Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Copper-Catalyzed Arylation of Polycyclic Aromatic Hydrocarbons by P=O Group

Yuan Niu[a], Zhichao Qi[a], Qinxin Lou[a], Pengbo Bai[a], Shangdong Yang[ab]*

[a] State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P. R. China. †

[b] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China.

*E-mail: yangshd@lzu.edu.cn

Table of content

1. General information.....3

2. Synthesis of P-sources.....3

2.1 Synthesis of **1a**-**1d**, **1h**-**1k**, **1m**-**1n**
2.2 Synthesis of **1e**-**1g**
2.3 Synthesis of **1l**
2.4 Synthesis of **1o**

3. Synthesis of diaryliodonium salts.....10

3.1 Synthesis of **2a**-**2o**
3.2 Synthesis of asymmetric diaryliodonium salts and other symmetric diaryliodonium

4. Screening of reaction conditions.....10

5. General procedure for C7-selective C-H arylation of naphthalene or similar arylation of fused rings.....12

6. Crystallographic data.....22

7. Investigation of the reaction mechanism.....24

7.1 Kinetic isotope effect
7.2 Radical capture experiment
7.3 Reasonable reaction mechanism

8. Synthesis of potential fluorescent molecules **5** and **6**.....25

8.1 Synthesis of **5**
8.2 Synthesis of **6**

9. Photophysical properties.....27

9.1. Photophysical data and spectra of **1a**, **1k**, **3ka**, **5** and **6**
9.2. Photoluminescence lifetime of **1a**, **1k**, **3ka**, **5** and **6** in neat film

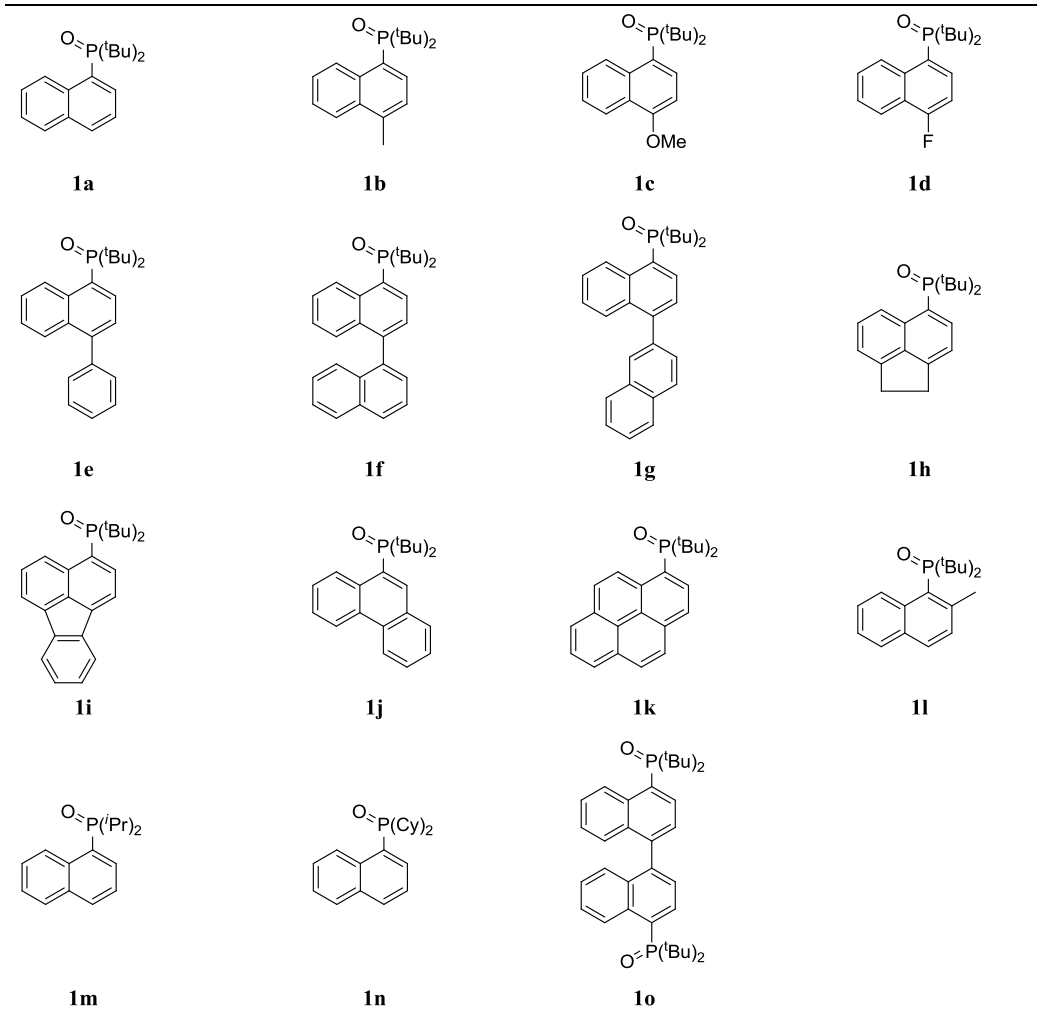
10. References.....28

11. Copies of NMR spectra.....29

1. General information

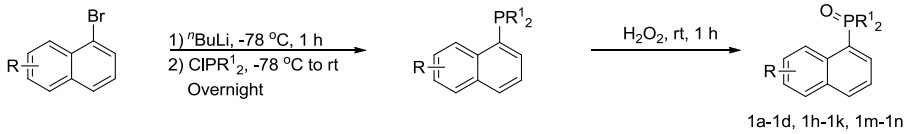
^{1}H and ^{13}C NMR spectra were recorded on a Bruker advance III 400 spectrometer (400 MHz for ^{1}H and 101 MHz for ^{13}C) in $CDCl_3$ with TMS as internal standard. Chemical shifts (δ) were measured in ppm relative to TMS δ = 0 for 1H, or to chloroform δ = 77.0 for ^{13}C as internal tandard.^{31}P and ^{19}F NMR were recorded on the same instrument. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), Coupling constants are reported in Hertz (Hz). High resolution mass spectroscopic (HRMS) and mass spectra were measured using Bruker micro TOF-Q mass spectrometer and Thermo Scientific DS II mass spectrometer. Analytical thin layer chromatography (TLC) was carried out using commercial silica-gel plates, spots were detected with UV light (254 nm) and revealed with phosphomolybdic acid solutions. The starting materials were purchased from Aldrich, Across Organics, J&K Chemicals or TCI and used without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Column chromatography was carried out on silica gel (particle size 200-400 mesh ASTM).

2. Synthesis of P-sources



Scheme S1. Scope of P-souces.

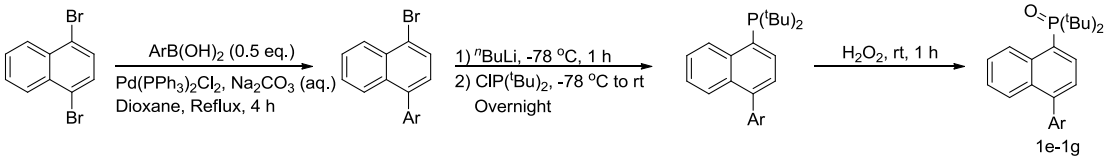
2.1 Synthesis of 1a-1d, 1h-1k, 1m-1n



General procedure 1 (GP1):

To a distilled THF solution (50 mL) of aryl bromide (10 mmol) was added dropwise ^{n}BuLi (5 mL, 12 mmol, 2.4 M in hexane) at -78 ℃ under Ar_2 atmosphere. The reaction mixture was stirred for 1 hour, then R_2PCl (11 mmol) was added at -78 ℃, then the temperature was slowly raised to room temperature and stirred overnight. H_2O_2 (2.5 mL, 30% aq) was added dropwise under ice bath. Water (30 mL) was added and the organic phase was extracted with ethyl acetate (2 × 40 mL), dried over anhydrous Na_2SO_4, filtered and the solvent was removed in vacuo, the residue was purified by preparative plate chromatography (silica gel) and eluted with petroleum ether/ethyl acetate to afford the desire products.

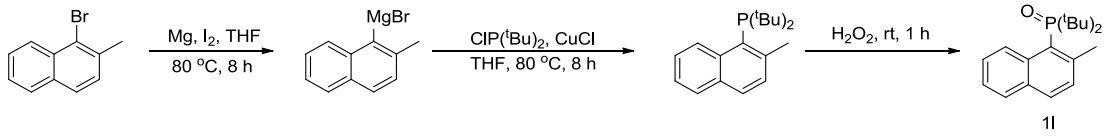
2.2 Synthesis of 1e-1g



General procedure 2 (GP2):

In a 50 mL round bottomed flask were mixed 1,4-dibromonaphtalene (2.84 g, 10 mmol), arylboronic acid (5 mmol, 0.5 equiv) and bis(triphenylphosphine)palladium(II) dichloride (140 mg, 0.2 mmol), aqueous sodium carbonate (2M, 24 mL), and dioxane (40 mL). The mixture was refluxed under argon for 6 h. Partition of the crude reaction between ethyl acetate (2 × 50 mL)/H_2O (100 mL) followed by column chromatography (petroleum ether) afforded 1-bromo-4-arylnaphthalene. Then followed GP1.

2.3 Synthesis of 1l

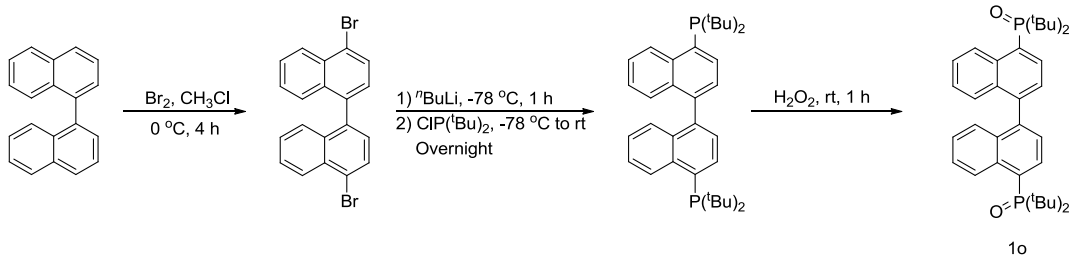


Procedure 3 (P3):

In a 50 mL round bottomed flask were mixed chloro-di-tert-butylphosphine (1.08 g, 6 mmol), copper(I) chloride (12 mg, 0.12 mmol) and 15 ml of tetrahydrofuran were placed. A solution of 2-methyl-1-naphthylmagnesium 1M in tetrahydrofuran, which was prepared from 1-bromo-2-methylnaphthalene (1.98 g, 9 mmol), I_2 (20 mg), magnesium turning (0.5 g) and THF (9.5 mL), the reaction mixture was heated at 80 ℃ under nitrogen atmosphere for 10 h. 9 ml (1.5 equiv.) was added at room temperature and the mixture was stirred for 20 min under nitrogen atmosphere. Then the resulting yellow mixture was heated at 80 ℃ for another 8h. After cooling to room temperature, H_2O_2 (2 mL, 30% aq) was added dropwise under ice bath. Water (30 mL) was added and the organic phase was extracted with ethyl acetate (2 × 20 mL), dried over anhydrous Na_2SO_4, filtered and the solvent was removed in vacuo, the residue was purified by preparative plate chromatography (silica gel) and eluted with petroleum ether/ethyl acetate (3:1 to 2:1) to afford 1l as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.0 Hz, 1H), 7.79 (d,

J = 7.9 Hz, 2H), 7.48 – 7.39 (m, 2H), 7.35 (dd, *J* = 8.4, 2.5 Hz, 1H), 3.06 (d, *J* = 1.1 Hz, 3H), 1.38 (d, *J* = 13.8 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 66.99 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.98 (d, *J* = 4.7 Hz), 133.96 (d, *J* = 11.9 Hz), 133.13 (d, *J* = 11.4 Hz), 131.99 (d, *J* = 8.5 Hz), 130.99 (d, *J* = 2.8 Hz), 128.86 (d, *J* = 5.1 Hz), 128.52 (s), 127.20 (d, *J* = 70.4 Hz), 124.63 (d, *J* = 50.5 Hz), 40.39 (d, *J* = 54.1 Hz), 28.39 (s), 25.24 (d, *J* = 1.8 Hz). GRMS calcd for $C_{19}H_{27}OP$: $[M+H]^+$ 303.1872, found 303.1613.

2.4 Synthesis of 1o

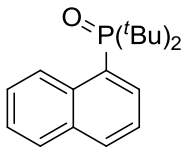


1o

Procedure 4 (P4):

Step 1: A stirred solution of 1,1′-binaphthalene (2.54 g, 10 mmol) in chloroform (60 mL) was cooled to 0 ℃. Bromine (6.3 g, 2.2 mL, 40 mmol) was added dropwise over 10 min in the dark while maintaining the temperature at 0 ℃ and with a steady magnetic stirring. The mixture was stirred for 4 h in the dark at 0 ℃. At this point, aqueous $NaHSO_3$ solution was added to quench the excess of bromine. The organic layer was separated and washed successively with aqueous $NaHSO_3$ solution, aqueous NaOH solution (2 M), and water. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness to afford the crude compound, which was recrystallized from boiling chloroform. White needle crystals, yield: 3.36 g, 82%.

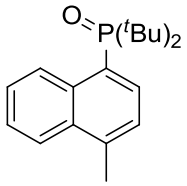
Step 2: To a distilled THF solution (30 mL) of 4,4'-dibromo-1,1'-binaphthalene (3.28 g, 8 mmol) was added dropwise ^{n}BuLi (8 mL, 19.2 mmol, 2.4 M in hexane) at -78 ℃ under Ar_2 atmosphere. The reaction mixture was stirred for 1 hour, then $(^t$Bu$)_2$PCl (3.4 mL, 17.6mmol) was added at -78 ℃, then the temperature was slowly raised to room temperature and stirred overnight. H_2O_2 (3 mL, 30% aq) was added dropwise under ice bath. Water (30 mL) was added and the organic phase was extracted with ethyl acetate (2 × 40 mL), dried over anhydrous Na_2SO_4, filtered and the solvent was removed in vacuo, the residue was purified by preparative plate chromatography (silica gel) and eluted with (petroleum ether : ethyl acetate = 1:1) to afford **1o** as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (d, *J* = 8.8 Hz, 2H), 7.88 (dd, *J* = 12.3, 7.4 Hz, 2H), 7.58 – 7.52 (m, 2H), 7.48 (dd, *J* = 7.4, 2.3 Hz, 2H), 7.35 – 7.30 (m, 4H), 1.44 (dd, *J* = 13.5, 5.4 Hz, 36H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.22 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.94 (d, *J* = 2.0 Hz), 137.37 (d, *J* = 4.7 Hz), 133.13 (d, *J* = 8.2 Hz), 130.07 (d, *J* = 11.2 Hz), 128.32 (s), 126.98 (s), 126.70 (d, *J* = 75.1 Hz), 126.47 (d, *J* = 7.1 Hz), 124.57 (d, *J* = 12.9 Hz), 37.88 (dd, *J* = 58.7, 1.7 Hz), 27.66 (d, *J* = 2.9 Hz). GRMS calcd for $C_{36}H_{48}O_2P_2$: $[M+H]^+$ 575.3202, found 575.2844.



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

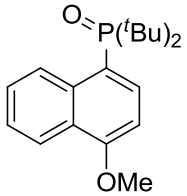
Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **1a** as a white solid under GP1. ^{1}H NMR (400 MHz, $CDCl^3$) δ 9.92 (d, J = 8.7 Hz, 1H), 7.96 (d, J = 8.1 Hz,

1H), 7.82 (d, J = 8.0 Hz, 1H), 7.76 (ddd, J = 12.4, 7.2, 1.0 Hz, 1H), 7.59 – 7.42 (m, 3H), 1.35 (d, J = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, CDCl3) δ 59.01 (s). ^{13}C NMR (101 MHz, CDCl3) δ 137.23 (d, J = 4.7 Hz), 134.08 (d, J = 8.0 Hz), 132.22 (d, J = 2.9 Hz), 130.75 (d, J = 11.1 Hz), 128.33 (s), 128.07 (d, J = 2.0 Hz), 126.96 (s), 126.86 (s), 126.12 (s), 122.72 (d, J = 13.0 Hz), 37.67 (d, J = 58.7 Hz), 27.55 (s). GRMS calcd for $C_{18}H_{25}OP$: $[M+H]^+$ 289.1716, found 289.1530.



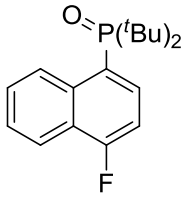
Di-tert-butyl(4-methylnaphthalen-1-yl)phosphine oxide. (**1b**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **1b** as a white solid under GP1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 – 9.91 (m, 1H), 8.05 – 7.96 (m, 1H), 7.65 (dd, *J* = 12.5, 7.4 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.31 (dd, *J* = 7.3, 1.5 Hz, 1H), 2.73 (s, 3H), 1.34 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 58.81 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.74 (d, *J* = 3.0 Hz), 137.23 (d, *J* = 4.9 Hz), 133.18 (d, *J* = 8.2 Hz), 130.62 (d, *J* = 11.1 Hz), 128.59 (s), 126.56 (s), 125.98 (s), 124.75 (s), 123.99 (s), 123.89 (d, *J* = 13.1 Hz), 37.68 (d, *J* = 58.9 Hz), 27.59 (s), 20.06 (s). GRMS calcd for $C_{19}H_{27}OP$: $[M+H]^+$ 303.1872, found 303.1643.



Di-tert-butyl(4-methoxynaphthalen-1-yl)phosphine oxide. (**1c**)

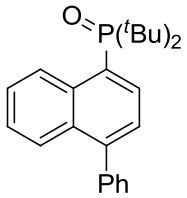
Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **1c** as a white solid under GP1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (d, *J* = 8.6 Hz, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 7.69 (dd, *J* = 12.4, 8.1 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.51 – 7.45 (m, 1H), 6.81 (dd, *J* = 8.1, 1.7 Hz, 1H), 4.04 (s, 3H), 1.34 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 58.63 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.99 (d, *J* = 2.9 Hz), 138.46 (d, *J* = 5.8 Hz), 131.64 (d, *J* = 12.2 Hz), 127.79 (s), 127.41 (s), 125.95 (d, *J* = 8.9 Hz), 125.45 (s), 121.63 (s), 117.50 (d, *J* = 81.7 Hz), 101.20 (d, *J* = 13.9 Hz), 55.56 (s), 37.71 (d, *J* = 59.3 Hz), 27.57 (s). GRMS calcd for $C_{19}H_{27}O_2P$: $[M+H]^+$ 319.1821, found 319.1541.



Di-tert-butyl(4-fluoronaphthalen-1-yl)phosphine oxide. (**1d**)

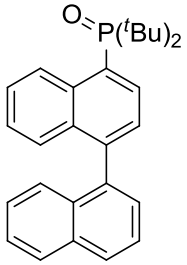
Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **1d** as a pale yellow solid under GP1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.1 Hz, 1H), 7.76 – 767 (m, 1H), 7.64 – 7.54 (m, 2H), 7.19 – 7.10 (m, 1H), 1.34 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 58.76 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.60 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.89 (dd, *J* = 258.0, 3.2 Hz), 139.46 – 139.12 (m), 130.91 (dd, *J* = 12.3, 9.1 Hz), 128.04 (s), 127.93 (s), 126.50 (d, *J* = 2.1 Hz), 124.28 (dd, *J* = 14.3, 9.0 Hz), 122.46 (dd, *J*

= 77.2, 5.2 Hz), 120.27 (d, *J* = 7.0 Hz), 106.91 (dd, *J* = 20.3, 13.7 Hz), 37.70 (d, *J* = 59.1 Hz), 27.47 (s). GRMS calcd for $C_{18}H_{24}FOP$: $[M+H]^+$ 307.1622, found 307.1358.



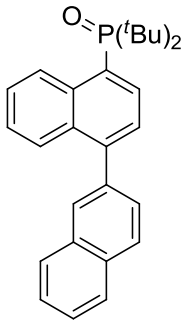
Di-tert-butyl(4-phenylnaphthalen-1-yl)phosphine oxide. (**1e**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **1e** as a white solid under GP2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (d, *J* = 8.7 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.80 (dd, *J* = 12.3, 7.4 Hz, 1H), 7.59 – 7.52 (m, 1H), 7.52 – 7.36 (m, 7H), 1.39 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 58.97 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.08 (d, *J* = 2.9 Hz), 140.27 (s), 137.71 (d, *J* = 4.8 Hz), 132.28 (d, *J* = 8.2 Hz), 130.28 (d, *J* = 11.1 Hz), 129.97 (s), 128.34 (s), 128.24 (d, *J* = 2.1 Hz), 127.68 (s), 126.72 (s), 126.27 (s), 126.16 (s), 126.13 (s), 125.37 (s), 123.86 (d, *J* = 13.0 Hz), 37.84 (d, *J* = 58.8 Hz), 27.65 (s). GRMS calcd for $C_{24}H_{29}OP$: $[M+H]^+$ 365.2029, found 365.1742.



[1,1'-binaphthalen]-4-yldi-tert-butylphosphine oxide. (**1f**)

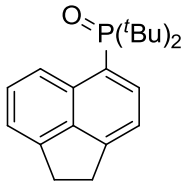
Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **1f** as a white solid under GP2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (d, *J* = 8.8 Hz, 1H), 7.95 (t, *J* = 7.9 Hz, 2H), 7.87 (dd, *J* = 12.4, 7.4 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.55 – 7.44 (m, 4H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.32 – 7.25 (m, 3H), 1.43 (dd, *J* = 13.5, 7.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.22 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.56 (d, *J* = 3.0 Hz), 137.95 (s), 137.39 (d, *J* = 4.8 Hz), 133.54 (s), 133.52 (s), 133.46 (s), 132.52 (s), 130.21 (d, *J* = 11.1 Hz), 128.27 (s), 128.20 (d, *J* = 2.1 Hz), 127.66 (s), 126.83 (s), 126.59 (s), 126.34 – 126.15 (m), 125.99 (s), 125.84 (s), 125.36 (s), 124.77 (d, *J* = 12.9 Hz), 37.89 (dd, *J* = 58.7, 3.9 Hz), 27.69 (d, *J* = 10.6 Hz). GRMS calcd for $C_{28}H_{31}OP$: $[M+H]^+$ 415.2185, found 415.1835.



[1,2'-binaphthalen]-4-yldi-tert-butylphosphine oxide. (**1g**)

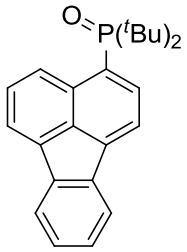
Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **1g** as a white solid under GP2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (d, *J* = 8.7 Hz, 1H), 7.98 – 7.90 (m,

4H), 7.88 (dd, *J* = 6.0, 3.4 Hz, 1H), 7.83 (dd, *J* = 12.3, 7.4 Hz, 1H), 7.62 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.59 – 7.51 (m, 3H), 7.48 (dd, *J* = 7.4, 2.4 Hz, 1H), 7.45 – 7.39 (m, 1H), 1.40 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.19 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.06 (d, *J* = 2.9 Hz), 137.83 (d, *J* = 0.7 Hz), 137.75 (d, *J* = 4.8 Hz), 133.35 (s), 132.76 (s), 132.44 (d, *J* = 8.2 Hz), 130.31 (d, *J* = 11.1 Hz), 128.83 (s), 128.31 (d, *J* = 2.0 Hz), 128.15 (d, *J* = 3.3 Hz), 127.81 (s), 126.82 (s), 126.51 (s), 126.37 (d, *J* = 3.4 Hz), 126.28 (s), 126.25 (s), 125.50 (s), 124.18 (d, *J* = 13.0 Hz), 37.88 (d, *J* = 58.7 Hz), 27.66 (s). GRMS calcd for $C_{28}H_{31}OP$: $[M+H]^+$ 415.2185, found 415.1816.



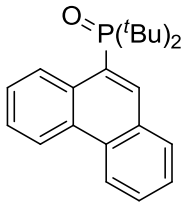
Di-tert-butyl(1,2-dihydroacenaphthylen-5-yl)phosphine oxide. (**1h**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **1h** as a yellow oil under GP1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (d, *J* = 8.7 Hz, 1H), 7.69 (dd, *J* = 11.9, 7.2 Hz, 1H), 7.49 (dd, *J* = 8.6, 6.9 Hz, 1H), 7.31 (d, *J* = 6.8 Hz, 1H), 7.27 (d, *J* = 6.4 Hz, 1H), 3.39 (s, 4H), 1.34 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.12 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.62 (d, *J* = 2.8 Hz), 145.75 (s), 139.40 (d, *J* = 9.2 Hz), 135.76 (d, *J* = 5.1 Hz), 132.32 (d, *J* = 11.9 Hz), 128.80 (s), 123.96 (s), 121.78 (d, *J* = 79.8 Hz), 119.92 (s), 116.96 (d, *J* = 13.0 Hz), 37.39 (d, *J* = 58.9 Hz), 30.29 (s), 30.00 (s), 27.45 (s). GRMS calcd for $C_{20}H_{27}OP$: $[M+H]^+$ 315.1872, found 315.1619.



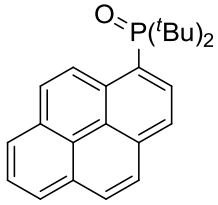
Di-tert-butyl(fluoranthen-3-yl)phosphine oxide. (**1i**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **1i** as a yellow solid under GP1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (d, *J* = 8.6 Hz, 1H), 7.92 – 7.82 (m, 5H), 7.64 (dd, *J* = 8.7, 6.9 Hz, 1H), 7.42 – 7.30 (m, 2H), 1.35 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.19 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.15 (d, *J* = 2.8 Hz), 140.00 (s), 138.16 (s), 136.86 (s), 134.38 (d, *J* = 4.7 Hz), 132.50 (d, *J* = 9.1 Hz), 132.17 (d, *J* = 11.7 Hz), 128.92 (s), 128.84 (s), 128.63 (s), 127.53 (s), 126.77 (s), 121.61 (d, *J* = 48.0 Hz), 120.77 (s), 117.27 (d, *J* = 12.6 Hz), 37.31 (d, *J* = 58.7 Hz), 27.45 (s). GRMS calcd for $C_{24}H_{27}OP$: $[M+H]^+$ 363.1872, found 363.1614.



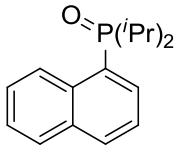
Di-tert-butyl(phenanthren-9-yl)phosphine oxide (**1j**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **1j** as a white solid under GP1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 – 9.97 (m, 1H), 8.70 (d, *J* = 7.9 Hz, 2H), 8.06 (d, *J* = 13.9 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.76 – 7.69 (m, 1H), 7.69 – 7.59 (m, 3H), 1.41 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.20 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.51 (d, *J* = 4.8 Hz), 133.23 (d, *J* = 10.9 Hz), 131.67 (d, *J* = 2.3 Hz), 130.44 (d, *J* = 7.5 Hz), 129.41 (s), 129.03 (d, *J* = 1.6 Hz), 128.86 (d, *J* = 13.5 Hz), 128.57 (s), 127.17 (s), 126.88 (s), 125.43 (d, *J* = 74.8 Hz), 122.52 (d, *J* = 30.5 Hz), 38.17 (d, *J* = 58.6 Hz), 27.70 (s). GRMS calcd for $C_{22}H_{27}OP$: $[M+H]^+$ 339.1872, found 339.1638.



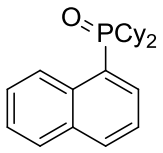
Di-tert-butyl(pyren-1-yl)phosphine oxide (**1k**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **1k** as a pale yellow solid under GP1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (d, *J* = 9.5 Hz, 1H), 8.25 – 8.08 (m, 6H), 8.06 – 7.97 (m, 2H), 1.38 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.55 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.36 (d, *J* = 4.5 Hz), 133.19 (d, *J* = 2.6 Hz), 131.07 (s), 130.58 (s), 129.50 (s), 129.01 (d, *J* = 11.7 Hz), 128.33 (s), 126.91 (s), 126.76 (d, *J* = 2.6 Hz), 126.27 (s), 125.88 (s), 125.59 (s), 125.30 (d, *J* = 9.2 Hz), 124.17 (s), 123.24 (d, *J* = 76.8 Hz), 122.27 (d, *J* = 12.4 Hz), 37.83 (d, *J* = 58.8 Hz), 27.67 (s). GRMS calcd for $C_{24}H_{27}OP$: $[M+H]^+$ 363.1872, found 363.1582.



Diisopropyl(naphthalen-1-yl)phosphine oxide (**1m**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **1m** as a white solid under GP1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.80 (dd, *J* = 12.2, 7.2 Hz, 1H), 7.61 – 7.46 (m, 3H), 2.62 – 2.41 (m, *J* = 7.1 Hz, 2H), 1.30 (dd, *J* = 14.9, 6.0 Hz, 6H), 1.05 (dd, *J* = 15.8, 7.2 Hz, 6H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.21 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.22 (d, *J* = 6.0 Hz), 133.86 (d, *J* = 8.4 Hz), 132.43 (d, *J* = 2.8 Hz), 131.94 (d, *J* = 8.4 Hz), 128.82 (s), 127.03 (s), 126.25 (d, *J* = 80.3 Hz), 126.19 (s), 124.15 (d, *J* = 12.1 Hz), 27.16 (d, *J* = 66.5 Hz), 16.43 (d, *J* = 2.3 Hz), 15.82 (d, *J* = 3.1 Hz). GRMS calcd for $C_{16}H_{21}OP$: $[M+H]^+$ 261.1403, found 261.1205.



Dicyclohexyl(naphthalen-1-yl)phosphine oxide (**1n**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **1n** as a colorless oil under GP1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.79 (s, 1H), 7.63 – 7.41 (m, 3H), 2.29 – 2.09 (m, 4H), 1.83 (d, *J* = 10.8 Hz, 2H), 1.74 – 1.53 (m, 6H), 1.50 – 1.08 (m, 10H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 50.19 (s). ^{13}C

NMR (101 MHz, $CDCl_3$) δ 133.83 (d, *J* = 8.4 Hz), 132.32 (d, *J* = 2.8 Hz), 128.85 (s), 127.01 (s), 126.90 (s), 126.33 (d, *J* = 81.1 Hz), 126.15 (s), 124.22 (d, *J* = 12.1 Hz), 37.19 (d, *J* = 66.7 Hz), 26.49 (dd, *J* = 12.6, 2.9 Hz), 25.77 (d, *J* = 1.0 Hz)., 25.67 (d, *J* = 2.6 Hz), 25.51 (d, *J* = 3.0 Hz). GRMS calcd for $C_{22}H_{29}OP$: $[M+H]^+$ 341.2029, found 341.1793.

3. Synthesis of diaryliodonium salts

3.1 Synthesis of 2a-2o

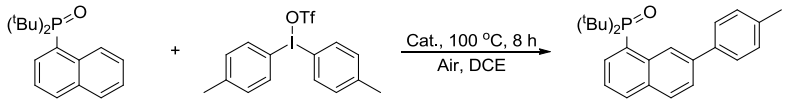
2a-2o were synthesized according to corresponding literatures[1]. Aryl boronic acid (10 mmol, 1.0 equiv) and CH_2Cl_2 (40 mL) were combined in a dried round-bottom flask. The mixture was cooled to 0 ℃ for 5 min, BF_3•OEt_2 (1.12 mL, 1.10 equiv) was added, and the mixture was stirred for 10 min. A solution of 2-(diacetoxyiodo)arene (1.05 equiv) in CH_2Cl_2 (20 mL) was added slowly for 10-15 min and stirred for additional 10 min. The mixture was warmed to room temperature and stirred for 1 h. The reaction was cooled to 0 ℃ again and TfOH (1.67 mL, 1.1 equiv) was dropped into the mixture. Then, the mixture was stirred for 10 min at 0 ℃ and warmed to room temperature for additional 10 min. At this time, the solvent was removed under reduced pressure and the residual ran through a short silica gel column (about 5 cm) with 5% of MeOH in CH_2Cl_2 quickly. The mixture was concentrated under vacuum and Et_2O (100 mL) was added to the residual. Filtrated and obtained the diaryliodonium salts **2a-2o** as solid.

3.2 Synthesis of asymmetric diaryliodonium salts and other symmetric diaryliodonium

Asymmetric diaryliodonium salts were synthesized according to corresponding literatures[2]. Ph_2IBF_4 was synthesized according to corresponding literatures[3]. Ph_2IBr and Ph_2IPF_6 were commercial available and used as substrates.

4. Screening of reaction conditions

Table S1. Catalyst screening [a].



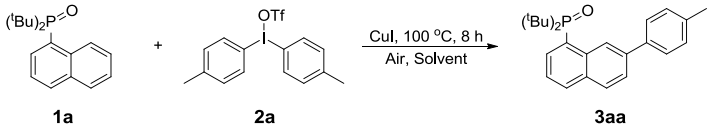
1a **2a** **3aa**

Entry	Cat. (10%)	DCE	Yield [b]
1	$Cu(OAc)_2$	1 mL	51%
2	$Cu(acac)_2$	1 mL	59%
3	CuO	1 mL	56%
4	$CuCl_2$	1 mL	53%
5	CuCl	1 mL	59%
6	CuBr	1 mL	56%
7	CuI	1 mL	69%
8	CuCN	1 mL	21%
9	Cu_2O	1 mL	30%
10	$Cu(CH_3CN)_4PF_6$	1 mL	24%
11	-	1 mL	N.R.
12	$Pd(OAc)_2$	1 mL	N.R.

13	$Fe(OTf)_2$	1 mL	N.R.
14	$Co(acac)_2$	1 mL	N.R.
15	$Ni(COD)_2$	1 mL	N.R.

[a] Reaction conditions: **1a** (0.1 mmol 1.0 equiv), **2a** (0.1 mmol 1.0 equiv), catalyst in DCE for 8 h at 100 °C under air. [b] Isolated yield.

Table S2. Solvent screening [a].

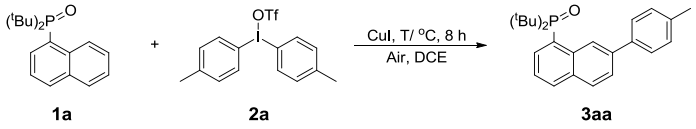


1a **2a** **3aa**

Entry	CuI	Solvent (0.1M)	Yield [b]
1	10%	DCE	69%
2	10%	Dioxane	37%
3	10%	Toluene	56%
4	10%	CH_3CN	N.R.
5	10%	DME	30%
6	10%	THF	42%
7	10%	TFE	N.R.

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

T**able S3.** Temperture screening [a].

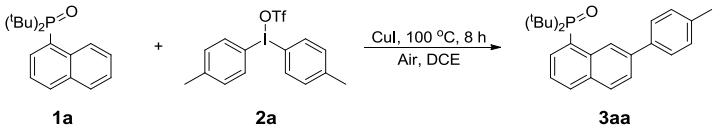


1a **2a** **3aa**

Entry	CuI	DCE	T/ °C	Yield [b]
1	10%	1 mL	40	N.R.
2	10%	1 mL	60	50%
3	10%	1 mL	80	60%
4	10%	1 mL	100	69%
5	10%	1 mL	120	62%

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

T**able S4.** Selection of reactant ratio and solvent concentration [a].

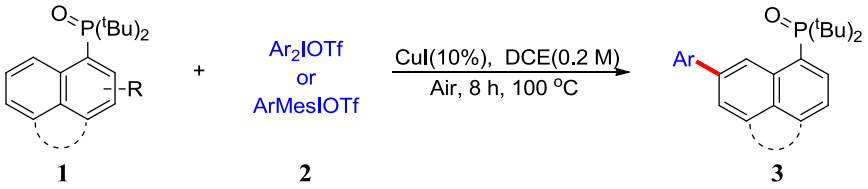


1a **2a** **3aa**

Entry	CuI	DCE	**2a**	Yield [b]
1	10%	1 mL	0.1 mmol	72%
2	10%	1 mL	0.12 mmol	78%
3	10%	1 mL	0.15 mmol	81%
4	10%	1 mL	0.2 mmol	78%
5	**10%**	**0.5 mL**	**0.15 mmol**	**88%**
6	10%	2 mL	0.2 mmol	78%
7	10%	3 mL	0.2 mmol	56%
8	5%	0.5 mL	0.2 mmol	71%

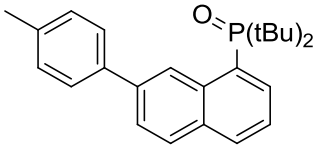
[a] Reaction conditions: **1a** (0.1 mmol 1.0 equiv), **2a** (0.1 X mmol X equiv), CuI in DCE for 8 h at 100 °C under air. [b] Isolated yield.

5. General procedure for C7-selective C-H arylation of naphthalene or similar arylation of fused rings



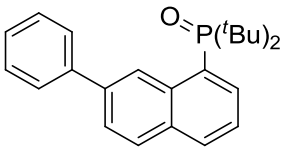
1 **2** **3**

A 15.00 mL test tube equipped with a rubber septum and magnetic stir bar was charged **1** (0.1 mmol, 1.0 equiv), diaryliodonium salts (0.15 mmol, 1.5 equiv), CuI (0.01 mmol, 10 mol %) and DCE (0.5 mL) under air. The mixture was stirred at 100 °C for 8 h (monitored by TLC). After cooling to room temperature, the solvent was removed under vaccum directly. The crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate.



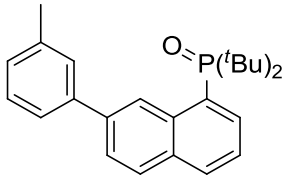
Di-tert-butyl(7-(p-tolyl)naphthalen-1-yl)phosphine oxide (**3aa**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1) to afford **3aa** as a pale yellow colloid in 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (s, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.86 (dd, *J* = 23.8, 8.2 Hz, 2H), 7.81 – 7.71 (m, 3H), 7.44 (t, *J* = 6.5 Hz, 1H), 7.27 (d, *J* = 6.4 Hz, 2H), 2.40 (s, 3H), 1.38 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.73 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.88 (s), 137.96 (s), 137.58 (d, *J* = 4.6 Hz), 137.09 (s), 133.17 (d, *J* = 8.0 Hz), 131.92 (d, *J* = 2.8 Hz), 131.24 (d, *J* = 11.1 Hz), 129.61 (s), 128.83 (s), 127.31 (s), 126.53 (d, *J* = 75.6 Hz), 125.47 (d, *J* = 2.0 Hz), 125.33 (s), 122.58 (d, *J* = 12.9 Hz), 37.71 (d, *J* = 58.6 Hz), 27.64 (s), 21.18 (s). HRMS calcd for $C_{25}H_{31}OP$: $[M+H]^+$ 379.2185, found 379.2181.



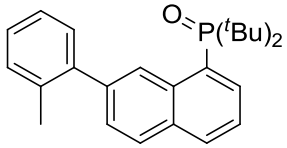
Di-tert-butyl(7-phenylnaphthalen-1-yl)phosphine oxide (**3ab**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1) to afford **3ab** as a pale yellow colloid in 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.29 (s, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 7.3 Hz, 3H), 7.78 (dd, *J* = 12.3, 7.2 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 3H), 7.34 (t, *J* = 7.4 Hz, 1H), 1.38 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.51 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.89 (s), 138.99 (s), 137.52 (d, *J* = 4.6 Hz), 133.27 (d, *J* = 7.9 Hz), 131.95 (d, *J* = 2.9 Hz), 131.31 (d, *J* = 11.0 Hz), 128.90 (s), 127.51 (s), 127.33 (s), 126.57 (d, *J* = 75.6 Hz), 125.90 (d, *J* = 1.9 Hz), 125.44 (s), 122.79 (d, *J* = 12.9 Hz), 37.71 (d, *J* = 58.6 Hz), 27.63 (s). HRMS calcd for $C_{24}H_{29}OP$: $[M+H]^+$ 365.2029, found 365.2026.



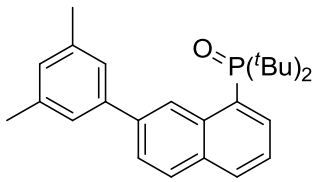
Di-tert-butyl(7-(m-tolyl)naphthalen-1-yl)phosphine oxide (**3ac**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1) to afford **3ac** as a pale yellow colloid in 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.84 – 7.74 (m, 2H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.58 (s, 1H), 7.45 (td, *J* = 7.8, 2.4 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 2.44 (s, 3H), 1.38 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.53 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.06 (s), 139.35 (s), 138.24 (s), 137.51 (d, *J* = 4.7 Hz), 133.25 (d, *J* = 8.1 Hz), 131.96 (d, *J* = 2.9 Hz), 131.27 (d, *J* = 11.1 Hz), 128.84 (d, *J* = 4.1 Hz), 128.14 (d, *J* = 6.6 Hz), 126.56 (d, *J* = 75.8 Hz), 125.89 (d, *J* = 1.8 Hz), 125.73 (s), 124.93 (s), 122.67 (d, *J* = 13.1 Hz), 37.71 (d, *J* = 58.6 Hz), 27.65 (s), 21.72 (s). HRMS calcd for $C_{25}H_{31}OP$: $[M+H]^+$ 379.2185, found 379.2183.



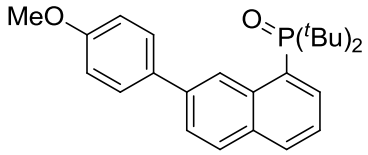
Di-tert-butyl(7-(o-tolyl)naphthalen-1-yl)phosphine oxide (**3ad**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1) to afford **3ad** as a pale yellow solid in 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.79 (dd, *J* = 12.3, 7.2 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.51 – 7.44 (m, 1H), 7.38 – 7.31 (m, 1H), 7.27 – 7.23 (m, 3H), 2.36 (s, 3H), 1.36 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.22 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.95 (s), 140.33 (s), 136.99 (d, *J* = 4.6 Hz), 135.66 (s), 132.83 (d, *J* = 7.8 Hz), 132.00 (d, *J* = 3.0 Hz), 131.15 (d, *J* = 11.2 Hz), 130.34 (d, *J* = 20.6 Hz), 128.13 (d, *J* = 1.9 Hz), 128.04 (s), 127.14 (s), 126.38 (d, *J* = 75.7 Hz), 125.81 (s), 122.69 (d, *J* = 12.9 Hz), 37.65 (d, *J* = 58.6 Hz), 27.58 (s), 20.89 (s). HRMS calcd for $C_{25}H_{31}OP$: $[M+H]^+$ 379.2185, found 379.2180.



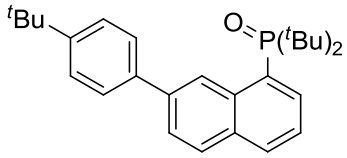
Di-tert-butyl(7-(3,5-dimethylphenyl)naphthalen-1-yl)phosphine oxide (**3ae**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1) to afford **3ae** as a pale yellow colloid in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.81 – 7.74 (m, 2H), 7.44 (td, *J* = 7.8, 2.3 Hz, 1H), 7.37 (s, 2H), 6.98 (s, 1H), 2.40 (s, 6H), 1.38 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.53 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.34 (s), 139.78 (s), 138.19 (s), 137.50 (d, *J* = 4.6 Hz), 133.23 (d, *J* = 8.0 Hz), 131.99 (d, *J* = 2.9 Hz), 131.26 (d, *J* = 11.1 Hz), 129.05 (s), 128.74 (s), 126.57 (d, *J* = 75.9 Hz), 126.14 (s), 125.83 (d, *J* = 2.0 Hz), 125.64 (s), 122.56 (d, *J* = 13.0 Hz), 37.72 (d, *J* = 58.5 Hz), 27.69 (s), 21.60 (s). HRMS calcd for $C_{26}H_{33}OP$: $[M+H]^+$ 393.2342, found 393.2338.



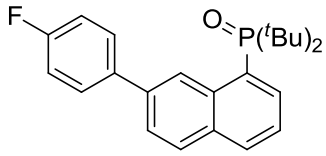
Di-tert-butyl(7-(4-methoxyphenyl)naphthalen-1-yl)phosphine oxide (**3af**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 2:1 to 1:1) to afford **3af** as a pale yellow colloid in 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.87 (dd, *J* = 8.6, 1.1 Hz, 1H), 7.83 – 7.73 (m, 4H), 7.47 – 7.39 (m, 1H), 7.02 – 6.97 (m, 2H), 3.85 (s, 3H), 1.38 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.50 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.24 (s), 138.56 (s), 137.62 (d, *J* = 4.6 Hz), 133.45 (s), 132.96 (d, *J* = 8.0 Hz), 131.93 (d, *J* = 2.9 Hz), 131.27 (d, *J* = 11.1 Hz), 128.84 (s), 128.53 (s), 126.35 (d, *J* = 75.8 Hz), 125.16 (s), 125.02 (d, *J* = 2.0 Hz), 122.47 (d, *J* = 13.0 Hz), 114.34 (s), 55.37 (s), 37.71 (d, *J* = 58.6 Hz), 27.64 (s). HRMS calcd for $C_{25}H_{31}O_2P$: $[M+H]^+$ 395.2134, found 395.2131.



Di-tert-butyl(7-(4-(tert-butyl)phenyl)naphthalen-1-yl)phosphine oxide (**3ag**)

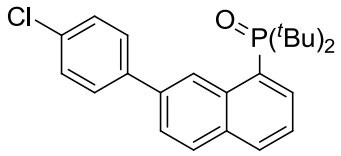
Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1) to afford **3ag** as a pale yellow colloid in 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.80 – 7.74 (m, 3H), 7.50 – 7.41 (m, 3H), 1.39 (s, 9H), 1.36 (s, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.36 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.25 (s), 138.95 (s), 138.08 (s), 137.57 (d, *J* = 4.6 Hz), 133.14 (d, *J* = 8.0 Hz), 131.91 (d, *J* = 2.9 Hz), 131.21 (d, *J* = 11.2 Hz), 128.77 (s), 127.16 (s), 126.51 (d, *J* = 75.6 Hz), 125.85 (s), 125.76 (d, *J* = 1.9 Hz), 125.38 (s), 122.59 (d, *J* = 12.8 Hz), 37.72 (d, *J* = 58.6 Hz), 34.53 (s), 31.38 (s), 27.63 (s). HRMS calcd for $C_{28}H_{37}OP$: $[M+H]^+$ 421.2655, found 421.2650.



Di-tert-butyl(7-(4-fluorophenyl)naphthalen-1-yl)phosphine oxide (**3ah**)

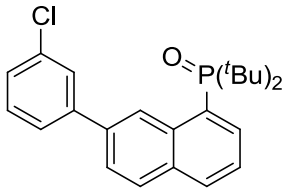
Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1) to afford **3ah** as a pale yellow colloid in 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.82 – 7.74 (m, 4H), 7.46 (td, *J* = 8.0, 2.2 Hz, 1H), 7.14 (t, *J* = 8.7 Hz, 2H), 1.38 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.64 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.80 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.58 (d, *J* = 246.3 Hz), 137.99 (s), 137.51

(d, *J* = 4.6 Hz), 137.04 (d, *J* = 3.0 Hz), 133.19 (d, *J* = 7.9 Hz), 131.94 (d, *J* = 2.8 Hz), 131.36 (d, *J* = 11.0 Hz), 129.05 (d, *J* = 8.1 Hz), 128.98 (s), 126.55 (d, *J* = 75.5 Hz), 125.70 (d, *J* = 1.2 Hz), 125.20 (s), 122.82 (d, *J* = 12.9 Hz), 115.71 (d, *J* = 21.4 Hz), 37.72 (d, *J* = 58.6 Hz), 27.59 (s). HRMS calcd for $C_{24}H_{28}FOP$: $[M+H]^+$ 383.1935, found 383.1930.



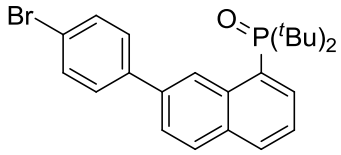
Di-tert-butyl(7-(4-chlorophenyl)naphthalen-1-yl)phosphine oxide (**3ai**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1) to afford **3ai** as a white solid in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.28 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.82 – 7.73 (m, 4H), 7.50 – 7.44 (m, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 1.37 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.60 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.35 (s), 137.64 (s), 137.47 (d, *J* = 4.6 Hz), 133.39 (s), 133.32 (s), 131.95 (d, *J* = 2.9 Hz), 131.44 (d, *J* = 11.0 Hz), 129.09 (s), 128.86 (d, *J* = 29.9 Hz), 126.64 (d, *J* = 75.3 Hz), 125.85 (d, *J* = 1.9 Hz), 125.02 (s), 123.03 (d, *J* = 12.9 Hz), 37.70 (d, *J* = 58.6 Hz), 27.60 (s). HRMS calcd for $C_{24}H_{28}ClOP$: $[M+H]^+$ 399.1639, found 399.1637.



Di-tert-butyl(7-(3-chlorophenyl)naphthalen-1-yl)phosphine oxide (**3aj**)

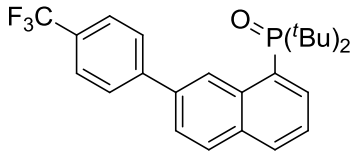
Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1) to afford **3aj** as a pale yellow colloid in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.26 (s, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.91 (dd, *J* = 8.6, 1.1 Hz, 1H), 7.83 – 7.70 (m, 4H), 7.52 – 7.45 (m, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.33 – 7.29 (m, 1H), 1.38 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.71 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.01 (s), 137.78 (s), 137.41 (d, *J* = 4.4 Hz), 134.55 (s), 133.49 (d, *J* = 7.9 Hz), 131.98 (d, *J* = 2.8 Hz), 131.45 (d, *J* = 11.0 Hz), 130.23 (s), 129.12 (s), 127.36 (d, *J* = 9.9 Hz), 126.72 (d, *J* = 75.2 Hz), 126.23 (d, *J* = 1.9 Hz), 126.03 (s), 125.27 (s), 123.12 (d, *J* = 12.8 Hz), 37.71 (d, *J* = 58.6 Hz), 27.60 (s). HRMS calcd for $C_{24}H_{28}ClOP$: $[M+H]^+$ 399.1639, found 399.1635.



(7-(4-bromophenyl)naphthalen-1-yl)di-tert-butylphosphine oxide (**3ak**)

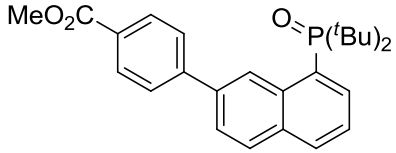
Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1) to afford **3ak** as a white solid in 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.28 (s, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.90 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.83 – 7.76 (m, 2H), 7.72 – 7.67 (m, 2H), 7.60 – 7.55 (m, 2H), 7.48 (td, *J* = 7.9, 2.4 Hz, 1H), 1.38 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.73 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.81 (s), 137.68 (s), 137.45 (d, *J* = 4.5 Hz), 133.38 (d, *J* = 7.9 Hz), 131.96 (s), 131.46 (d, *J* = 11.1 Hz), 129.12 (s), 129.07 (s), 126.59 (d, *J* = 75.4 Hz), 125.83 (d, *J* = 1.8 Hz),

124.97 (s), 123.06 (d, *J* = 13.0 Hz), 121.64 (s), 37.70 (d, *J* = 58.6 Hz), 27.60 (s). HRMS calcd for $C_{24}H_{28}BrOP$: $[M+H]^+$ 443.1134, found 443.1130.



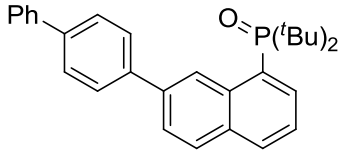
Di-tert-butyl(7-(4-(trifluoromethyl)phenyl)naphthalen-1-yl)phosphine oxide (**3al**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **3al** as a white solid in 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.35 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.93 (t, *J* = 7.4 Hz, 3H), 7.85 – 7.78 (m, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.50 (td, *J* = 7.8, 2.3 Hz, 1H), 1.38 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.82 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.35 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.49 (s), 137.51 (s), 137.40 (d, *J* = 4.4 Hz), 133.65 (d, *J* = 7.9 Hz), 131.99 (d, *J* = 2.8 Hz), 131.50 (d, *J* = 11.0 Hz), 129.25 (d, *J* = 32.5 Hz), 129.22 (s), 127.75 (s), 126.81 (d, *J* = 75.2 Hz), 126.65 (d, *J* = 1.9 Hz), 125.80 (dd, *J* = 7.5, 3.7 Hz), 125.10 (s), 123.34 (d, *J* = 12.8 Hz), 37.73 (d, *J* = 58.6 Hz), 27.57 (s). HRMS calcd for $C_{25}H_{28}F_3OP$: $[M+H]^+$ 433.1903, found 433.1899.



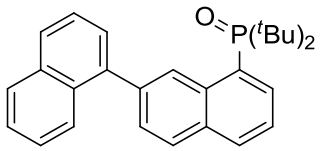
Methyl 4-(8-(di-tert-butylphosphoryl)naphthalen-2-yl)benzoate (**3am**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 2:1) to afford **3am** as a white solid in 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.37 (s, 1H), 8.12 (d, *J* = 8.3 Hz, 2H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.91 (t, *J* = 10.0 Hz, 3H), 7.86 – 7.77 (m, 2H), 7.53 – 7.46 (m, 1H), 3.94 (s, 3H), 1.38 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.62 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.13 (s), 145.41 (s), 137.75 (s), 137.42 (d, *J* = 4.5 Hz), 133.66 (d, *J* = 7.9 Hz), 131.95 (d, *J* = 2.8 Hz), 131.45 (d, *J* = 11.0 Hz), 130.20 (s), 129.13 (s), 128.84 (s), 127.39 (s), 126.88 (d, *J* = 75.1 Hz), 126.59 (d, *J* = 1.9 Hz), 125.20 (s), 123.26 (d, *J* = 12.8 Hz), 52.09 (s), 37.71 (d, *J* = 58.6 Hz), 27.59 (s). HRMS calcd for $C_{26}H_{31}O_3P$: $[M+H]^+$ 423.2084, found 423.2079.



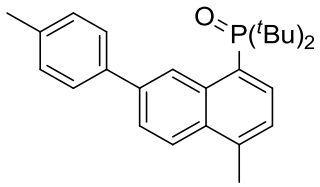
(7-([1,1'-biphenyl]-4-yl)naphthalen-1-yl)di-tert-butylphosphine oxide (**3an**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **3an** as a pale yellow colloid in 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.36 (s, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.96 – 7.85 (m, 4H), 7.79 (dd, *J* = 12.2, 7.2 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 2H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 3H), 7.35 (t, *J* = 7.2 Hz, 1H), 1.39 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.50 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.90 (s), 139.98 (d, *J* = 28.0 Hz), 138.45 (s), 137.59 (d, *J* = 4.6 Hz), 133.35 (d, *J* = 7.9 Hz), 131.95 (d, *J* = 2.8 Hz), 131.32 (d, *J* = 11.1 Hz), 128.96 (s), 128.81 (s), 127.74 (d, *J* = 20.1 Hz), 127.27 (s), 127.09 (s), 126.65 (d, *J* = 75.6 Hz), 125.86 (d, *J* = 1.8 Hz), 125.25 (s), 122.80 (d, *J* = 13.0 Hz), 37.74 (d, *J* = 58.6 Hz), 27.64 (s). HRMS calcd for $C_{30}H_{33}OP$: $[M+H]^+$ 441.2342, found 441.2338.



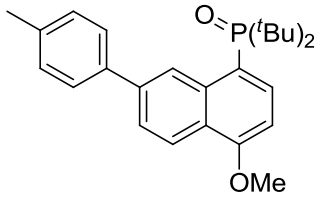
[1,2'-binaphthalen]-8'-yldi-tert-butylphosphine oxide (**3ao**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **3ao** as a pale yellow solid in 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.86 – 7.78 (m, 2H), 7.71 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.57 (dd, *J* = 7.0, 1.4 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.46 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.41 – 7.36 (m, 1H), 1.37 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.14 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.37 (s), 139.38 (s), 137.33 (d, *J* = 4.6 Hz), 133.86 (s), 133.20 (d, *J* = 8.0 Hz), 132.08 (d, *J* = 2.8 Hz), 131.67 (s), 131.27 (d, *J* = 11.1 Hz), 129.06 (d, *J* = 2.0 Hz), 128.85 (s), 128.27 (s), 128.00 (s), 127.67 (d, *J* = 12.7 Hz), 126.59 (d, *J* = 75.5 Hz), 126.16 (s), 125.85 (s), 125.60 (d, *J* = 1.8 Hz), 122.89 (d, *J* = 12.9 Hz), 37.68 (d, *J* = 58.6 Hz), 27.61 (s). HRMS calcd for $C_{28}H_{31}OP$: $[M+H]^+$ 415.2185, found 415.2180



Bi-tert-butyl(4-methyl-7-(p-tolyl)naphthalen-1-yl)phosphine oxide (**3ba**)

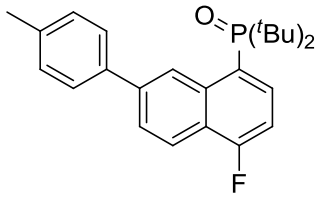
Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **3ba** as a pale yellow solid in 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.31 (s, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 2H), 7.66 (dd, *J* = 12.4, 7.4 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 3H), 2.75 (s, 3H), 2.39 (s, 3H), 1.37 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.20 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.59 (d, *J* = 2.8 Hz), 138.30 (s), 137.86 (s), 137.64 (d, *J* = 4.7 Hz), 137.05 (s), 132.25 (d, *J* = 8.2 Hz), 131.12 (d, *J* = 11.0 Hz), 129.61 (s), 127.24 (s), 125.95 (s), 125.01 (s), 124.55 (s), 124.47 (d, *J* = 77.6 Hz), 123.72 (d, *J* = 13.0 Hz), 37.71 (d, *J* = 58.8 Hz), 27.67 (s), 21.17 (s), 19.99 (s). HRMS calcd for $C_{26}H_{33}OP$: $[M+H]^+$ 393.2342, found 393.2336.



Di-tert-butyl(4-methoxy-7-(p-tolyl)naphthalen-1-yl)phosphine oxide (**3ca**)

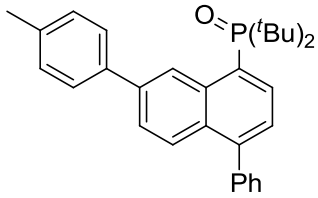
Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **3ca** as a pale yellow solid in 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (d, *J* = 1.3 Hz, 1H), 8.34 (d, *J* = 8.8 Hz, 1H), 7.81 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.70 (dd, *J* = 12.4, 8.1 Hz, 1H), 7.27 – 7.23 (m, 2H), 6.79 (dd, *J* = 8.1, 1.3 Hz, 1H), 4.05 (s, 3H), 2.39 (s, 3H), 1.36 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 58.93 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.00 (d, *J* = 2.8 Hz), 139.18 (s), 138.91 (d, *J* = 5.6 Hz), 137.93 (s), 137.07 (s), 132.15 (d, *J* = 12.2 Hz), 129.57 (s), 127.28 (s), 125.25 (s), 124.94 (d, *J* = 8.7 Hz), 124.49 (s), 122.23 (s), 117.64 (d, *J* =

81.7 Hz), 101.13 (d, *J* = 13.8 Hz), 55.59 (s), 37.75 (d, *J* = 59.2 Hz), 27.67 (s), 21.17 (s). HRMS calcd for $C_{26}H_{33}O_2P$: $[M+H]^+$ 409.2291, found 409.2289.



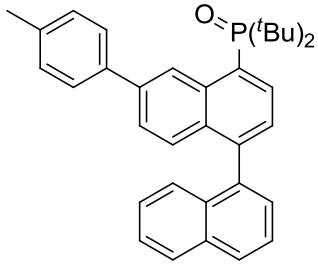
Di-tert-butyl(4-fluoro-7-(p-tolyl)naphthalen-1-yl)phosphine oxide (**3da**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **3da** as a white solid in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.28 (s, 1H), 8.19 (d, *J* = 8.7 Hz, 1H), 7.92 – 7.87 (m, 1H), 7.80 – 7.65 (m, 3H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.15 – 7.08 (m, 1H), 2.40 (s, 3H), 1.37 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.28 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.68 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.97 (d, *J* = 257.9 Hz), 139.92 (s), 139.79 (t, *J* = 5.1 Hz), 137.51 (s), 131.49 (dd, *J* = 12.3, 9.1 Hz), 129.69 (s), 127.34 (s), 125.73 (d, *J* = 1.8 Hz), 125.35 (s), 123.21 (dd, *J* = 14.5, 8.9 Hz), 122.41 (dd, *J* = 77.5, 5.2 Hz), 120.91 (d, *J* = 6.6 Hz), 106.77 (dd, *J* = 20.2, 13.8 Hz), 37.74 (d, *J* = 59.0 Hz), 27.57 (s), 21.20 (s). HRMS calcd for $C_{25}H_{30}FOP$: $[M+H]^+$ 397.2091, found 397.2090.



Di-tert-butyl(4-phenyl-7-(p-tolyl)naphthalen-1-yl)phosphine oxide (**3ea**)

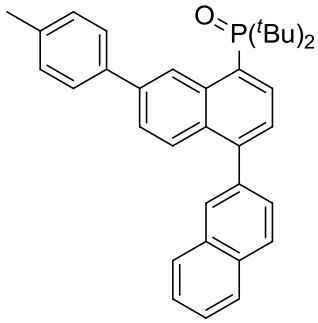
Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **3ea** as a pale yellow colloid in 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.37 (s, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.84 – 7.72 (m, 4H), 7.54 – 7.45 (m, 5H), 7.37 (dd, *J* = 7.4, 2.1 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 2H), 2.39 (s, 3H), 1.41 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.61 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.91 (d, *J* = 2.9 Hz), 140.26 (s), 138.50 (s), 138.10 (d, *J* = 4.7 Hz), 137.77 (s), 137.16 (s), 131.33 (d, *J* = 8.2 Hz), 130.78 (d, *J* = 11.2 Hz), 129.96 (s), 129.64 (s), 128.39 (s), 127.73 (s), 127.28 (s), 126.81 (s), 125.77 (d, *J* = 76.1 Hz), 125.58 (d, *J* = 1.9 Hz), 125.23 (s), 123.64 (d, *J* = 13.0 Hz), 37.86 (d, *J* = 58.7 Hz), 27.72 (s), 21.19 (s). HRMS calcd for $C_{31}H_{35}OP$: $[M+H]^+$ 455.2498, found 455.2492.



Di-tert-butyl(6-(p-tolyl)-[1,1'-binaphthalen]-4-yl)phosphine oxide (**3fa**)

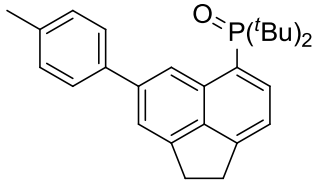
Flash slica gel chromatography (petroleum ether : ethyl acetate = 2:1) to afford **3fa** as a pale yellow colloid in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.39 (d, *J* = 1.6 Hz, 1H), 7.96 (t, *J* = 8.2 Hz, 2H), 7.87 (dd, *J* = 12.3, 7.4 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.63 – 7.57 (m, 2H), 7.53 – 7.41 (m, 4H), 7.38 – 7.28 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H), 1.45 (dd, *J* = 13.5, 8.7

Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.63 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.38 (d, *J* = 3.0 Hz), 138.68 (s), 137.93 (s), 137.80 (t, *J* = 2.3 Hz), 137.16 (s), 133.56 (s), 132.62 (s), 132.53 (s), 130.72 (d, *J* = 11.1 Hz), 129.64 (s), 128.30 (s), 127.51 (d, *J* = 31.1 Hz), 127.29 (s), 126.31 (d, *J* = 2.7 Hz), 126.26 (d, *J* = 75.9 Hz), 126.04 (s), 125.55 (d, *J* = 2.0 Hz), 125.37 (d, *J* = 7.5 Hz), 124.58 (d, *J* = 12.9 Hz), 37.92 (dd, *J* = 58.6, 5.1 Hz), 27.78 (d, *J* = 14.0 Hz), 21.19 (s). HRMS calcd for $C_{35}H_{37}OP$: $[M+H]^+$ 505.2655, found 505.2650.



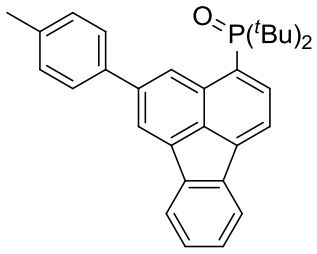
Di-tert-butyl(6-(p-tolyl)-[1,2'-binaphthalen]-4-yl)phosphine oxide (**3ga**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 2:1) to afford **3ga** as a pale yellow solid in 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (d, *J* = 1.7 Hz, 1H), 8.01 – 7.89 (m, 5H), 7.84 (dd, *J* = 12.3, 7.4 Hz, 1H), 7.77 – 7.72 (m, 3H), 7.65 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.54 (dd, *J* = 6.2, 3.3 Hz, 2H), 7.46 (dd, *J* = 7.4, 2.4 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 2.38 (s, 3H), 1.43 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.49 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.87 (d, *J* = 2.9 Hz), 138.60 (s), 138.17 (d, *J* = 4.7 Hz), 137.79 (d, *J* = 2.7 Hz), 137.20 (s), 133.09 (d, *J* = 58.7 Hz), 131.50 (d, *J* = 8.1 Hz), 130.81 (d, *J* = 11.0 Hz), 129.67 (s), 128.84 (s), 128.16 (s), 127.85 (d, *J* = 3.7 Hz), 127.30 (s), 126.92 (s), 126.54 (s), 126.38 (s), 125.96 (d, *J* = 75.9 Hz), 125.65 (d, *J* = 1.9 Hz), 125.35 (s), 123.97 (d, *J* = 12.9 Hz), 37.90 (d, *J* = 58.7 Hz), 27.75 (s), 21.20 (s). HRMS calcd for $C_{35}H_{37}OP$: $[M+H]^+$ 505.2655, found 505.2650.



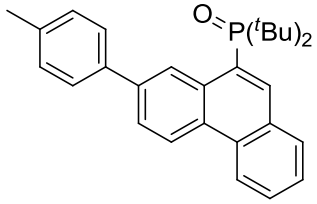
Di-tert-butyl(7-(p-tolyl)-1,2-dihydroacenaphthylen-5-yl)phosphine oxide (**3ha**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **3ha** as a yellow solid in 42% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.73 – 7.66 (m, 3H), 7.62 (s, 1H), 7.26 – 7.21 (m, 3H), 3.43 (s, 4H), 2.38 (s, 3H), 1.36 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.52 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.32 (d, *J* = 2.8 Hz), 146.36 (s), 141.51 (s), 139.08 (s), 138.73 (d, *J* = 9.2 Hz), 136.86 (s), 135.86 (d, *J* = 5.1 Hz), 132.81 (d, *J* = 11.9 Hz), 129.42 (s), 127.73 (s), 122.21 (d, *J* = 1.0 Hz), 121.91 (d, *J* = 79.7 Hz), 119.47 (s), 116.87 (d, *J* = 12.9 Hz), 37.42 (d, *J* = 58.8 Hz), 30.53 (s), 30.07 (s), 27.52 (s), 21.16 (s). HRMS calcd for $C_{27}H_{33}OP$: $[M+H]^+$ 405.2342, found 405.2339.



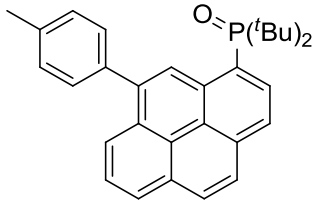
Di-tert-butyl(5-(p-tolyl)fluoranthen-3-yl)phosphine oxide (**3ia**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **3ia** as a pale yellow colloid in 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 8.22 (s, 1H), 7.96 – 7.87 (m, 4H), 7.77 (d, *J* = 7.9 Hz, 2H), 7.40 (dt, *J* = 15.7, 7.4 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 2.41 (s, 3H), 1.39 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.42 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.82 (s), 140.00 (s), 139.98 (s), 138.73 (s), 138.63 (d, *J* = 1.1 Hz), 137.39 (d, *J* = 0.9 Hz), 137.25 (s), 134.58 (d, *J* = 4.6 Hz), 132.59 (d, *J* = 11.8 Hz), 131.85 (d, *J* = 9.1 Hz), 129.57 (s), 128.63 (s), 127.65 (s), 127.15 (d, *J* = 76.4 Hz), 126.73 (d, *J* = 0.8 Hz), 121.90 (s), 121.40 (s), 120.46 (s), 116.98 (d, *J* = 12.6 Hz), 37.38 (d, *J* = 58.6 Hz), 27.52 (s), 21.18 (s). HRMS calcd for $C_{31}H_{33}OP$: $[M+H]^+$ 453.2342, found 453.2337.



Di-tert-butyl(7-(p-tolyl)phenanthren-9-yl)phosphine oxide (**3ja**)

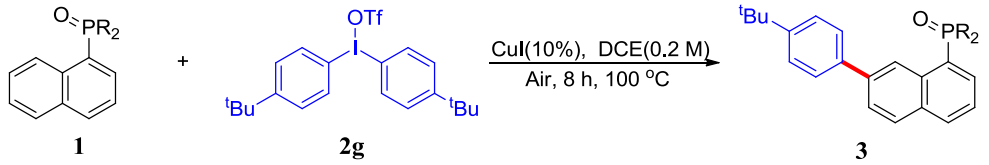
Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **3ja** as a white solid in 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 1H), 8.73 (dd, *J* = 15.7, 8.5 Hz, 2H), 8.08 (d, *J* = 13.9 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.84 – 7.70 (m, 3H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 2.41 (s, 3H), 1.44 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.62 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.99 (s), 137.65 (s), 137.15 (s), 134.91 (d, *J* = 4.7 Hz), 133.69 (d, *J* = 10.9 Hz), 131.55 (d, *J* = 2.2 Hz), 129.68 (s), 129.46 (s), 129.36 (d, *J* = 7.5 Hz), 128.79 (d, *J* = 13.6 Hz), 128.67 (s), 127.18 (s), 126.79 (s), 126.58 (d, *J* = 1.3 Hz), 125.48 (d, *J* = 74.6 Hz), 125.47 (s), 122.81 (d, *J* = 27.0 Hz), 38.18 (d, *J* = 58.5 Hz), 27.78 (s), 21.22 (s). HRMS calcd for $C_{29}H_{33}OP$: $[M+H]^+$ 429.2342, found 429.2337.



Di-tert-butyl(9-(p-tolyl)pyren-1-yl)phosphine oxide (**3ka**)

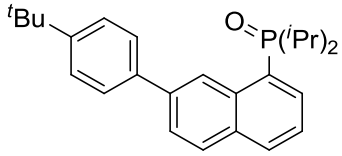
Flash slica gel chromatography (petroleum ether : ethyl acetate = 3:1 to 2:1) to afford **3ka** as a yellow solid in 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (s, 1H), 8.37 (d, *J* = 7.9 Hz, 1H), 8.28 – 8.18 (m, 3H), 8.13 (dd, *J* = 8.0, 1.8 Hz, 1H), 8.08 (d, *J* = 8.9 Hz, 1H), 7.98 (t, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 2H), 2.46 (s, 3H), 1.40 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.49 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.23 (s), 138.09 (s), 137.13 (d, *J* = 4.4 Hz), 136.91 (s), 133.12 (d, *J* = 2.5 Hz), 131.31 (s), 130.28 (s), 129.90 (s),

129.74 (s), 129.32 (d, *J* = 11.6 Hz), 129.08 (s), 127.22 (d, *J* = 2.7 Hz), 126.77 (s), 126.03 (s), 125.81 (s), 125.04 (s), 124.79 (d, *J* = 9.1 Hz), 124.58 (s), 123.18 (d, *J* = 77.2 Hz), 121.99 (d, *J* = 12.4 Hz), 37.86 (d, *J* = 58.7 Hz), 27.73 (s), 21.30 (s). HRMS calcd for $C_{31}H_{33}OP$: $[M+H]^+$ 453.2342, found 453.2337.



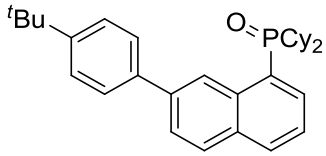
1 **2g** **3**

A 15.00 mL test tube equipped with a rubber septum and magnetic stir bar was charged **1** (0.1 mmol, 1.0 equiv), **2g** (0.15 mmol, 1.5 equiv), CuI (0.01 mmol, 10 mol %) and DCE (0.5 mL) under air. The mixture was stirred at 100 °C for 8 h (monitored by TLC). After cooling to room temperature, the solvent was removed under vaccum directly. The crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate.



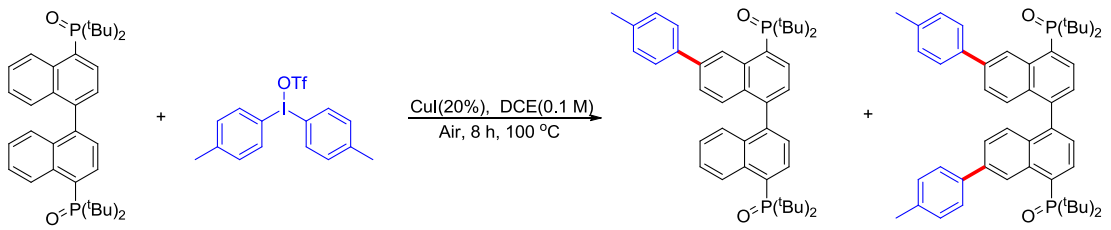
(7-(4-(tert-butyl)phenyl)naphthalen-1-yl)diisopropylphosphine oxide (**3ma**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 2:1) to afford **3ma** as a pale yellow colloid in 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.83 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.53 – 7.46 (m, 3H), 2.60 – 2.47 (m, 2H), 1.37 (s, 9H), 1.33 (dd, *J* = 14.9, 7.0 Hz, 6H), 1.08 (dd, *J* = 15.8, 7.2 Hz, 6H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.57 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.63 (s), 139.17 (s), 137.84 (s), 132.94 (d, *J* = 8.4 Hz), 132.37 (d, *J* = 6.5 Hz), 132.17 (d, *J* = 2.8 Hz), 129.23 (s), 127.10 (s), 125.93 (s), 125.64 (s), 124.73 (s), 124.03 (d, *J* = 12.1 Hz), 34.58 (s), 31.37 (s), 27.13 (d, *J* = 65.9 Hz), 16.20 (dd, *J* = 57.7, 2.5 Hz). HRMS calcd for $C_{26}H_{33}OP$: $[M+H]^+$ 393.2342, found 393.2337.



(7-(4-(tert-butyl)phenyl)naphthalen-1-yl)dicyclohexylphosphine oxide (**3na**)

Flash slica gel chromatography (petroleum ether : ethyl acetate = 4:1 to 2:1) to afford **3na** as a pale yellow colloid in 41% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.83 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 3H), 7.50 (d, *J* = 8.3 Hz, 3H), 2.32 – 2.13 (m, 4H), 1.84 (d, *J* = 10.3 Hz, 2H), 1.75 – 1.60 (m, 6H), 1.46 – 1.35 (m, 11H), 1.35 – 1.20 (m, 6H), 1.19 – 1.09 (m, 2H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 50.75 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.57 (s), 139.08 (s), 137.87 (s), 132.93 (d, *J* = 8.3 Hz), 132.01 (d, *J* = 2.8 Hz), 129.14 (s), 127.11 (s), 125.91 (s), 125.62 (s), 124.39 (dd, *J* = 77.4, 12.6 Hz), 36.97 (d, *J* = 61.0 Hz). 34.59 (s), 31.38 (s), 26.59 (d, *J* = 3.5 Hz), 26.47 (d, *J* = 2.7 Hz), 25.80 (s), 25.66 (d, *J* = 2.3 Hz), 25.41 (s). HRMS calcd for $C_{32}H_{41}OP$: $[M+H]^+$ 473.2968, found 473.2965.



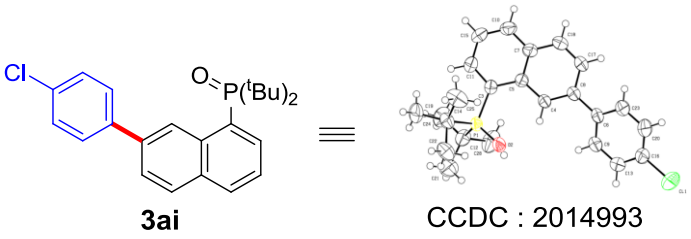
1o **2a** **3oa** **3oa'**

A 15.00 mL test tube equipped with a rubber septum and magnetic stir bar was charged **1o** (0.1 mmol, 1.0 equiv), **2a** (0.3 mmol, 3.0 equiv), CuI (0.02 mmol, 20 mol %) and DCE (1 mL) under air. The mixture was stirred at 100 °C for 8 h (monitored by TLC). After cooling to room temperature, the solvent was removed under vaccum directly. The crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (2:1 to 1:1) afforded **3oa** and **3oa'**respectively.

3oa as a pale yellow colloid in 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (d, *J* = 1.6 Hz, 1H), 10.07 (d, *J* = 8.8 Hz, 1H), 7.89 (dd, *J* = 12.3, 7.4 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.65 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.50 (dd, *J* = 7.4, 2.4 Hz, 1H), 7.45 (dd, *J* = 7.3, 2.3 Hz, 1H), 7.41 – 7.33 (m, 3H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.38 (s, 3H), 1.49 – 1.41 (m, 36H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.54 (s), 59.25 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.92 (d, *J* = 2.6 Hz), 141.74 (d, *J* = 2.2 Hz), 138.81 (s), 137.78 (d, *J* = 4.6 Hz), 137.63 (s), 137.39 (d, *J* = 4.8 Hz), 137.25 (s), 133.14 (d, *J* = 8.1 Hz), 132.19 (d, *J* = 8.0 Hz), 130.57 (d, *J* = 11.0 Hz), 130.10 (d, *J* = 11.1 Hz), 129.64 (s), 128.33 (d, *J* = 1.6 Hz), 127.24 (s), 127.02 (s), 126.52 (d, *J* = 5.7 Hz), 125.98 (dd, *J* = 75.4, 2.0 Hz), 125.55 (s), 124.57 (d, *J* = 13.3 Hz), 124.35 (d, *J* = 12.9 Hz), 37.90 (dd, *J* = 58.7, 2.4 Hz), 27.71 (dd, *J* = 7.3, 5.1 Hz), 21.15 (s). HRMS calcd for $C_{43}H_{54}O_2P_2$: $[M+H]^+$ 665.3672, found 665.3667.

3oa' as a white solid in 31% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.40 (d, *J* = 1.4 Hz, 2H), 7.91 (dd, *J* = 12.3, 7.4 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 4H), 7.67 (dd, *J* = 8.9, 1.7 Hz, 2H), 7.49 (d, *J* = 2.2 Hz, 1H), 7.48 – 7.45 (m, 2H), 7.44 (s, 1H), 7.25 (d, *J* = 6.5 Hz, 4H), 2.38 (s, 6H), 1.47 (dd, *J* = 13.5, 7.6 Hz, 36H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.82 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.75 (d, *J* = 2.2 Hz), 138.88 (s), 137.78 (d, *J* = 4.6 Hz), 137.63 (s), 137.29 (s), 132.20 (d, *J* = 8.0 Hz), 130.63 (d, *J* = 11.1 Hz), 129.67 (s), 127.27 (s), 127.08 (s), 126.67 (d, *J* = 75.4 Hz), 125.63 (s), 124.35 (d, *J* = 12.9 Hz), 37.93 (dd, *J* = 58.6, 3.1 Hz), 27.76 (d, *J* = 6.6 Hz), 21.18 (s). HRMS calcd for $C_{50}H_{60}O_2P_2$: $[M+H]^+$ 755.4141, found 755.4137.

6. Crystallographic data



3ai CCDC : 2014993

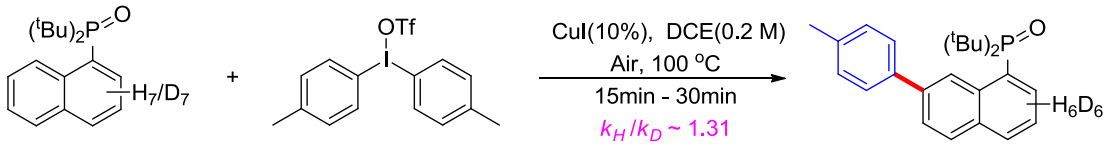
Table S5. Crystal data and structure refinement for **3ai**.

Identification code	3ai
Empirical formula	$C_{24}H_{28}ClOP$
Formula weight	398.88
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P-1
a/Å	11.7689(4)
b/Å	15.1355(6)
c/Å	13.0960(5)
α/°	90
β/°	111.370(4)
γ/°	90
Volume/$Å^3$	2172.39(15)
Z	4
ρcalcg/cm^3	1.22
μ/mm^{-1}	2.32
F(000)	848
Crystal size/mm^3	0.17×0.15×0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.15 to 69.875
Index ranges	$-14 \leq h \leq 13$, $-18 \leq k \leq 15$, $-10 \leq l \leq 15$
Reflections collected	7989
Independent reflections	3830
Data/restraints/parameters	3830/0/250
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0477, wR_2 = 0.1175
Final R indexes [all data]	R_1 = 0.0687, wR_2 = 0.1267
Largest diff. peak/hole / e $Å^{-3}$	0.350/-0.453

Single crystals of $C_{24}H_{28}ClOP$ (**3ai**) was collected. A suitable crystal was selected and collected on a SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation. Refined structure and crystallographic parameters are summarized in Figure S1 and Table S3. CCDC 2014993 contains the supplementary crystallographic data for **3ai**. The crystallographic data of the compound can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

7. Investigation of the reaction mechanism

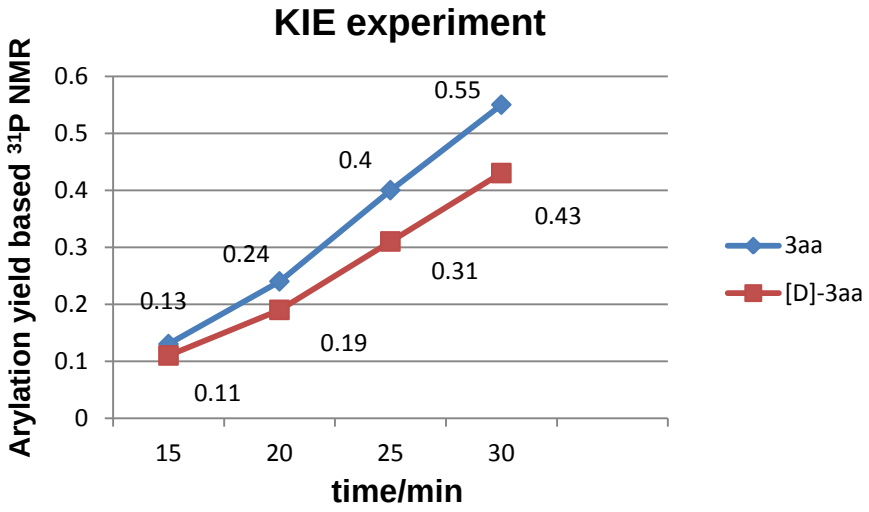
7.1 Kinetic isotope effect



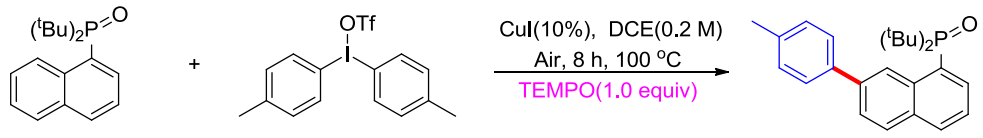
1a/[D_7]-1a **2a, 1.5 equiv** **3aa/[D_6]-3aa**

[D_7]-1a was prepared according to the reported literature[4] and then proceed to GP 1.

KIE measurement: Normal substrate **1a** (0.1 mmol, 1.0 equiv) or deuterated substrate **[D_7]-1a** (0.1 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), CuI (10 mol %), were suspended in 0.5 mL DCE. The tube was sealed and the mixture was then heated at 100 ℃. Four tubes were carried out in parallel. At the time point of 15, 20, 25 and 30 minutes, a tube was taken out from the oil bath. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (5 mL) and filtered through a celite pad. The organic layer was washed with saturated salt water (5 mL) and extracted with ethyl acetate (2×5 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The resulting residue and triphenyl phosphine oxide as an internal standard were dissolved in $CDCl_3$ for ^{31}P-NMR analysis. KH/KD (~1.31) was estimated based on the ratio of phosphorus yield.



7.2 Radical capture experiment

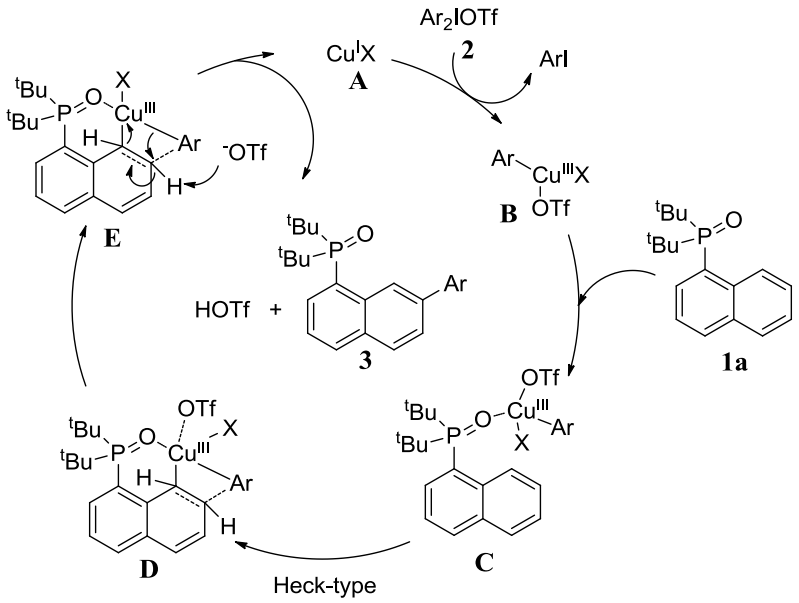


1a **2a, 1.5 equiv** **3aa, 50%**

A 15.00 mL test tube equipped with a rubber septum and magnetic stir bar was charged **1a** (0.1 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), CuI (0.01 mmol, 10 mol %) 2,2,6,6-tetramethylpiperidinooxy (0.1 mmol, 1.0 equiv) and DCE (0.5 mL) under air. The mixture was stirred at 100 °C for 8 h. After cooling to room temperature, the solvent was removed

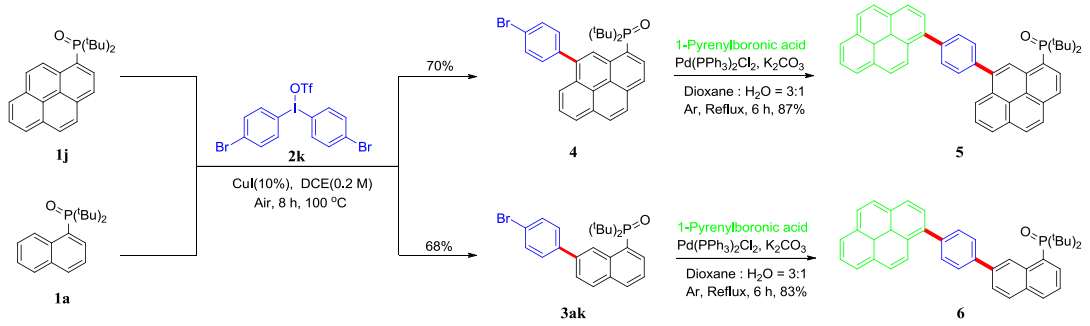
under vaccum directly. The crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (3:1) to afford **3aa** in 50% yield.

7.3 Reasonable reaction mechanism



A plausible reaction mechanism was shown in **7.3**. Firstly, oxidative addition of the CuI species to active intermediate B of Cu^{III} by diaryliodonium triflate salts occurred. Then Cu^{III} species coordinated to the oxygen atom of the P=O group leadind to the formation of complex C. Next, the bond of aryl group to copper inserted to naphthalene and generated four membered-ring transition state D via the Heck-type, leading to the formation of intermediate E with the departure of trifluoromethanesulfonic acid anion. Finally, arylated product was obtained with the generation of HOTf through a base-assisted E2-type elimination and Cu^{I} entered the next catalytic cycle.[5]

8. Synthesis of potential fluorescent molecules 5 and 6



8.1 Synthesis of 5

Step 1：A 15.00 mL test tube equipped with a rubber septum and magnetic stir bar was charged **1j** (0.1 mmol, 1.0 equiv), **2k** (0.15 mmol, 1.5 equiv), CuI (0.01 mmol, 10 mol %) and DCE (0.5 mL) under air. The mixture was stirred at 100 ^{o}C for 8 h (monitored by TLC). After cooling to room temperature, the solvent was removed under vaccum directly. The crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (3:1) to afford **4** as a pale yellow solid in 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 8.28 – 8.21 (m, 3H), 8.19 (d, *J* = 8.9 Hz, 1H), 8.16 (dd, *J* = 8.1, 2.3 Hz, 1H), 8.08 (d, *J* = 8.9 Hz, 1H), 7.98 (t, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 1.40 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.62 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.01 (s), 138.88 (s), 136.85 (d, *J* = 4.4 Hz), 133.12 (d, *J* = 2.6 Hz), 132.05 (s), 131.60 (s), 131.37 (s), 129.77 (s), 129.44 (d, *J* = 4.0 Hz),

129.35 (s), 127.48 (d, *J* = 2.6 Hz), 126.91 (s), 126.13 (d, *J* = 14.3 Hz), 124.91 (d, *J* = 9.0 Hz), 124.56 (s), 123.47 (d, *J* = 76.6 Hz), 122.42 (d, *J* = 12.4 Hz), 121.53 (s), 37.86 (d, *J* = 58.7 Hz), 27.70 (s). HRMS calcd for $C_{30}H_{30}BrOP$: $[M+H]^+$ 517.1290, found 517.1285.

Step 2 : To a solution of substrate **4** (0.1 mmol, 1.0 equiv) in dioxane (1.5 mL) was added 1-pyrenylboronic acid (0.15 mmol 1.5 equiv), $Pd(PPh_3)Cl_2$ (5% mol) and 4 M potassium carbonate aqueous solution (0.5 mL) at rt. The mixtue was refluxed for 6 h under Ar. After cooling to room temperature, the reaction mixture was diluted with water (5 mL) and extracted with ethyl acetate (2×5 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (3:1 to 2:1) to afford **5** as a yellow solid with fluorescence in 87%. ^1H NMR (400 MHz, $CDCl_3$) δ 10.42 (s, 1H), 8.56 (d, *J* = 7.7 Hz, 1H), 8.43 (d, *J* = 9.2 Hz, 1H), 8.32 – 8.15 (m, 7H), 8.15 – 8.09 (m, 5H), 8.08 (t, *J* = 6.1 Hz, 1H), 8.05 – 7.99 (m, 1H), 7.91 (d, *J* = 8.1 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 2H), 1.45 (d, *J* = 13.4 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.69 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.23 (s), 140.08 (s), 140.00 (d, *J* = 0.5 Hz), 137.81 (s), 137.14 (d, *J* = 4.4 Hz), 133.19 (d, *J* = 2.5 Hz), 131.56 (s), 131.41 (s), 131.14 (s), 130.66 (s), 130.63 (s), 130.46 (s), 129.84 (d, *J* = 4.3 Hz), 129.43 (d, *J* = 11.6 Hz), 128.68 (s), 127.78 (s), 127.49 (t, *J* = 7.3 Hz), 126.88 (s), 126.21 (s), 126.01 (s), 125.72 (s), 125.05 (s), 125.02 (s), 124.89 (s), 124.76 (s), 124.67 (s), 123.37 (d, *J* = 77.0 Hz), 122.23 (d, *J* = 12.3 Hz), 37.92 (d, *J* = 58.7 Hz), 27.78 (s). HRMS calcd for $C_{46}H_{39}OP$: $[M+H]^+$ 639.2811, found 639.2807.

8.2 Synthesis of 6

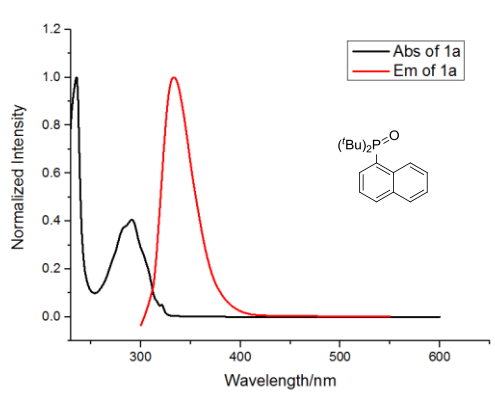
Step 1：A 15.00 mL test tube equipped with a rubber septum and magnetic stir bar was charged **1a** (0.1 mmol, 1.0 equiv), **2k** (0.15 mmol, 1.5 equiv), CuI (0.01 mmol, 10 mol %) and DCE (0.5 mL) under air. The mixture was stirred at 100 ^oC for 8 h (monitored by TLC). After cooling to room temperature, the solvent was removed under vaccum directly. The crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (3:1) to afford **3ak** as a white solid in 68%. (previously mentioned data)

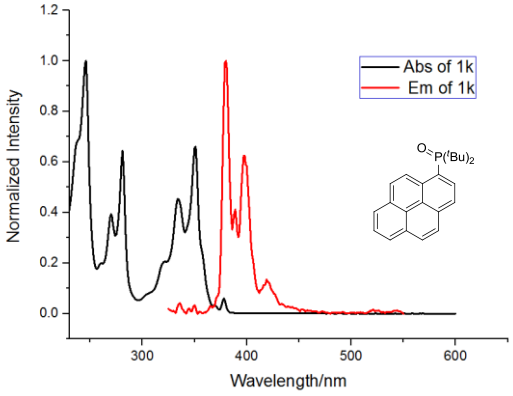
Step 2 : To a solution of substrate **3ak** (0.1 mmol, 1.0 equiv) in dioxane (1.5 mL) was added 1-pyrenylboronic acid (0.15 mmol 1.5 equiv), $Pd(PPh_3)Cl_2$ (5% mol) and 4 M potassium carbonate aqueous solution (0.5 mL) at rt. The mixtue was refluxed for 6 h under Ar. After cooling to room temperature, the reaction mixture was diluted with water (5 mL) and extracted with ethyl acetate (2×5 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (3:1 to 2:1) to afford **6** as a yellow solid with fluorescence in 83%. ^1H NMR (400 MHz, $CDCl_3$) δ 10.45 (s, 1H), 8.29 (d, *J* = 9.3 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 8.20 – 8.15 (m, 2H), 8.08 (s, 2H), 8.07 – 7.97 (m, 6H), 7.94 (s, 2H), 7.80 (dd, *J* = 12.3, 7.2 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.46 (td, *J* = 8.0, 2.1 Hz, 1H), 1.40 (d, *J* = 13.5 Hz, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.66 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.21 (s), 139.96 (s), 138.71 (s), 137.66 (d, *J* = 4.5 Hz), 137.53 (s), 133.41 (d, *J* = 8.0 Hz), 132.01 (d, *J* = 2.8 Hz), 131.54 (s), 131.41 (s), 131.30 (s), 131.20 (s), 131.09 (s), 130.63 (s), 129.05 (s), 128.60 (s), 127.61 (s), 127.53 (s), 127.44 (d, *J* = 3.8 Hz), 126.67 (d, *J* = 75.6 Hz), 126.07 (d, *J* = 1.9 Hz), 126.01 (s), 125.47 (d, *J* = 8.4 Hz), 125.07 (s), 124.99 (s), 124.80 (d, *J* = 14.7 Hz), 122.86 (d, *J* = 12.9 Hz), 37.78 (d, *J* = 58.5 Hz), 27.66 (s). HRMS calcd for $C_{40}H_{37}OP$: $[M+H]^+$ 565.2655, found 565.2653.

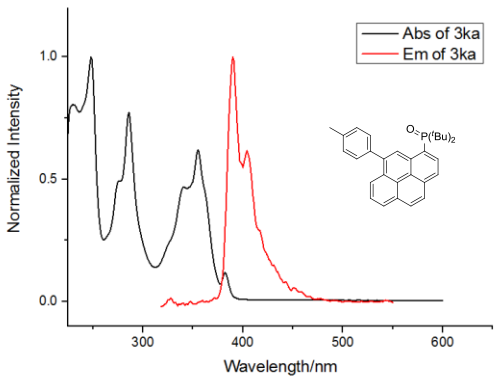
9. Photophysical properties

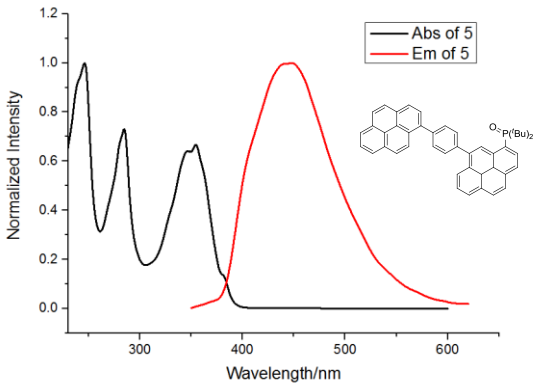
9.1. Photophysical data and spectra of 1a, 1k, 3ka, 5 and 6

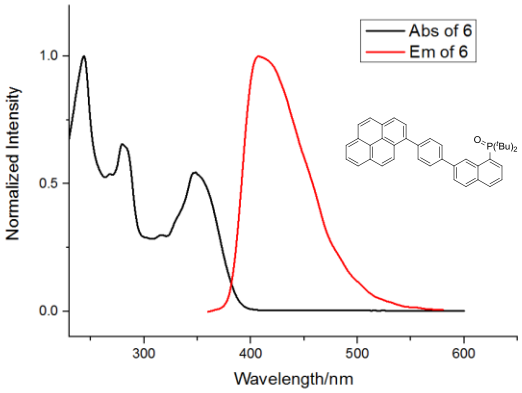
Compounds	$\lambda_{abs}{}^{a}$ (nm)	$\lambda_{em}{}^{b}$ (nm)	$\tau_F{}^{c}$ (ns)
1a	236, 291	333	6.88
1k	246, 270, 281, 334, 351, 378	380	26.16
3ka	230, 248, 286, 341, 355, 382	390	8.75
5	246, 285, 346, 354	448	3.42
6	244, 279, 348,	407	1.94





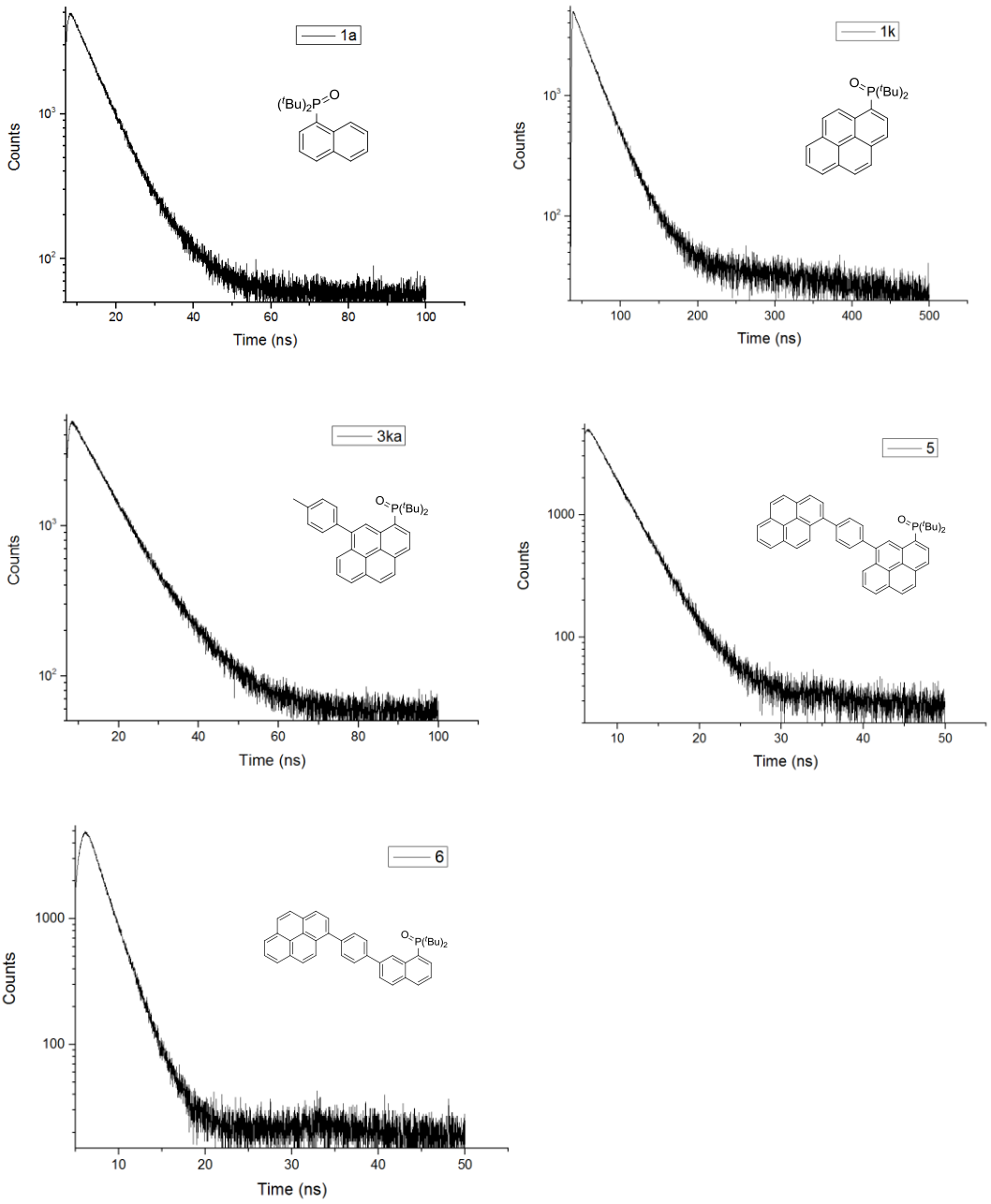






9.2. Photoluminescence lifetime of 1a, 1k, 3ka, 5 and 6 in neat film

Compounds	τ (ns)	χ^2
1a	6.88 (100%)	1.054
1k	26.16 (100%)	1.152
3ka	8.75 (100%)	1.091
5	3.42 (100%)	1.147
6	1.94 (100%)	1.266



10. Reference

[1] W.-M. Shi, X.-H. Li, C. Liang, D. L. Mo, *Adv. Synth. Catal.*, 2017, **359**, 4129.

[2] X. Li, P.-H. Cheng, G.-S. Liu, *Angew. Chem. Int. Ed.*, 2018, **57**, 15871.

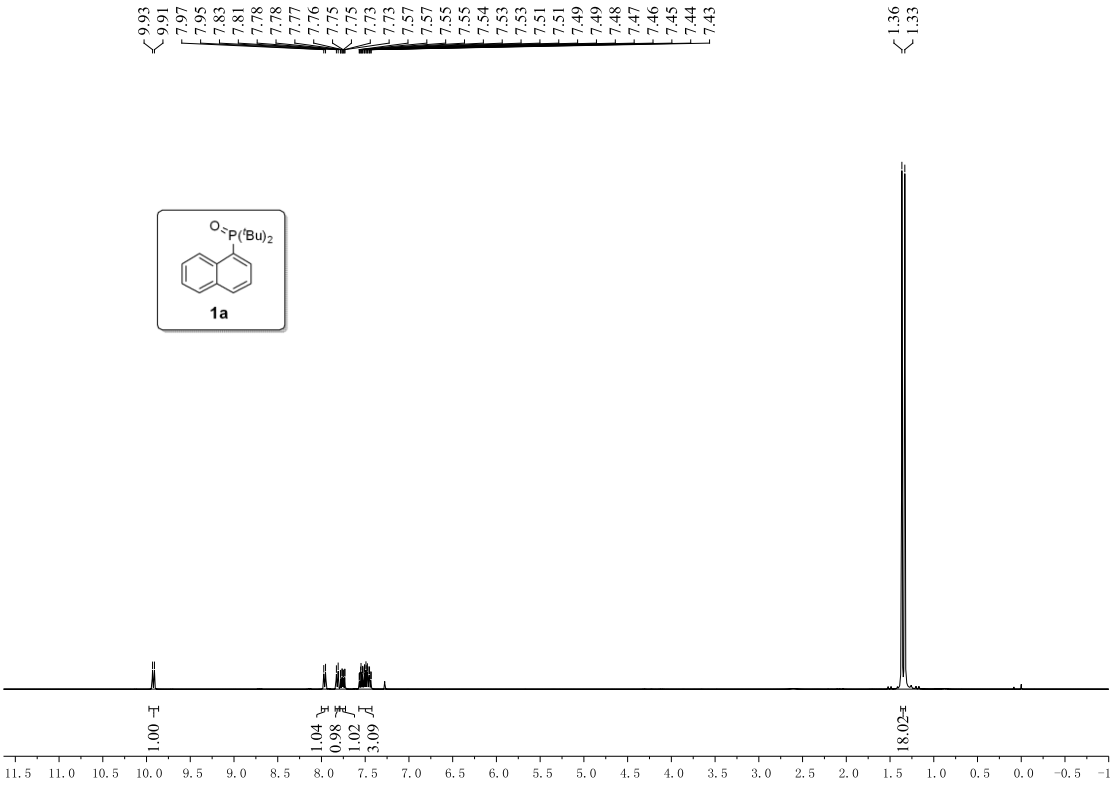
[3] M. Reitti, P. Villo, B. Olofsson, *Angew. Chem. Int. Ed.* 2016, **55**, 8928.

[4] A. J. Rago, G.-B. Dong, *Org. Lett.*, 2020, **22**, 3770.

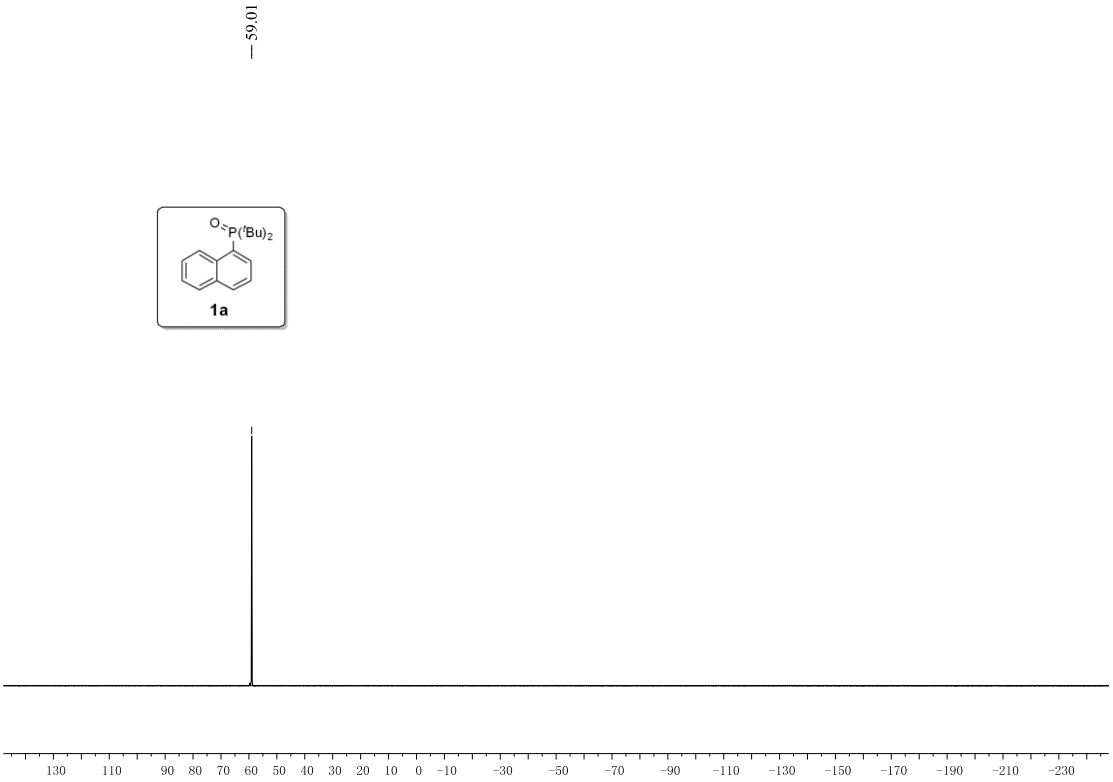
[5] a) B. Chen, X.-L. Hou, Y.-X. Li, Y.-D. Wu, *J. Am. Chem. Soc.*, 2011, **133**, 7668; b) T Wang, L.-Y. Zhou, Y.-Q. Yang, X.-H. Zhang, Z.-Z. Shi, Y.-D. Wu. *Org. Lett.* 2018, **20**, 6502.

11. Copies of NMR spectra

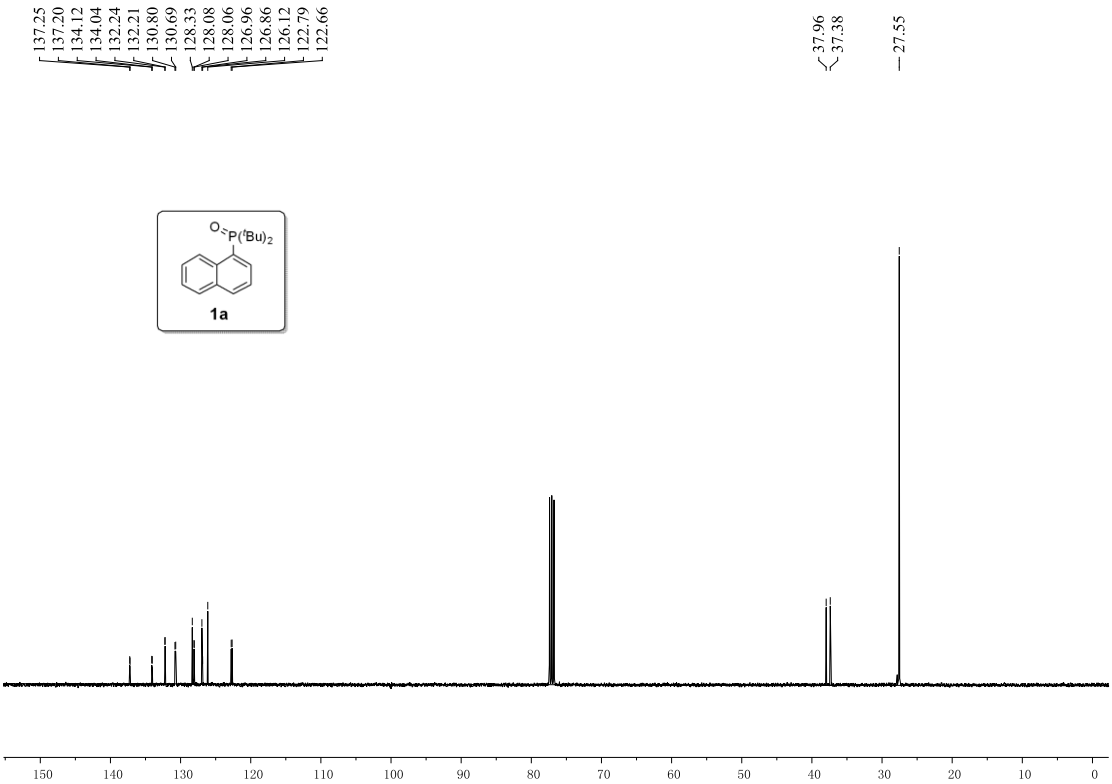
^{1}H NMR spectrum for **1a**



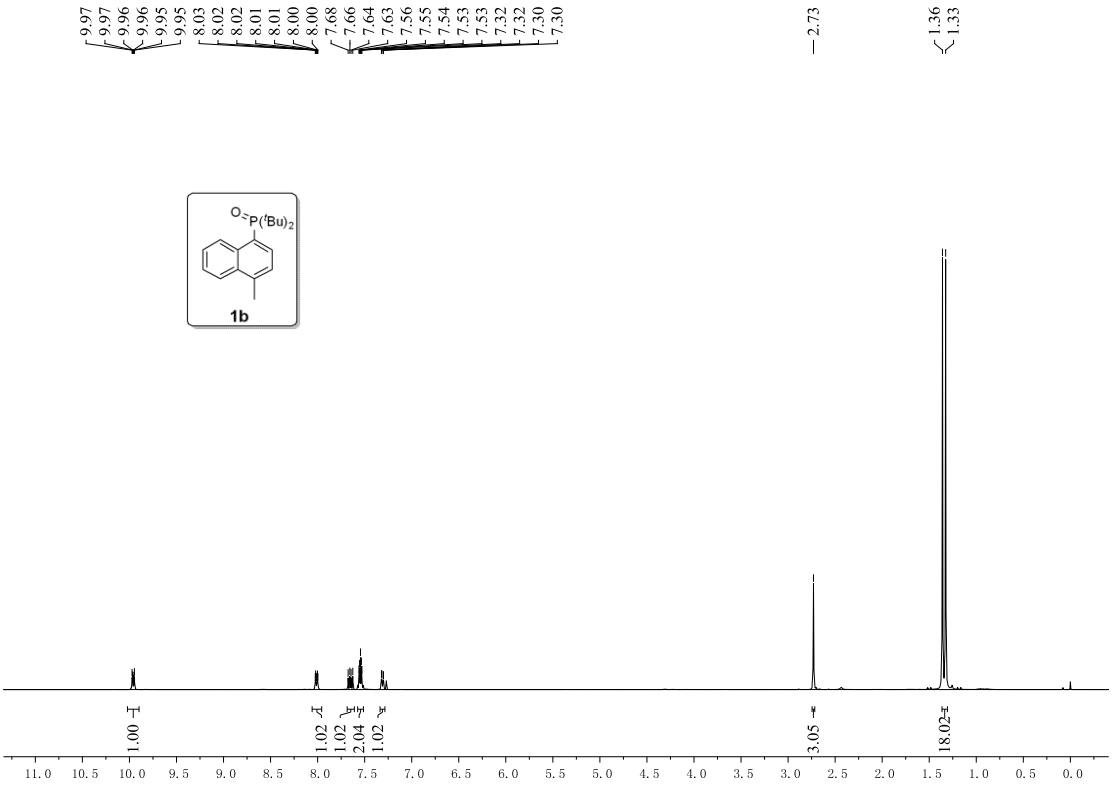
^{31}P NMR spectrum for **1a**



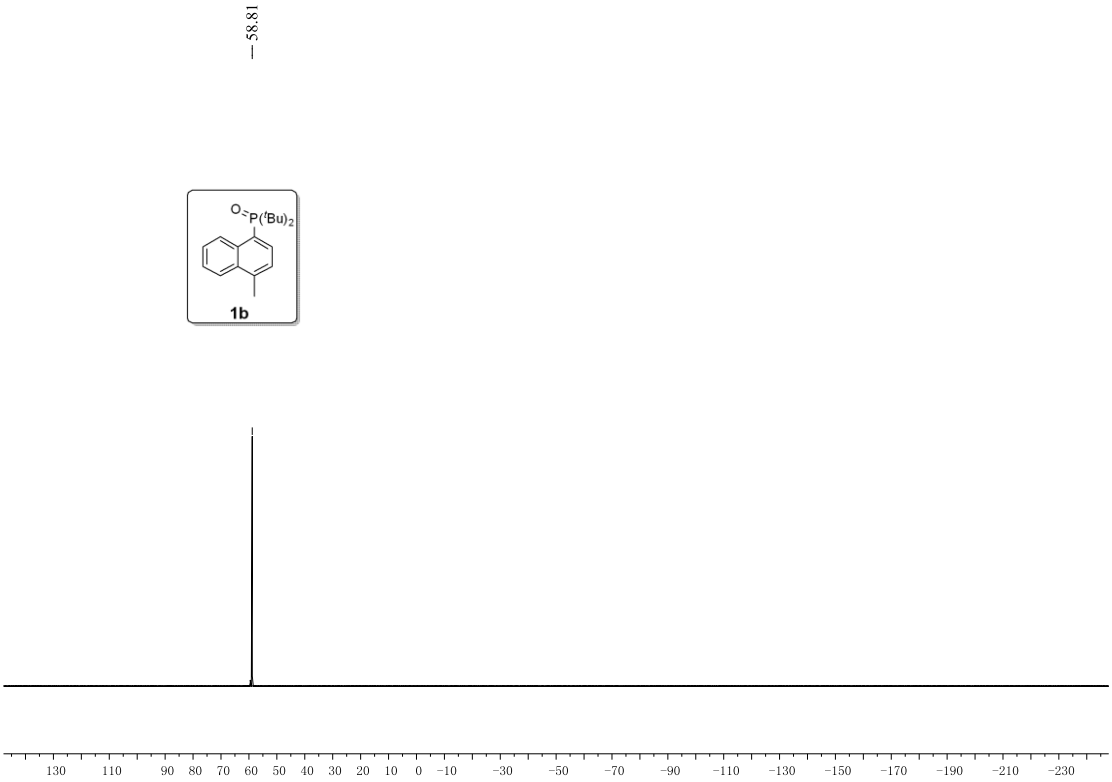
^{13}C NMR spectrum for **1a**



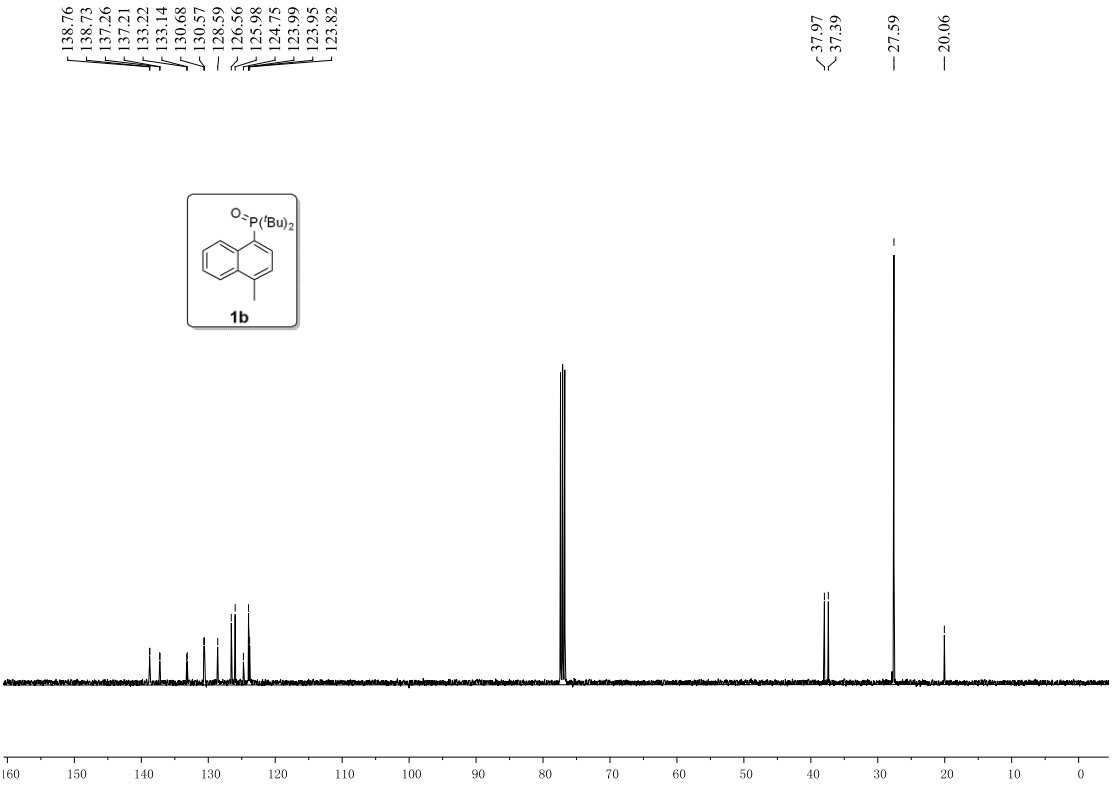
^{1}H NMR spectrum for **1b**



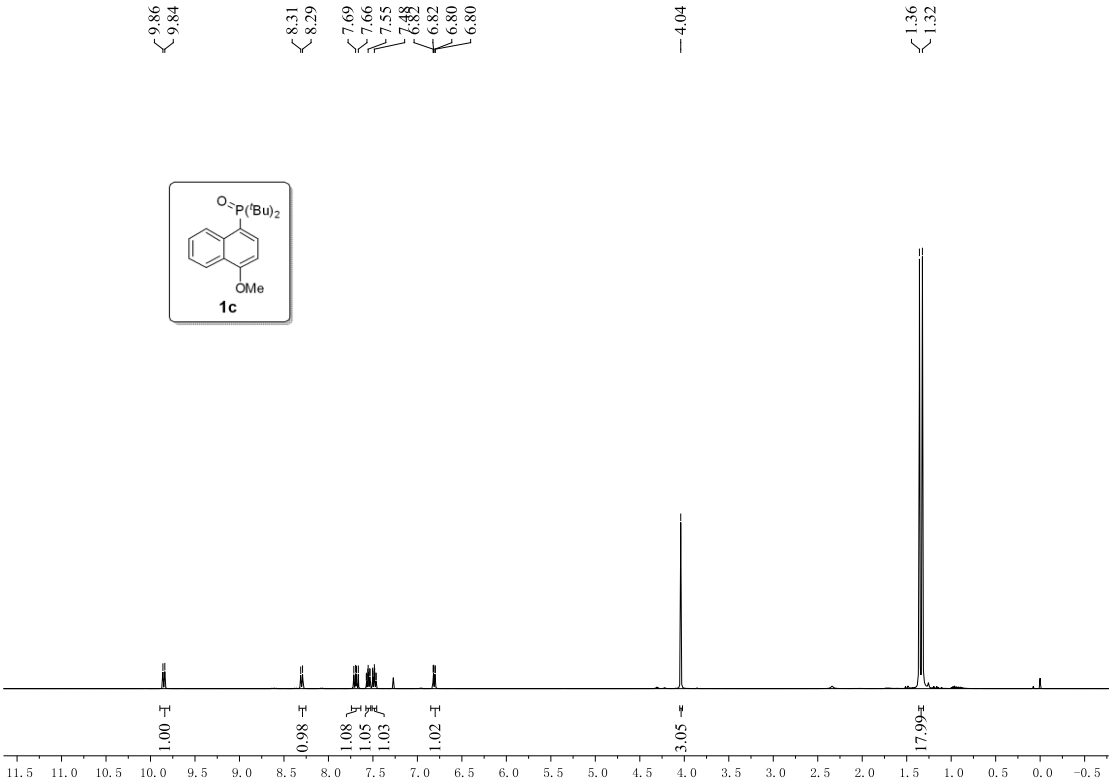
^{31}P NMR spectrum for **1b**



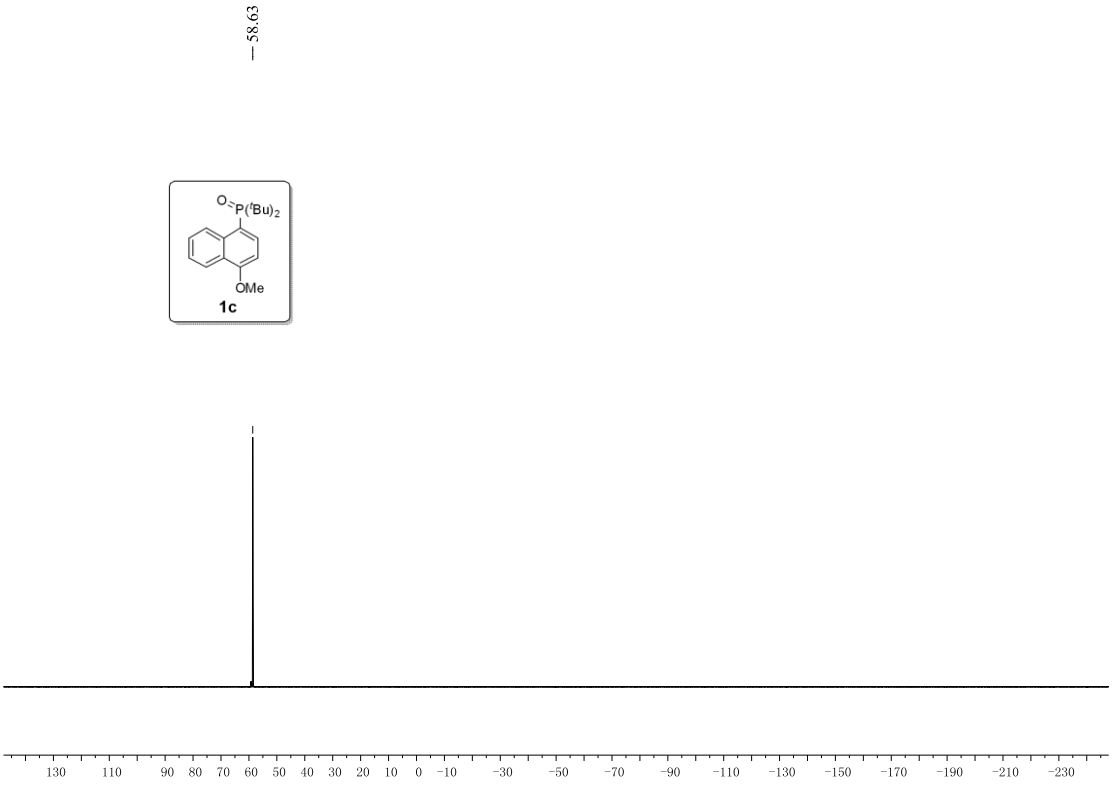
^{13}C NMR spectrum for **1b**



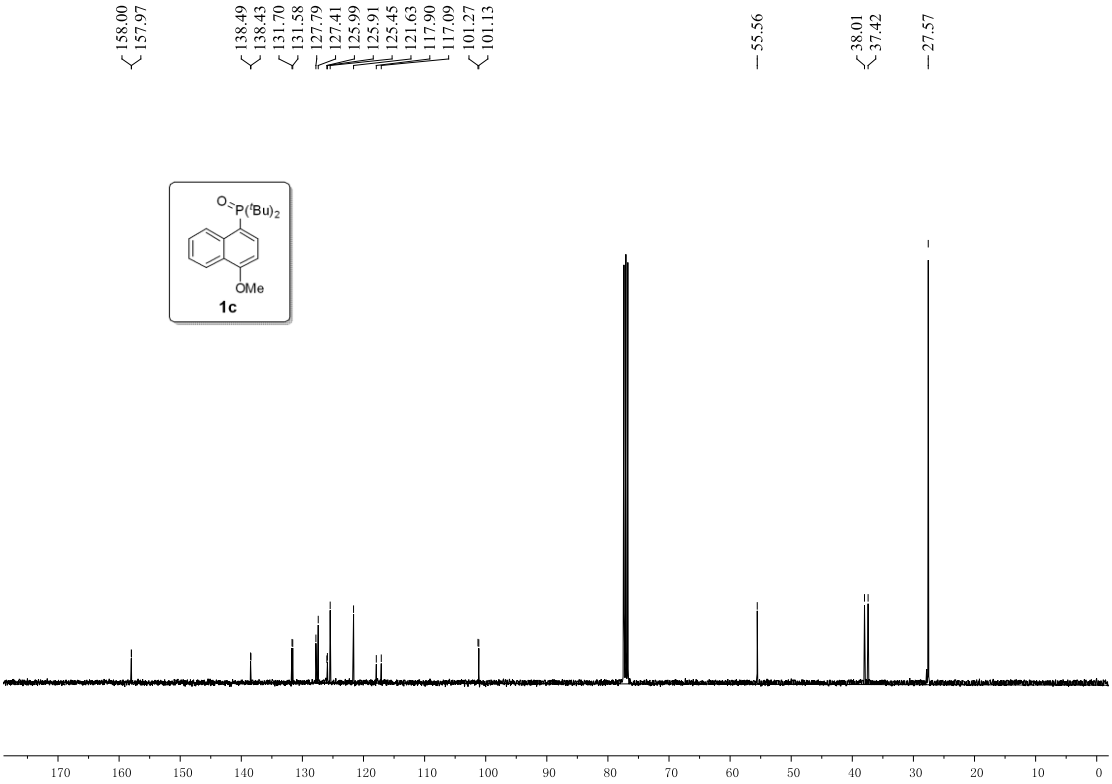
^{1}H NMR spectrum for **1c**



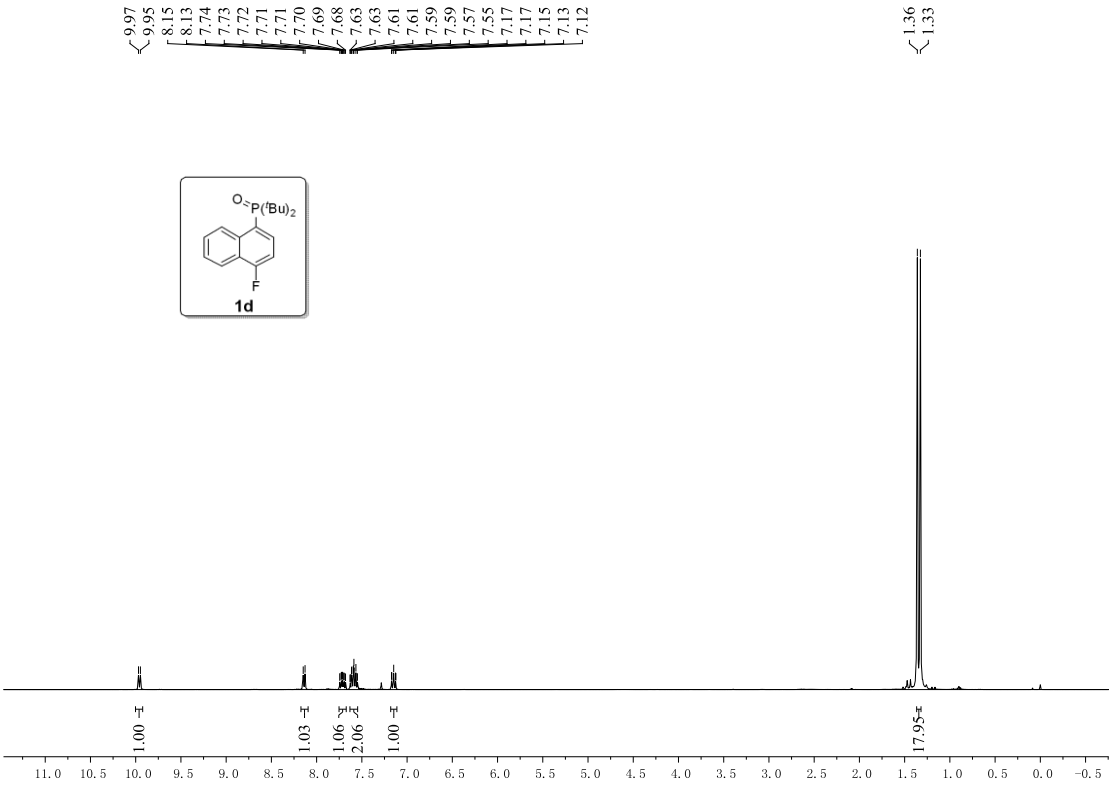
^{31}P NMR spectrum for **1c**



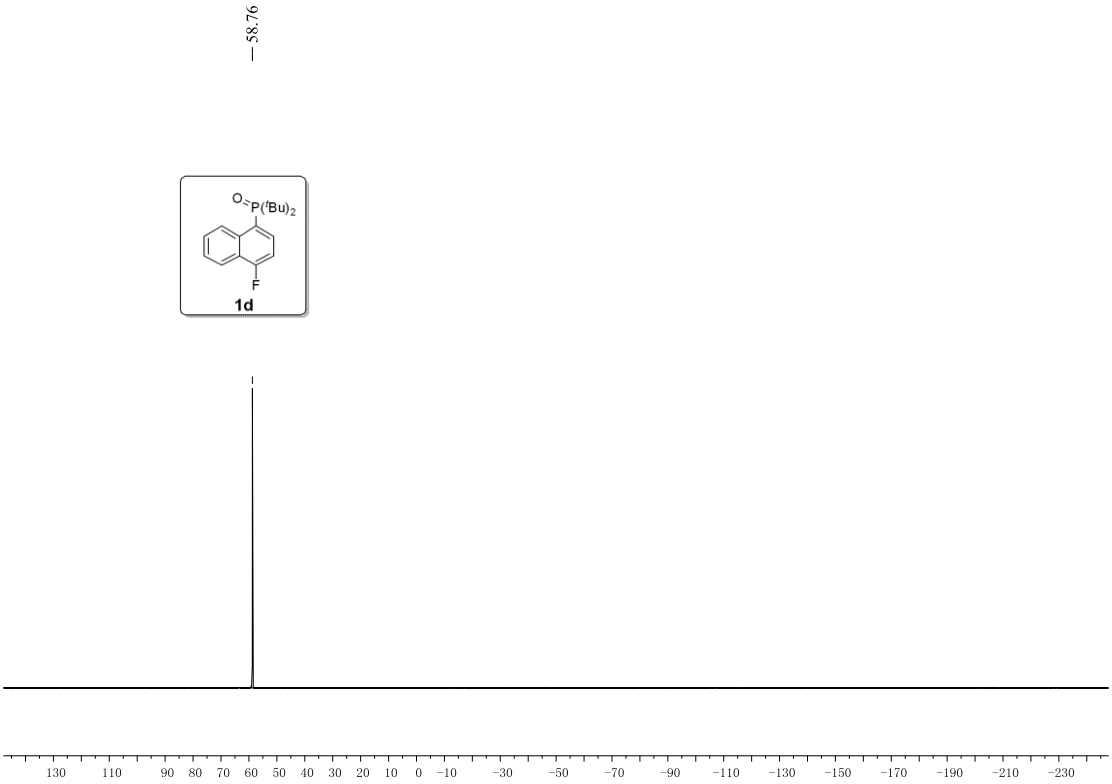
^{13}C NMR spectrum for **1c**



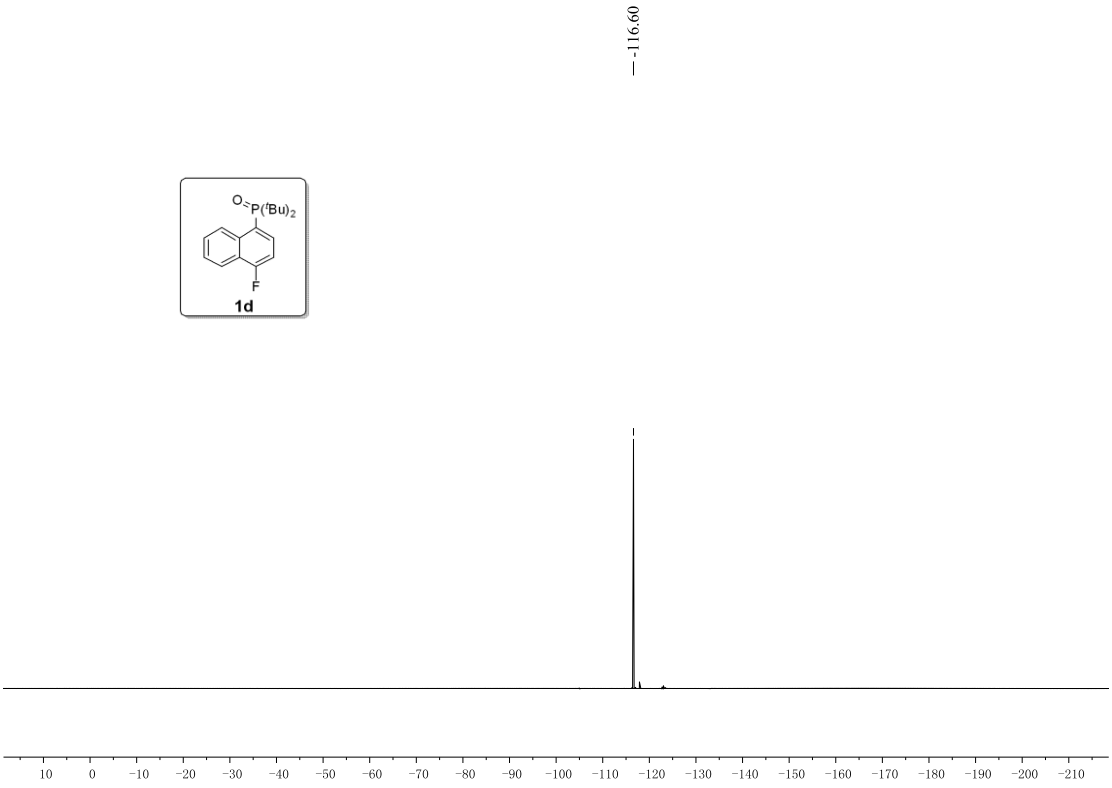
^{1}H NMR spectrum for **1d**



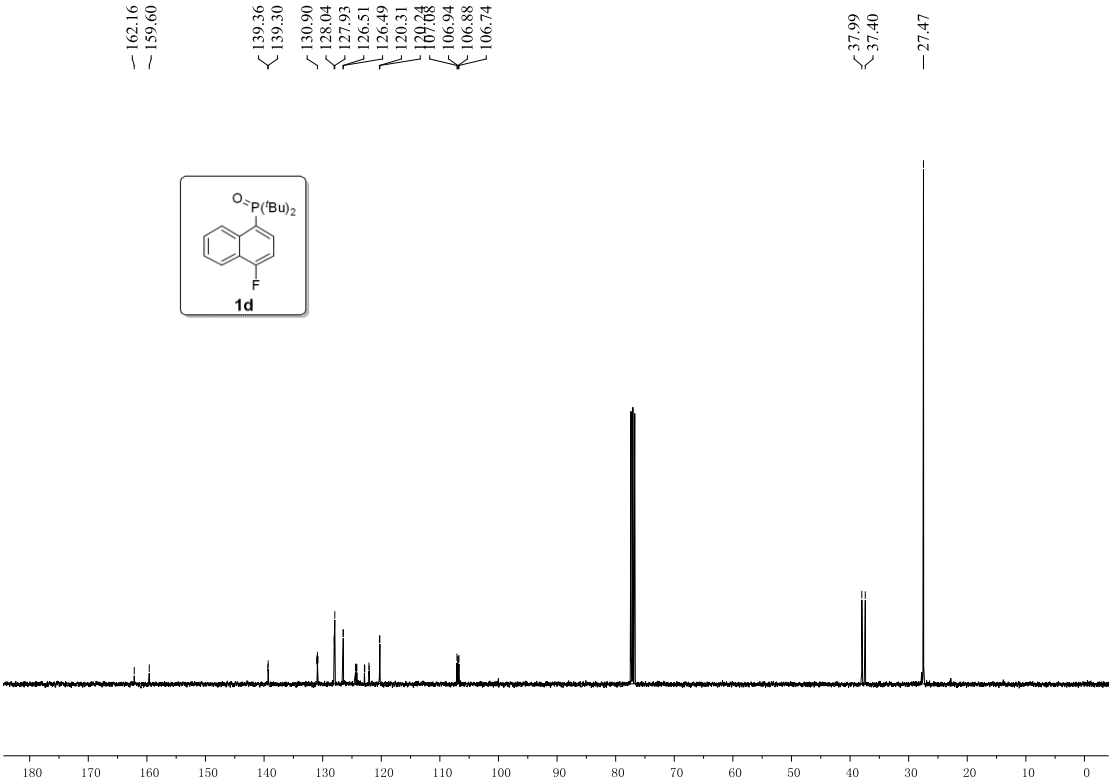
^{31}P NMR spectrum for **1d**



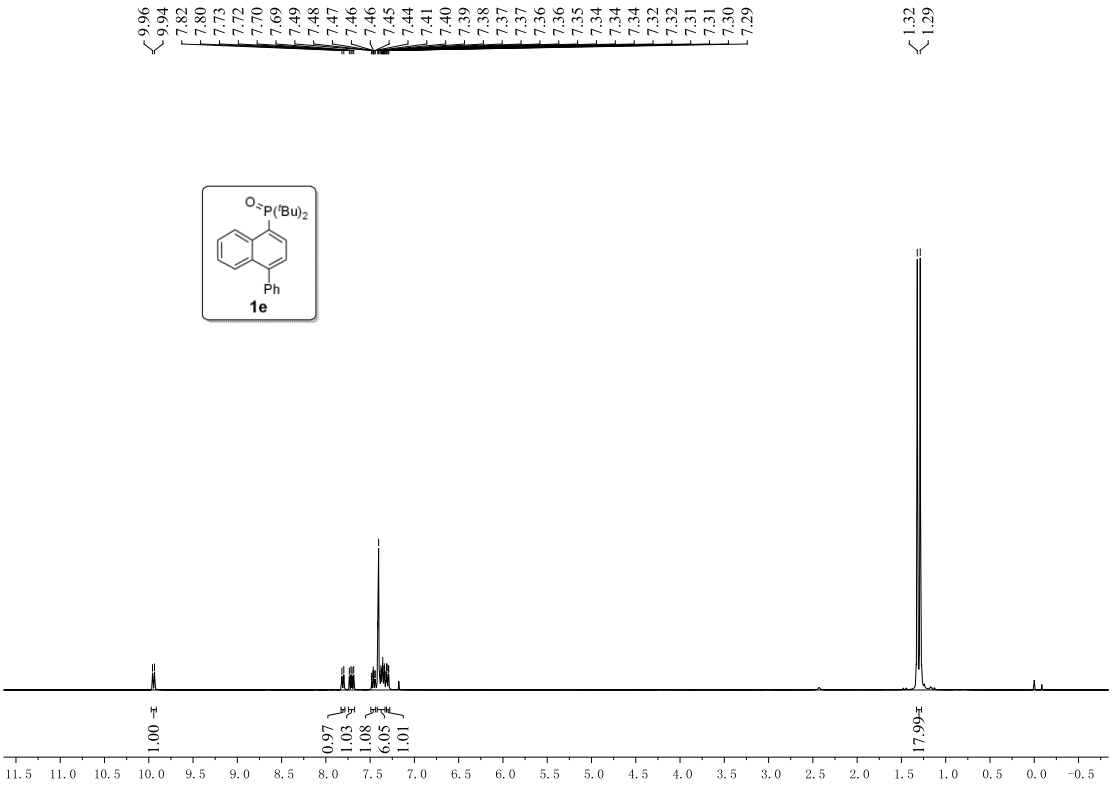
^{19}F NMR spectrum for **1d**



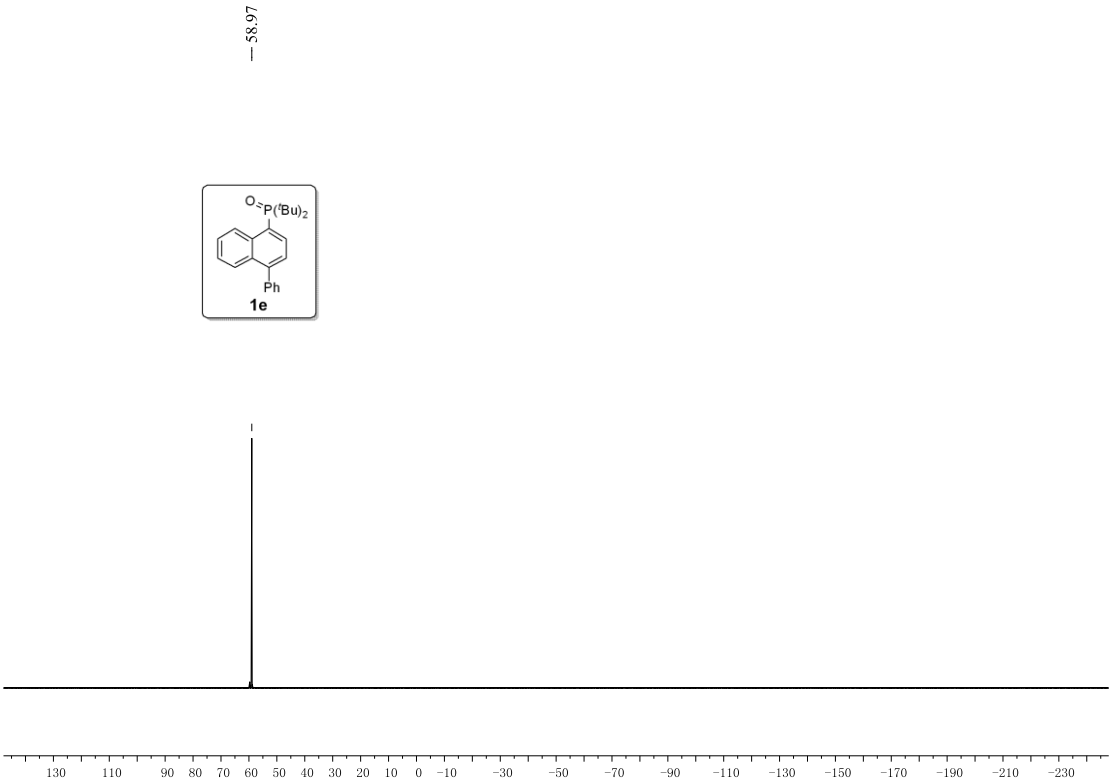
^{13}C NMR spectrum for **1d**



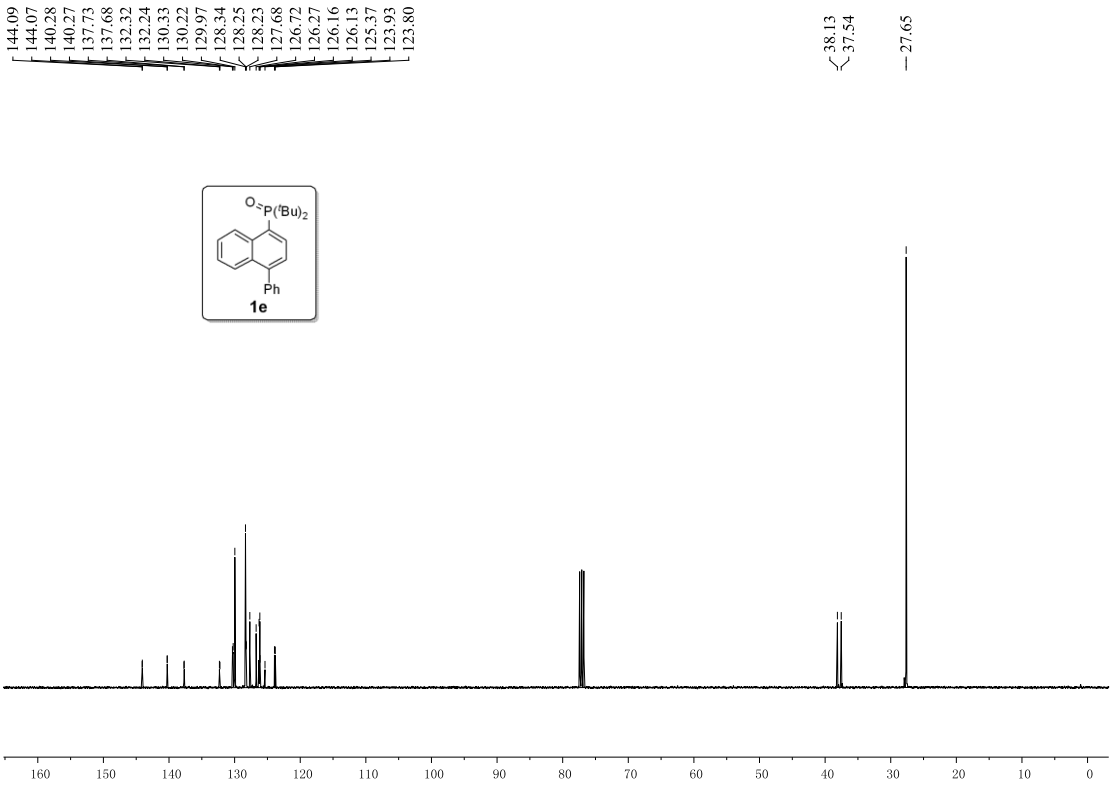
^{1}H NMR spectrum for **1e**



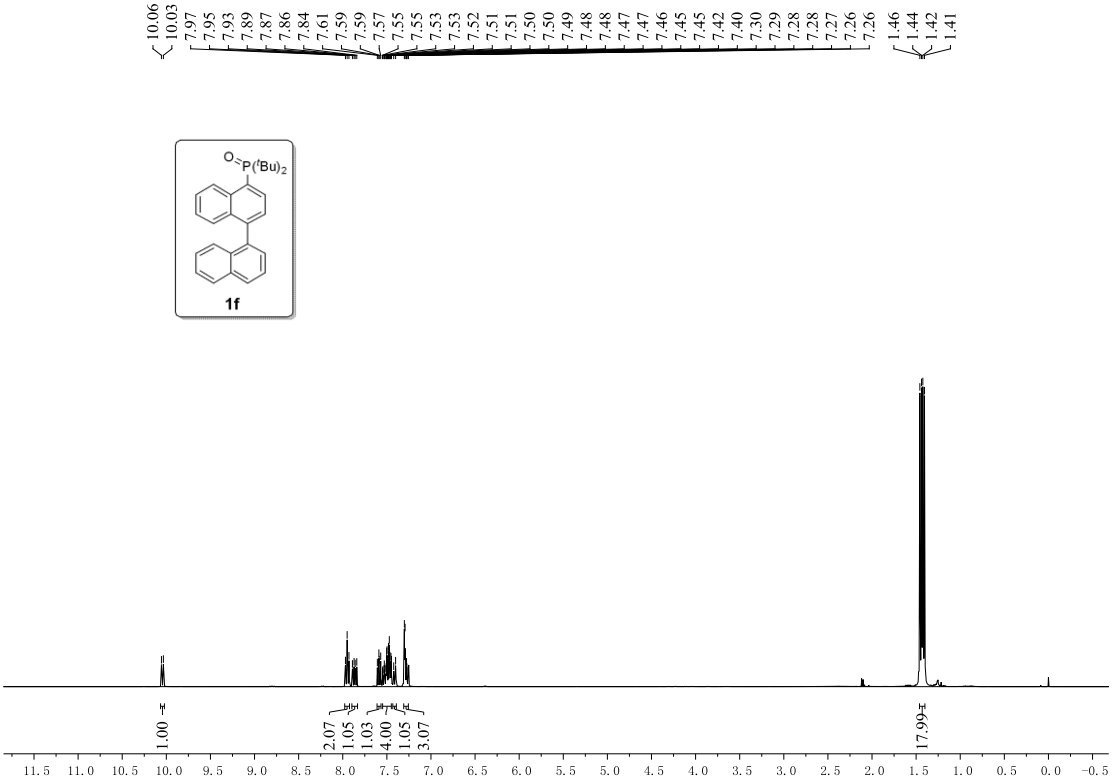
^{31}P NMR spectrum for **1e**



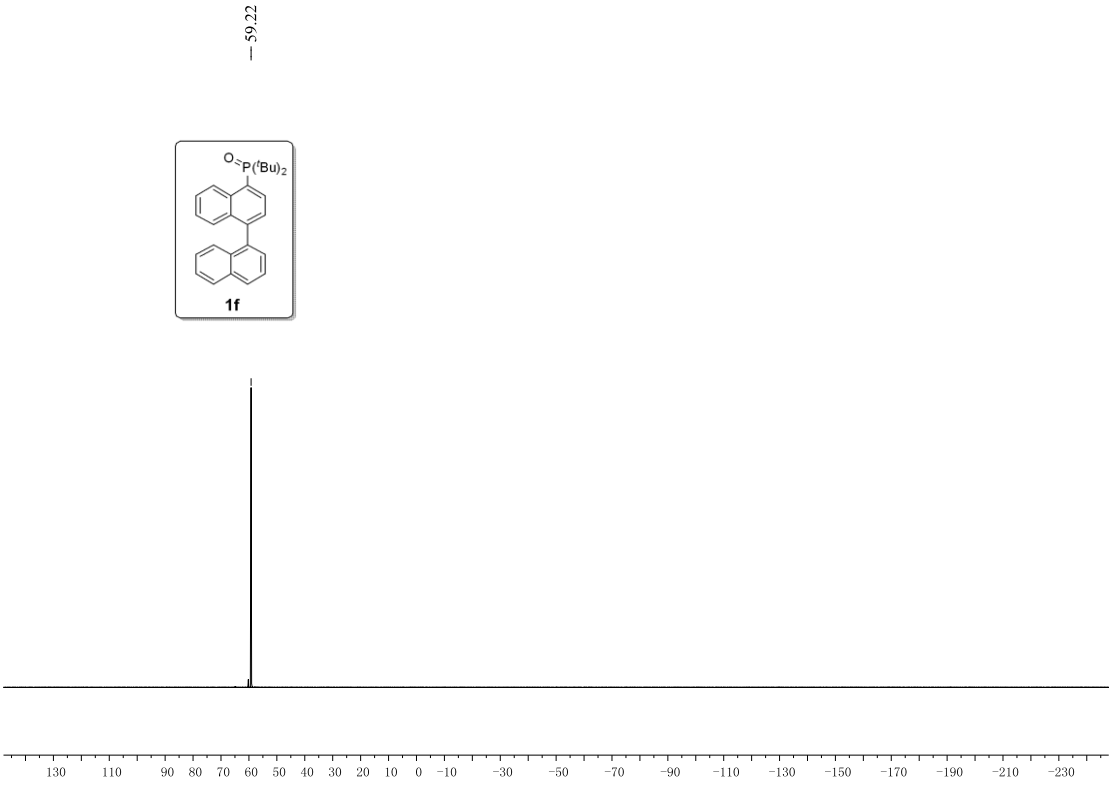
^{13}C NMR spectrum for **1e**



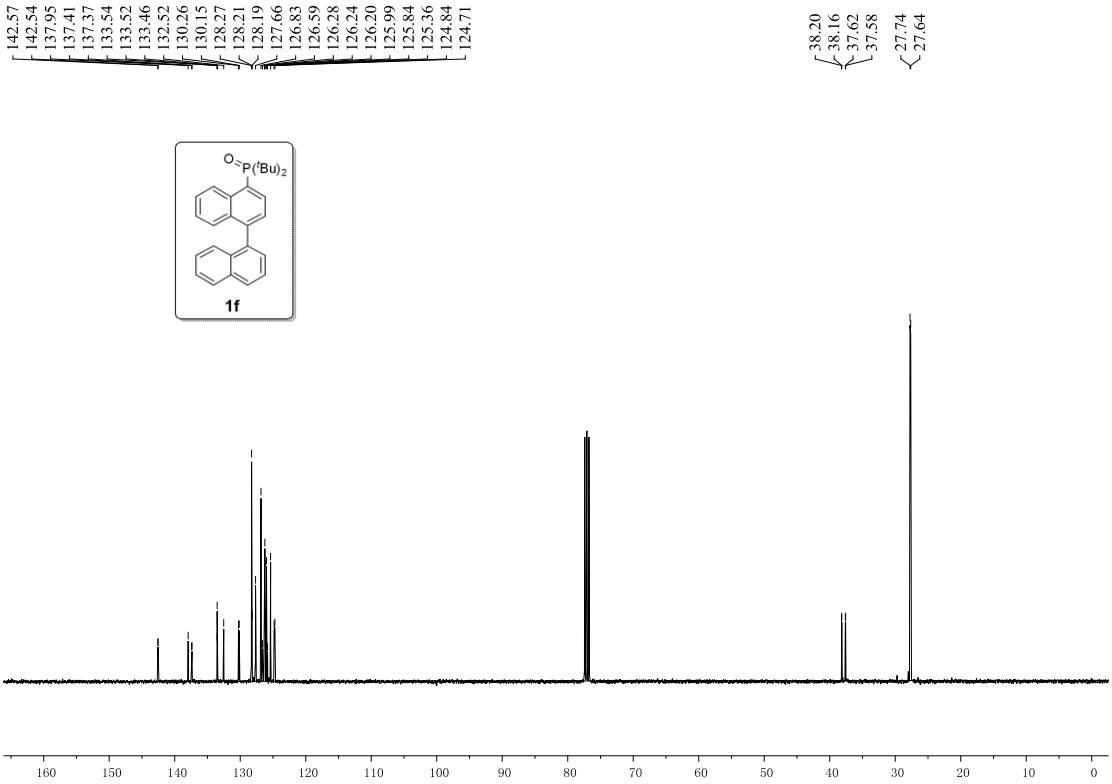
^{1}H NMR spectrum for **1f**



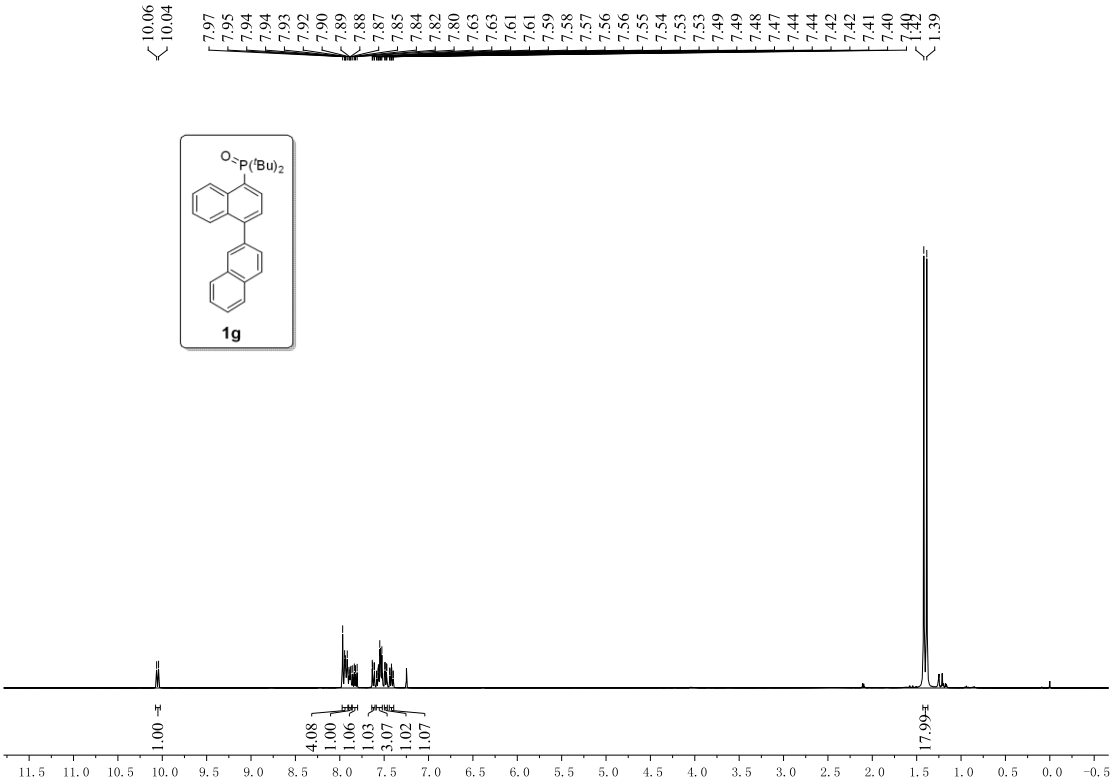
^{31}P NMR spectrum for **1f**



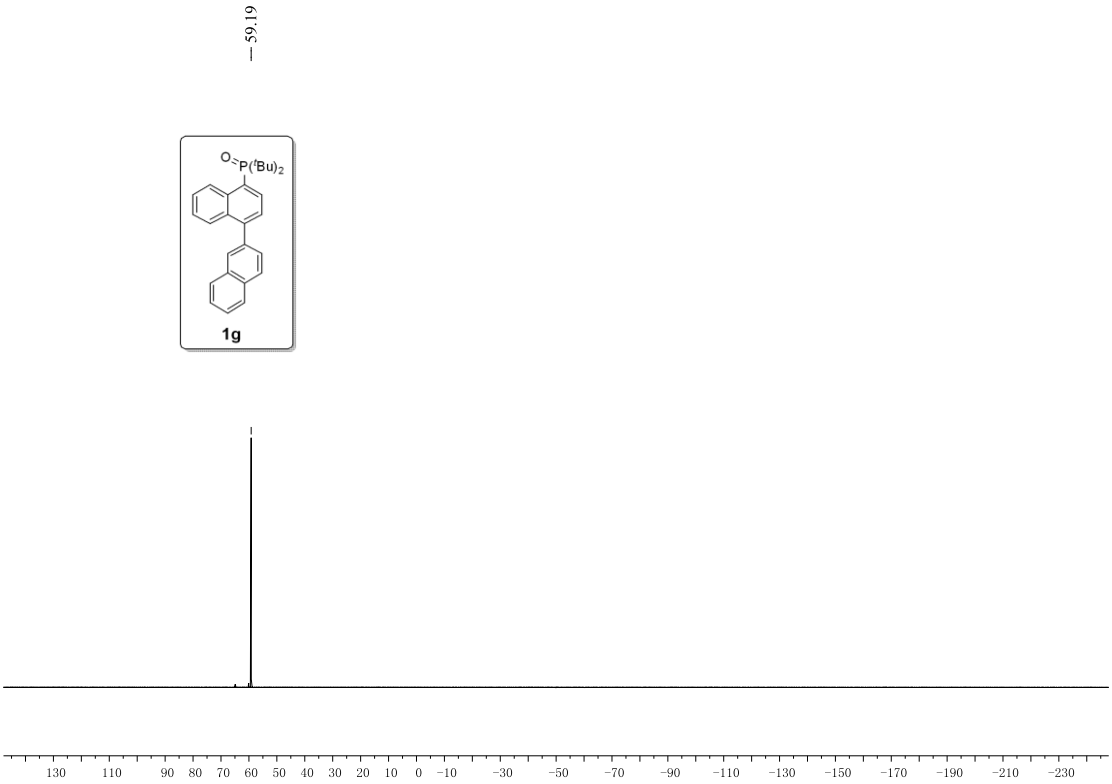
^{13}C NMR spectrum for **1f**



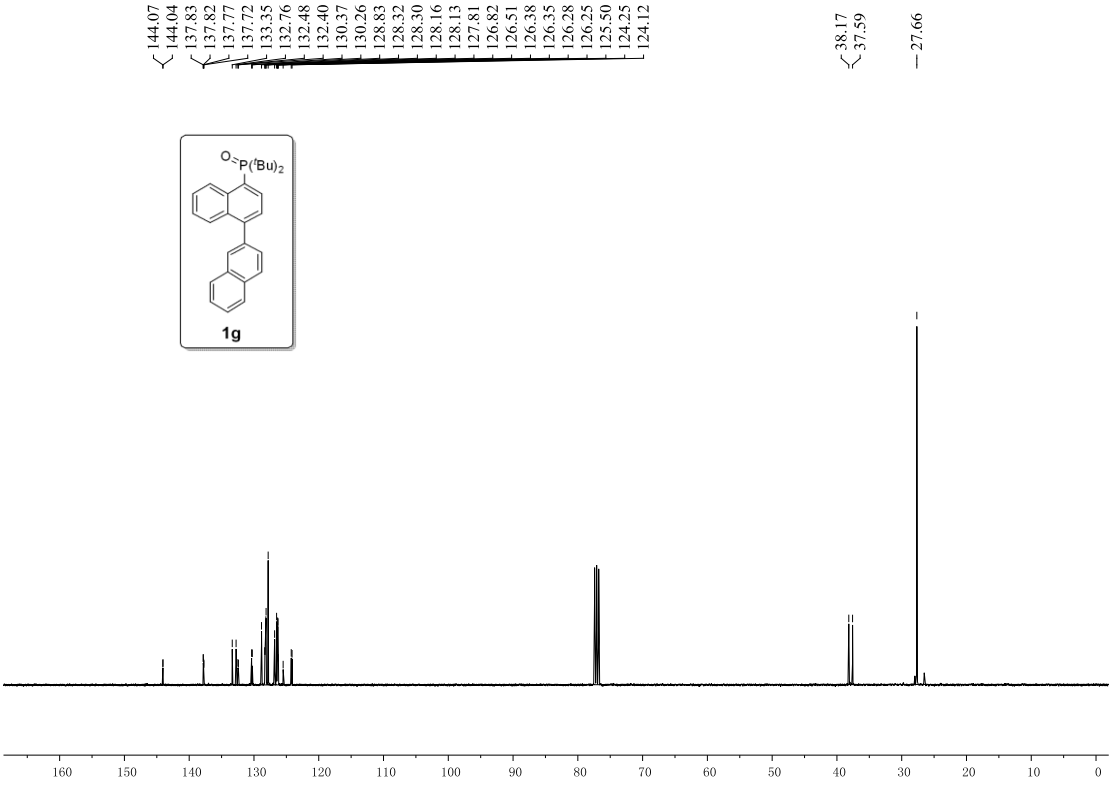
^{1}H NMR spectrum for **1g**



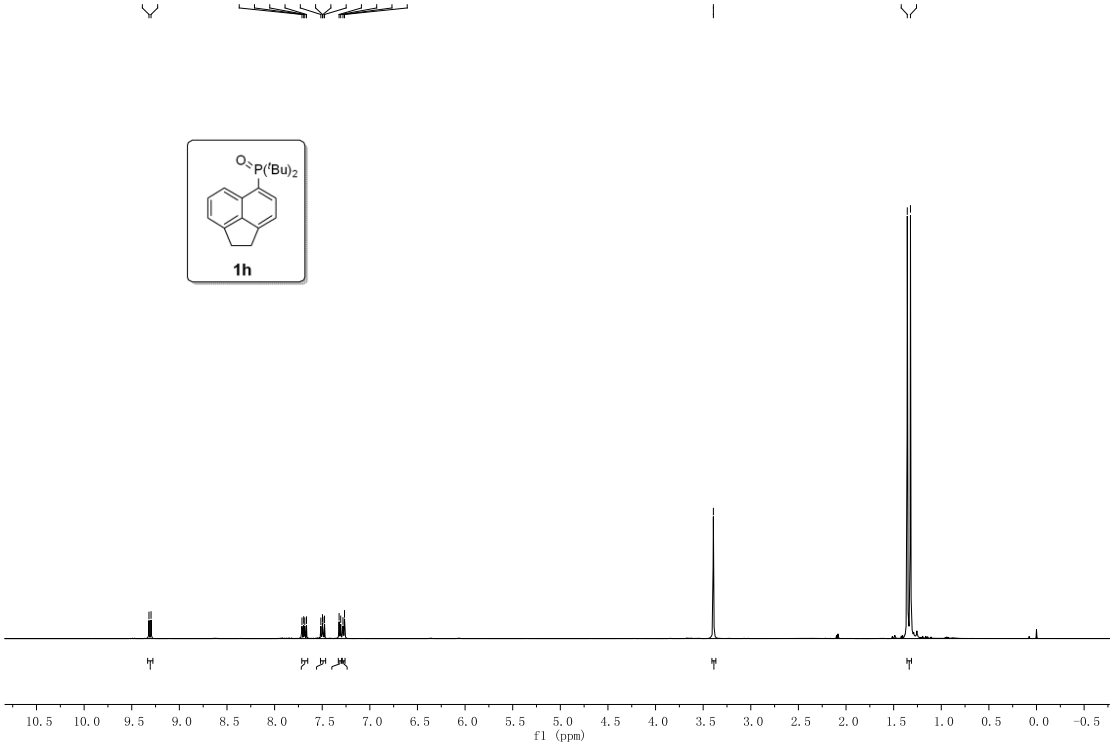
^{31}P NMR spectrum for **1g**



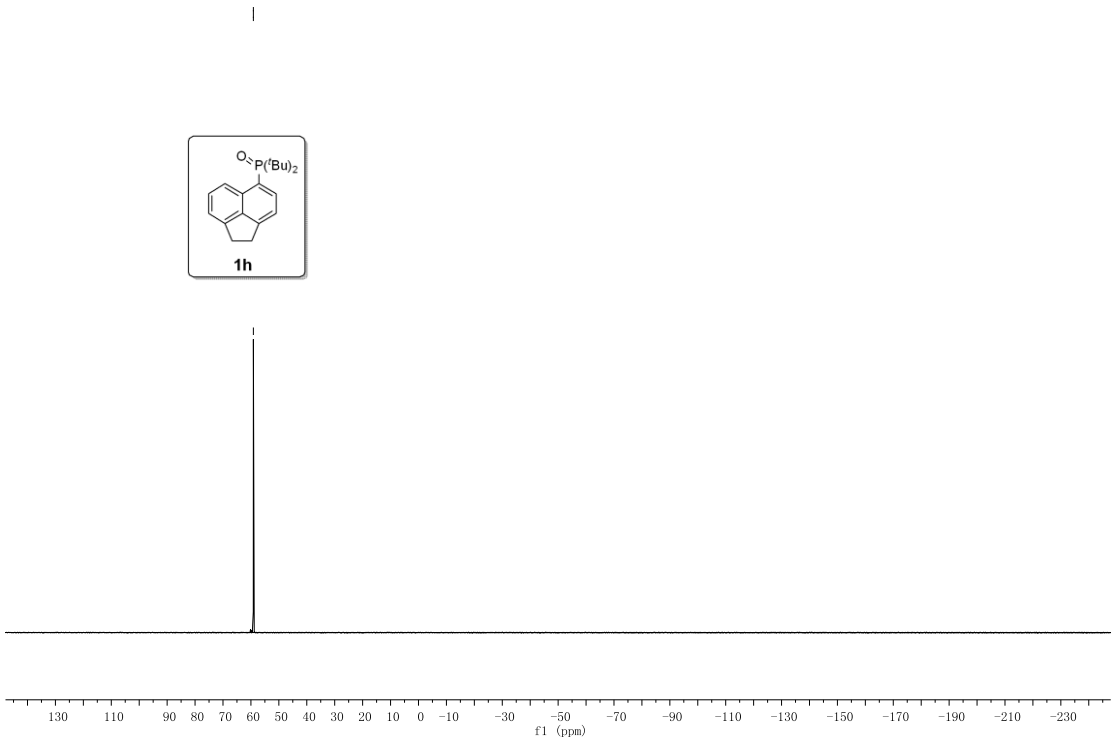
^{13}C NMR spectrum for **1g**



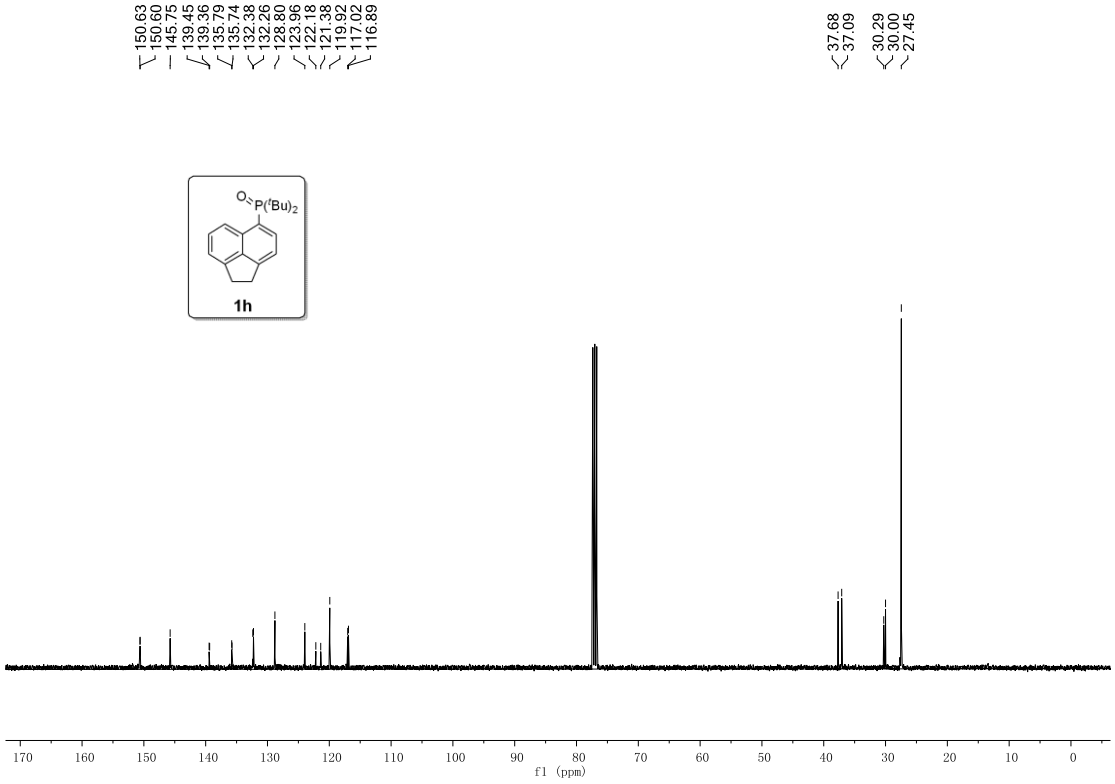
^{1}H NMR spectrum for **1h**



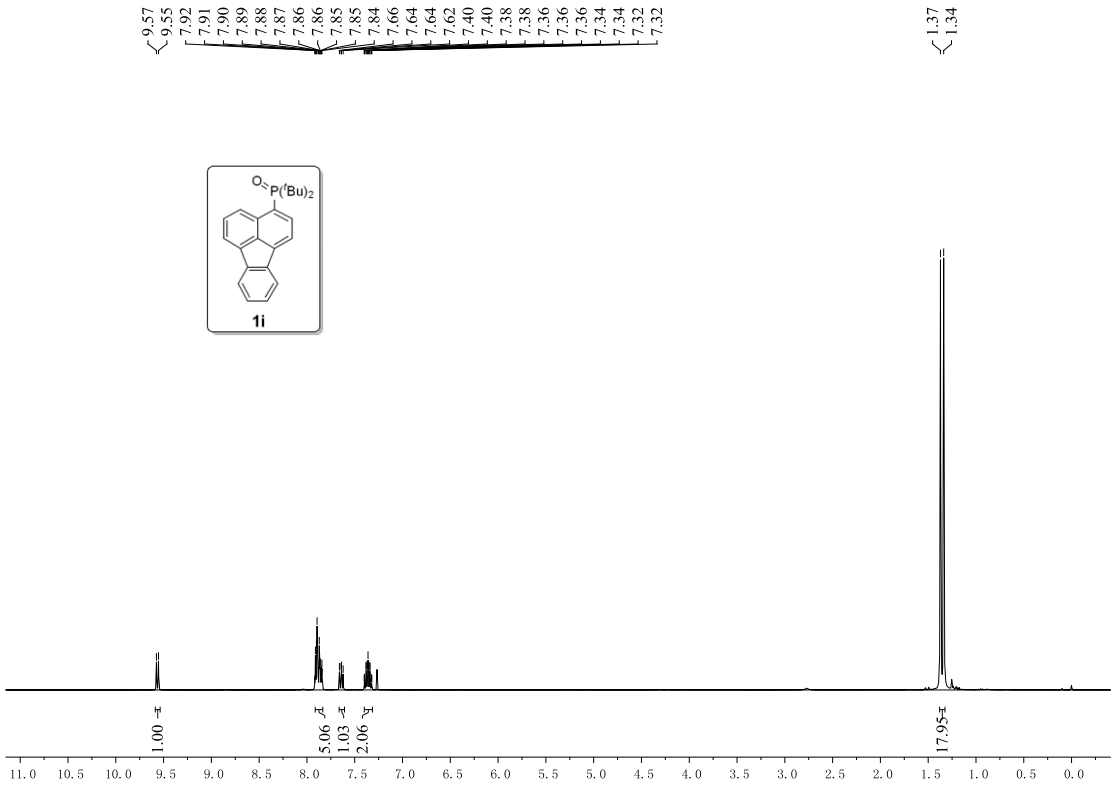
^{31}P NMR spectrum for **1h**



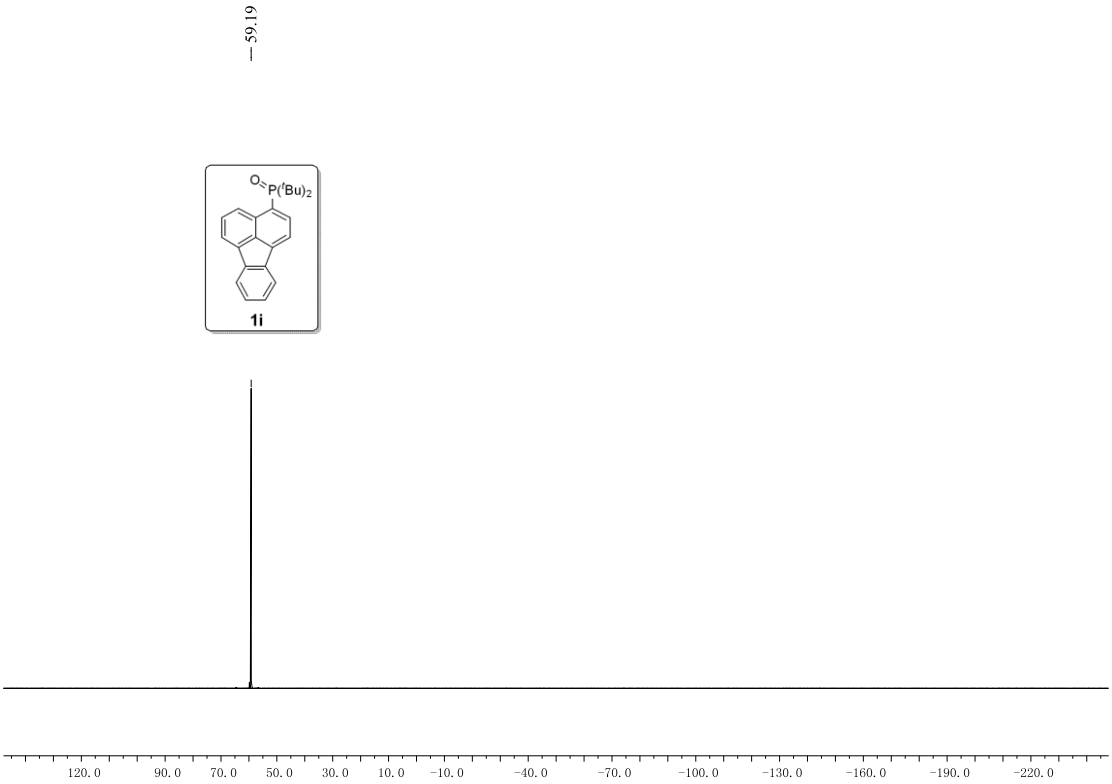
^{13}C NMR spectrum for **1h**



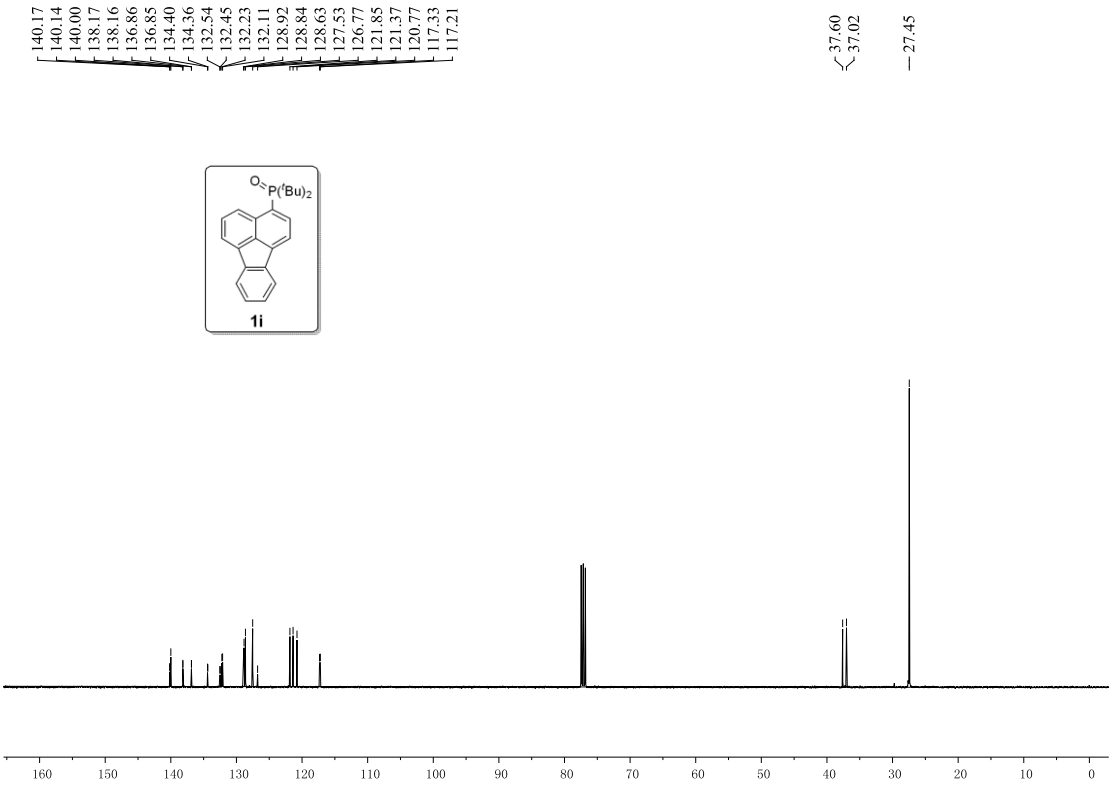
^{1}H NMR spectrum for **1i**



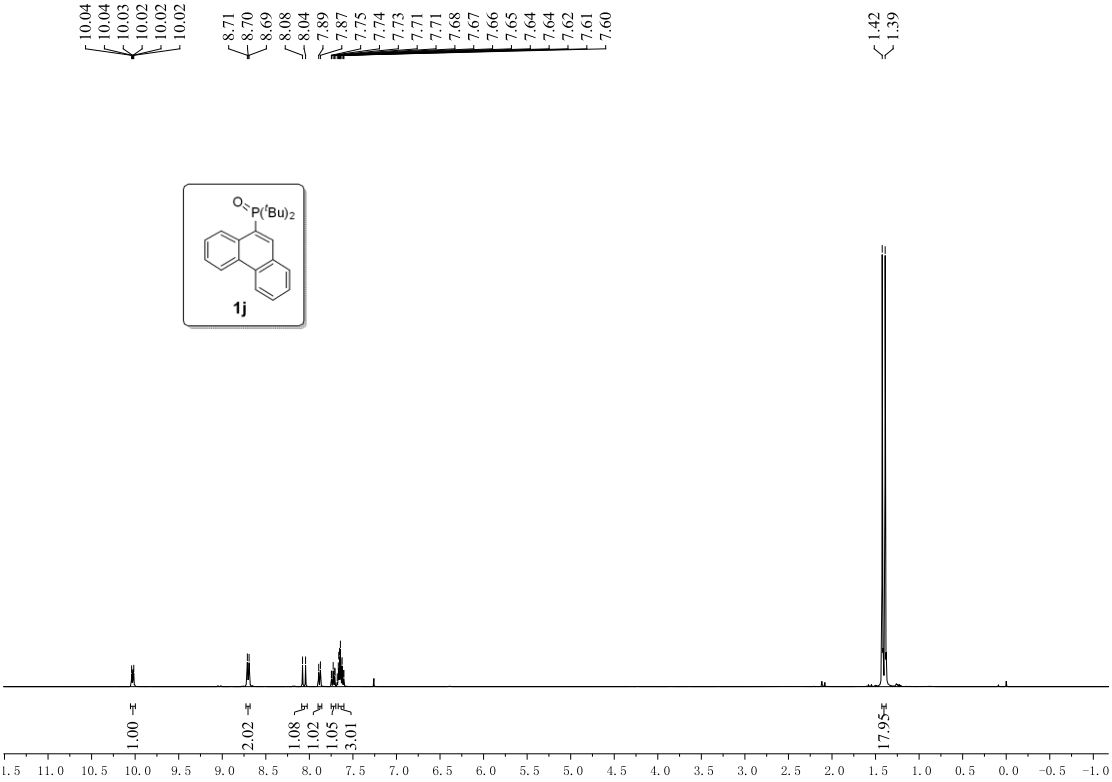
^{31}P NMR spectrum for **1i**



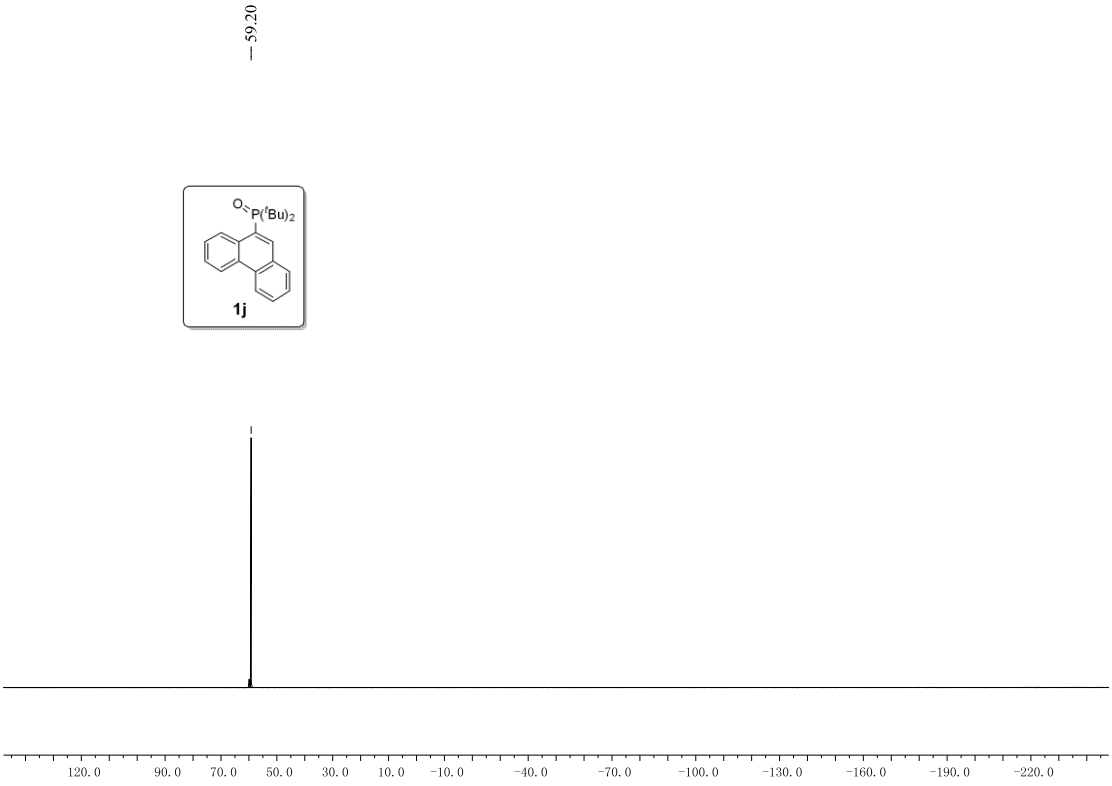
^{13}C NMR spectrum for **1i**



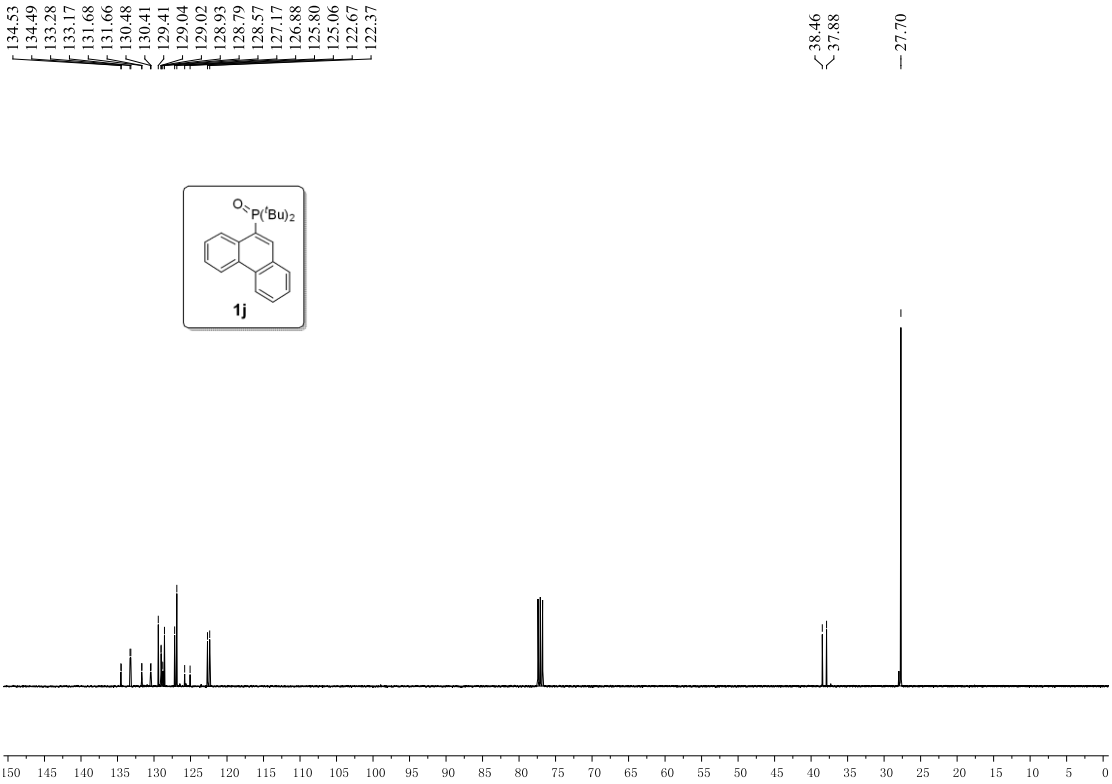
^{1}H NMR spectrum for **1j**



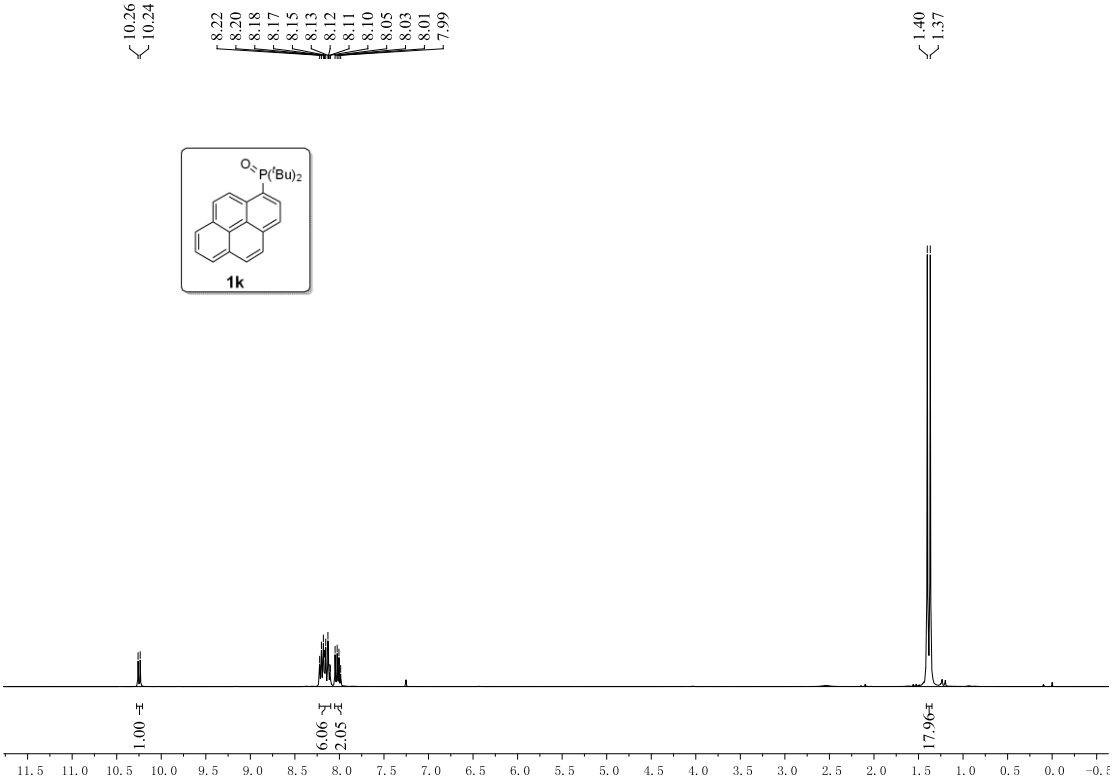
^{31}P NMR spectrum for **1j**



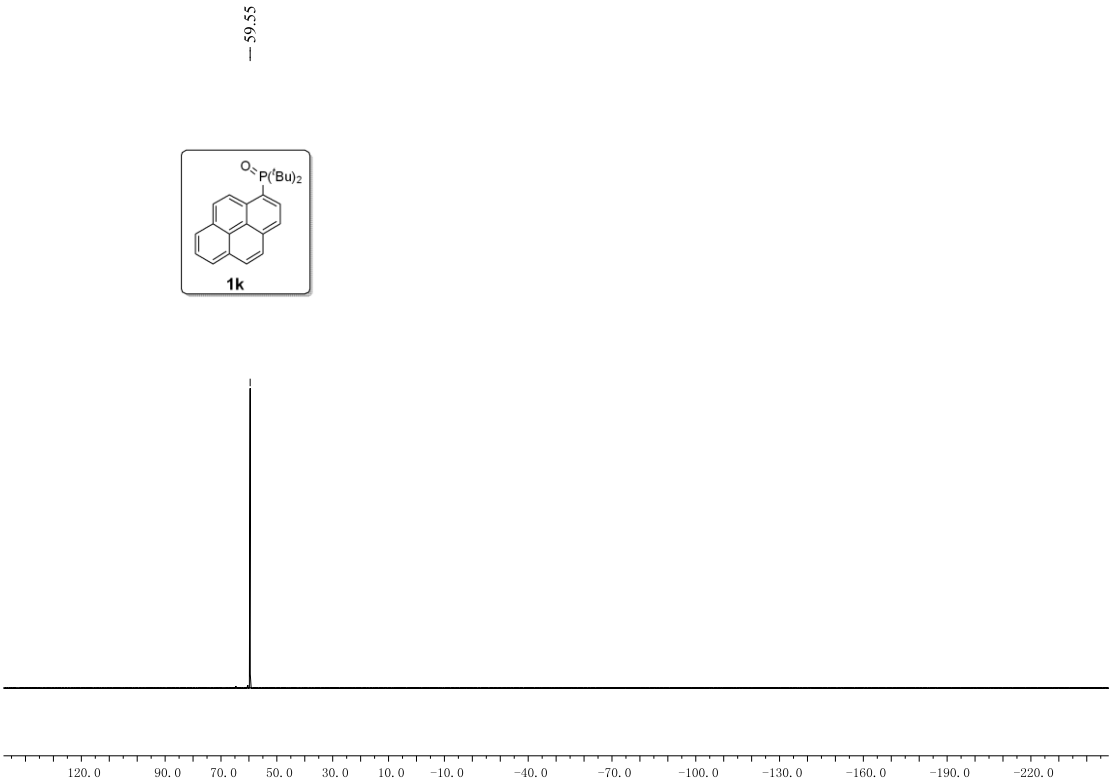
^{13}C NMR spectrum for **1j**



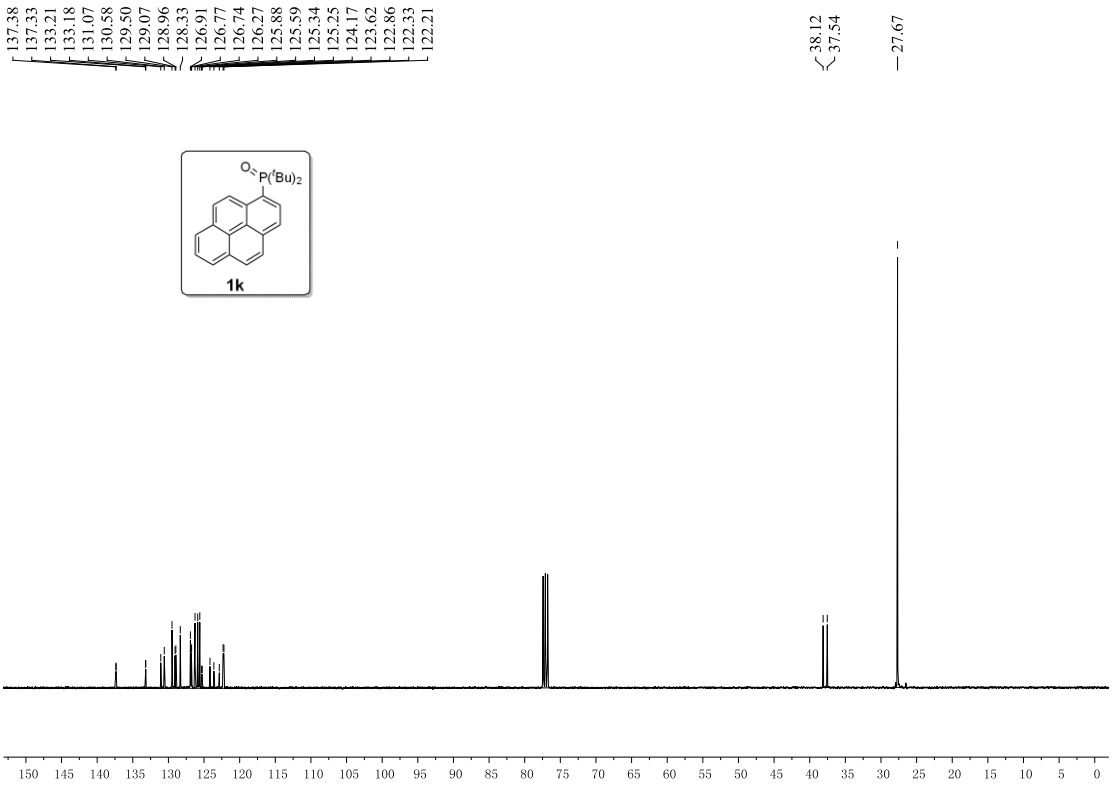
^{1}H NMR spectrum for **1k**



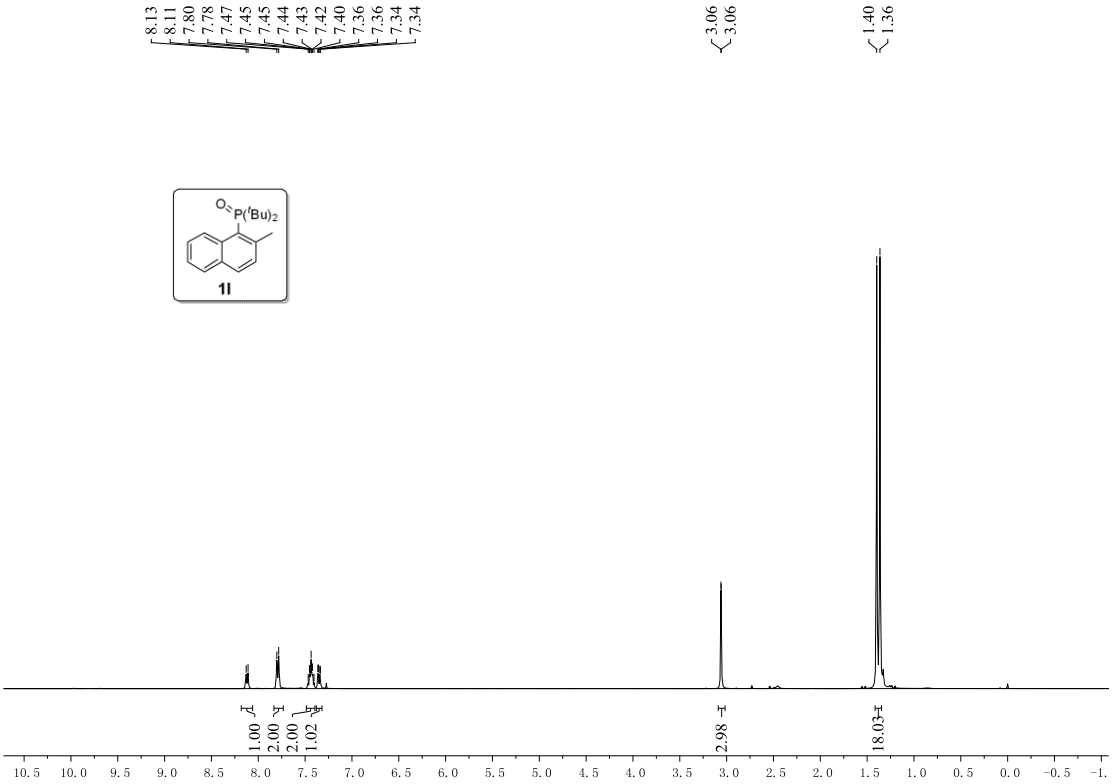
^{31}P NMR spectrum for **1k**



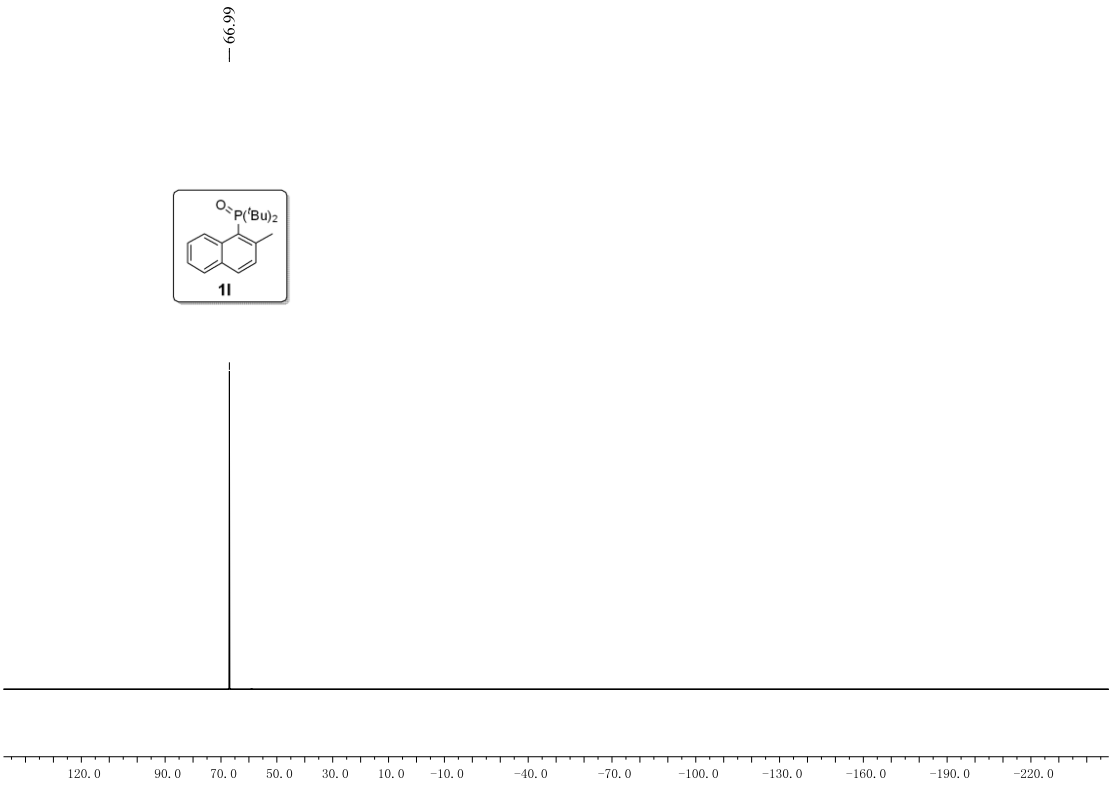
^{13}C NMR spectrum for **1k**



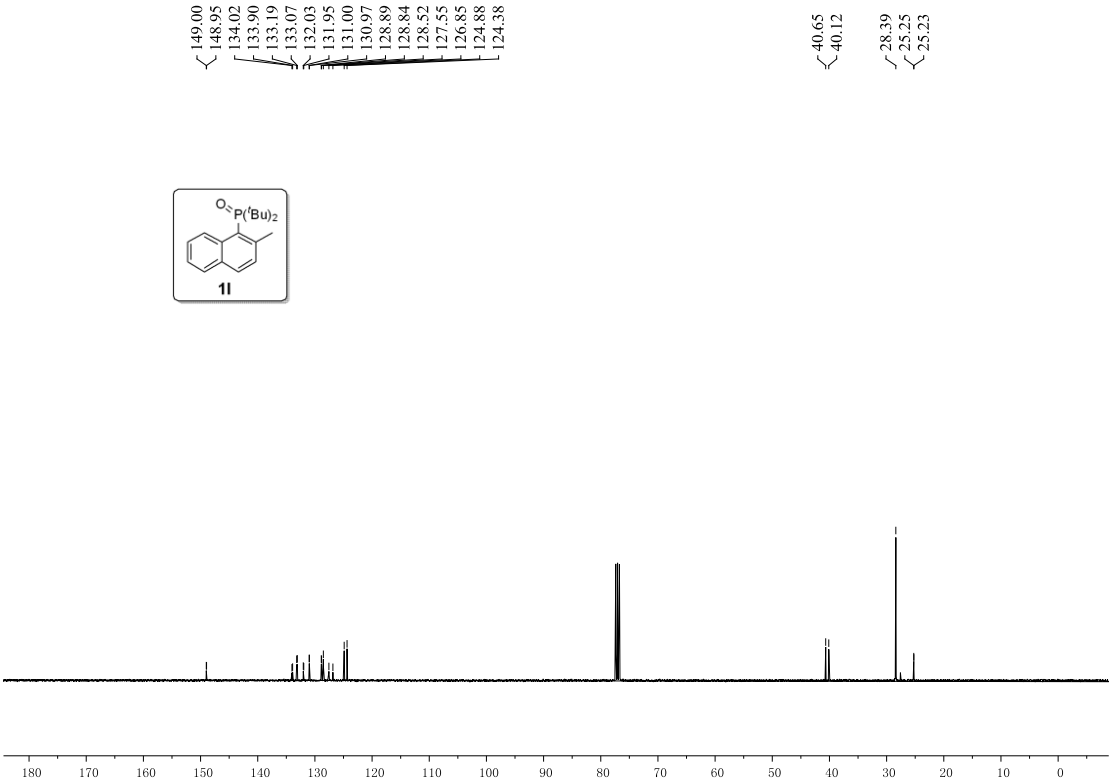
^{1}H NMR spectrum for **1l**



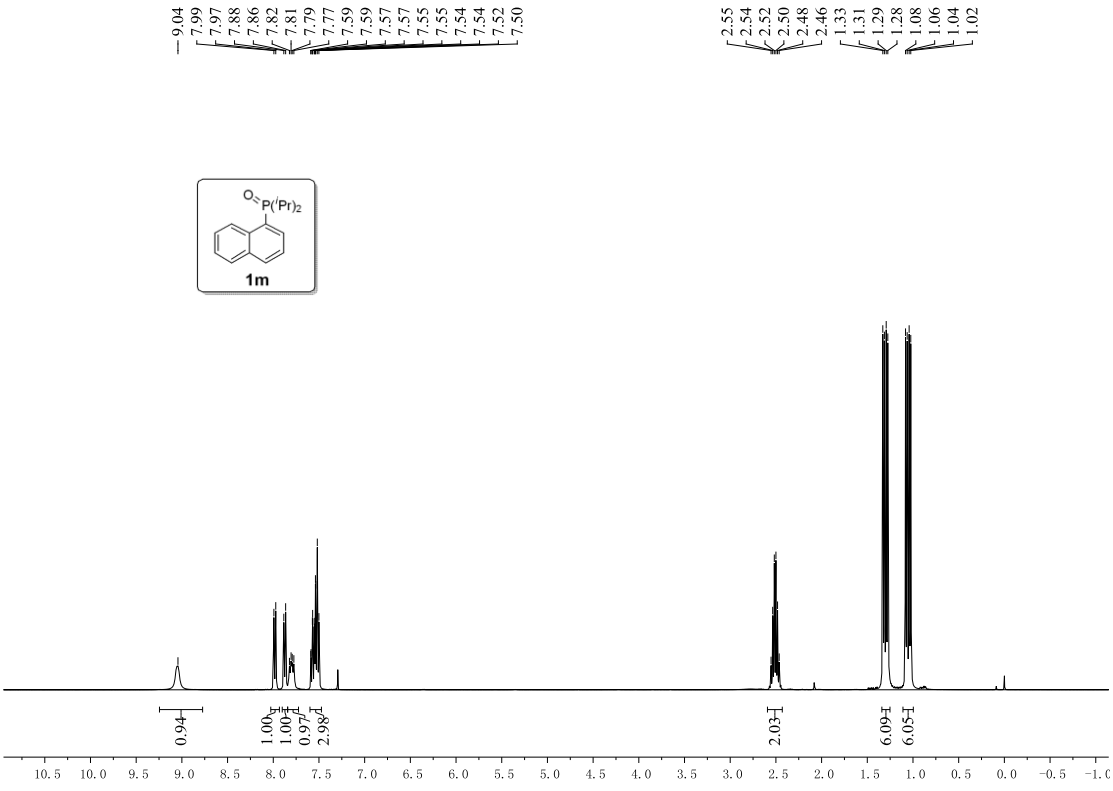
^{31}P NMR spectrum for **1l**



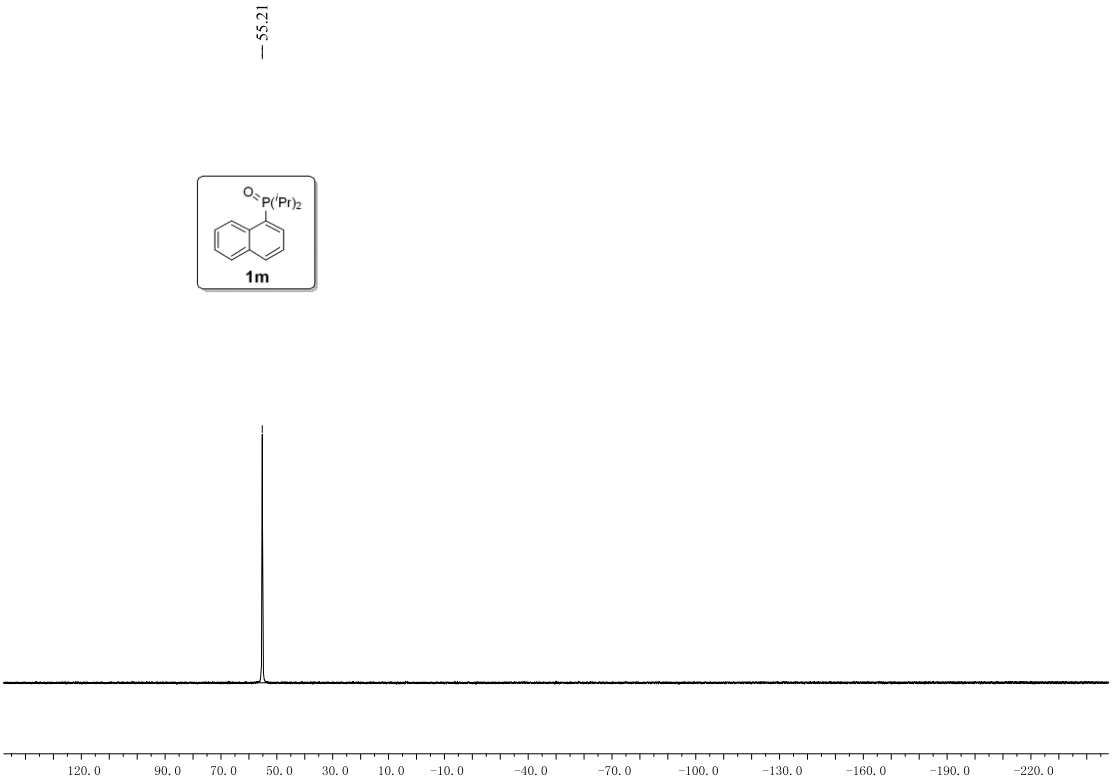
^{13}C NMR spectrum for **1l**



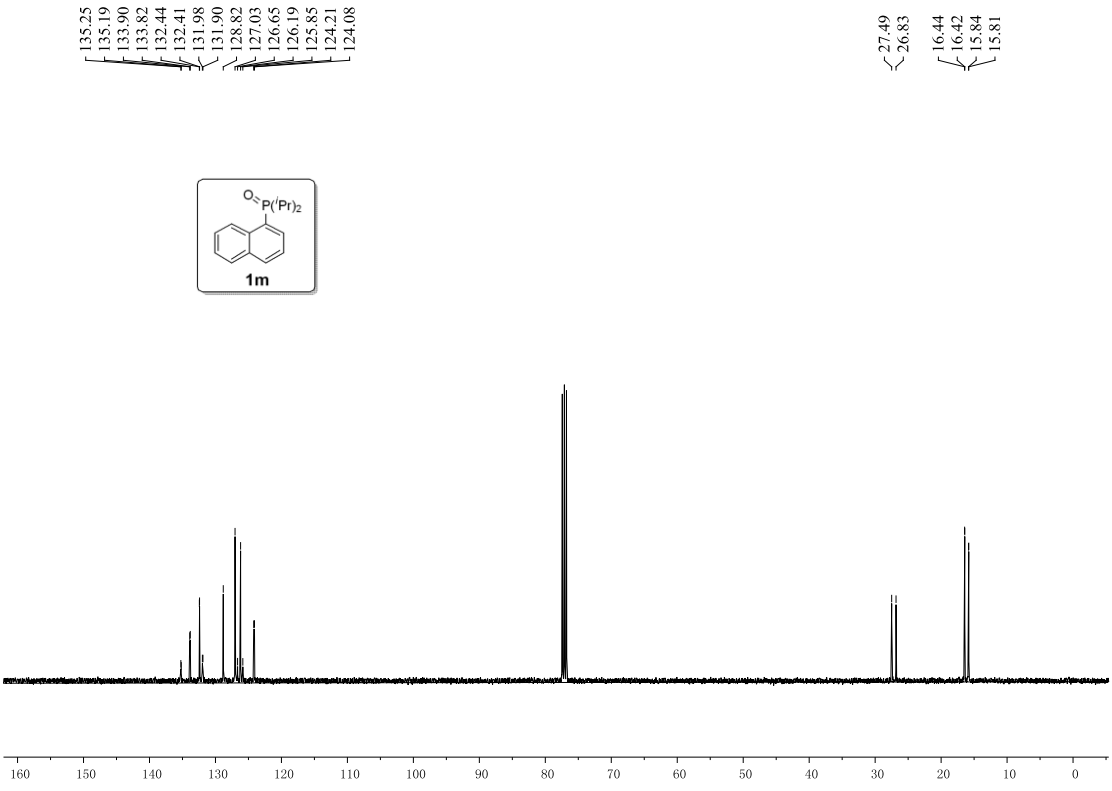
^{1}H NMR spectrum for **1m**



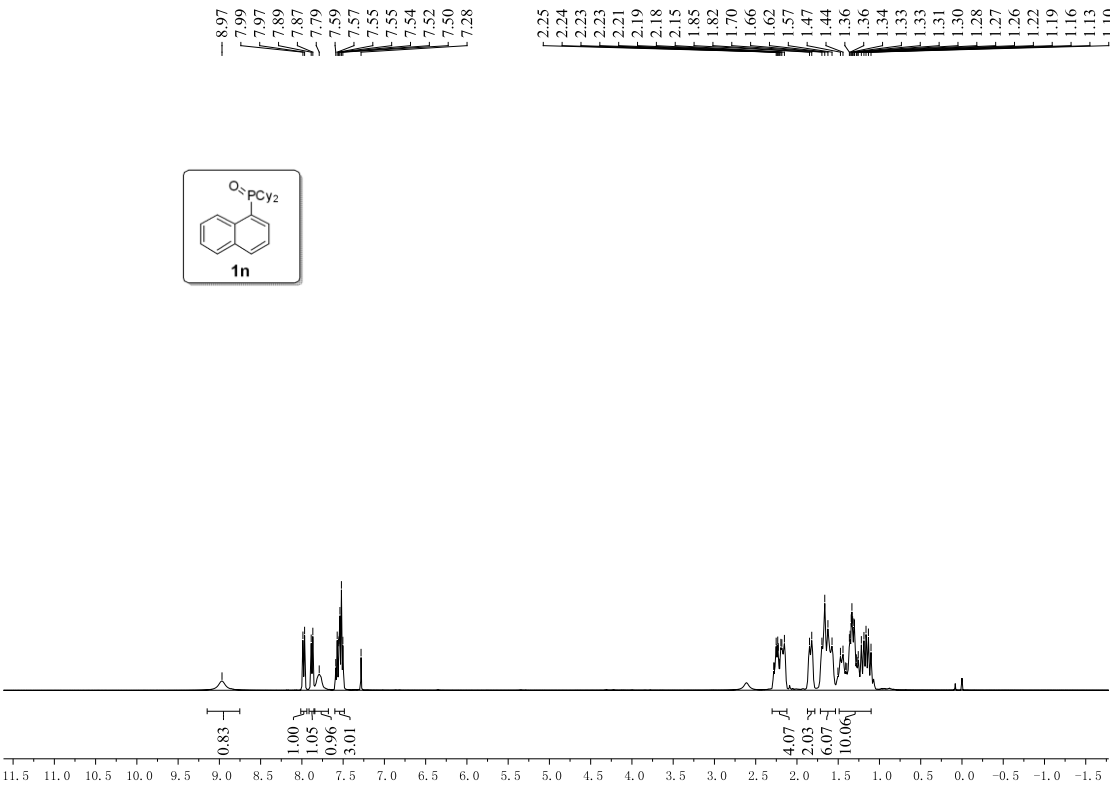
^{31}P NMR spectrum for **1m**



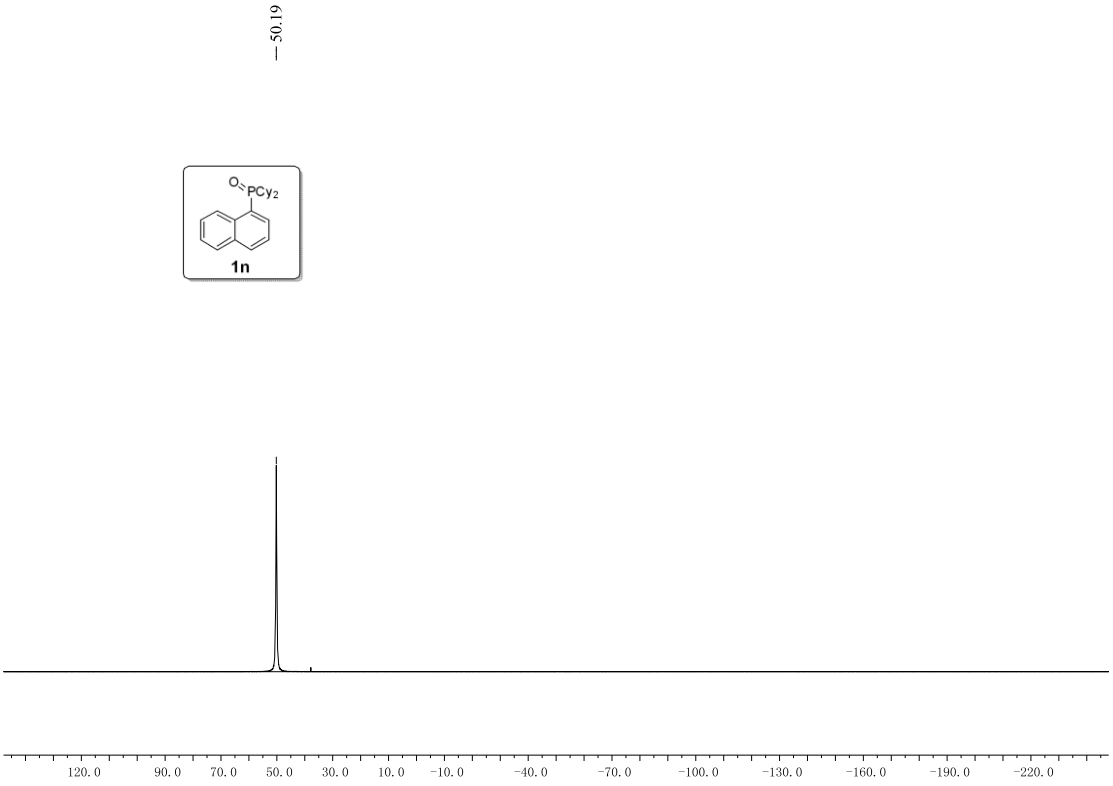
^{13}C NMR spectrum for **1m**



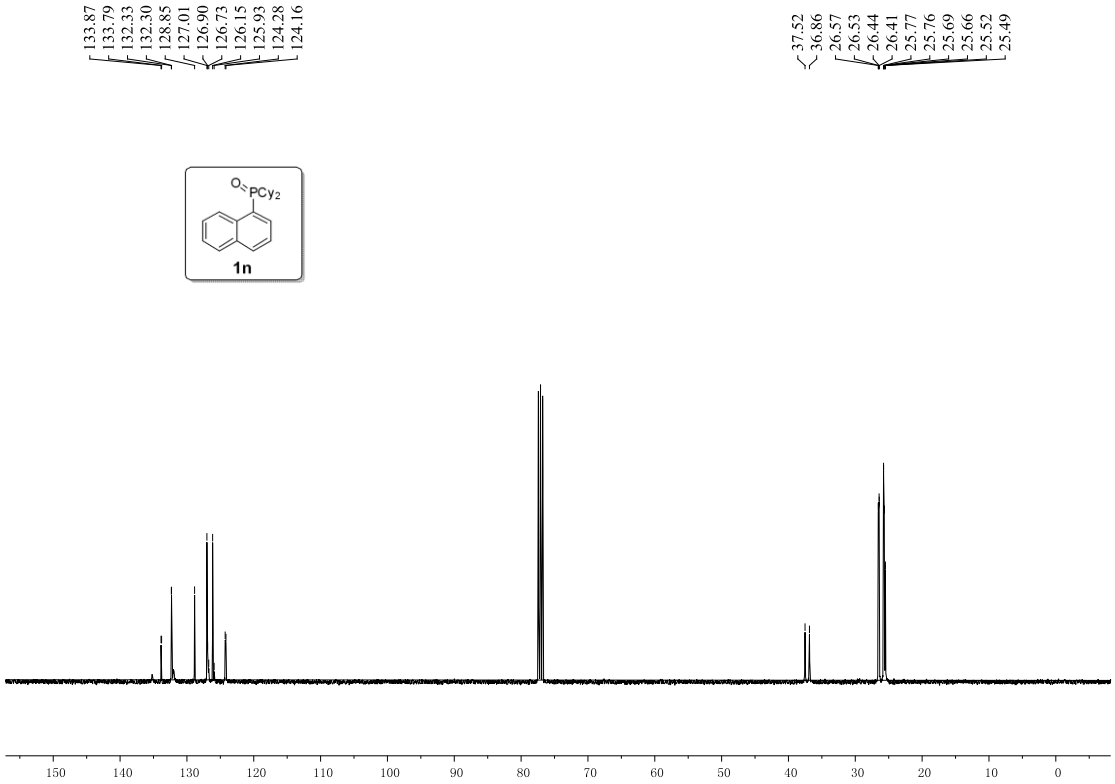
^{1}H NMR spectrum for **1n**



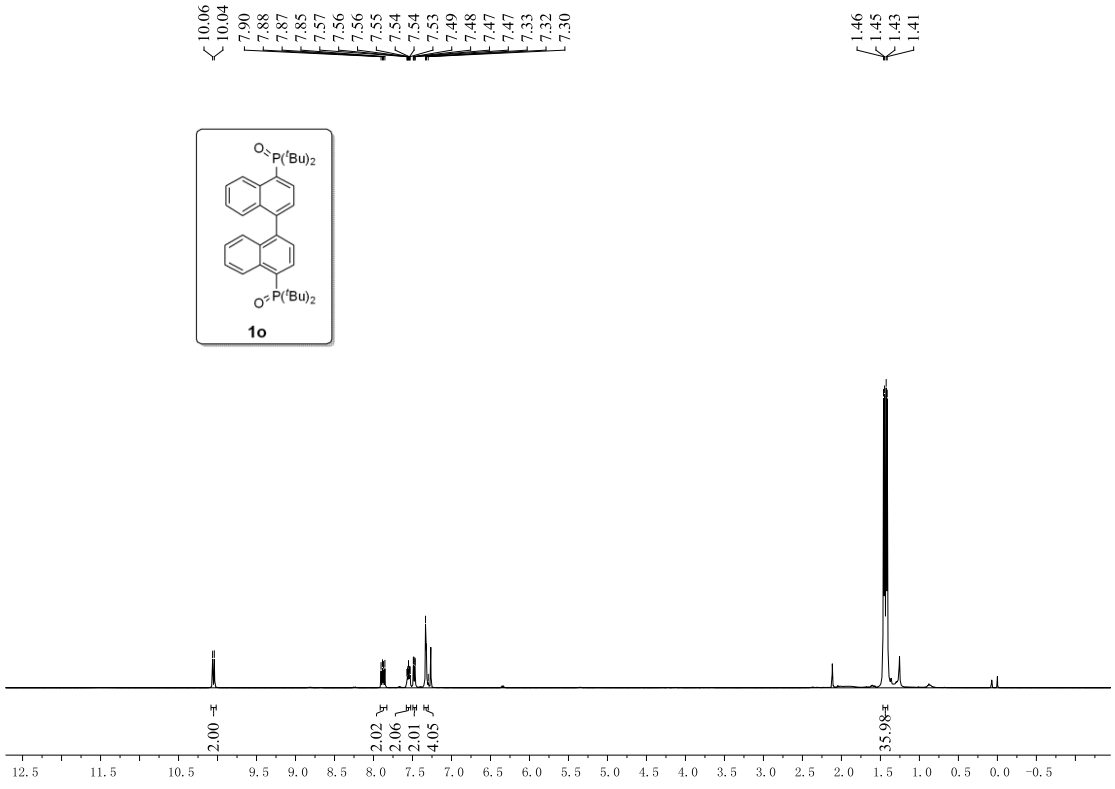
^{31}P NMR spectrum for **1n**



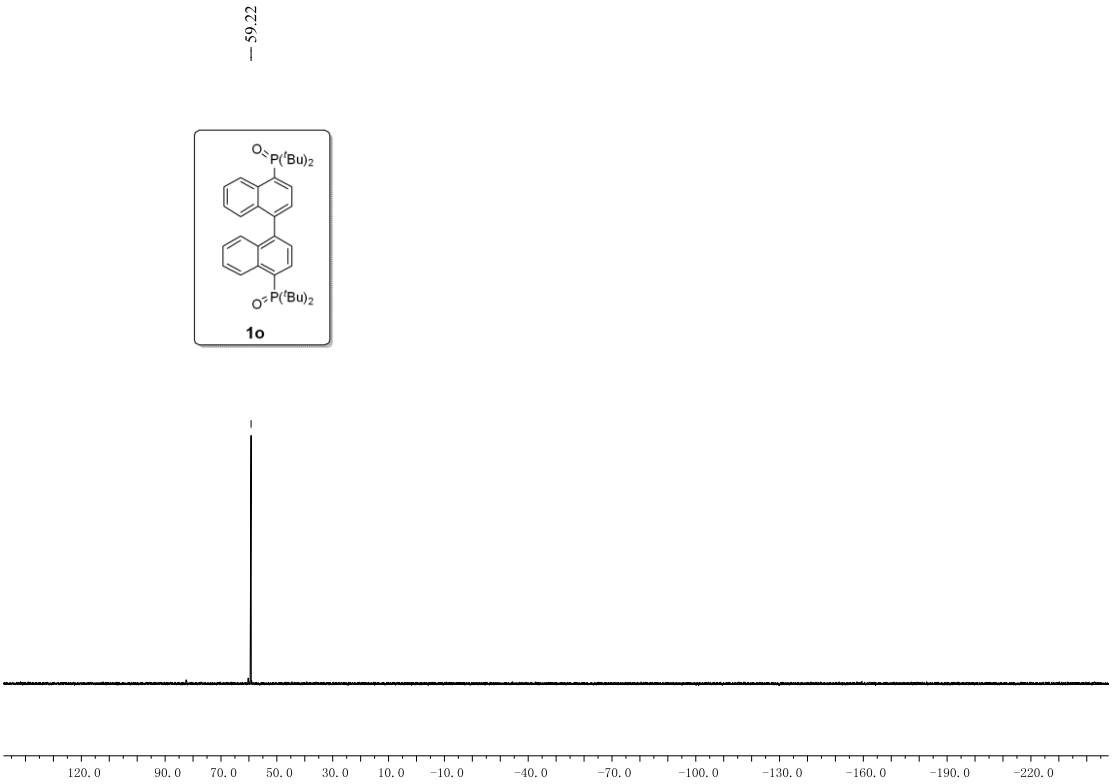
^{13}C NMR spectrum for **1n**



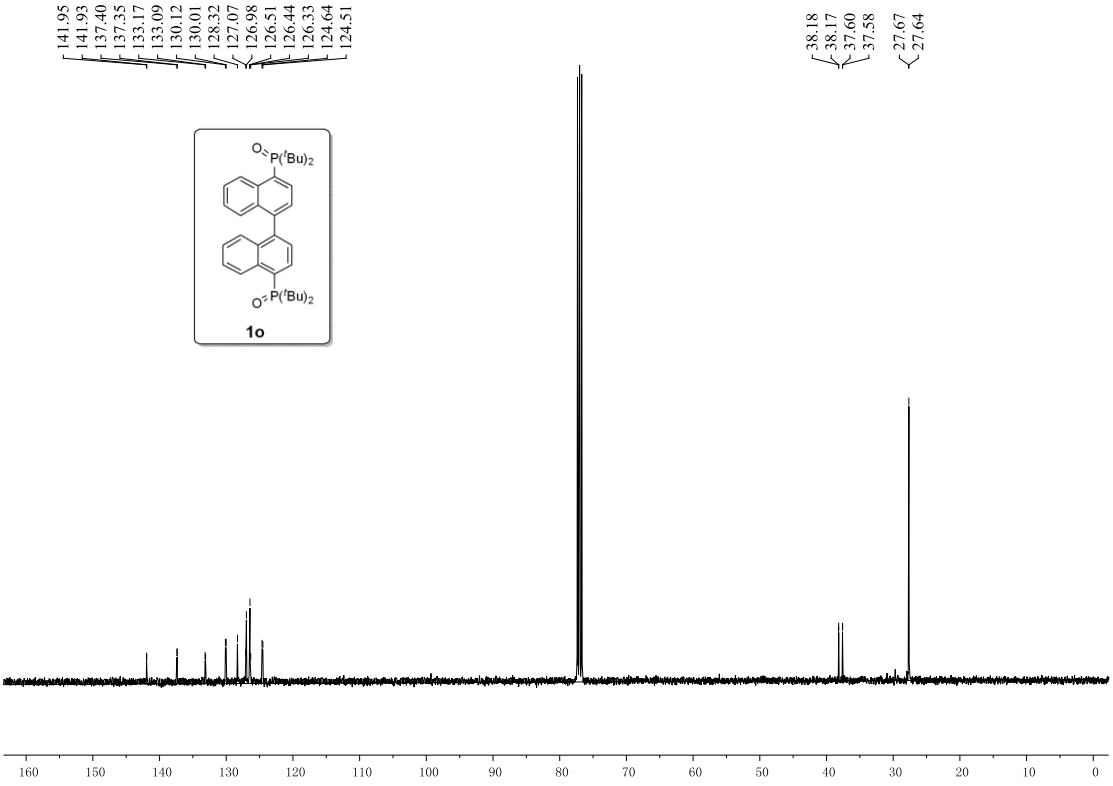
^{1}H NMR spectrum for **1o**



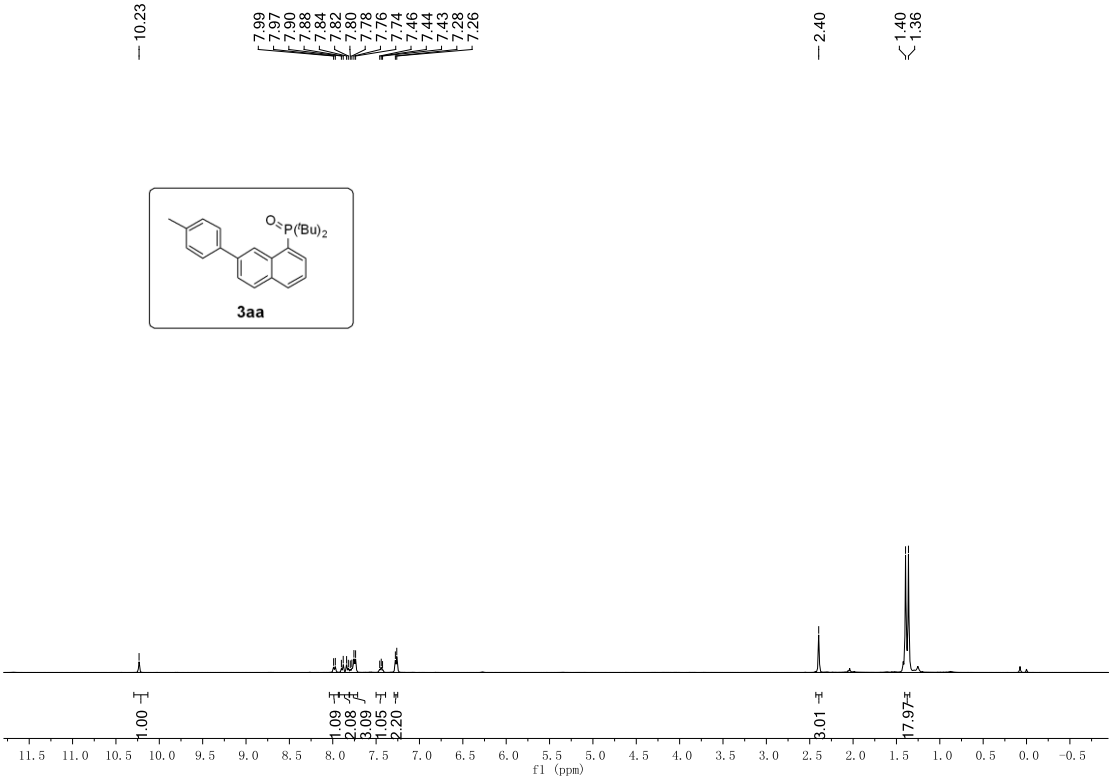
^{31}P NMR spectrum for **1o**



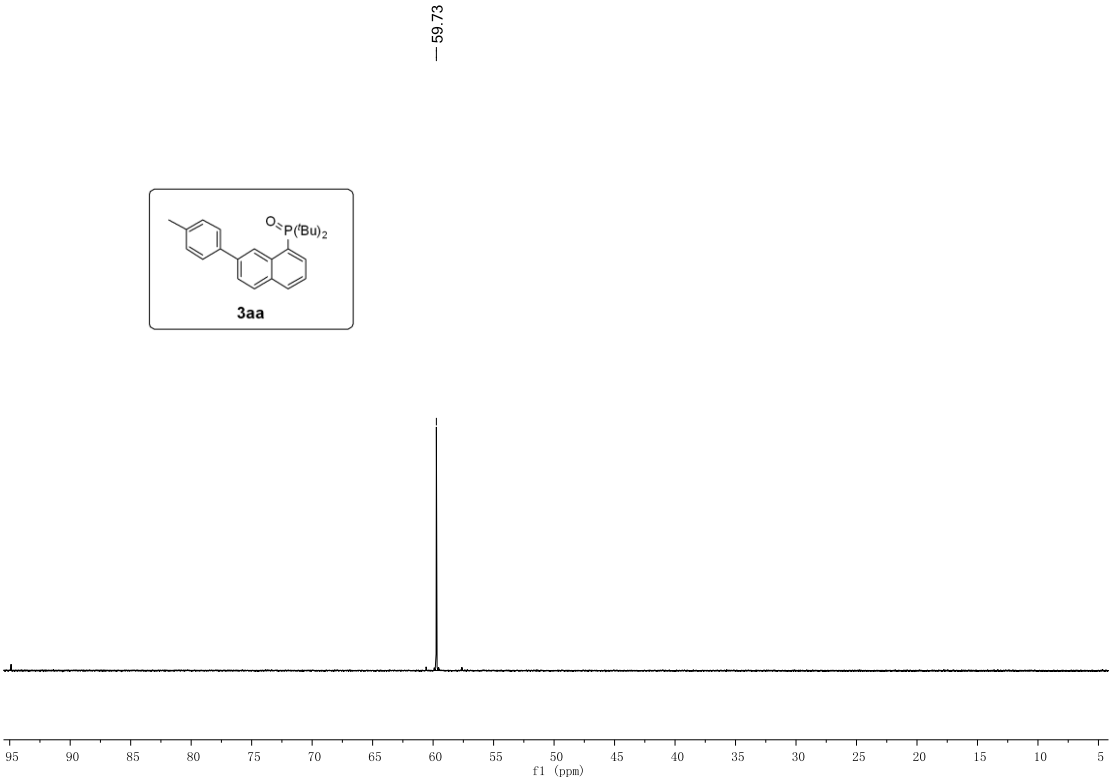
^{13}C NMR spectrum for **1o**



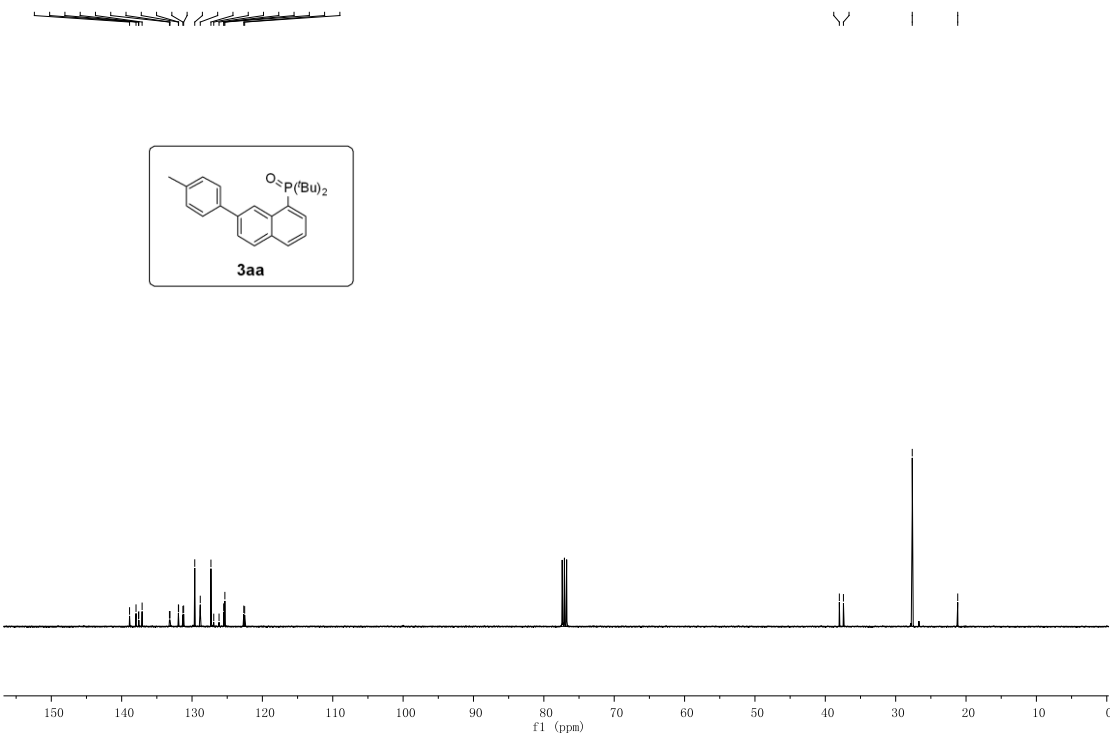
^{1}H NMR spectrum for **3aa**



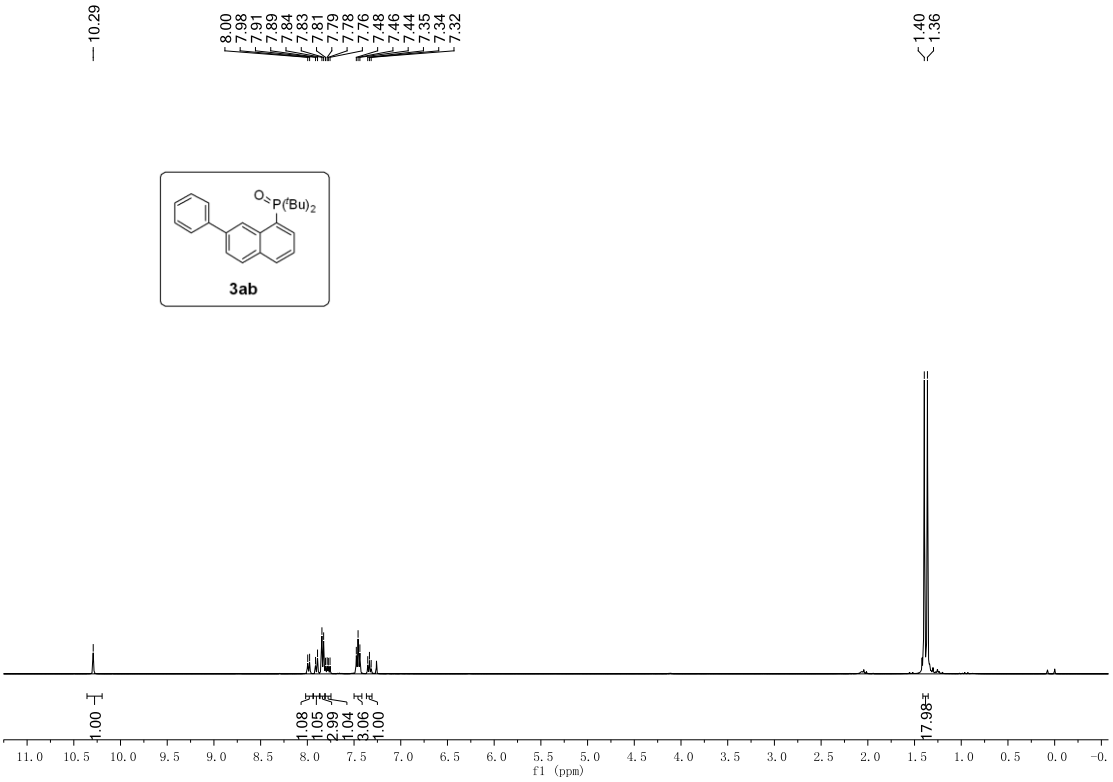
^{31}P NMR spectrum for **3aa**



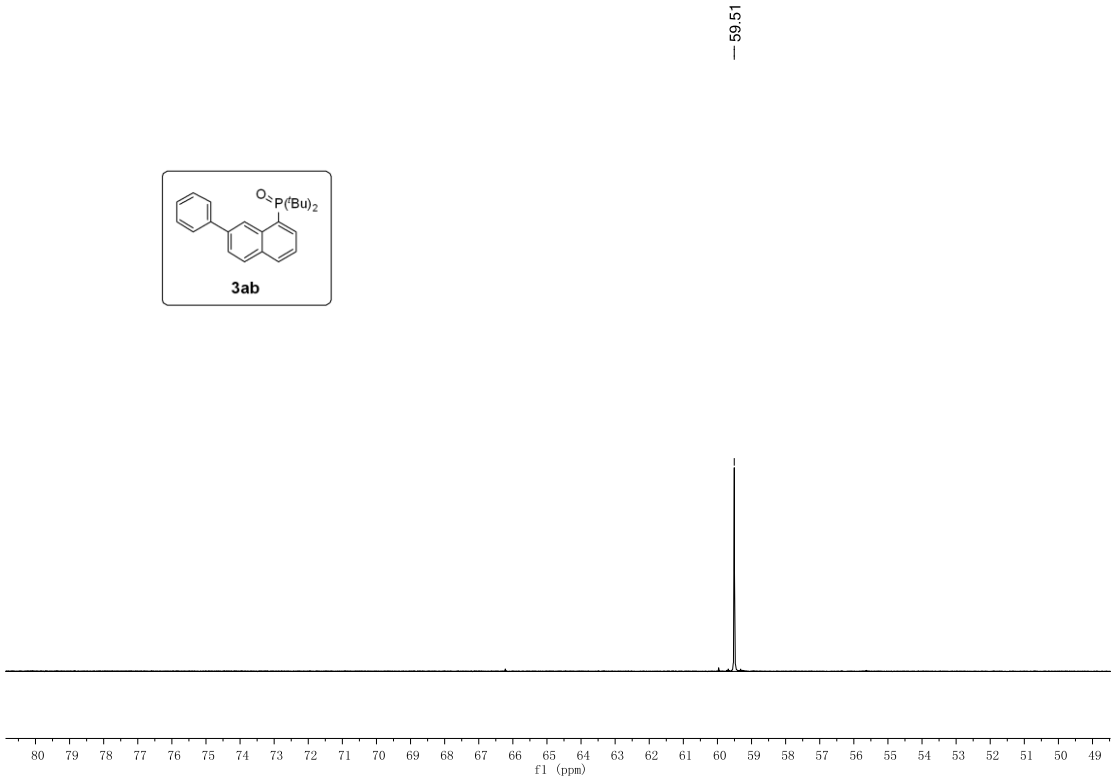
^{13}C NMR spectrum for **3aa**



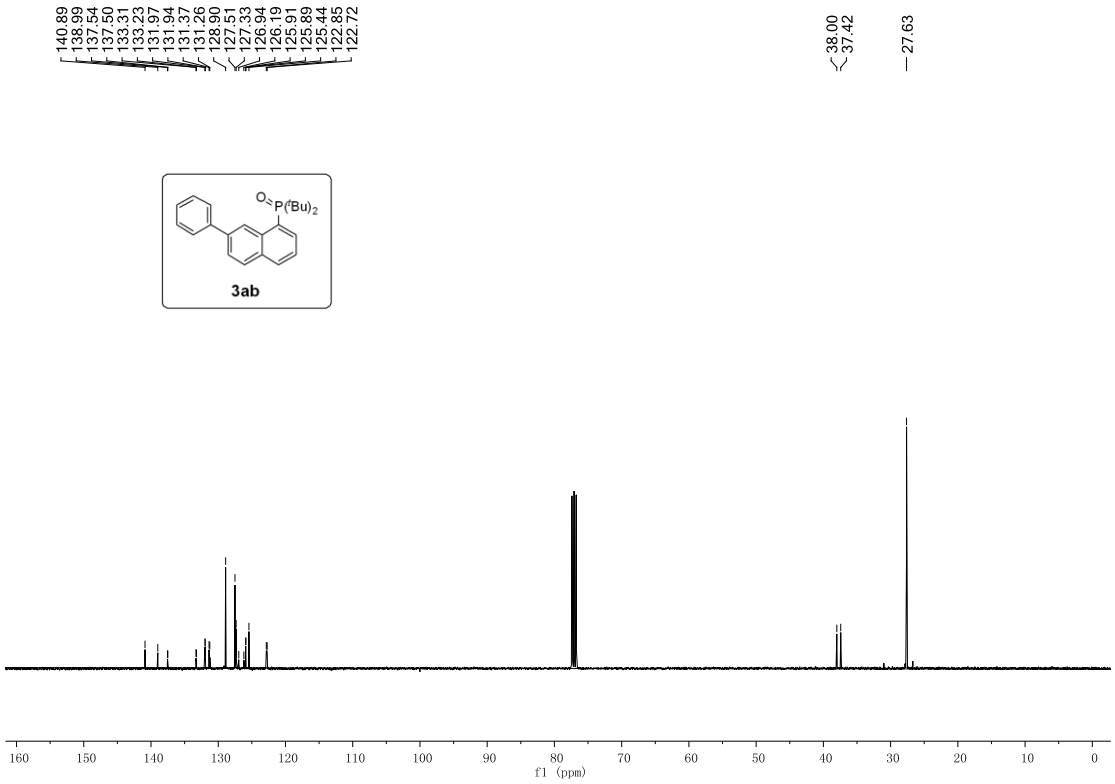
^{1}H NMR spectrum for **3ab**



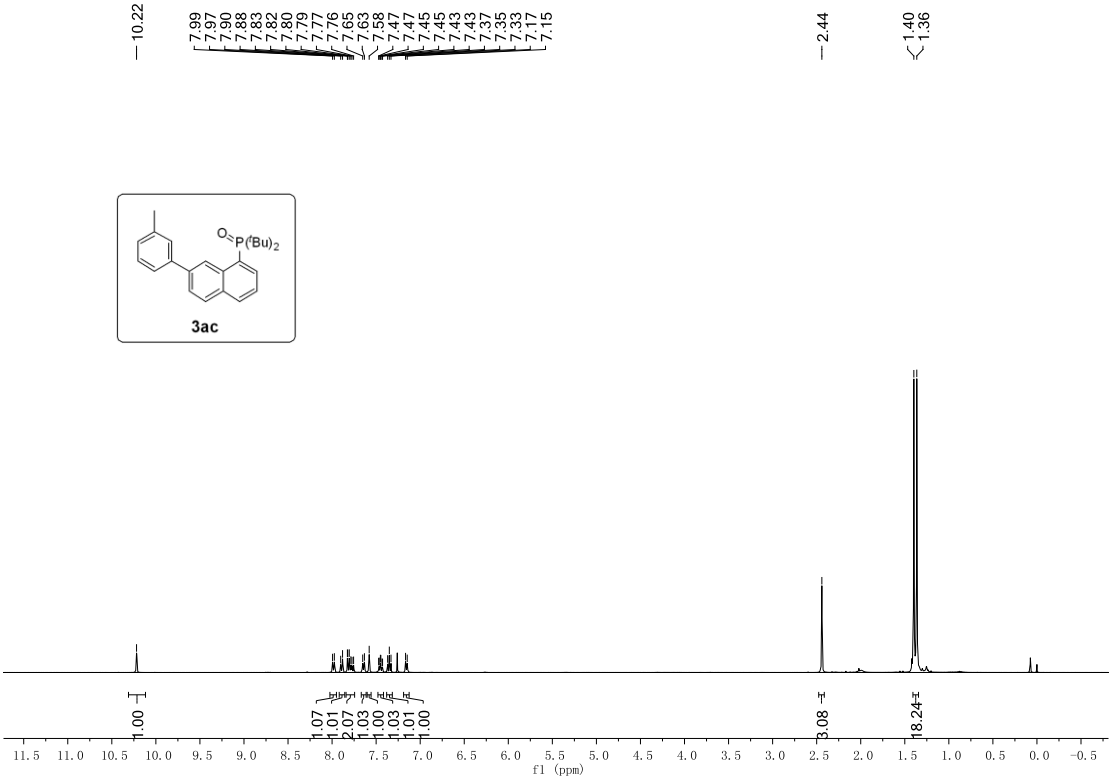
^{31}P NMR spectrum for **3ab**



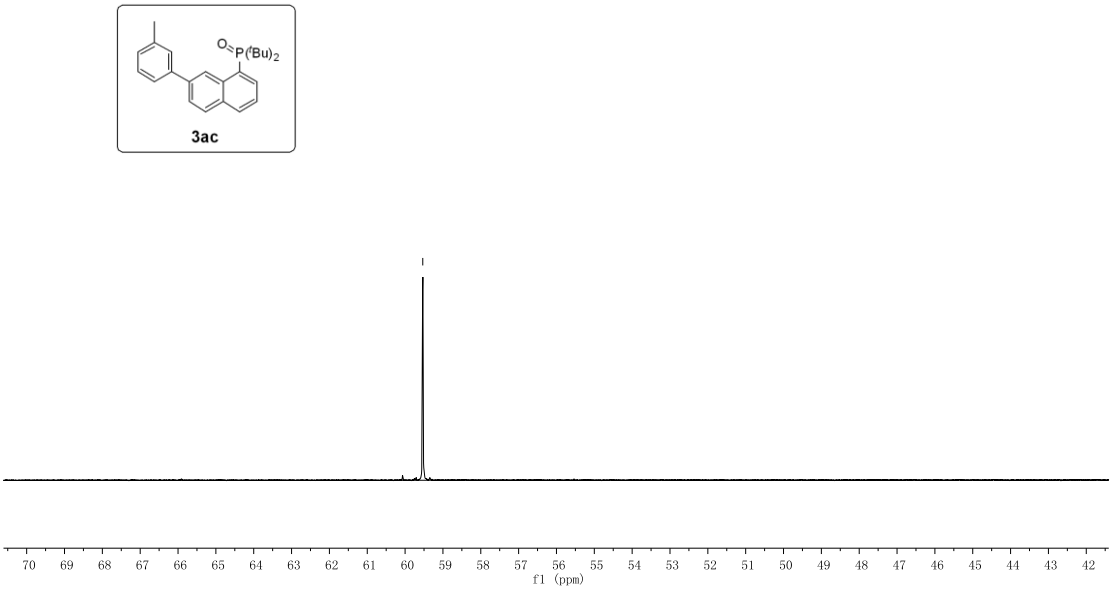
^{13}C NMR spectrum for **3ab**



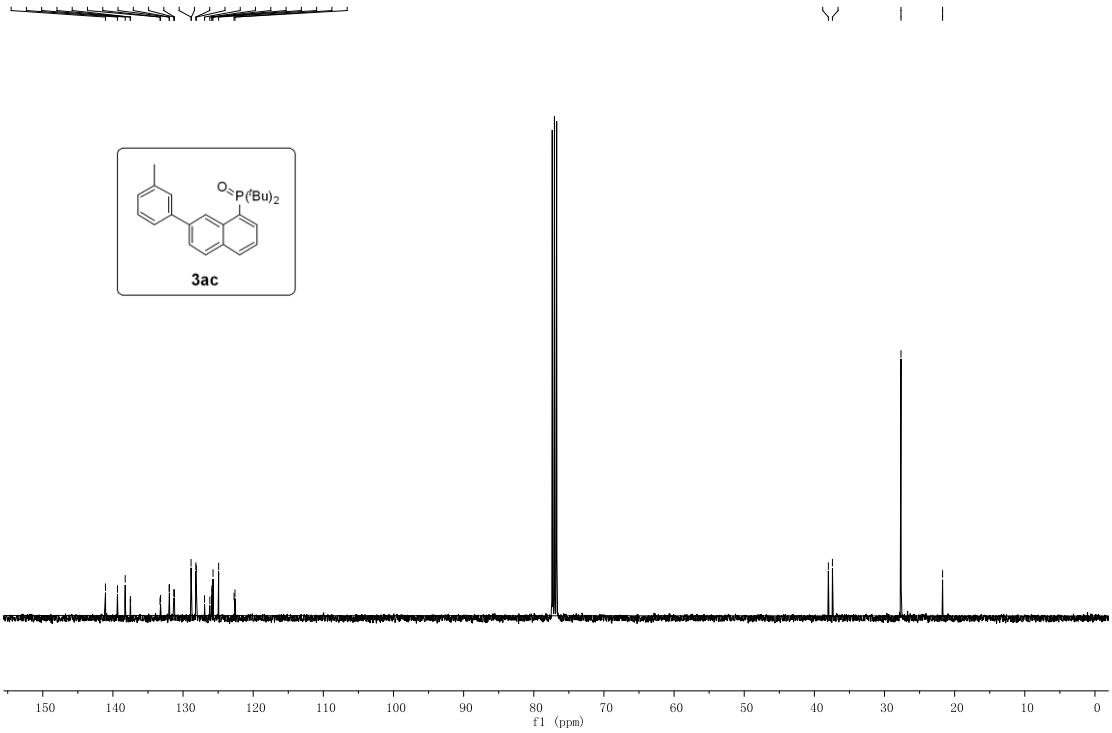
^{1}H NMR spectrum for **3ac**



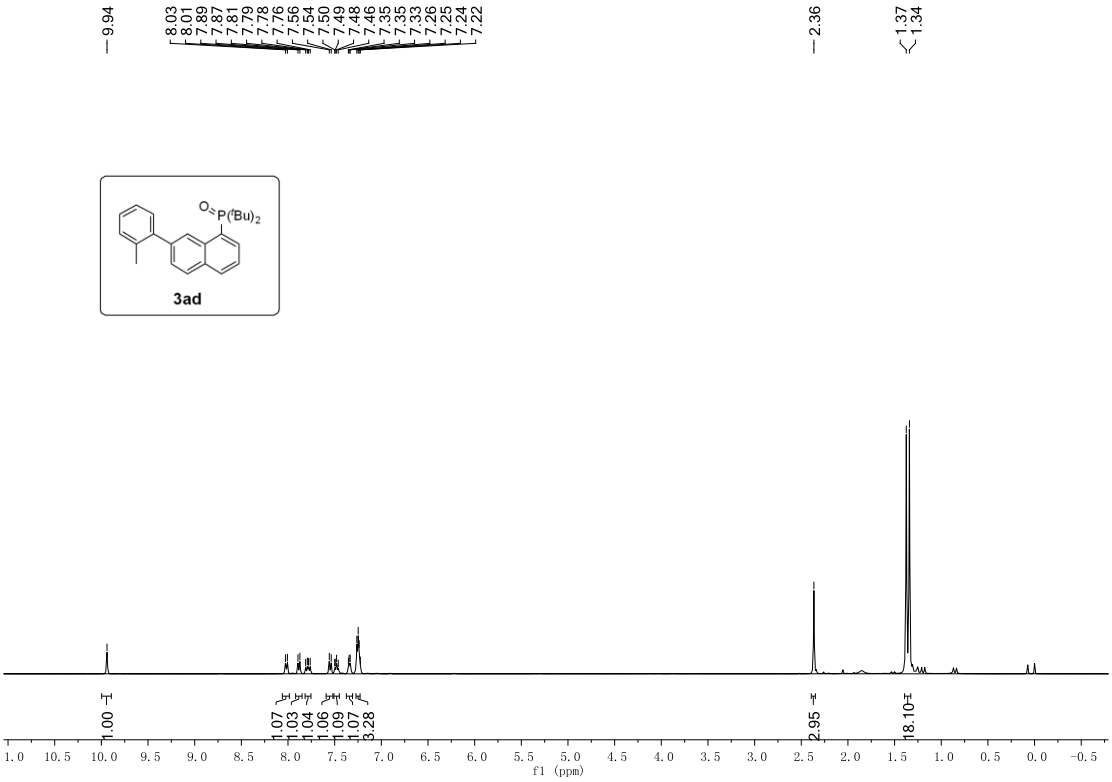
^{31}P NMR spectrum for **3ac**



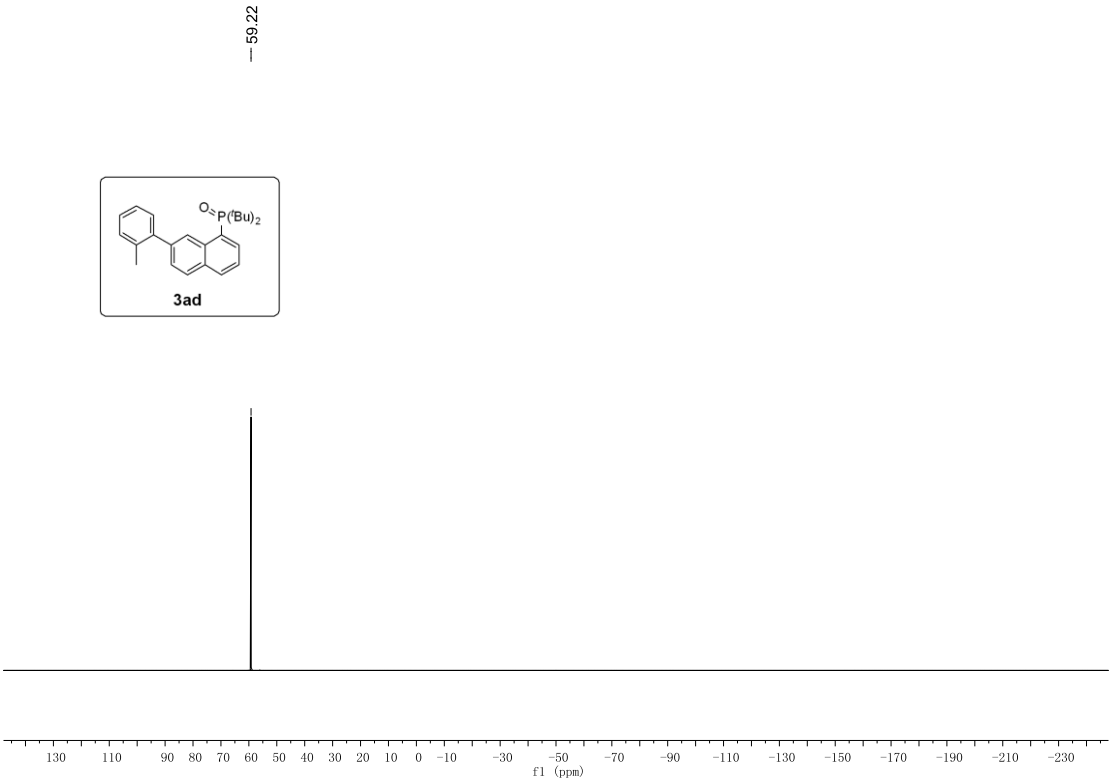
^{13}C NMR spectrum for **3ac**



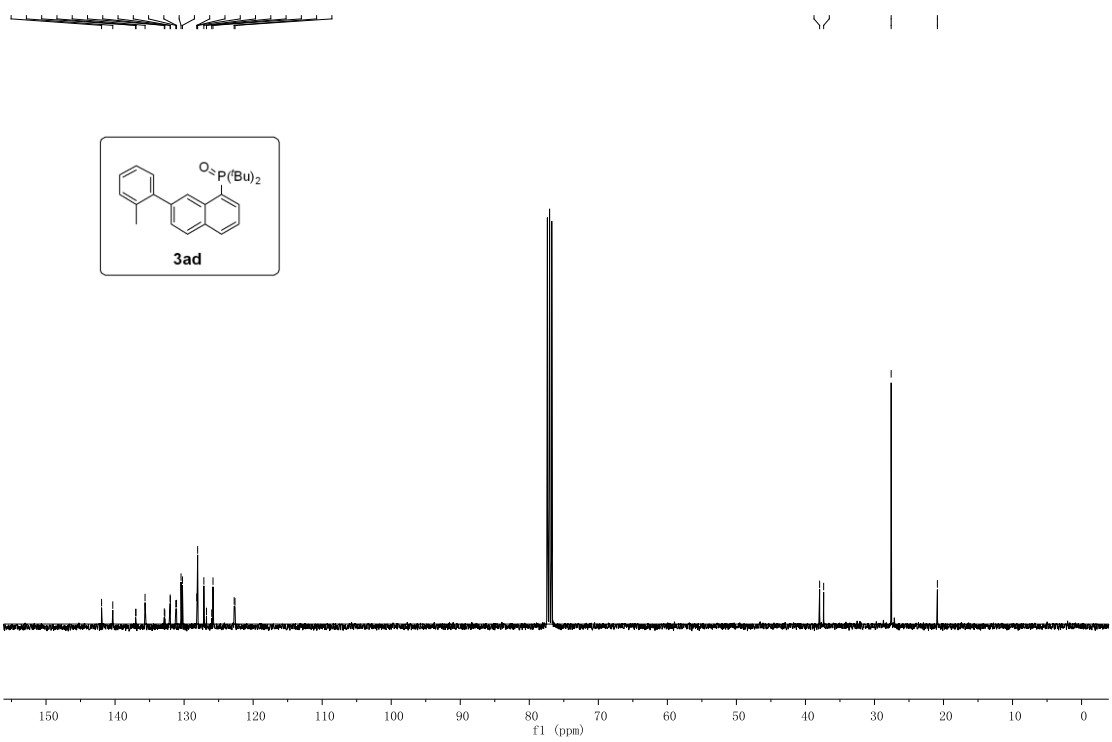
^{1}H NMR spectrum for **3ad**



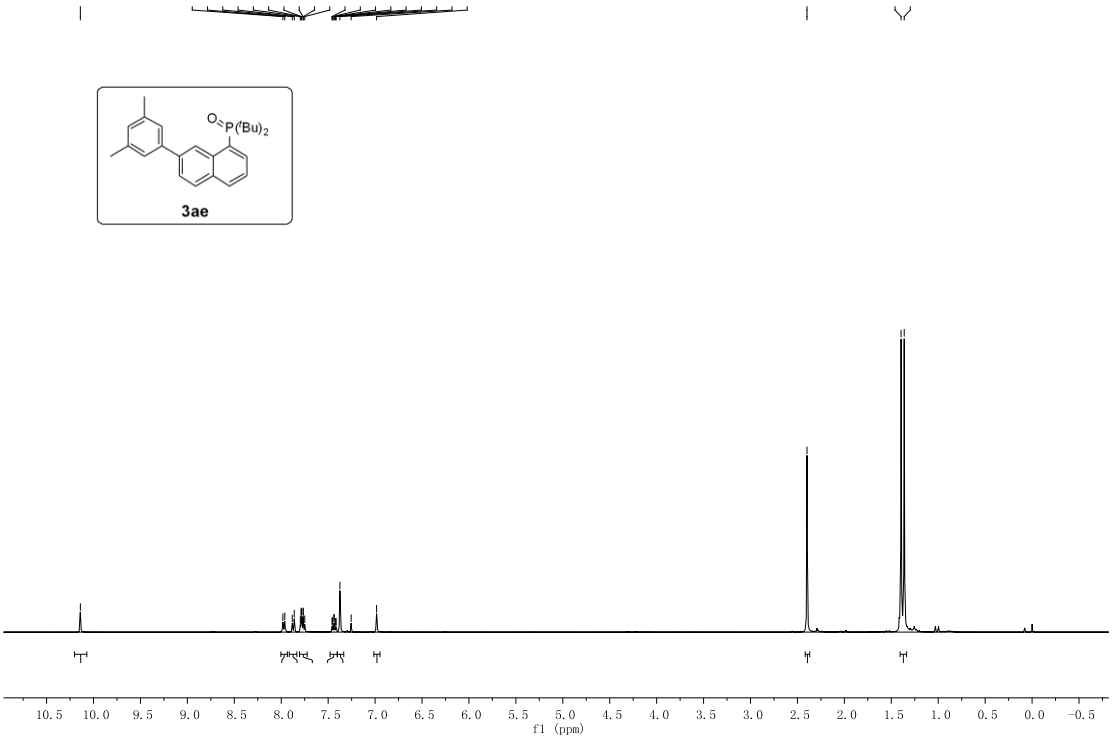
^{31}P NMR spectrum for **3ad**



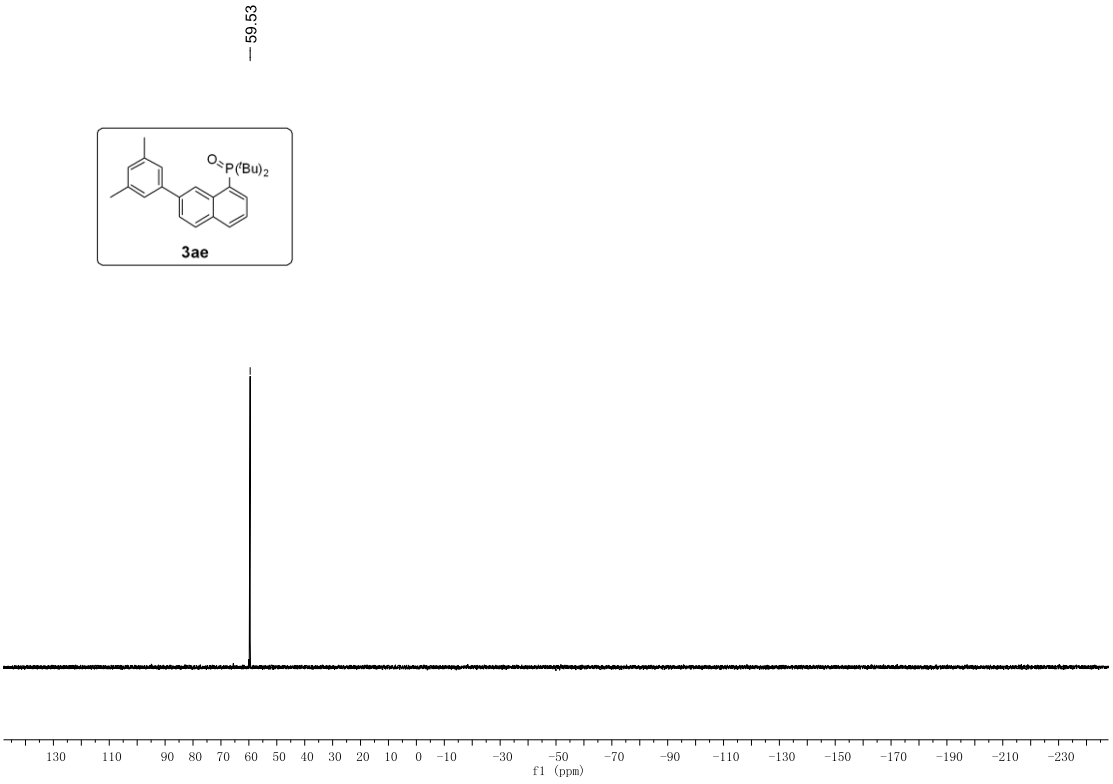
^{13}C NMR spectrum for **3ad**



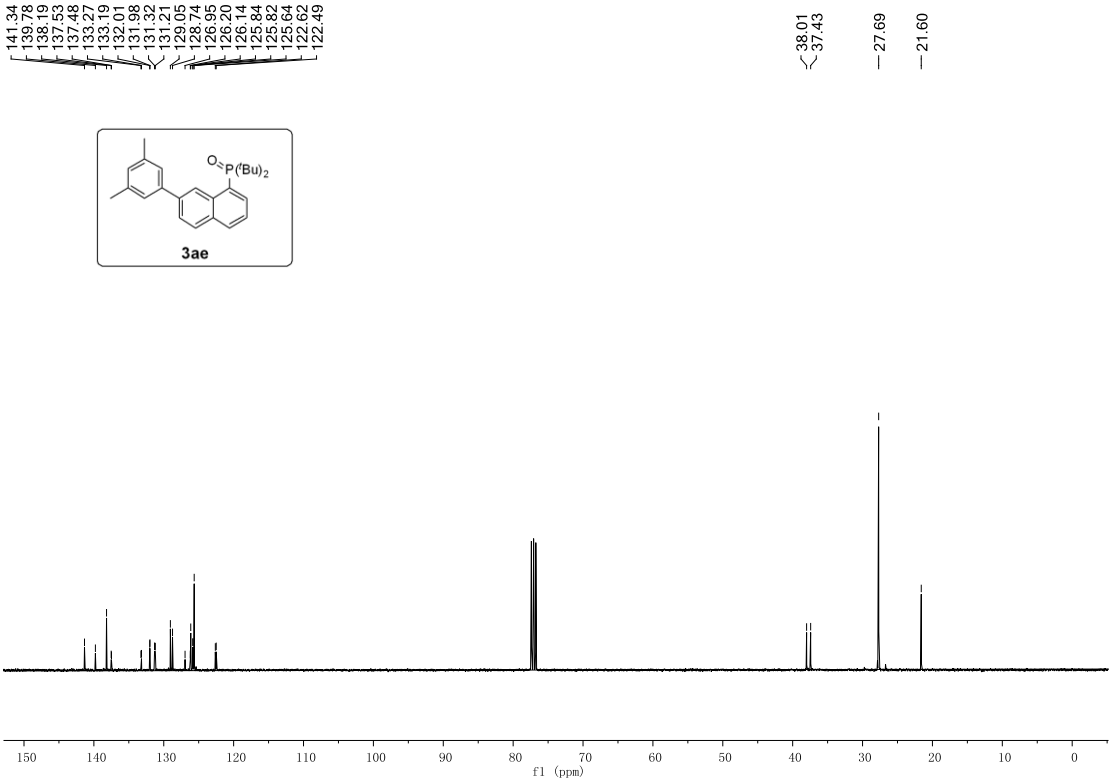
^{1}H NMR spectrum for **3ae**



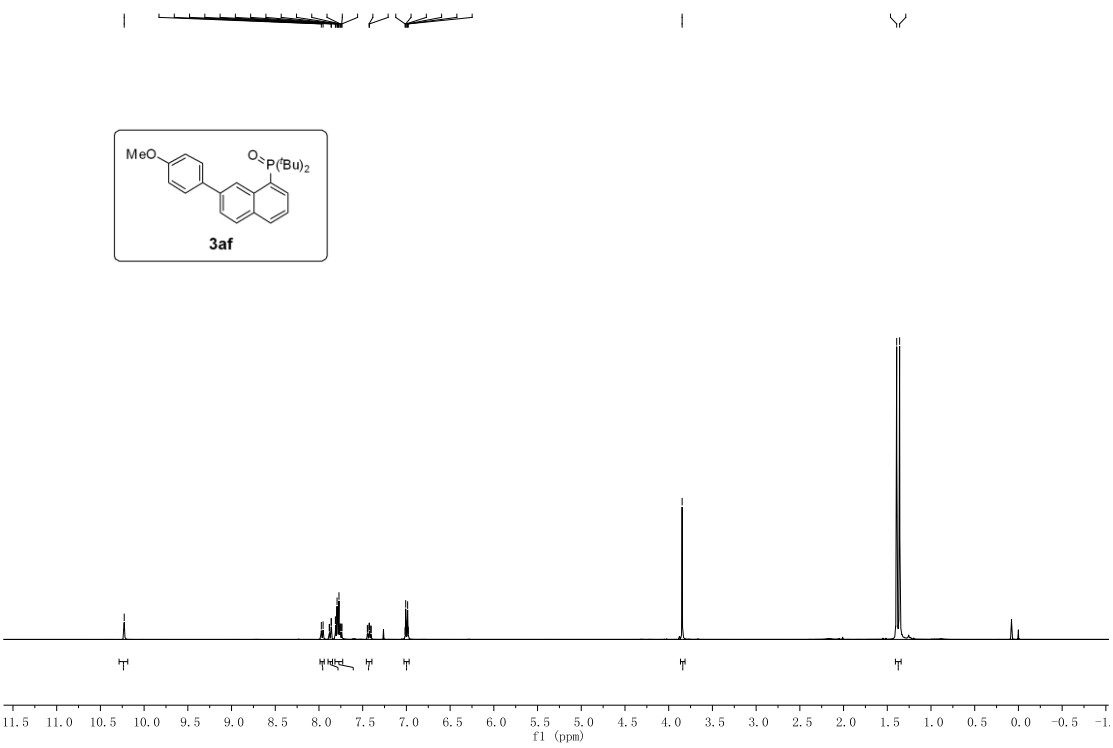
^{31}P NMR spectrum for **3ae**



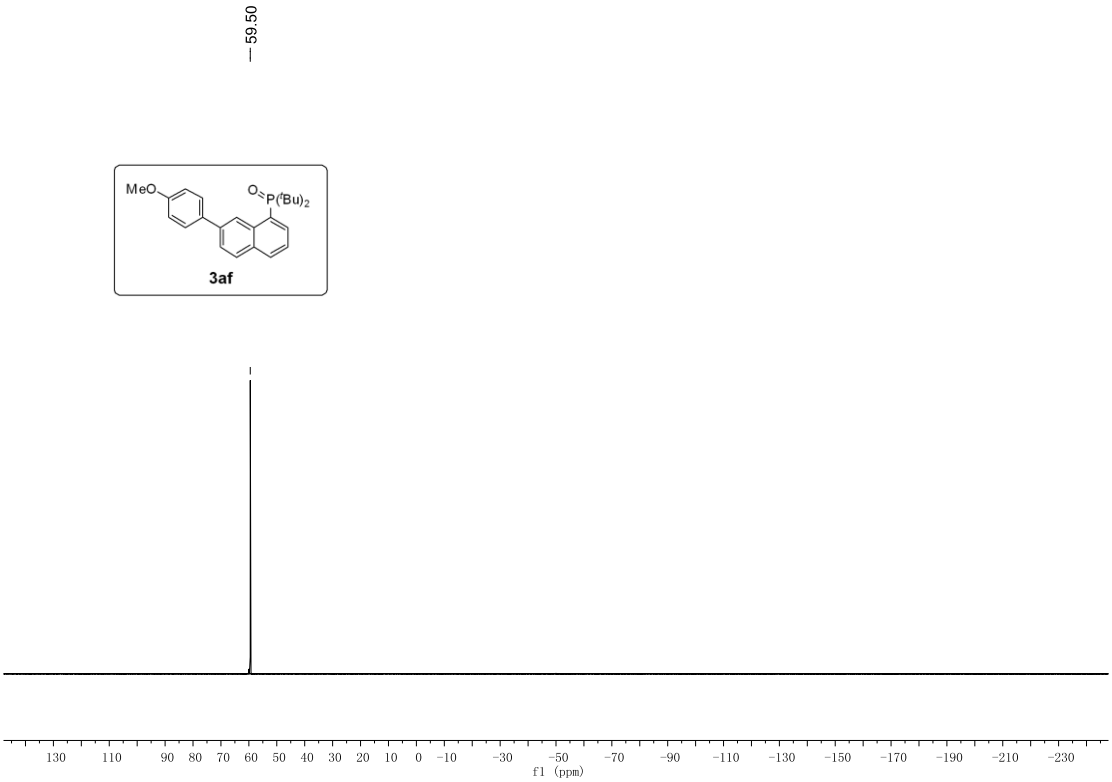
^{13}C NMR spectrum for **3ae**



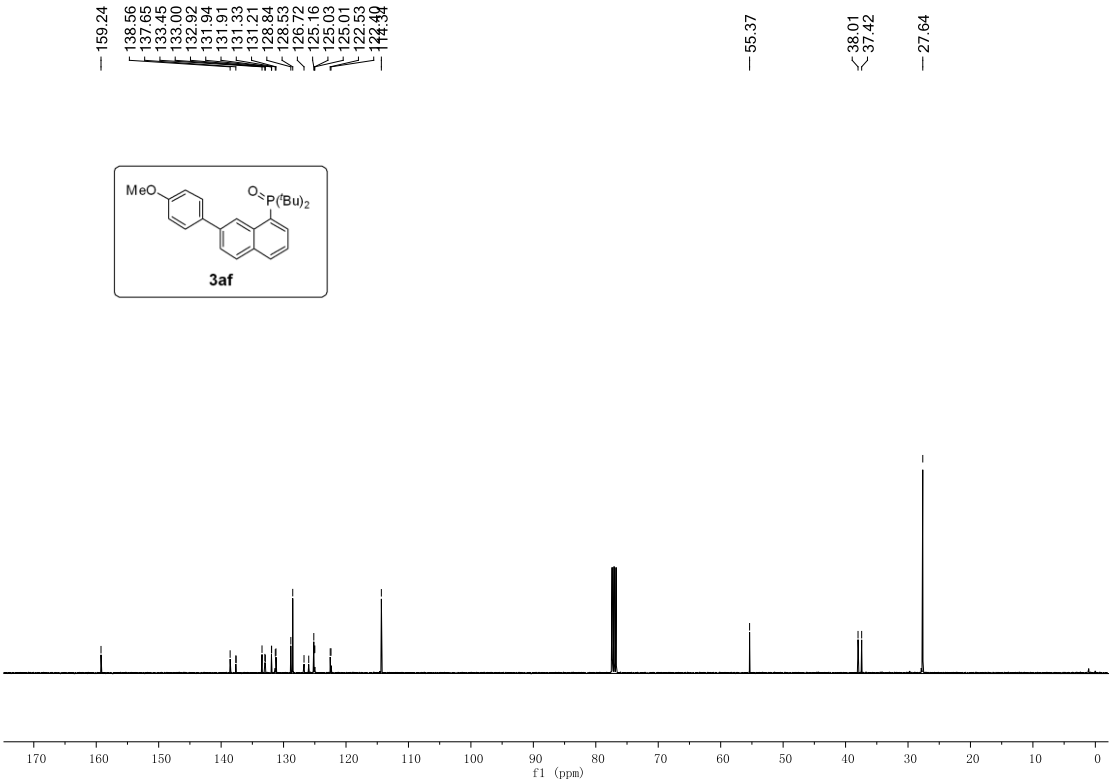
^{1}H NMR spectrum for **3af**



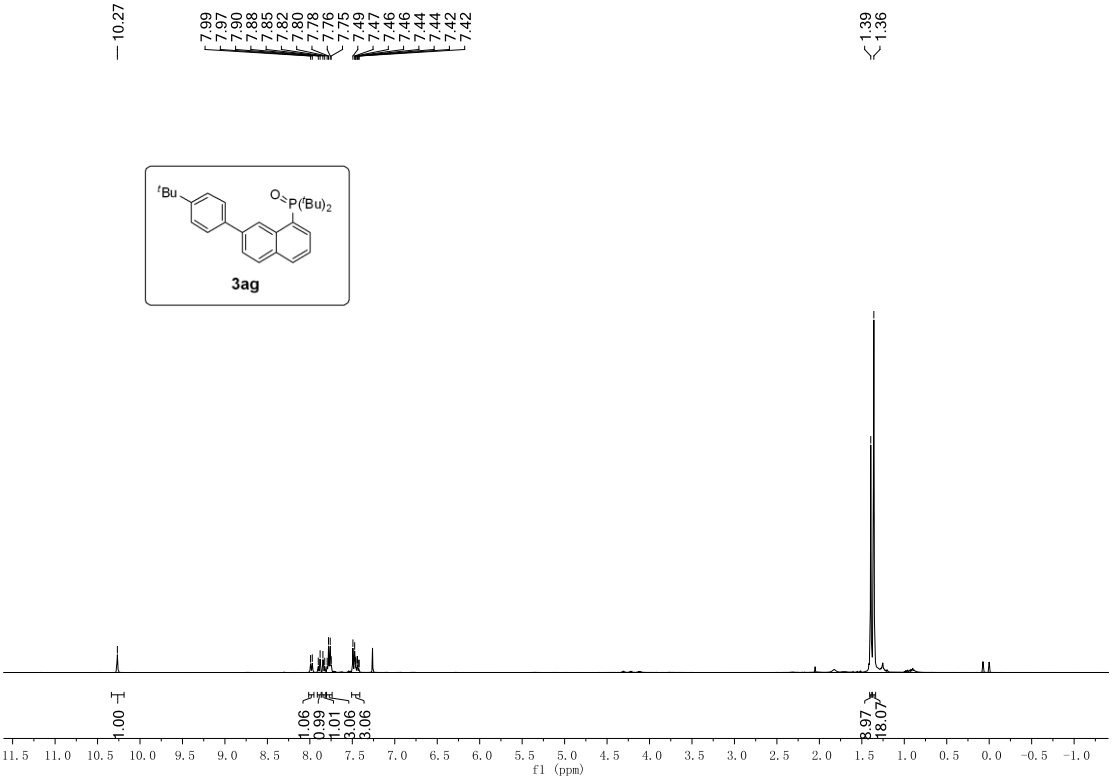
^{31}P NMR spectrum for **3af**



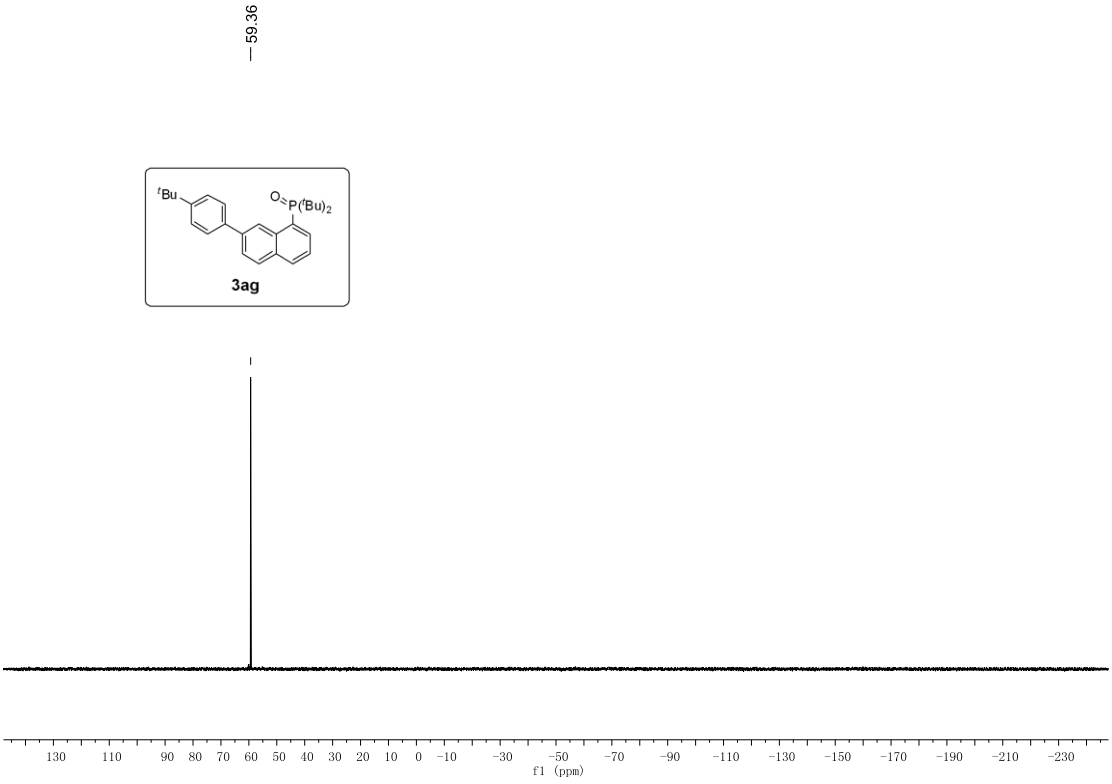
^{13}C NMR spectrum for **3af**



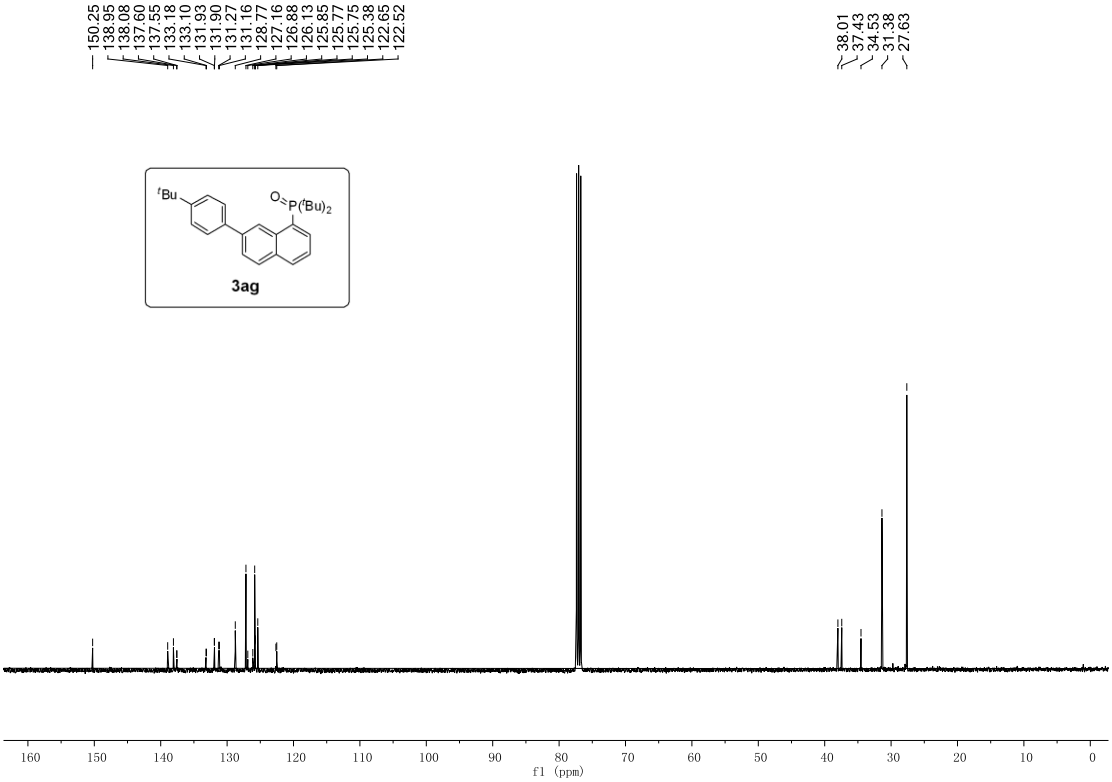
^{1}H NMR spectrum for **3ag**



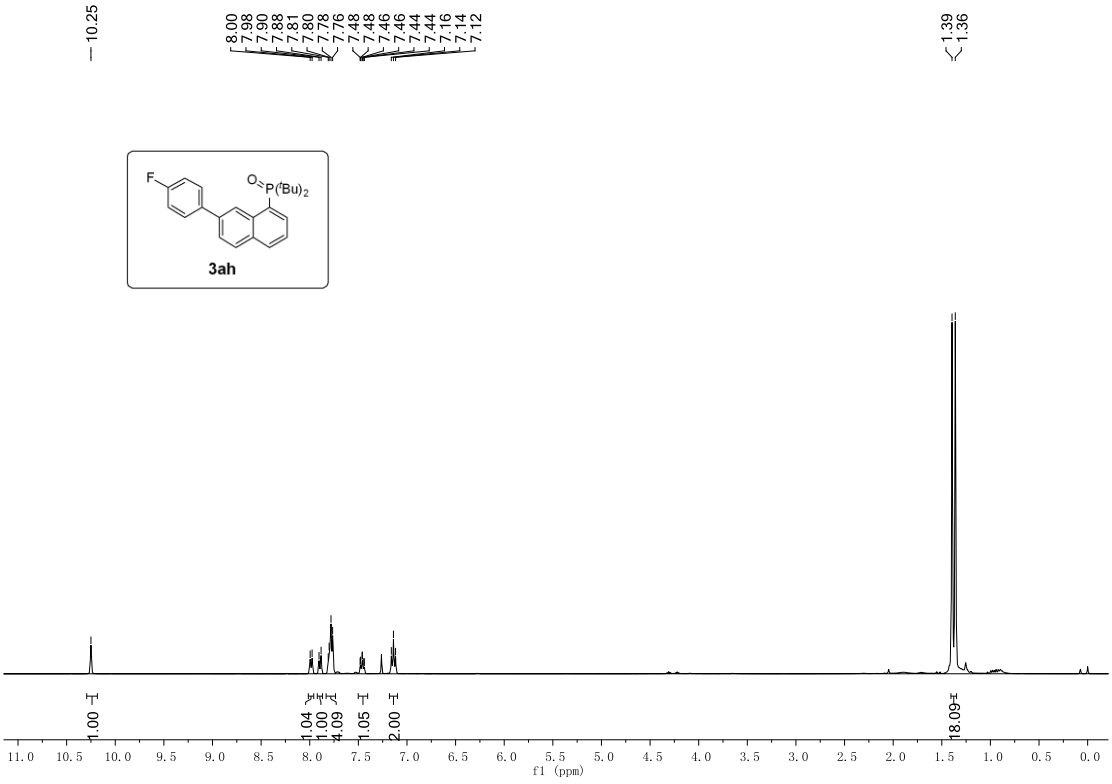
^{31}P NMR spectrum for **3ag**



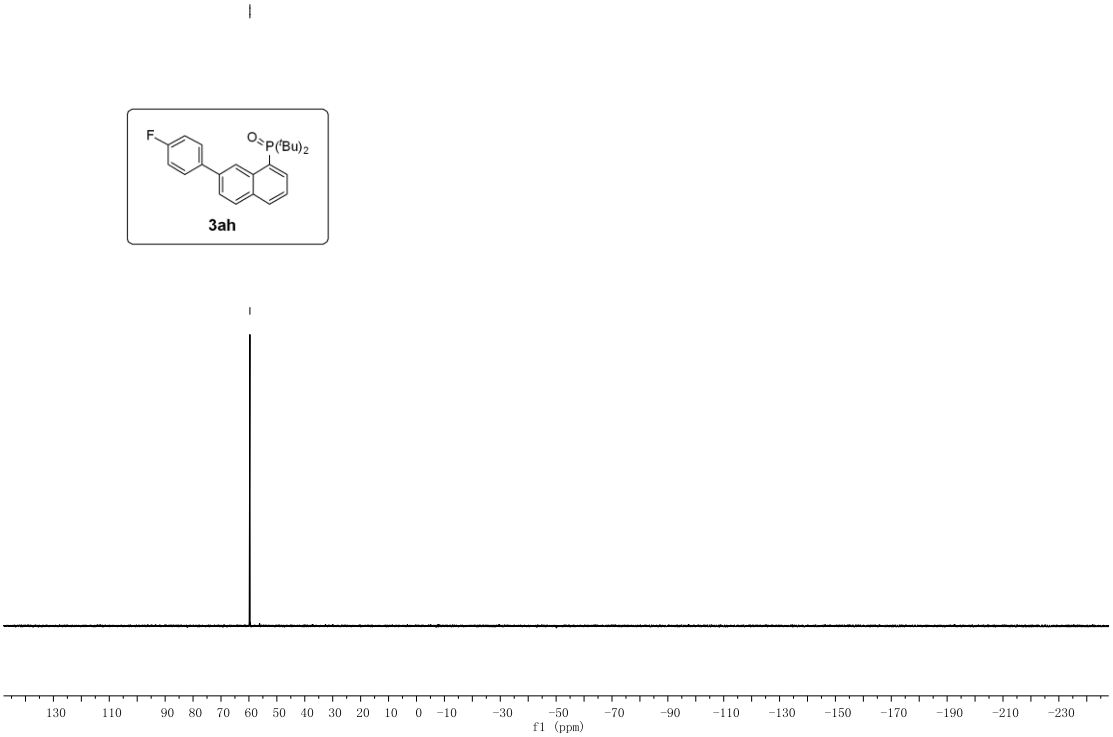
^{13}C NMR spectrum for **3ag**



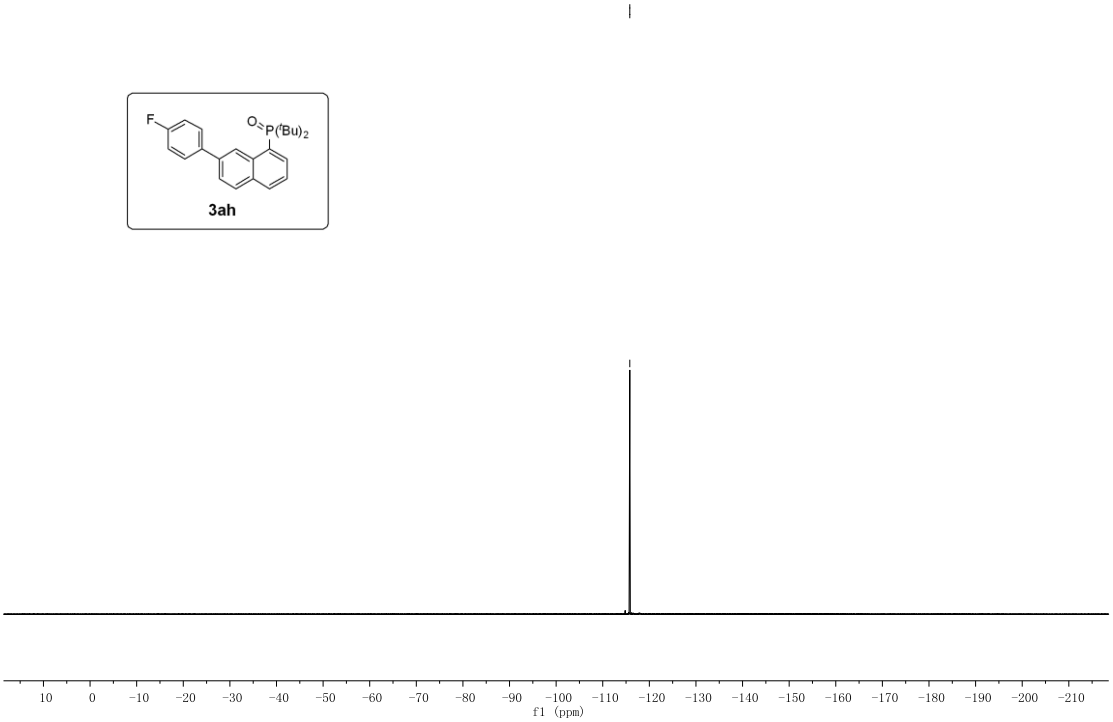
^{1}H NMR spectrum for **3ah**



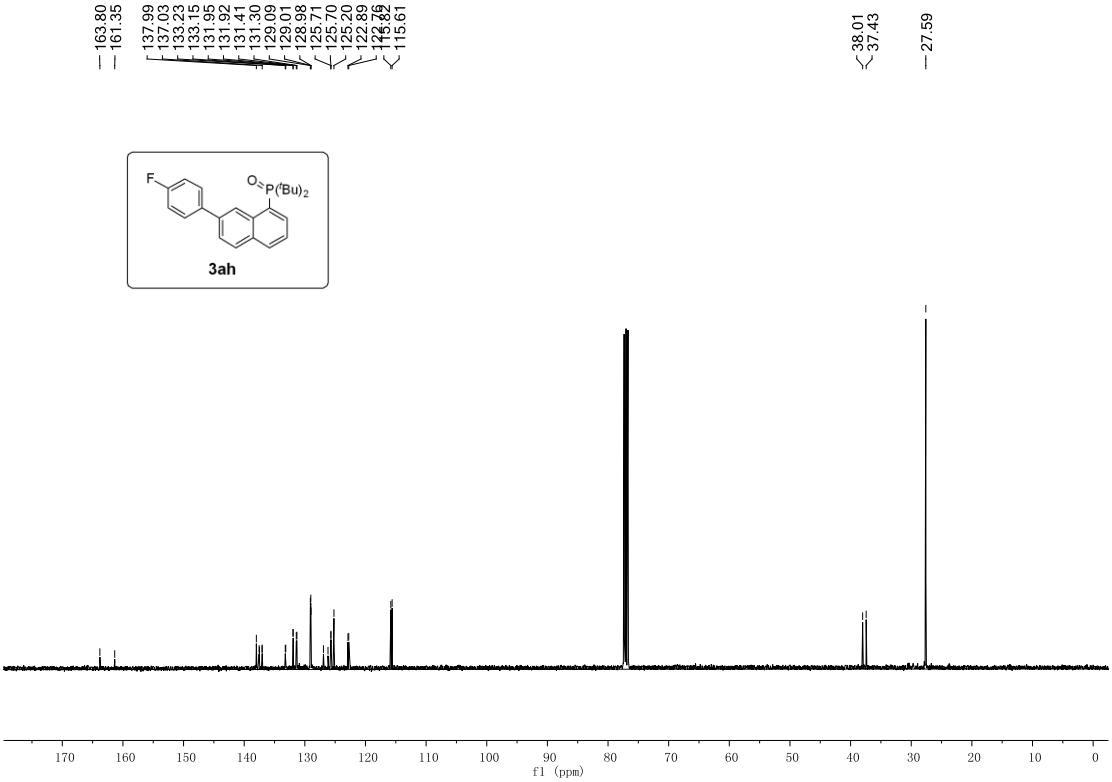
^{31}P NMR spectrum for **3ah**



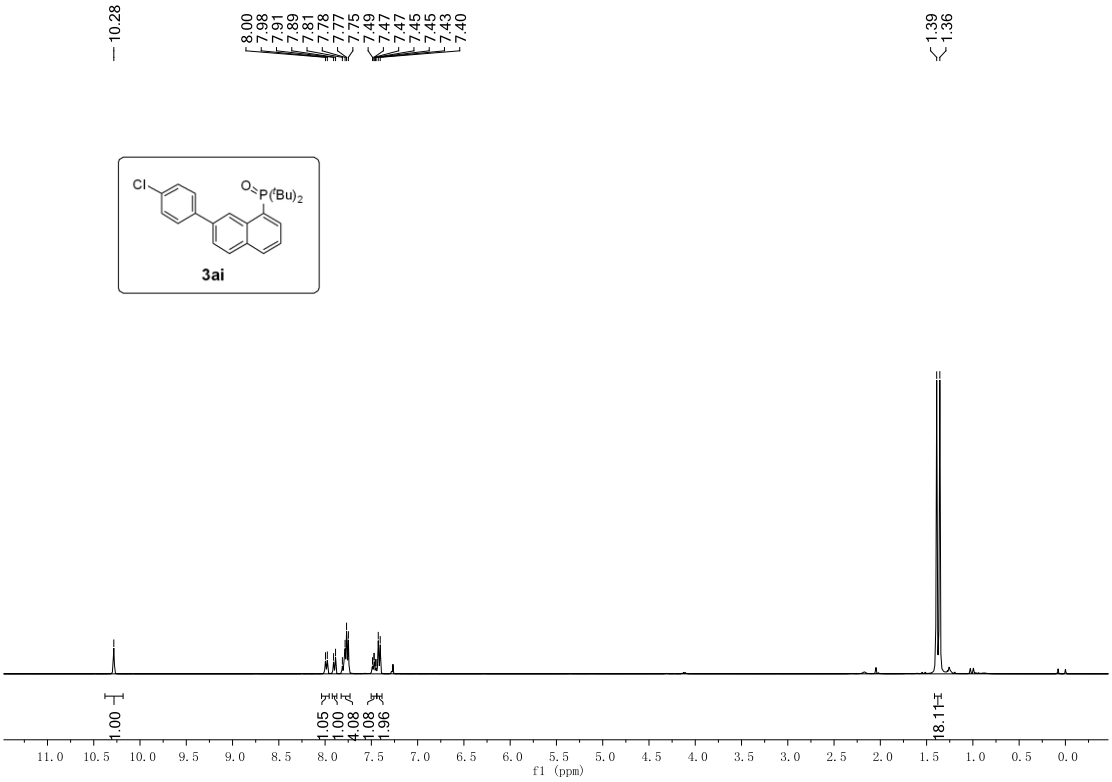
^{19}F NMR spectrum for **3ah**



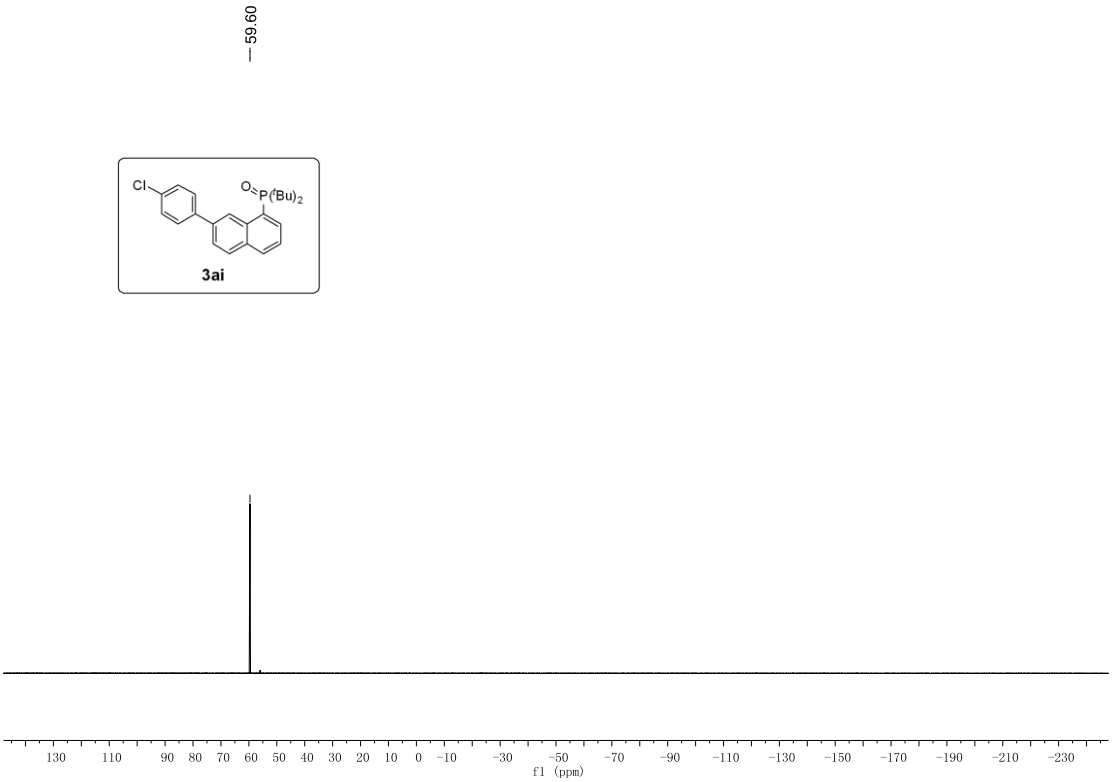
^{13}C NMR spectrum for **3ah**



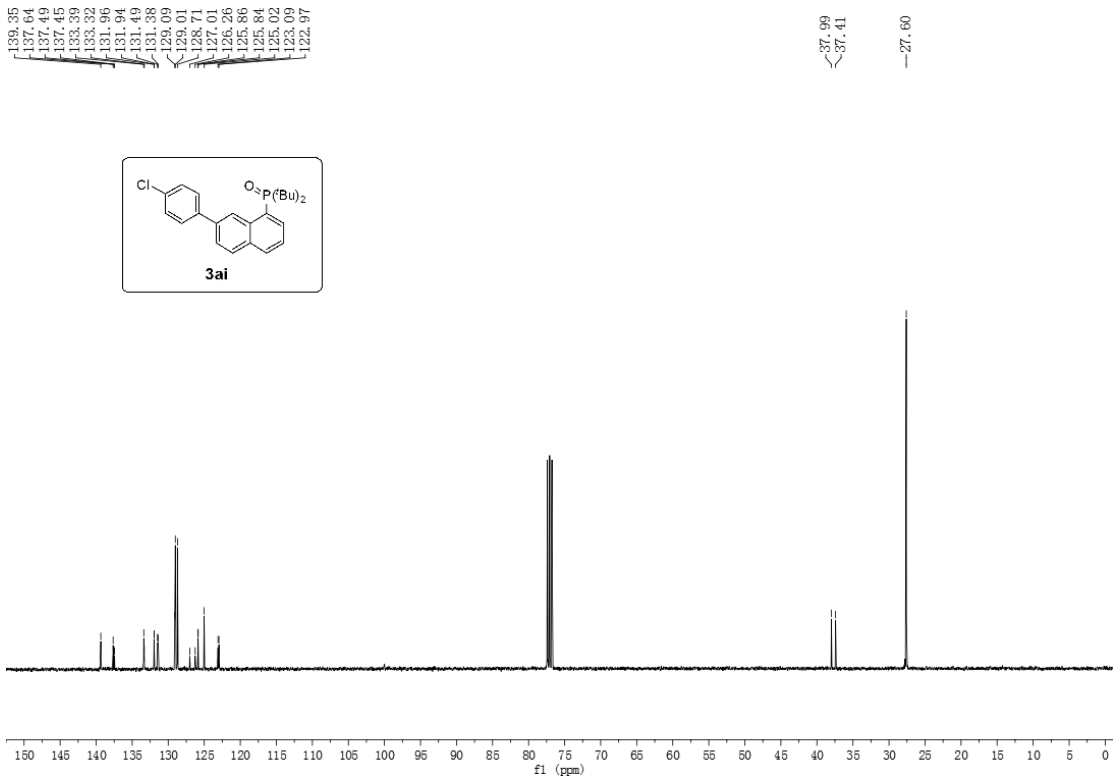
^{1}H NMR spectrum for **3ai**



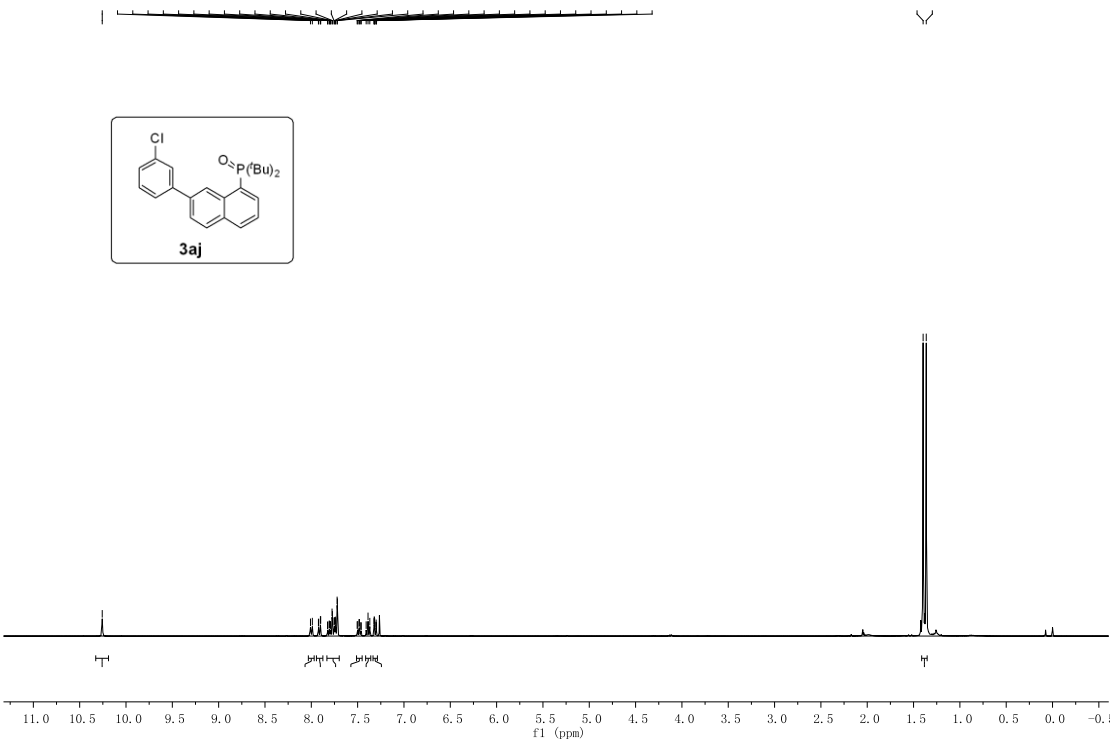
^{31}P NMR spectrum for **3ai**



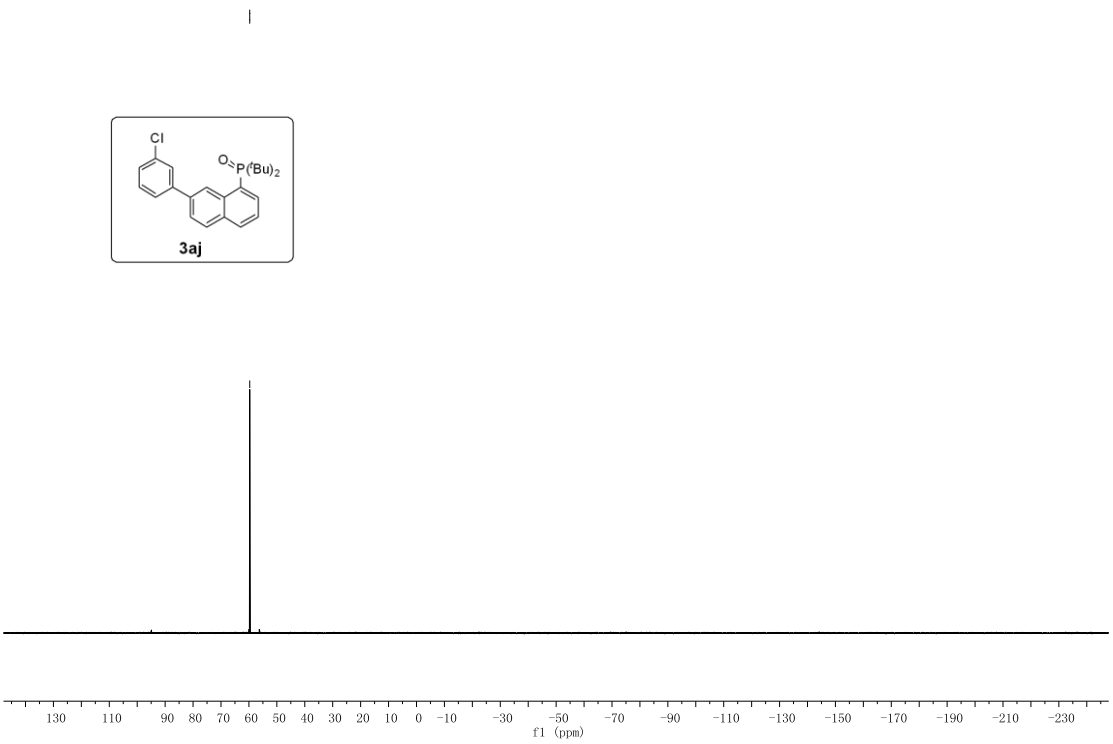
^{13}C NMR spectrum for **3ai**



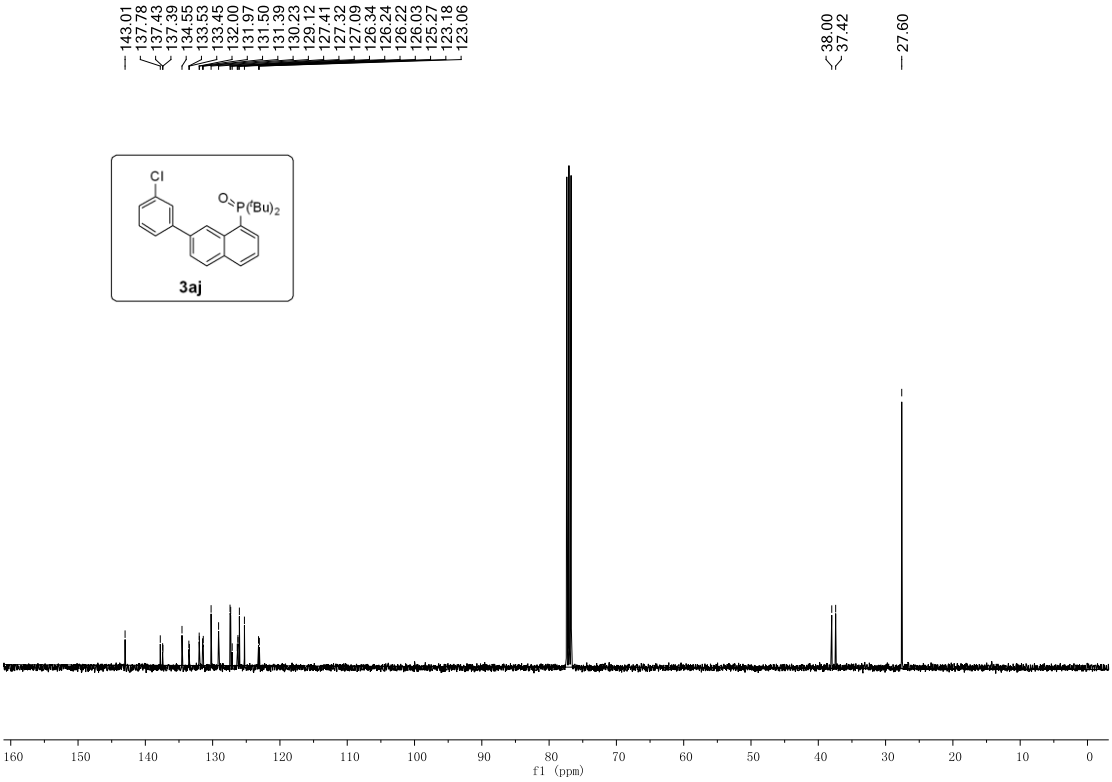
^{1}H NMR spectrum for **3aj**



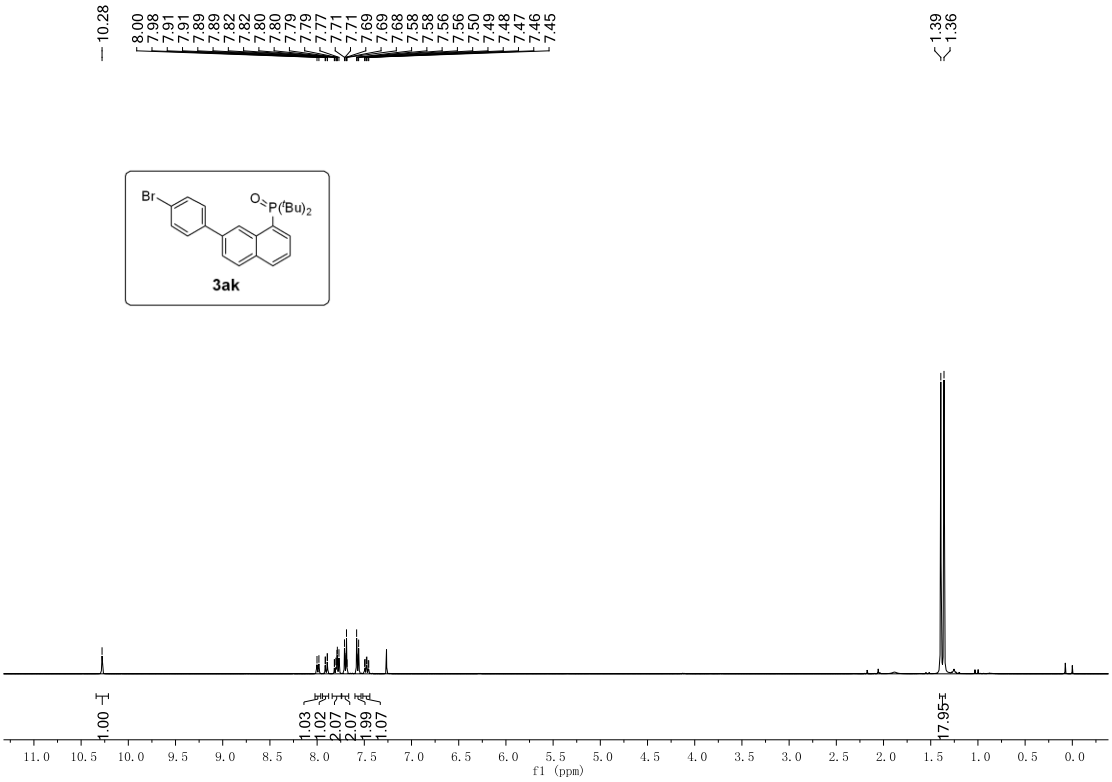
^{31}P NMR spectrum for **3aj**



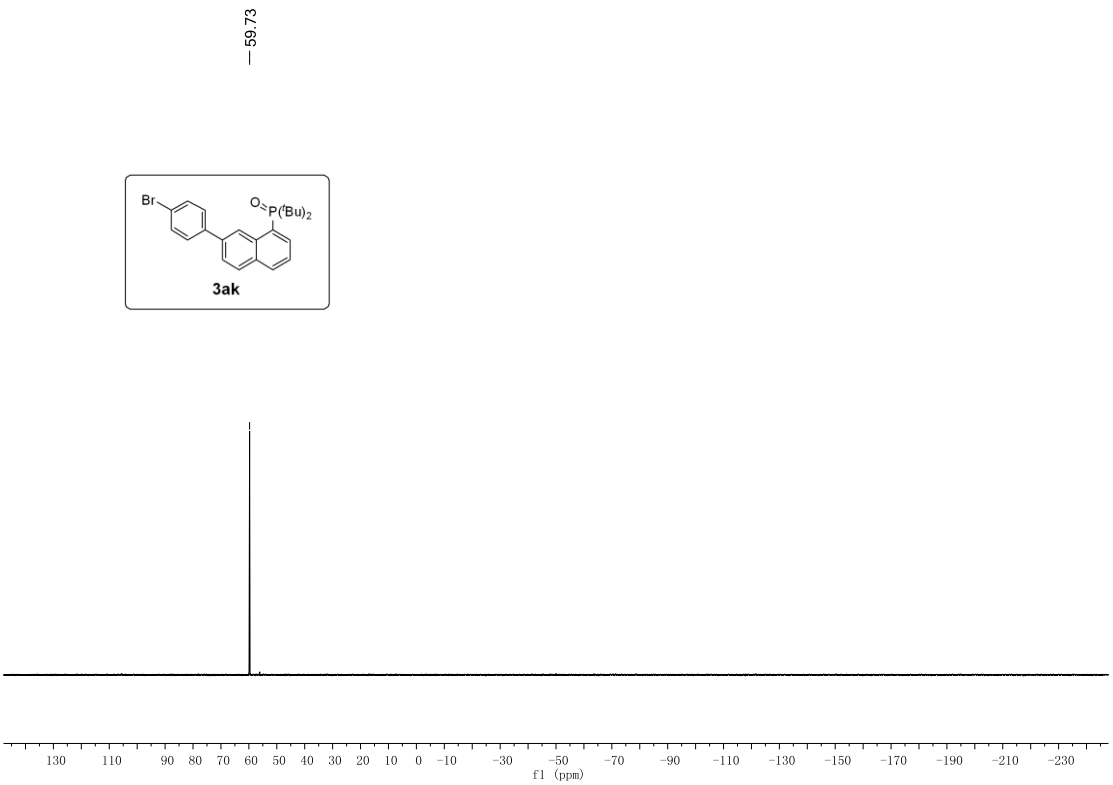
^{13}C NMR spectrum for **3aj**



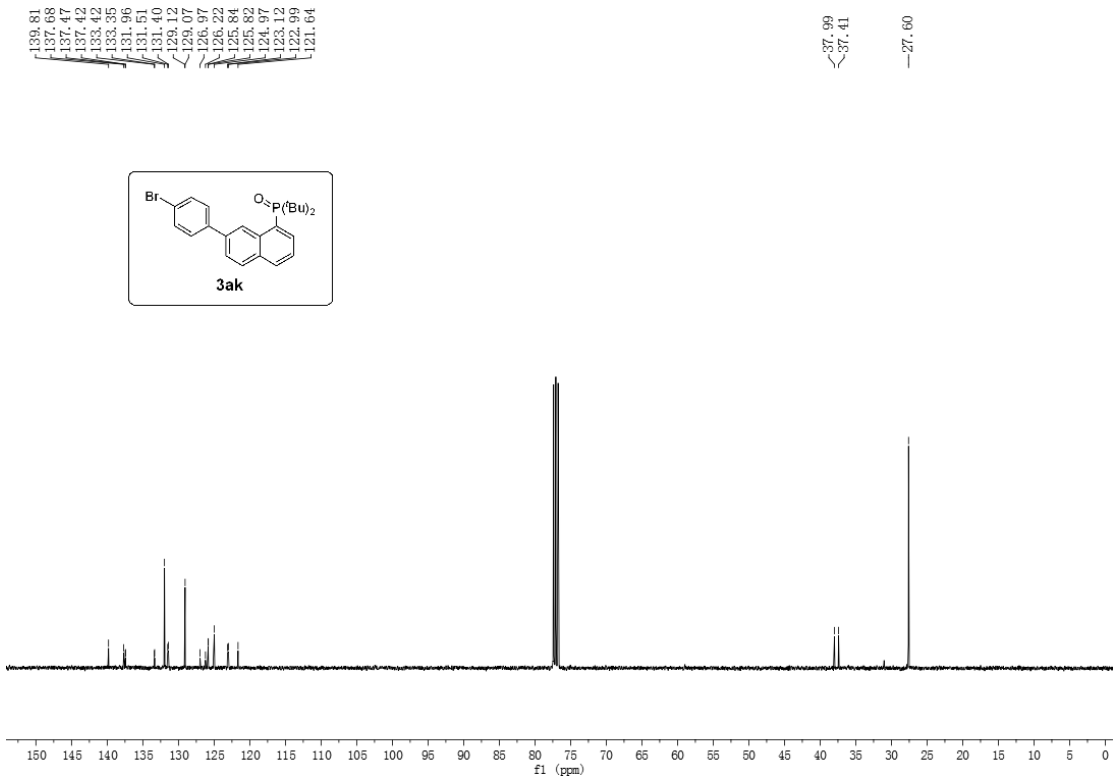
^{1}H NMR spectrum for **3ak**



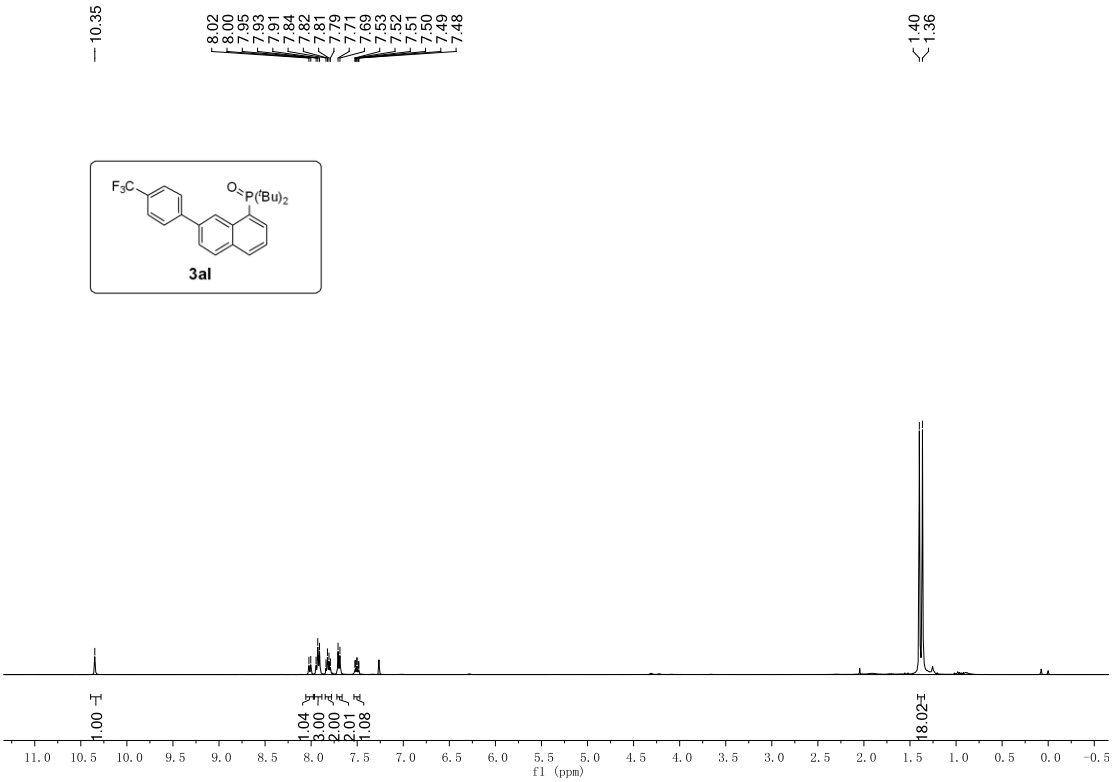
^{31}P NMR spectrum for **3ak**



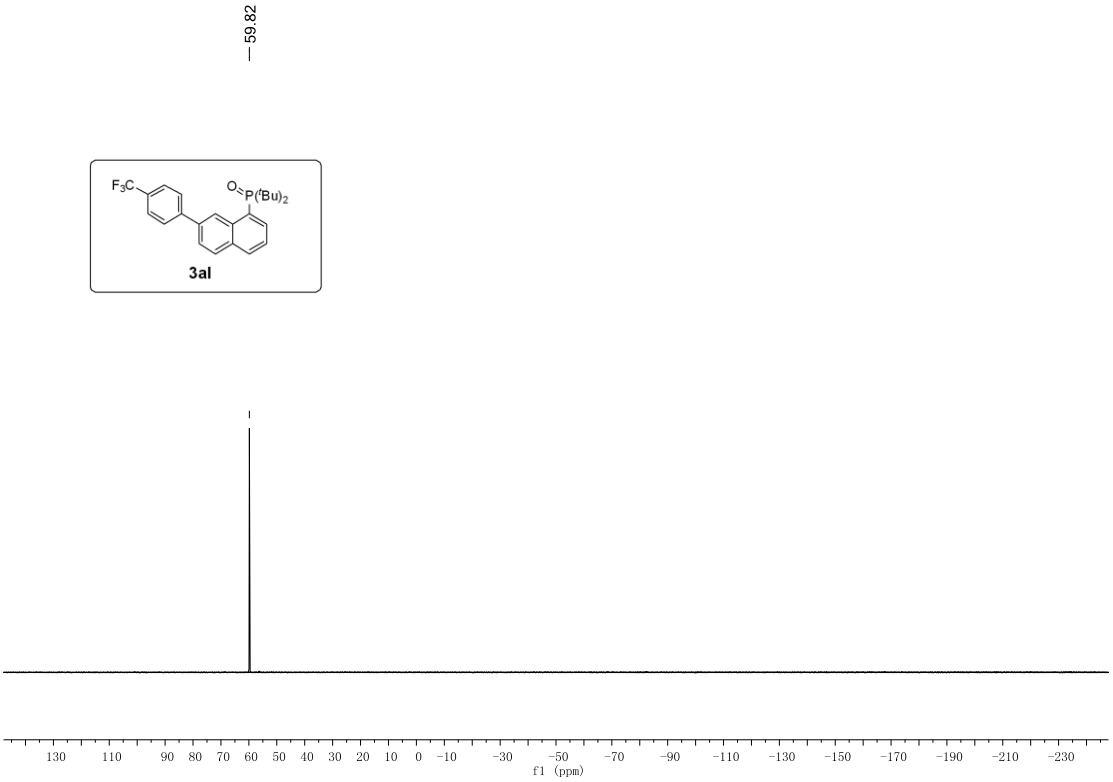
^{13}C NMR spectrum for **3ak**



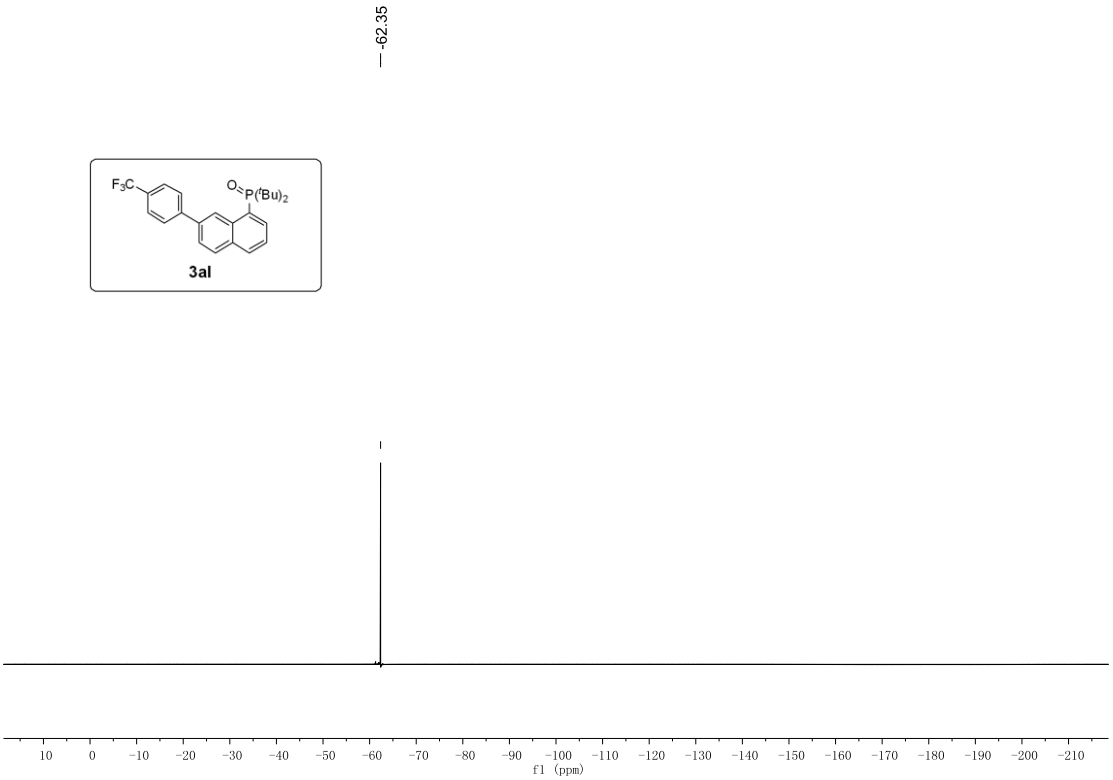
^{1}H NMR spectrum for **3al**



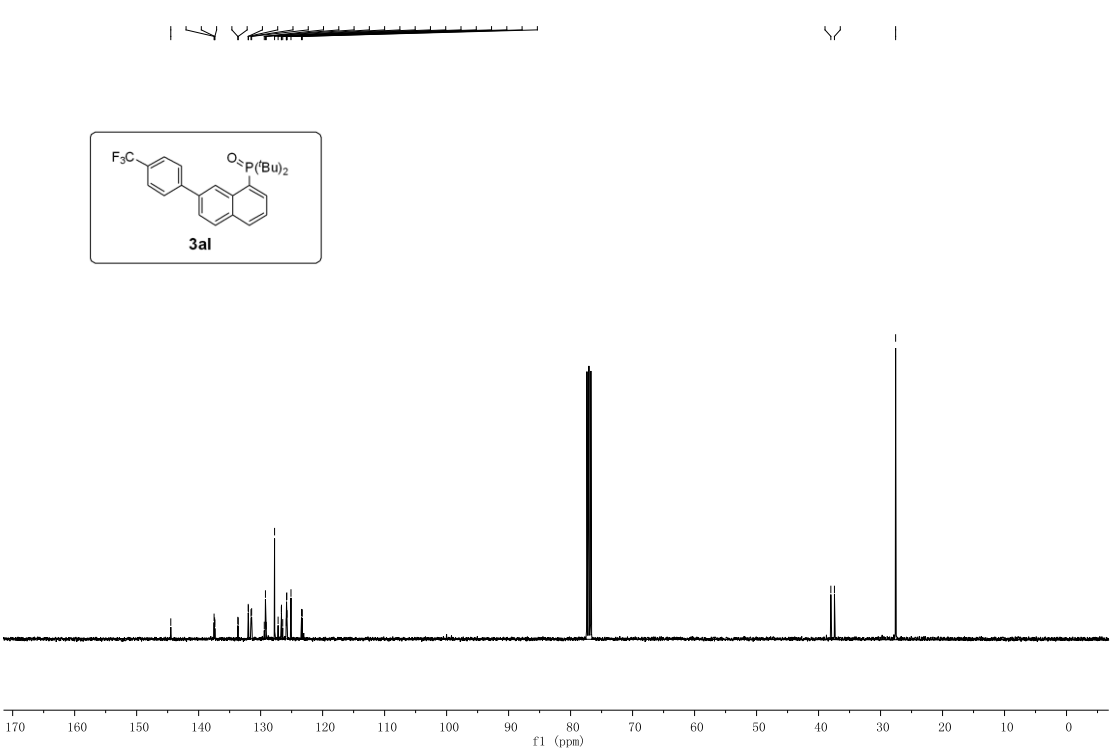
^{31}P NMR spectrum for **3al**



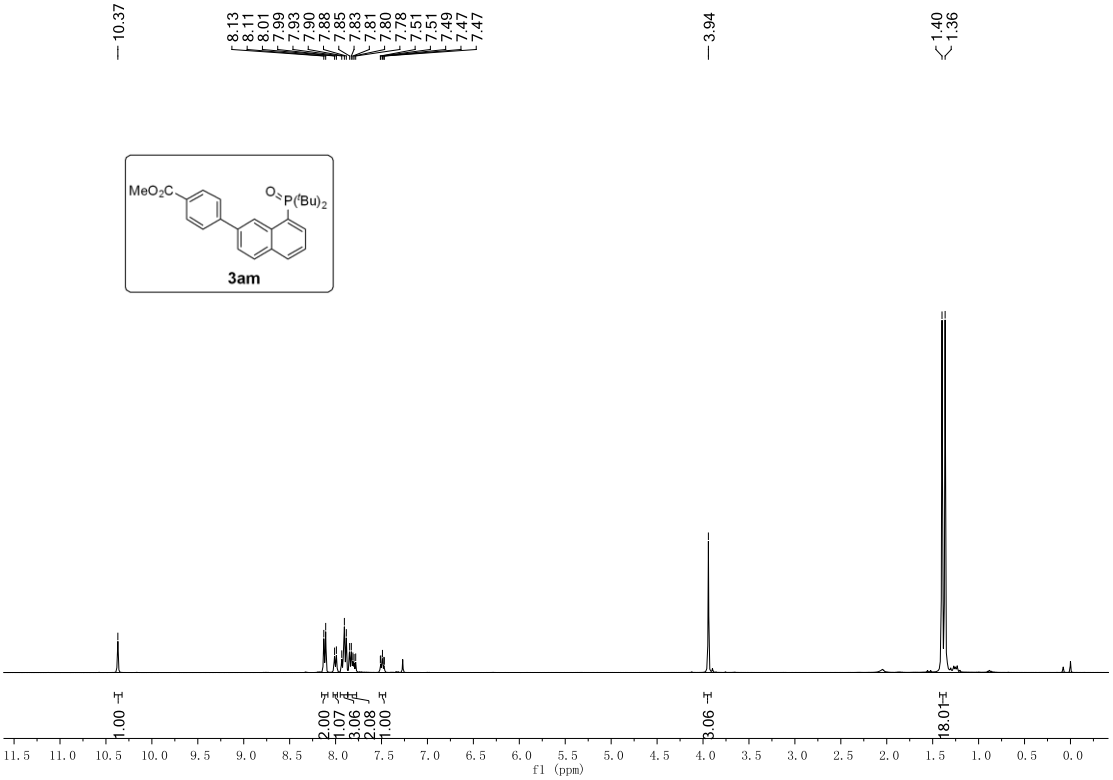
^{19}F NMR spectrum for **3al**



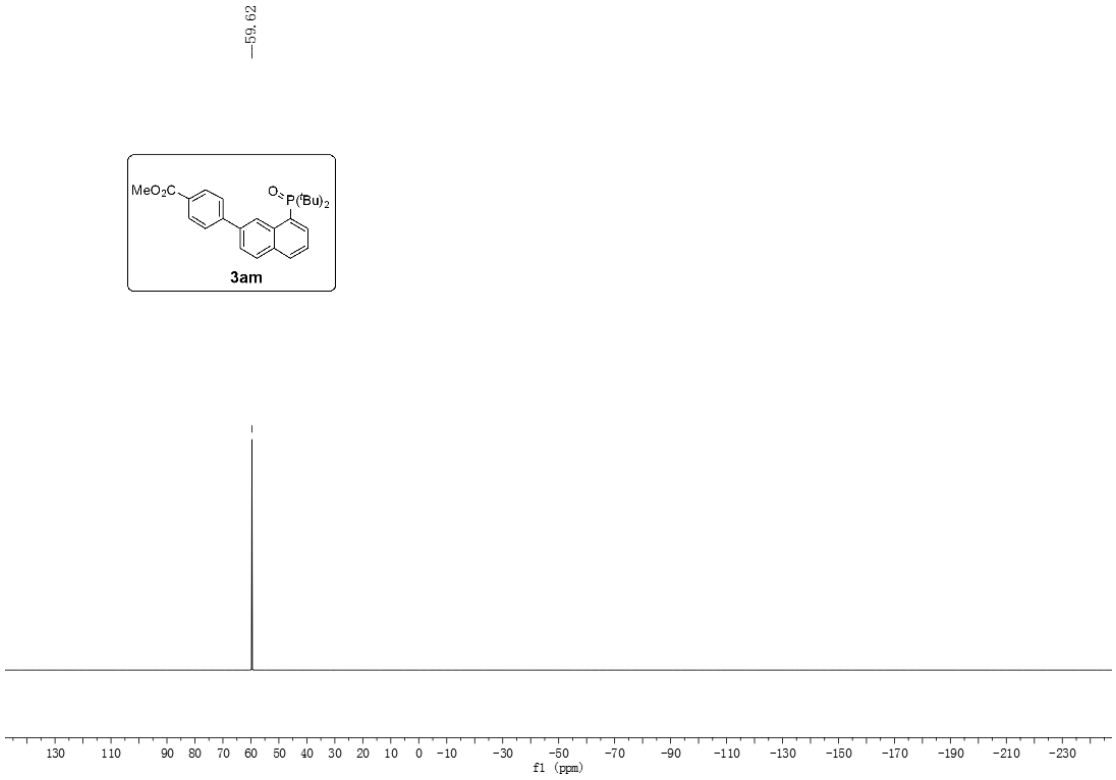
^{13}C NMR spectrum for **3al**



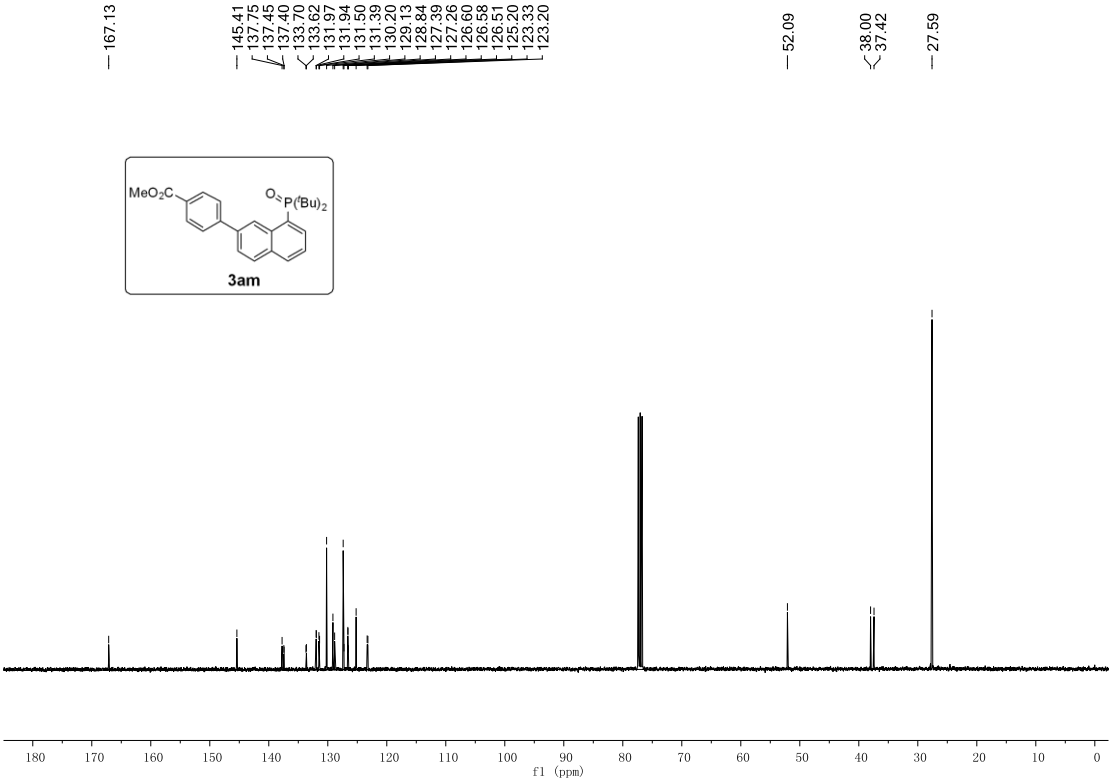
^{1}H NMR spectrum for **3am**



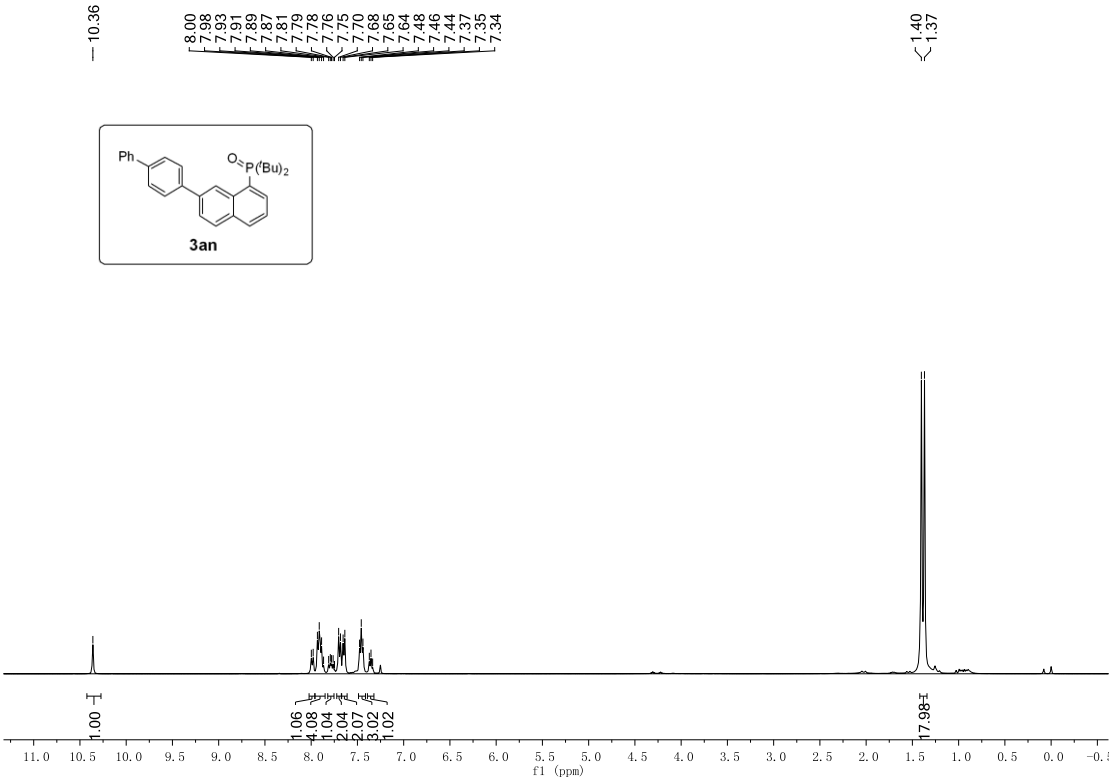
^{31}P NMR spectrum for **3am**



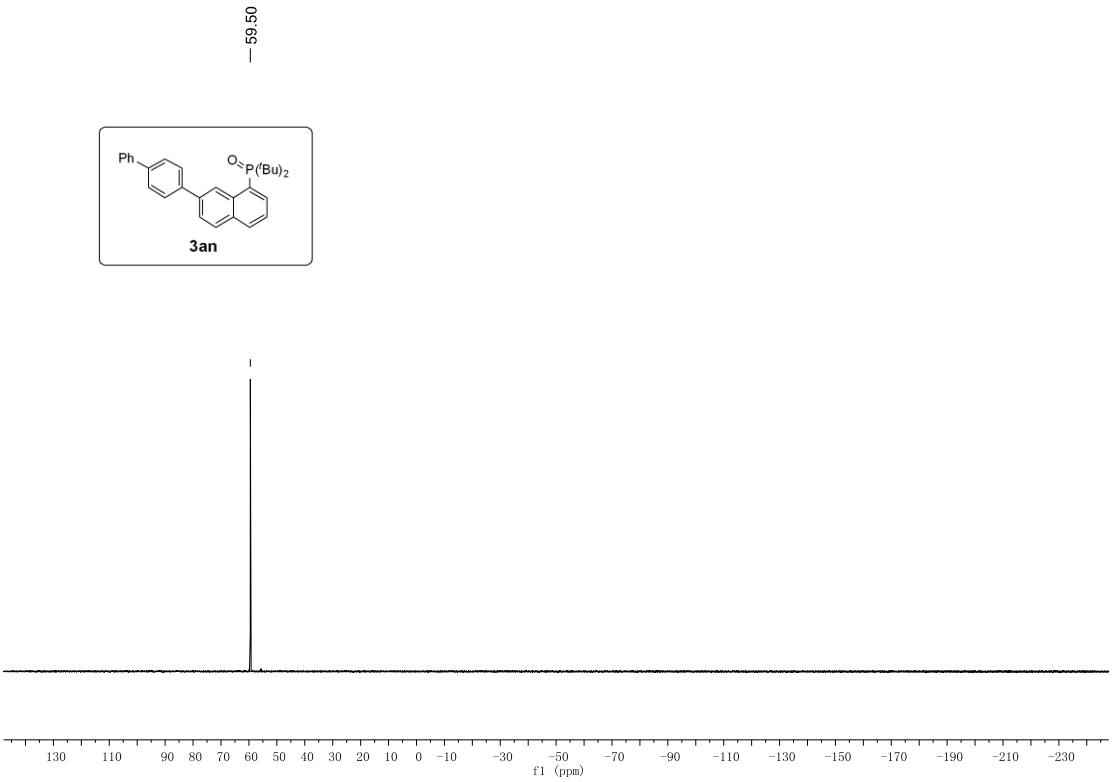
^{13}C NMR spectrum for **3am**



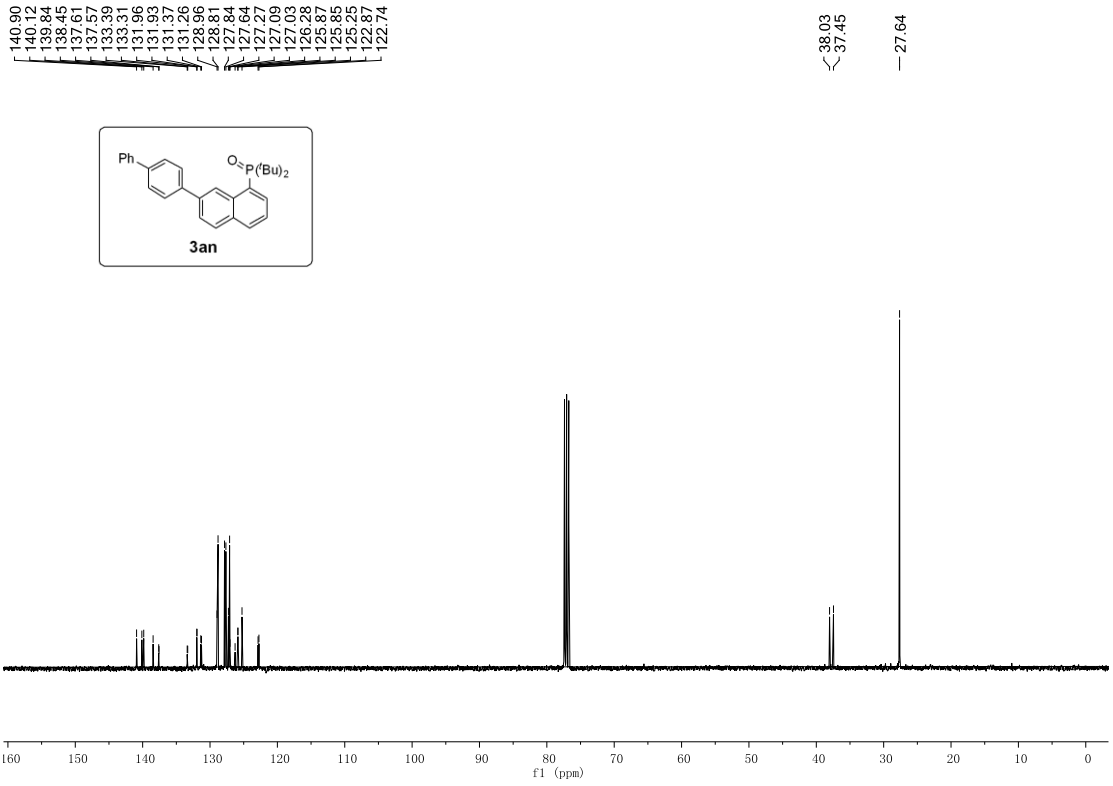
^{1}H NMR spectrum for **3an**



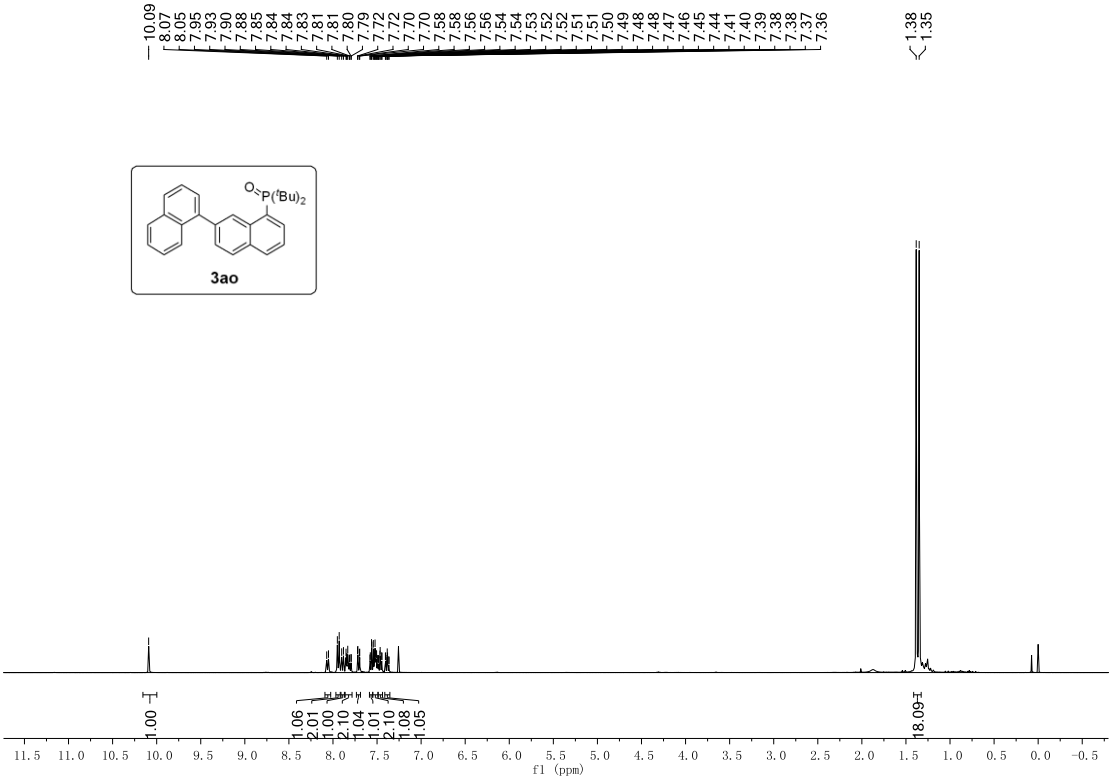
^{31}P NMR spectrum for **3an**



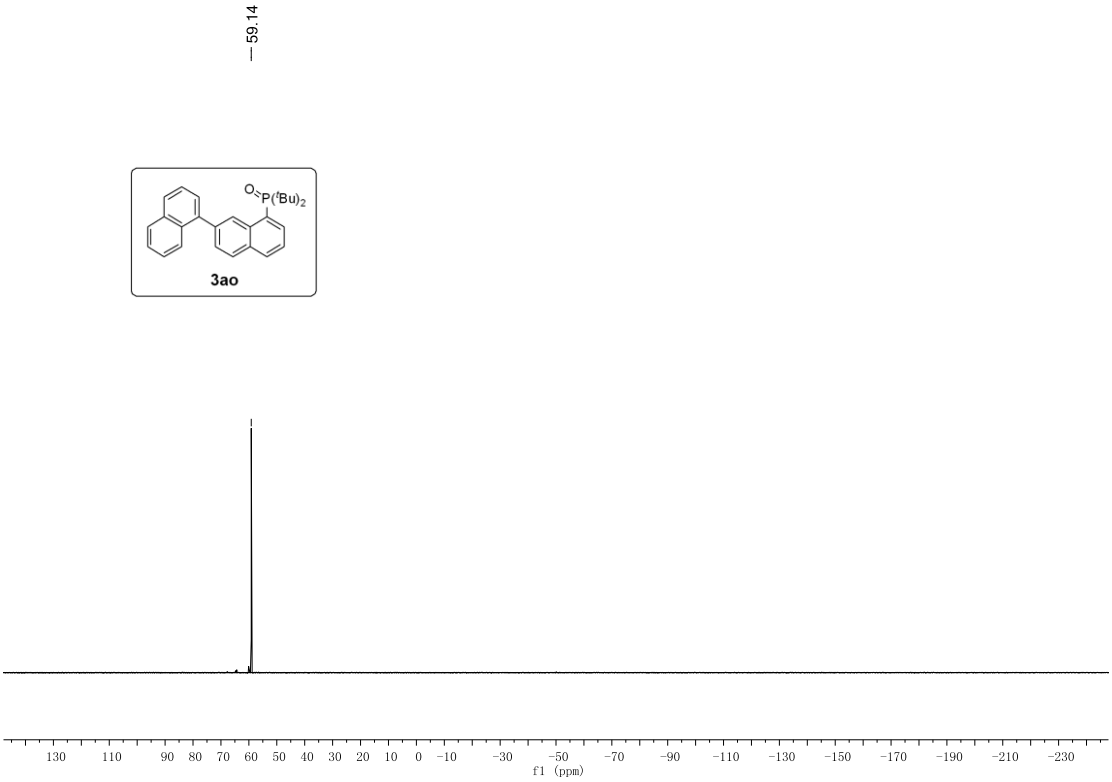
^{13}C NMR spectrum for **3an**



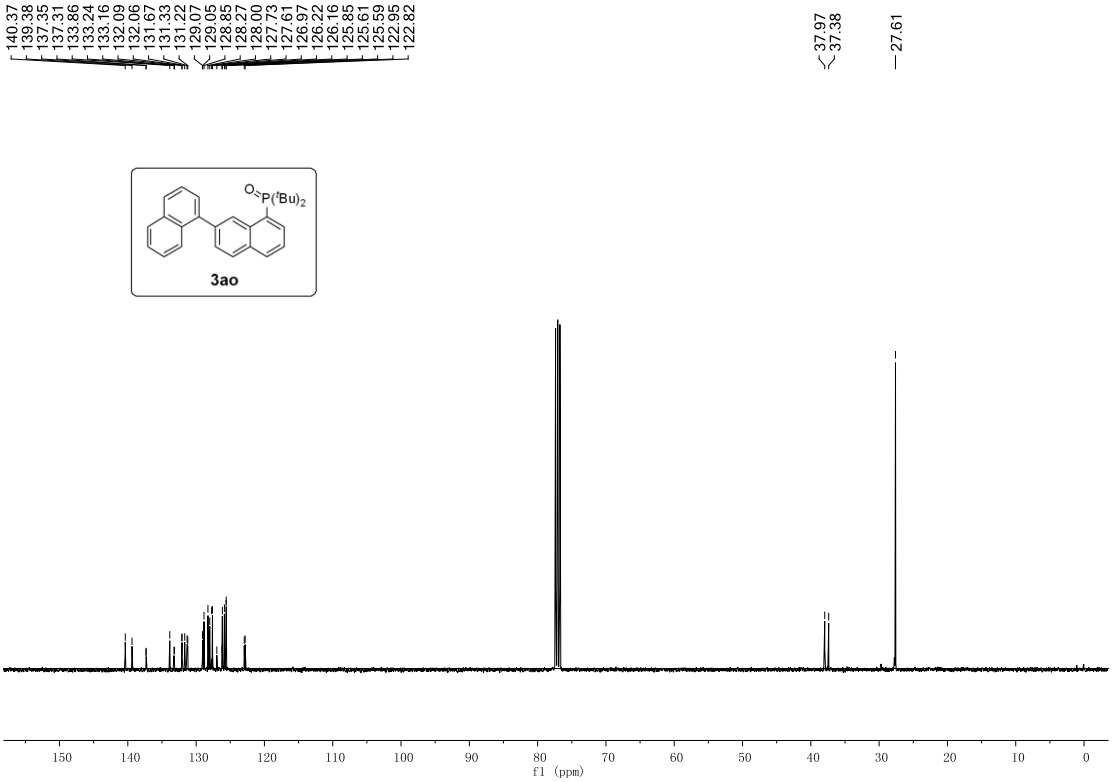
^{1}H NMR spectrum for **3ao**



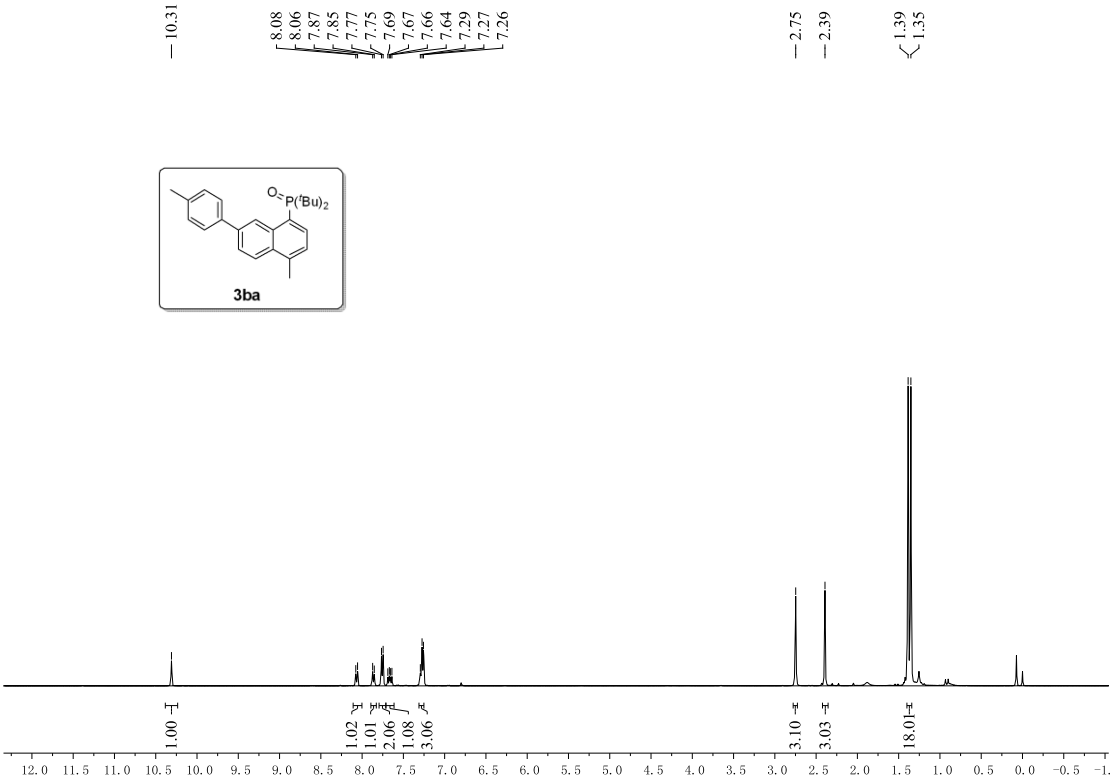
^{31}P NMR spectrum for **3ao**



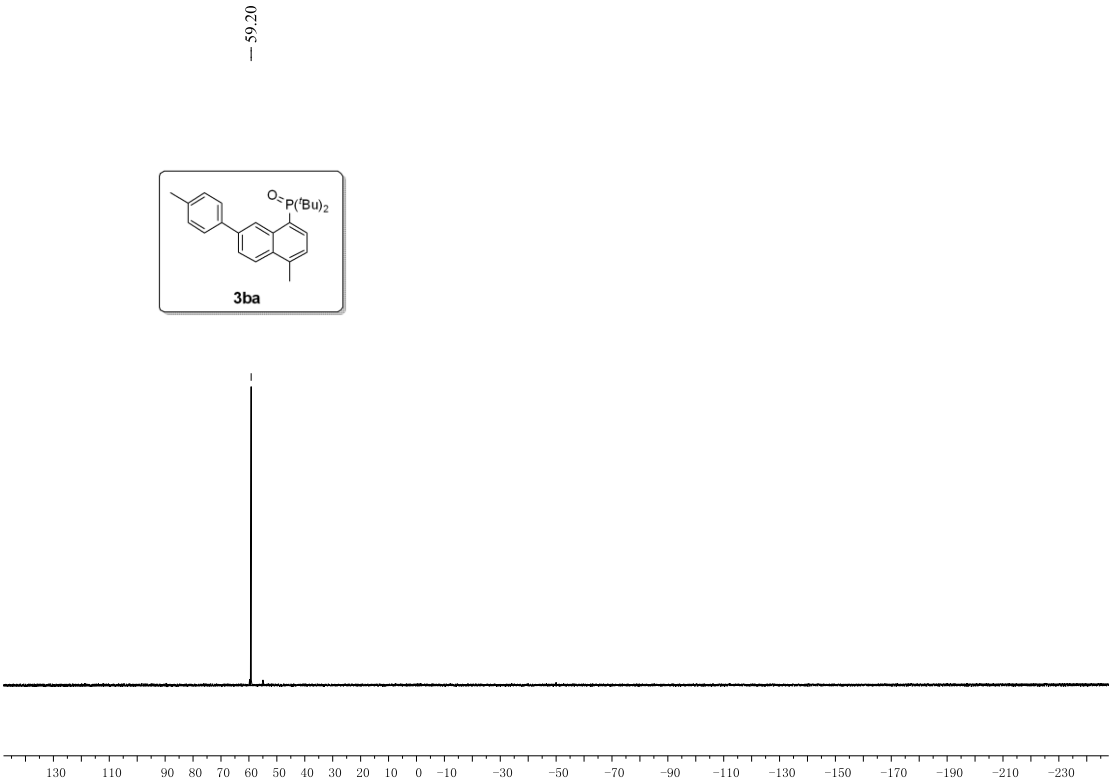
^{13}C NMR spectrum for **3ao**



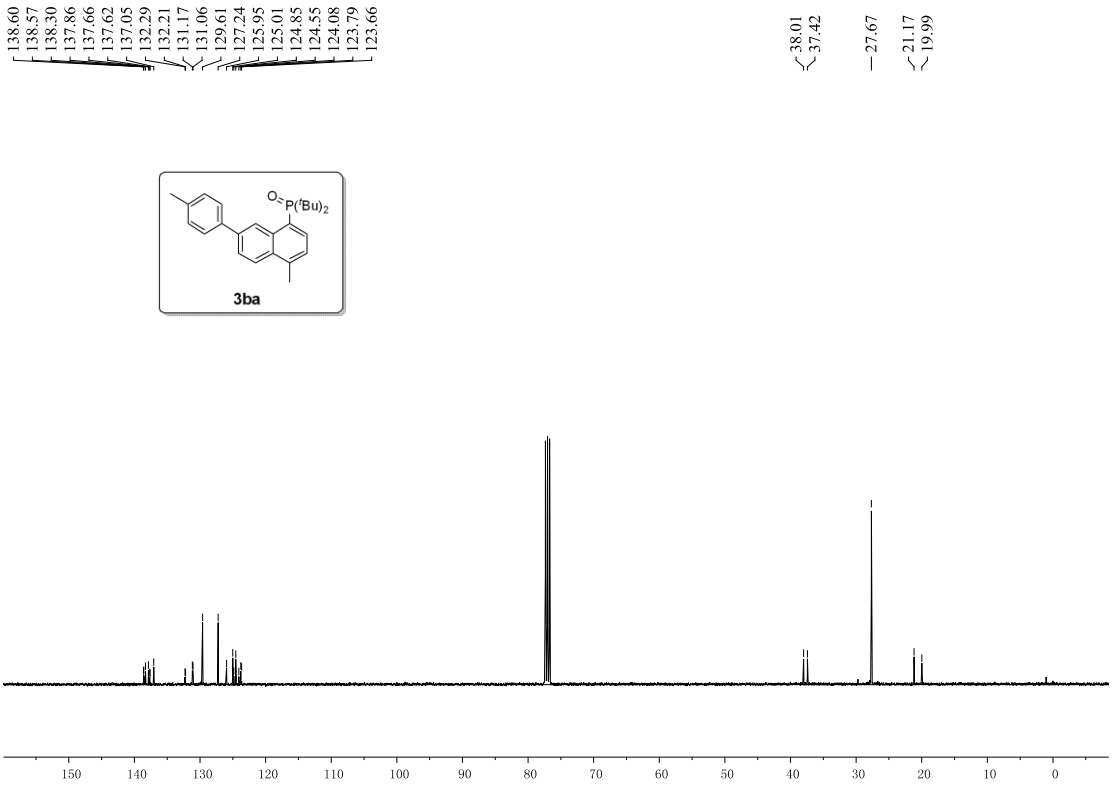
^{1}H NMR spectrum for **3ba**



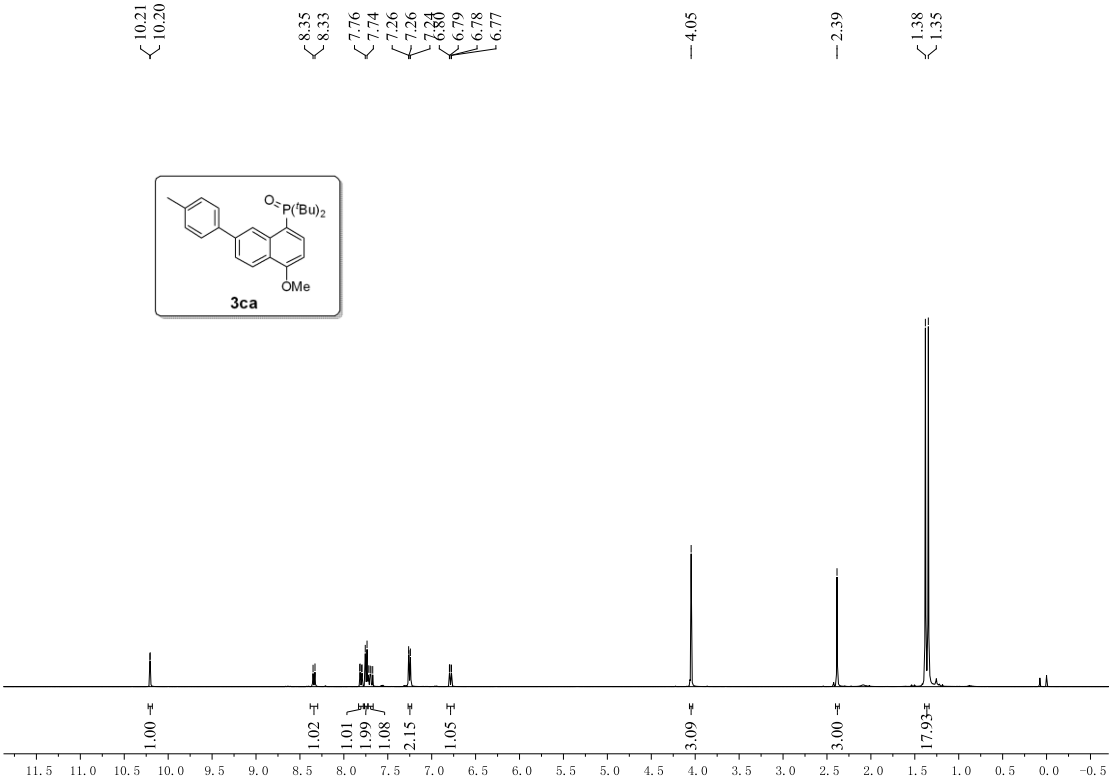
^{31}P NMR spectrum for **3ba**



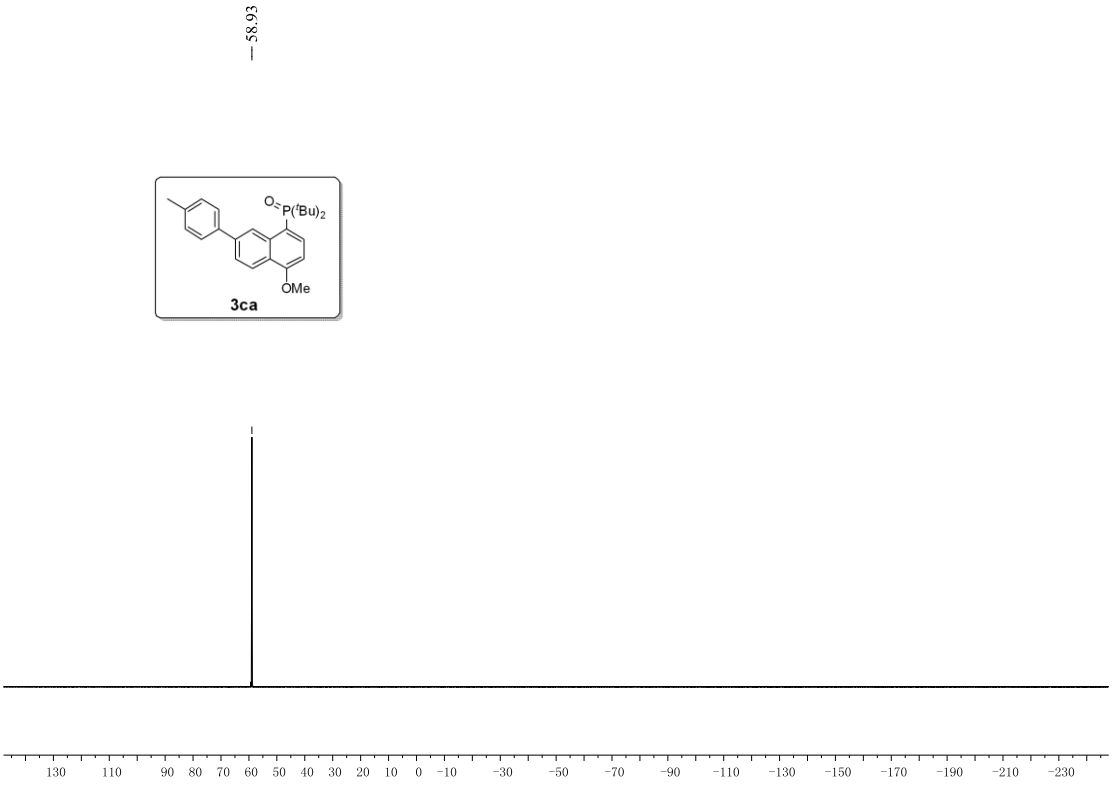
^{13}C NMR spectrum for **3ba**



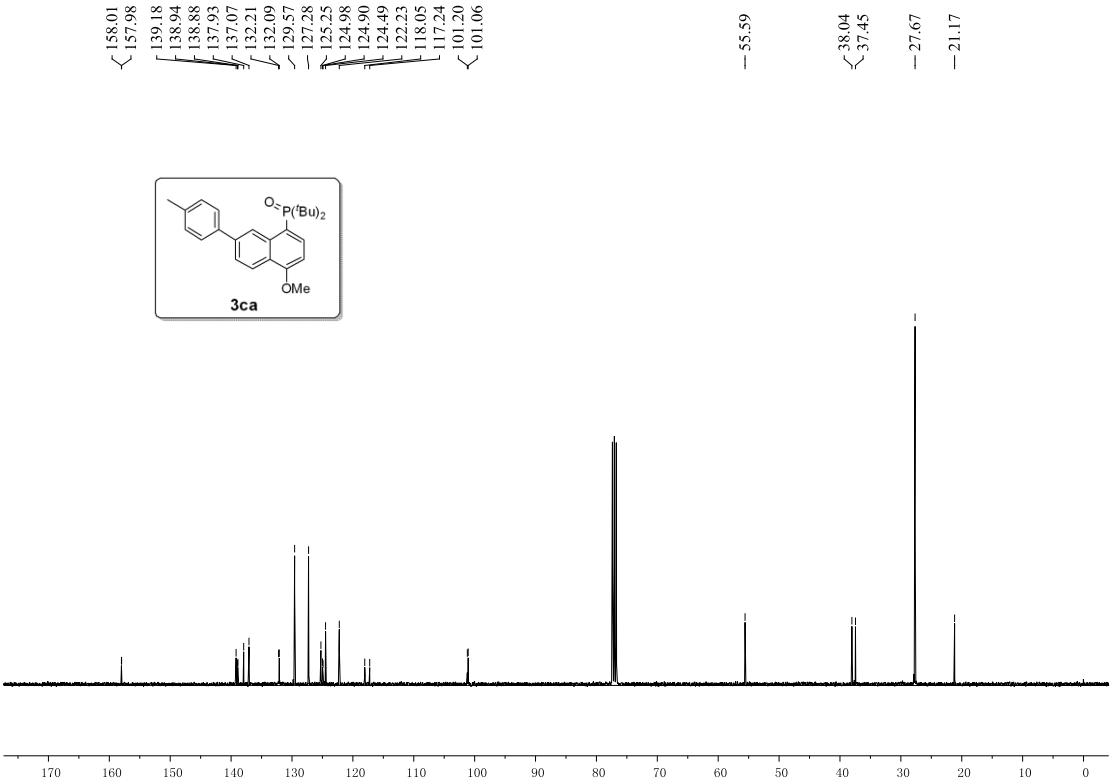
^{1}H NMR spectrum for **3ca**



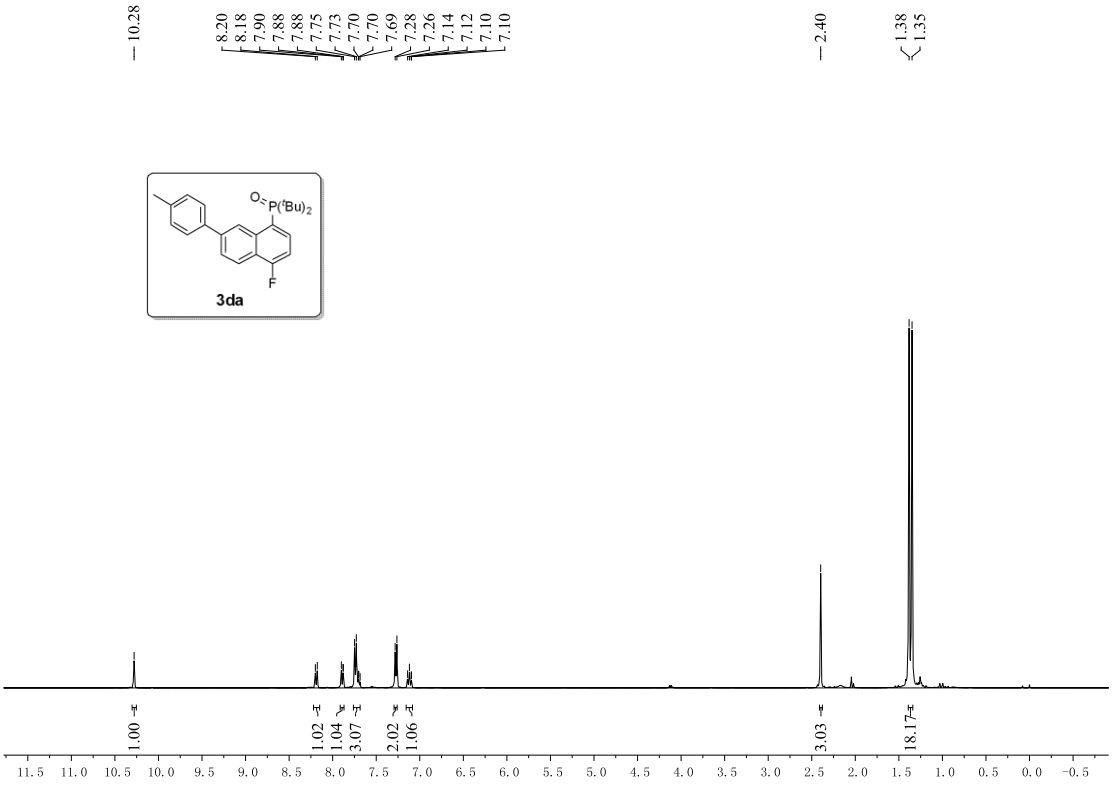
^{31}P NMR spectrum for **3ca**



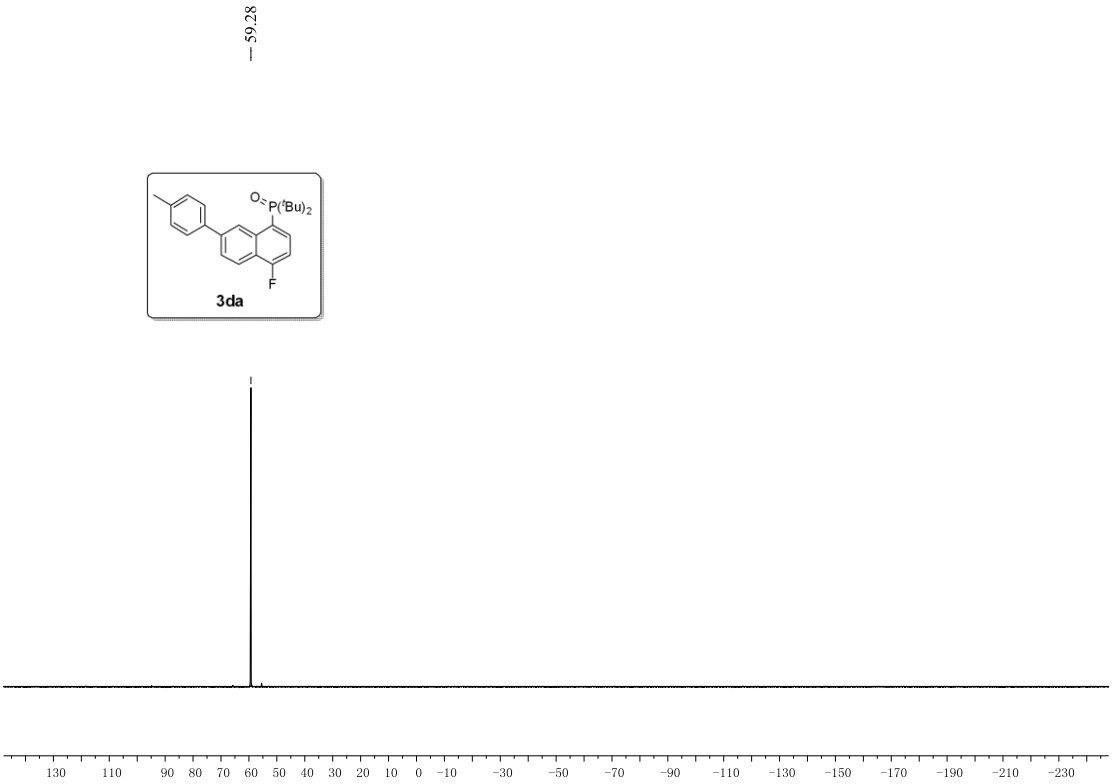
^{13}C NMR spectrum for **3ca**



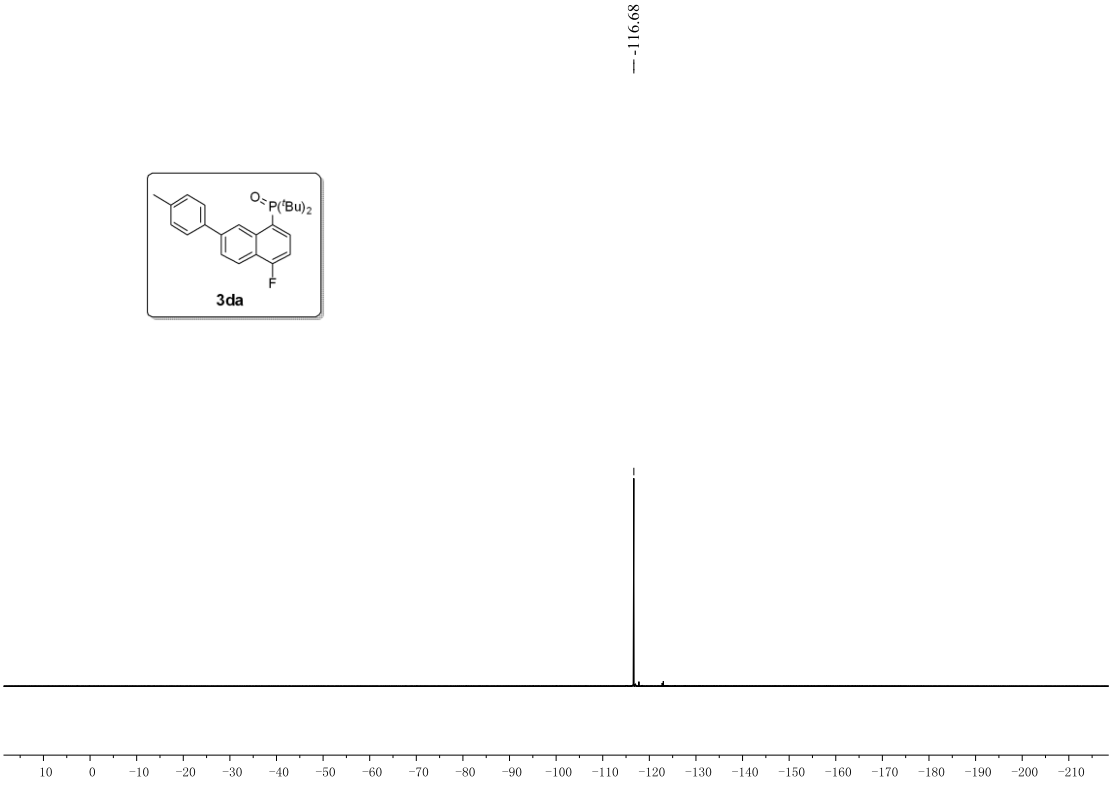
^{1}H NMR spectrum for **3da**



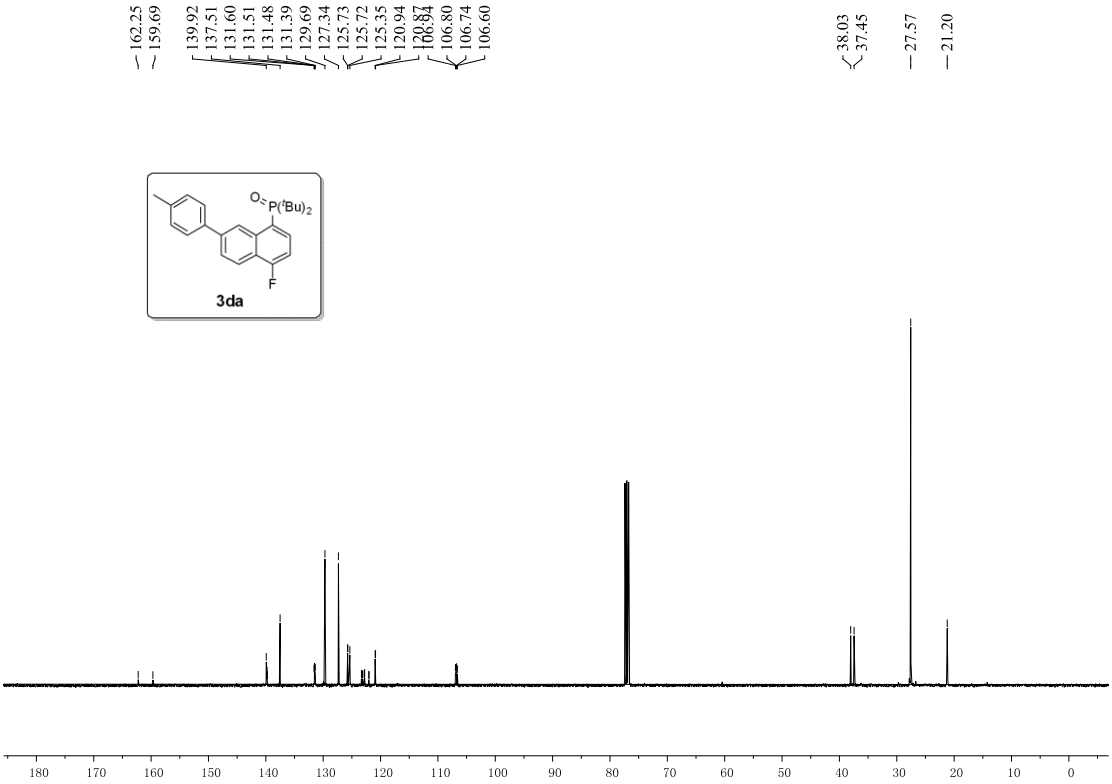
^{31}P NMR spectrum for **3da**



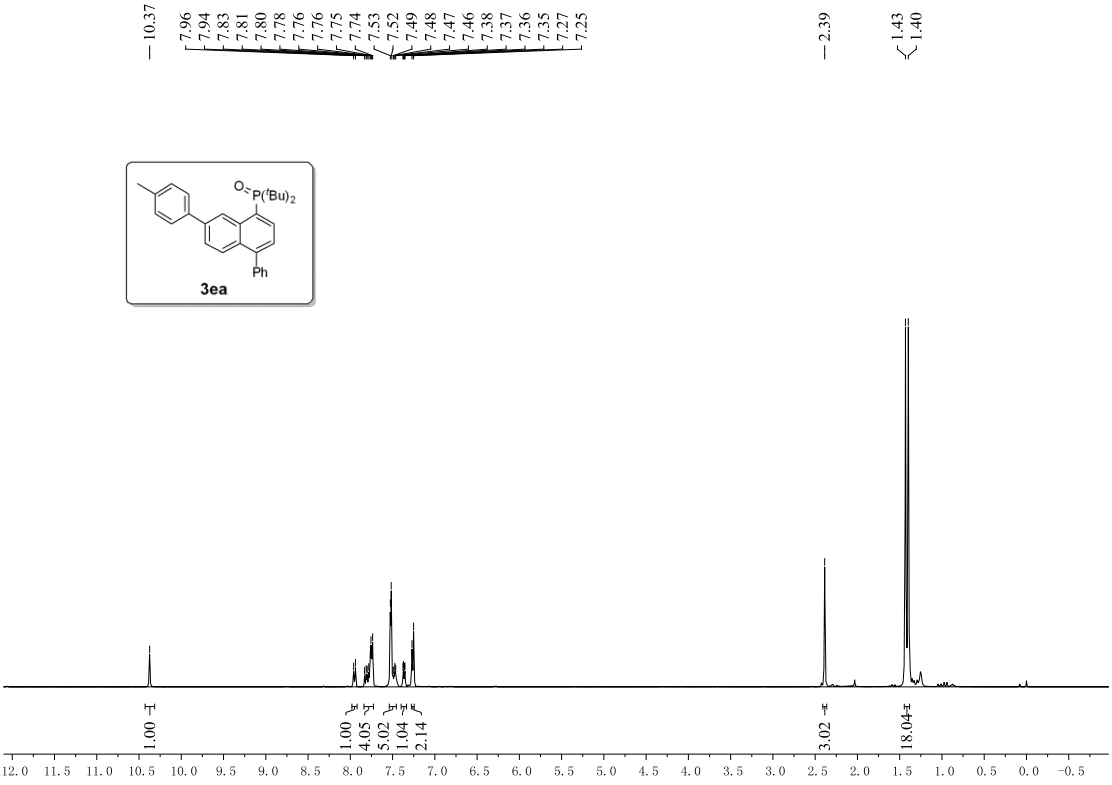
^{19}F NMR spectrum for **3da**



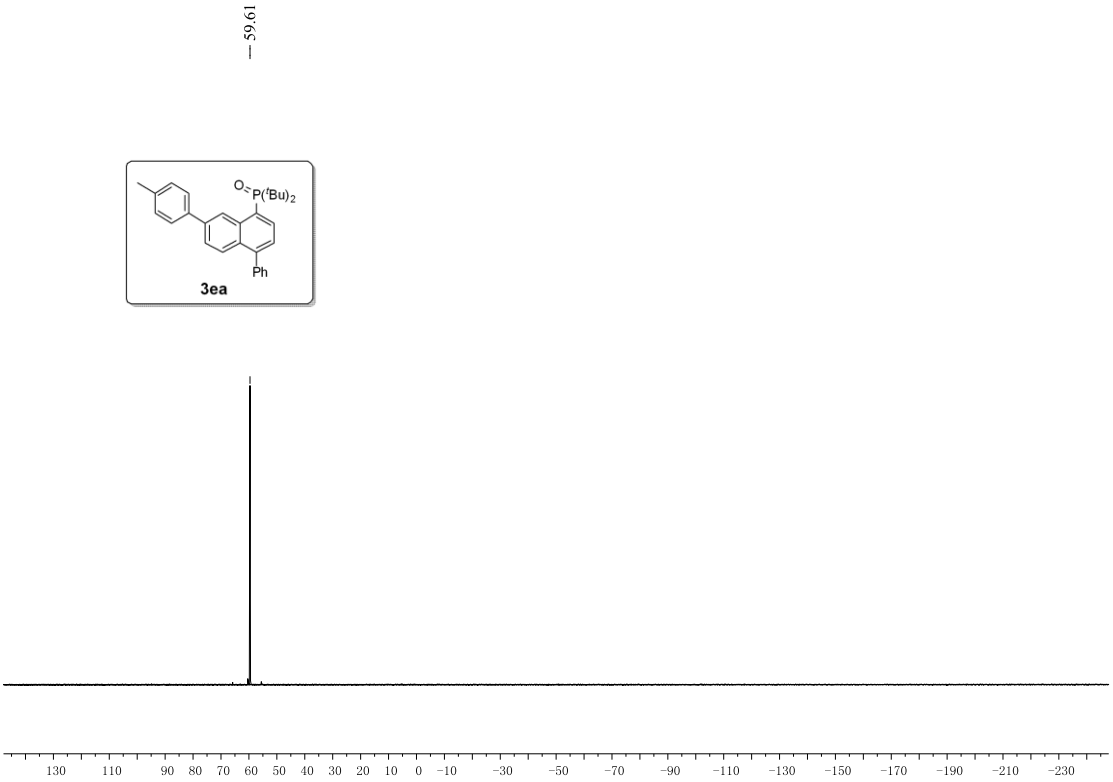
^{13}C NMR spectrum for **3da**



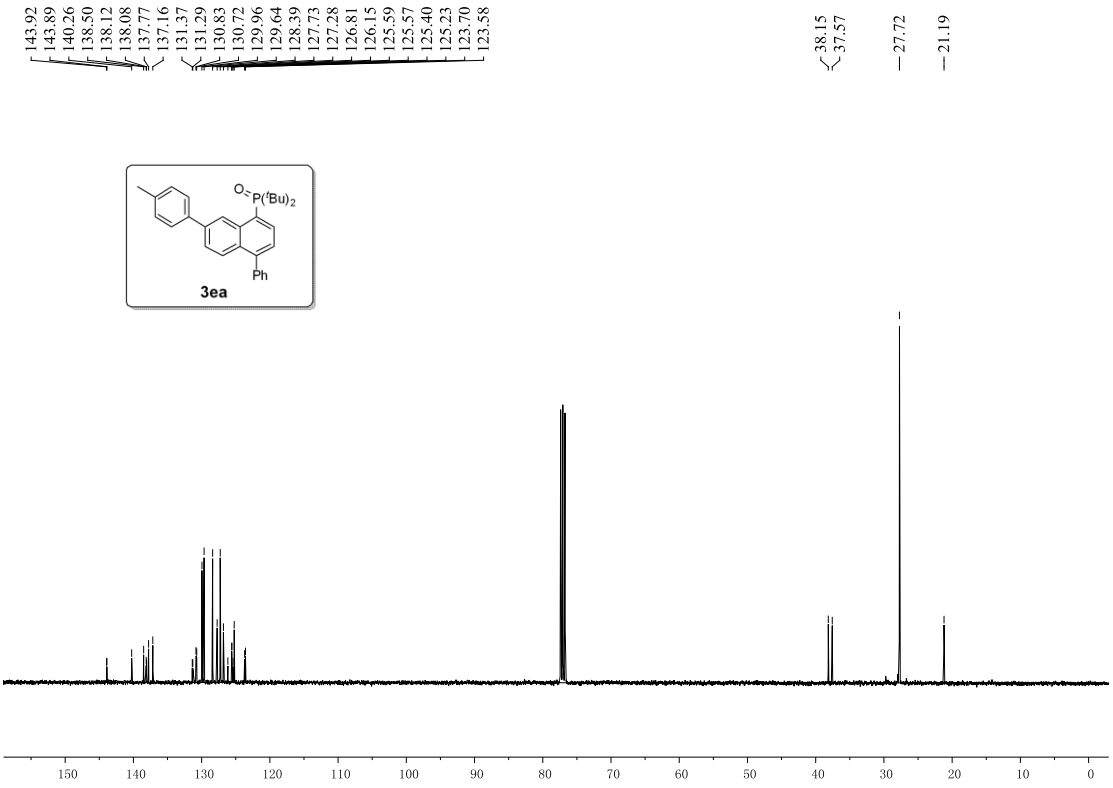
^{1}H NMR spectrum for **3ea**



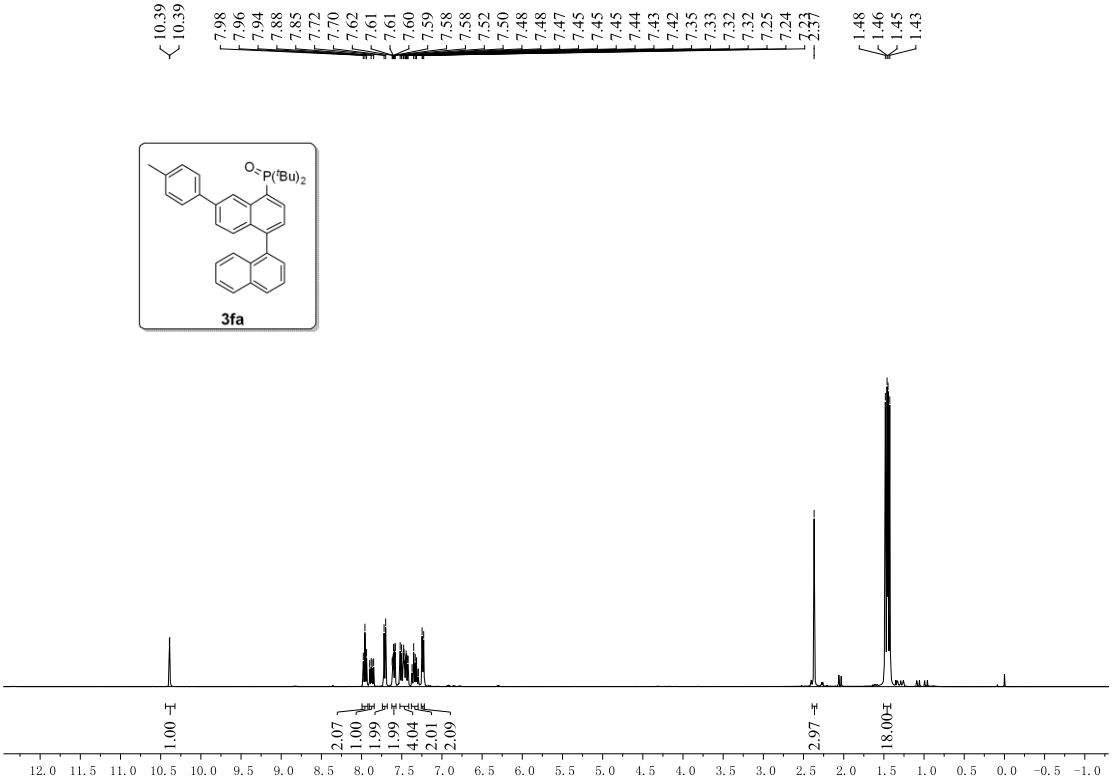
^{31}P NMR spectrum for **3ea**



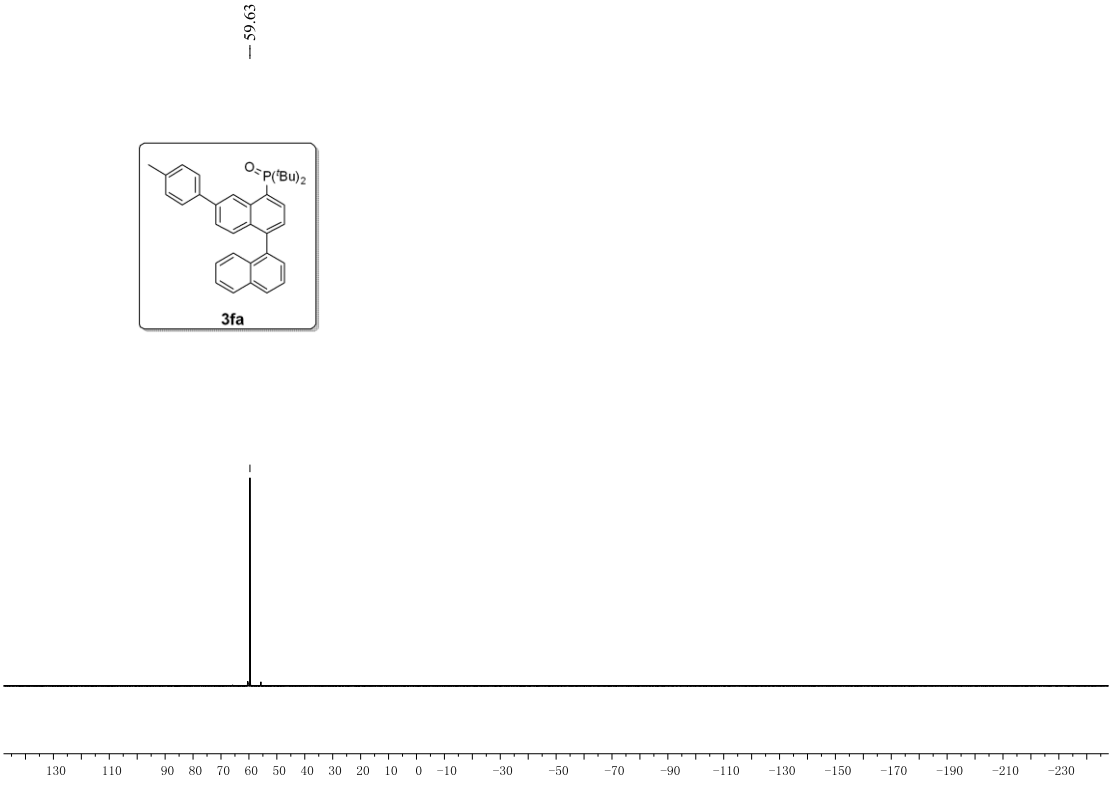
^{13}C NMR spectrum for **3ea**



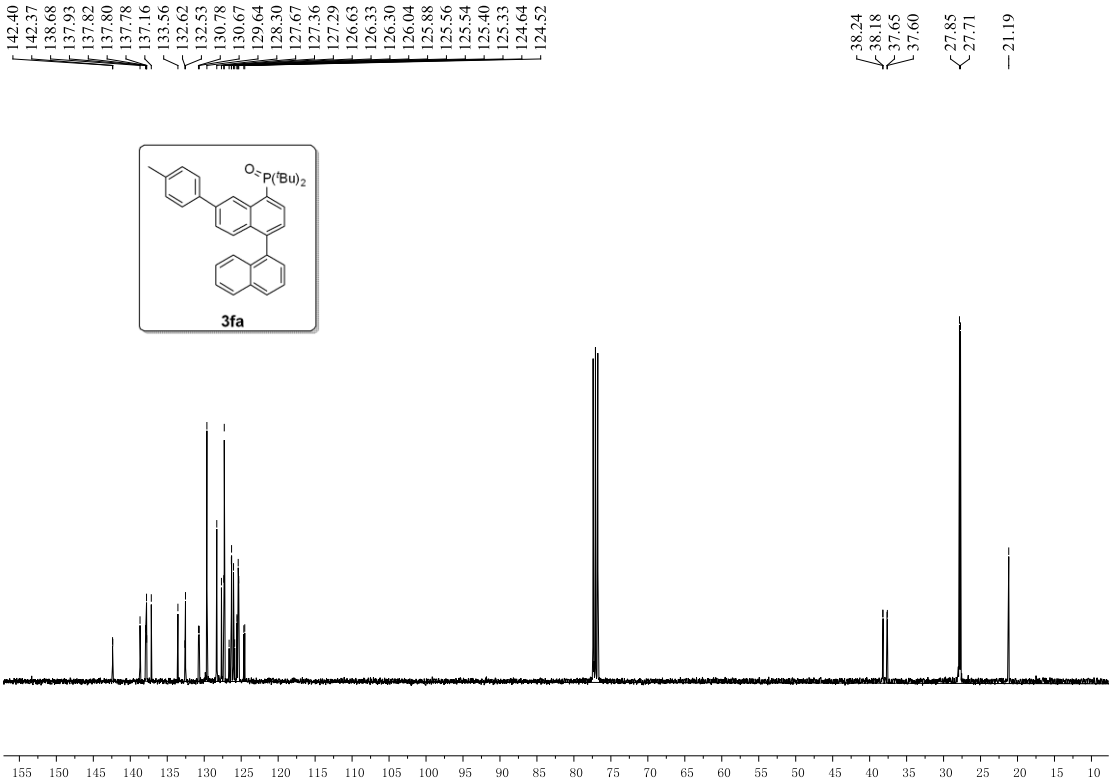
^{1}H NMR spectrum for **3fa**



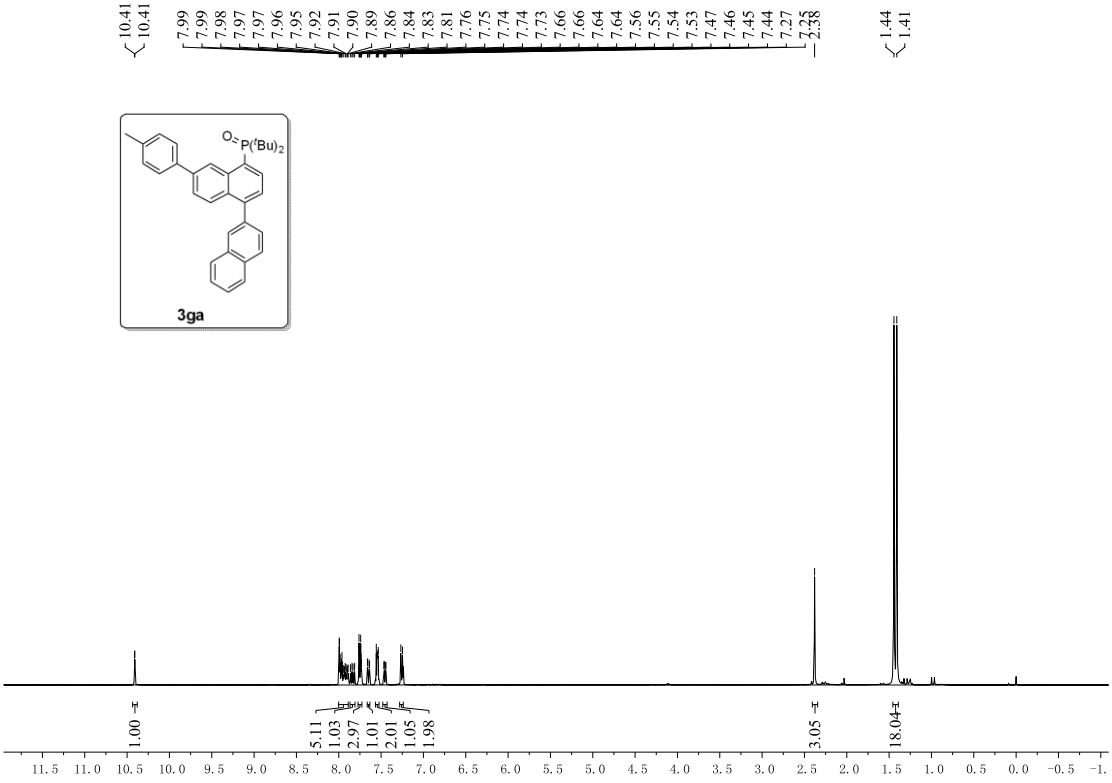
^{31}P NMR spectrum for **3fa**



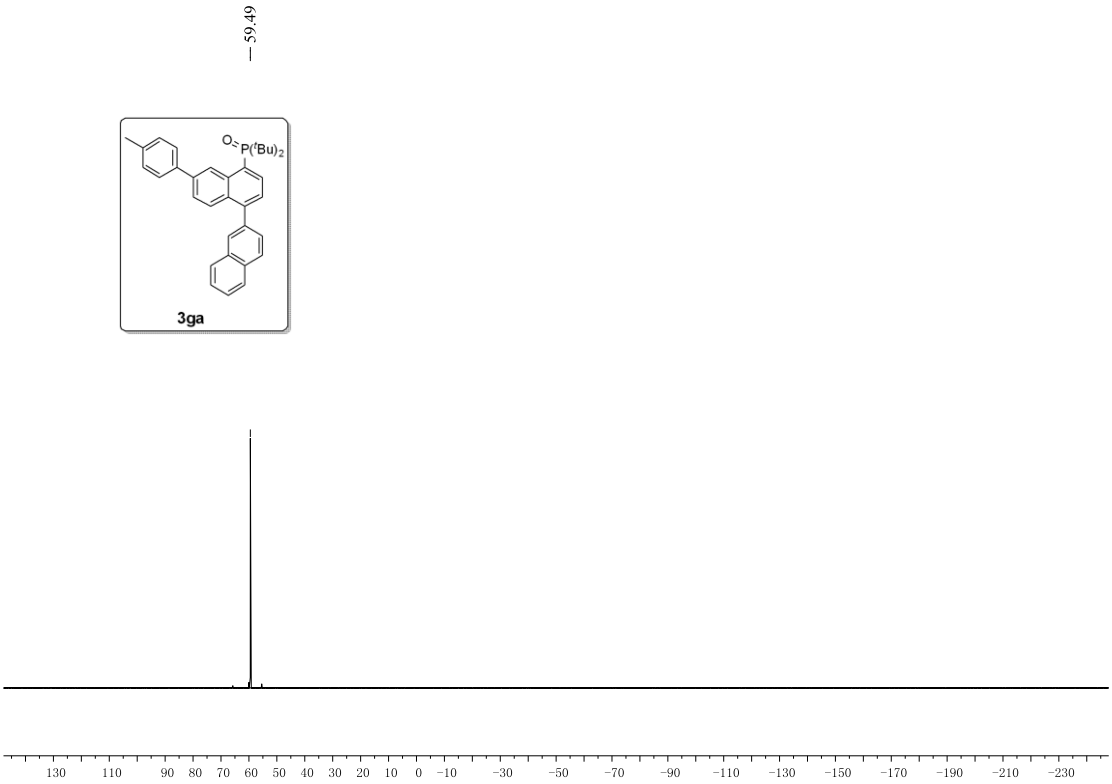
^{13}C NMR spectrum for **3fa**



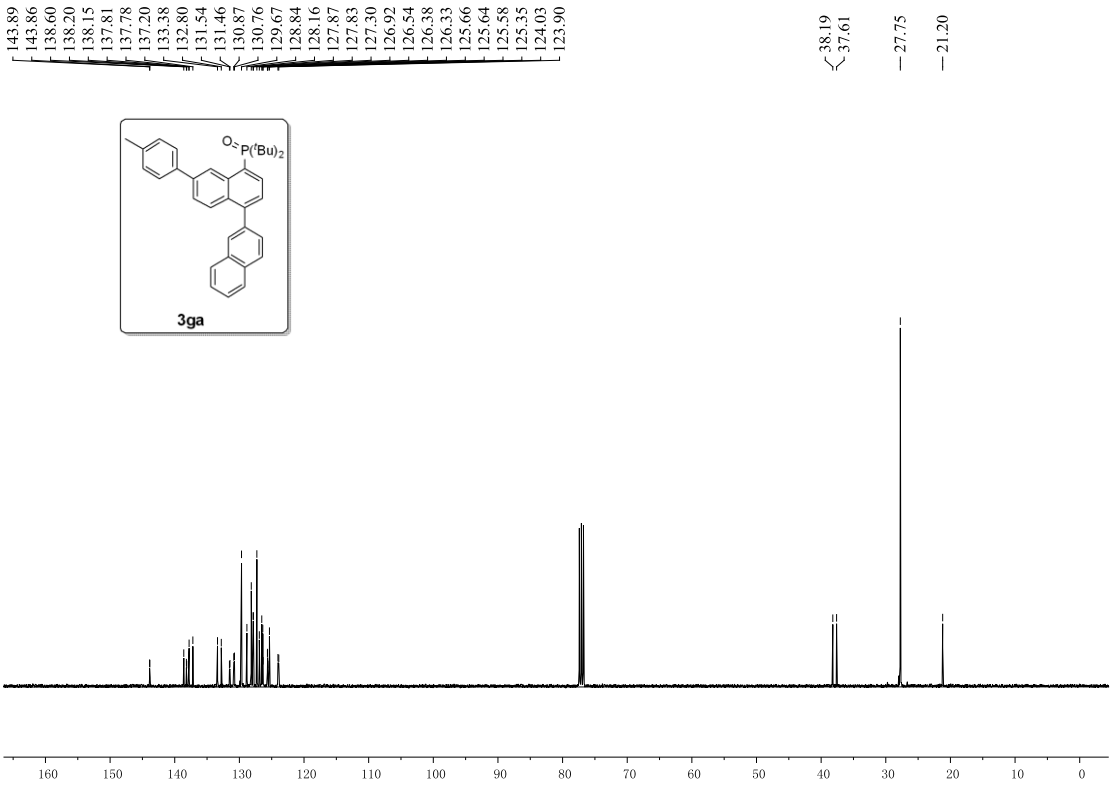
^{1}H NMR spectrum for **3ga**



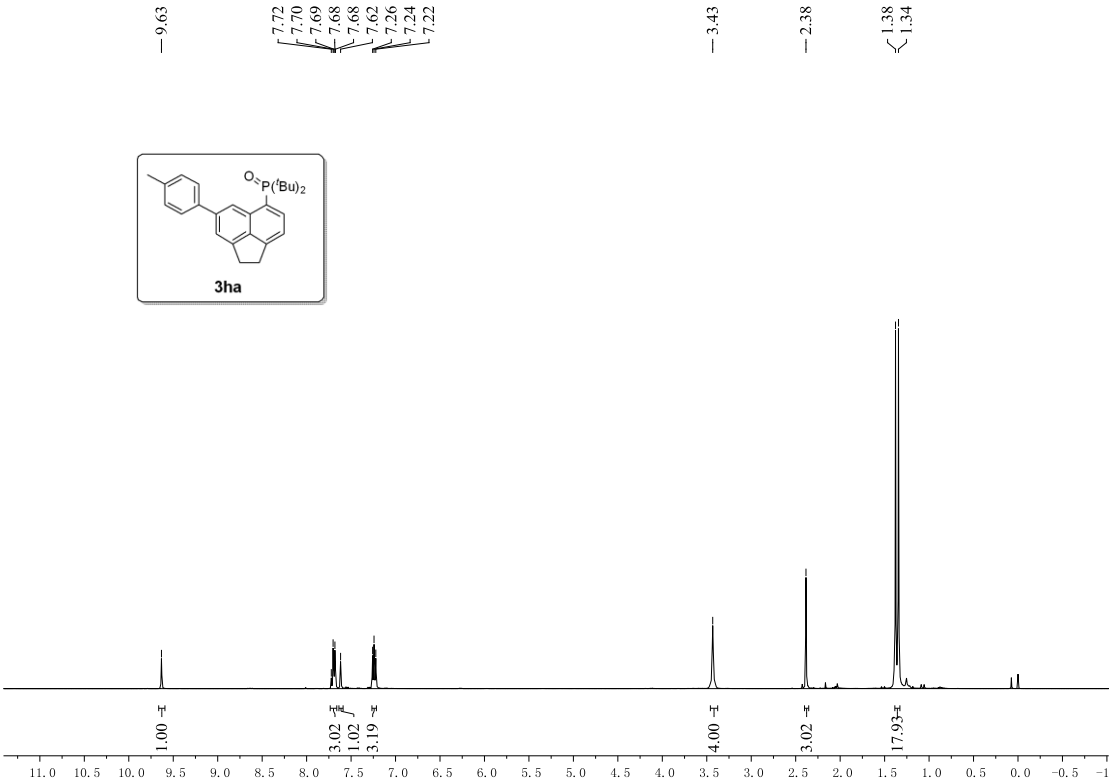
^{31}P NMR spectrum for **3ga**



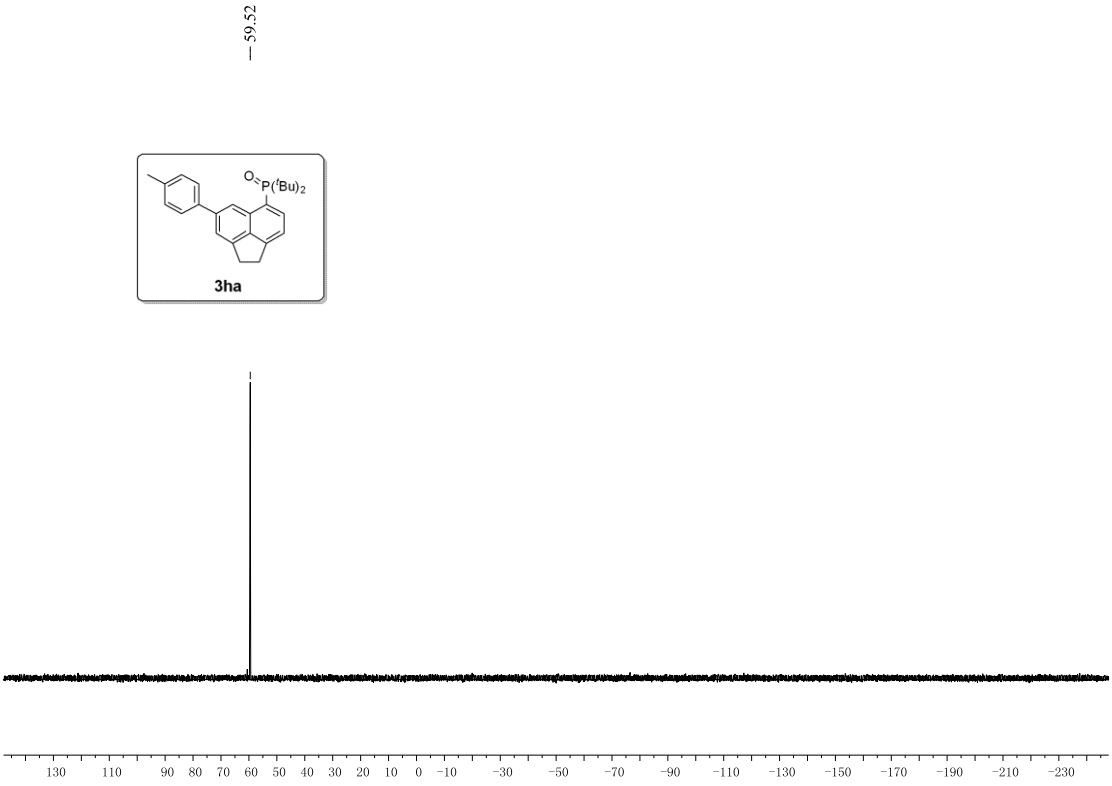
^{13}C NMR spectrum for **3ga**



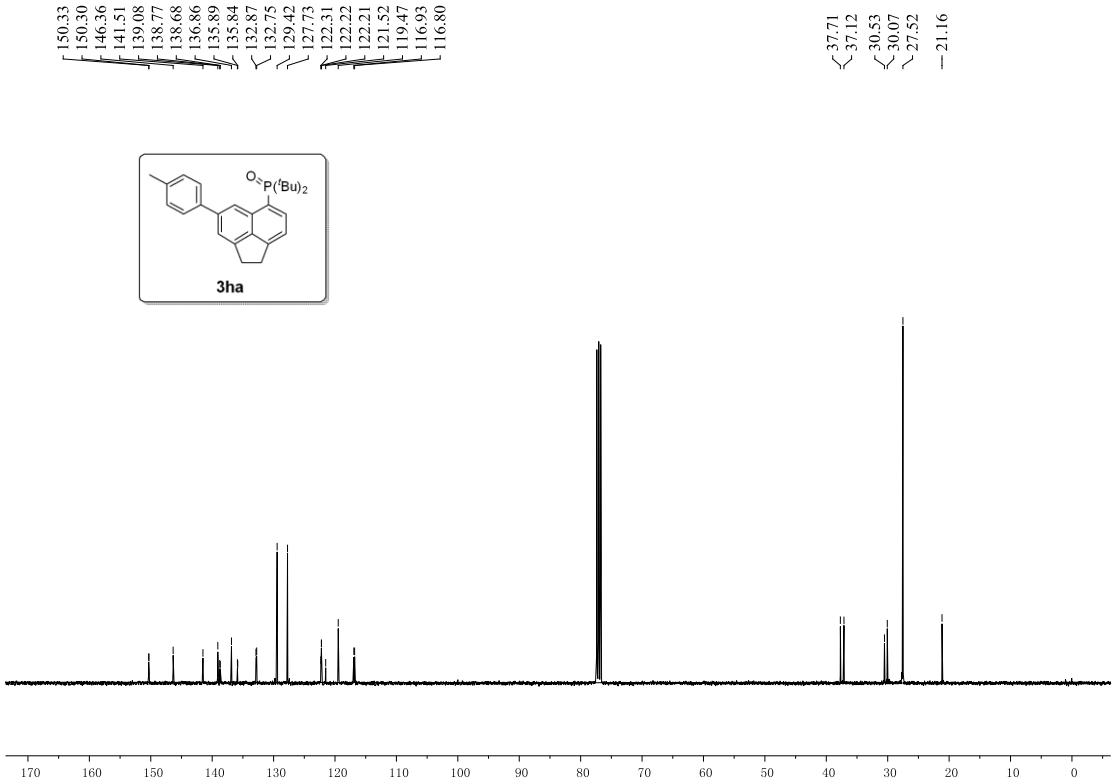
^{1}H NMR spectrum for **3ha**



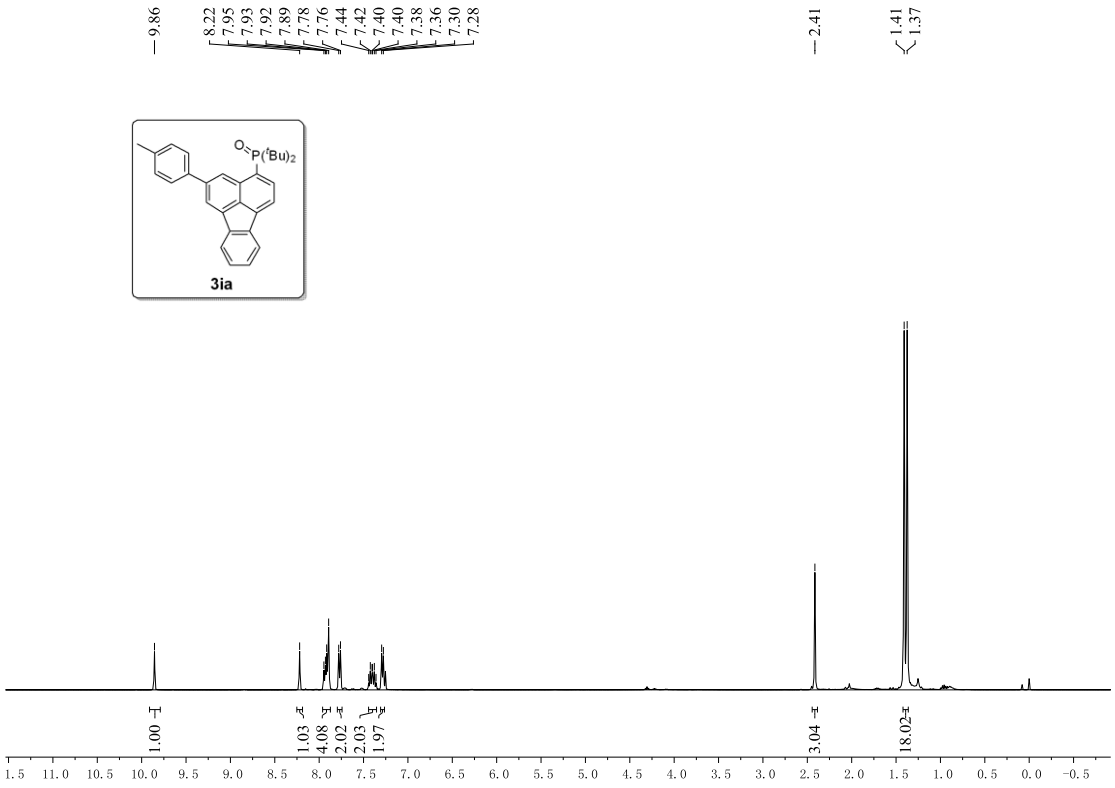
^{31}P NMR spectrum for **3ha**



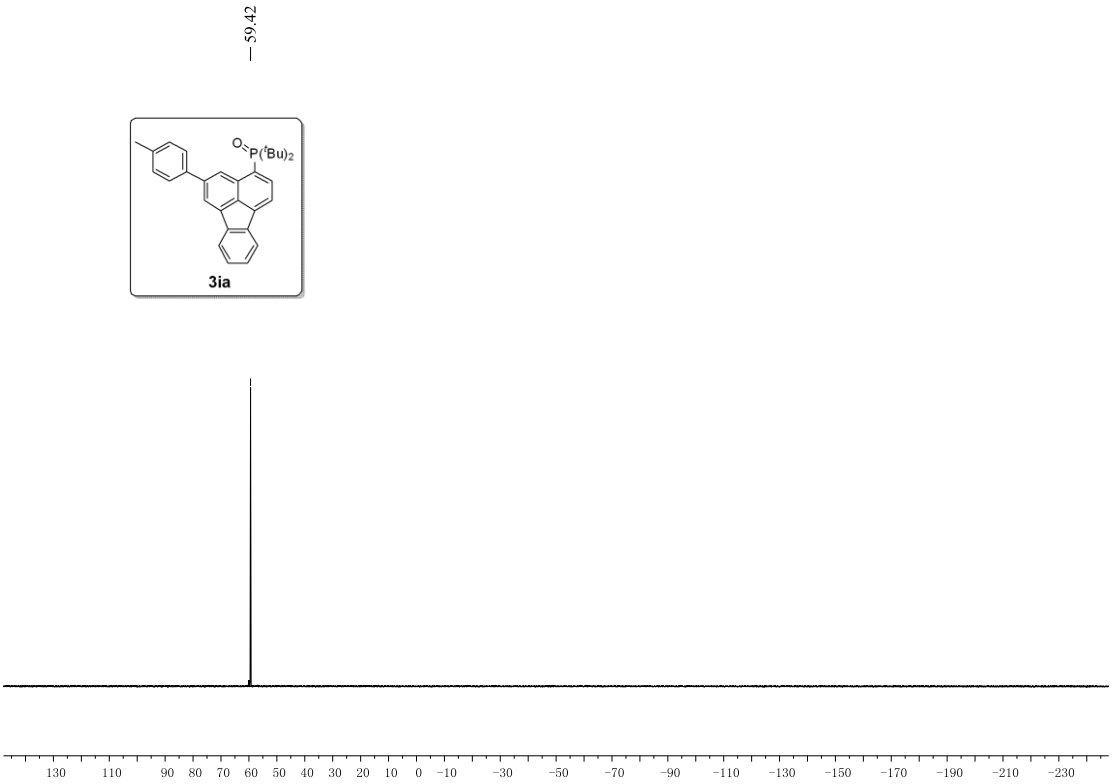
^{13}C NMR spectrum for **3ha**



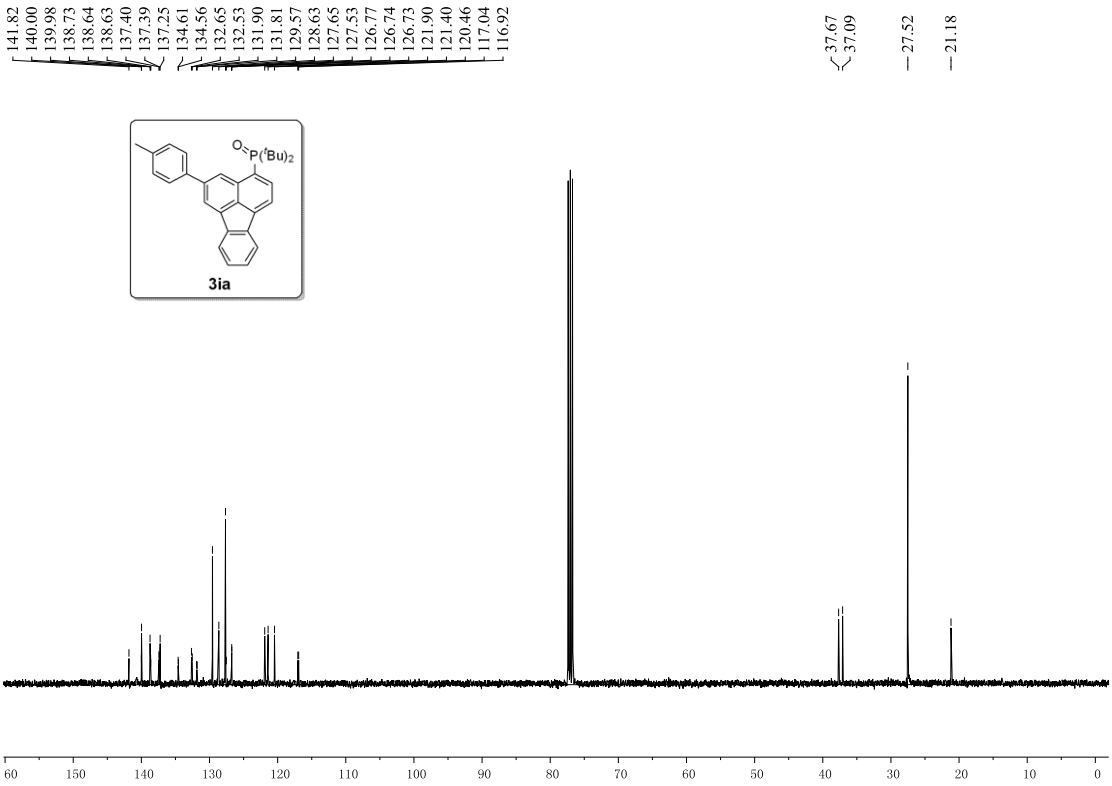
^{1}H NMR spectrum for **3ia**



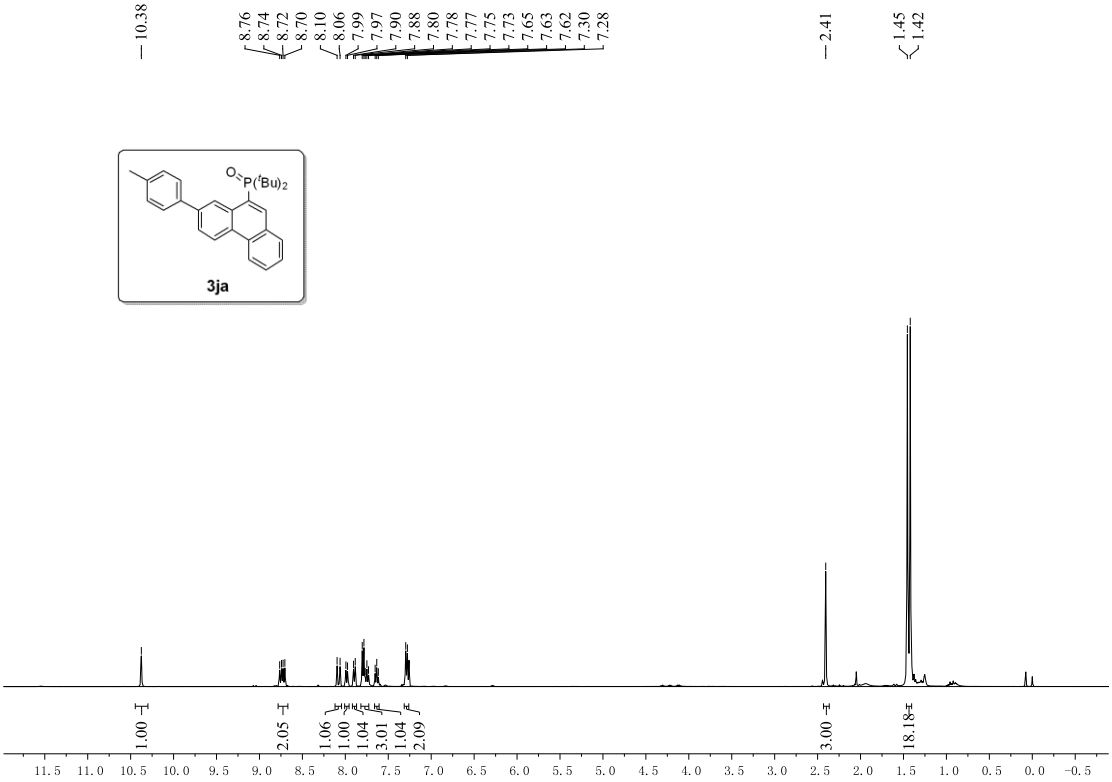
^{31}P NMR spectrum for **3ia**



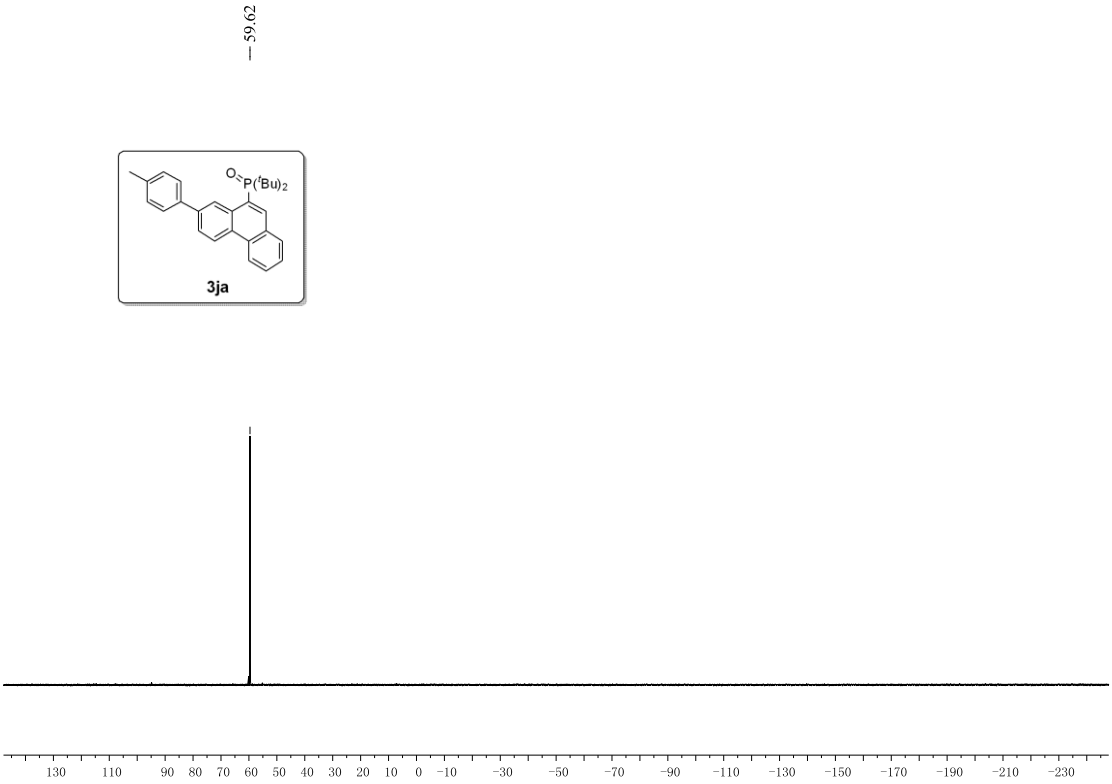
^{13}C NMR spectrum for **3ia**



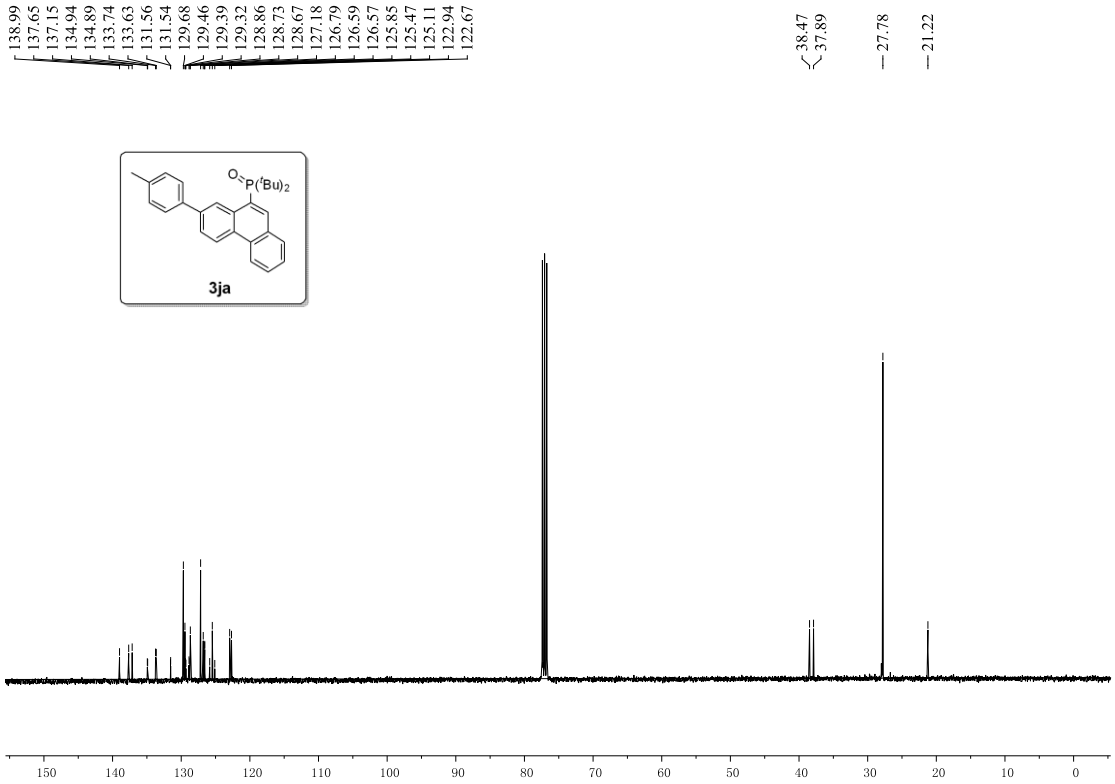
^{1}H NMR spectrum for **3ja**



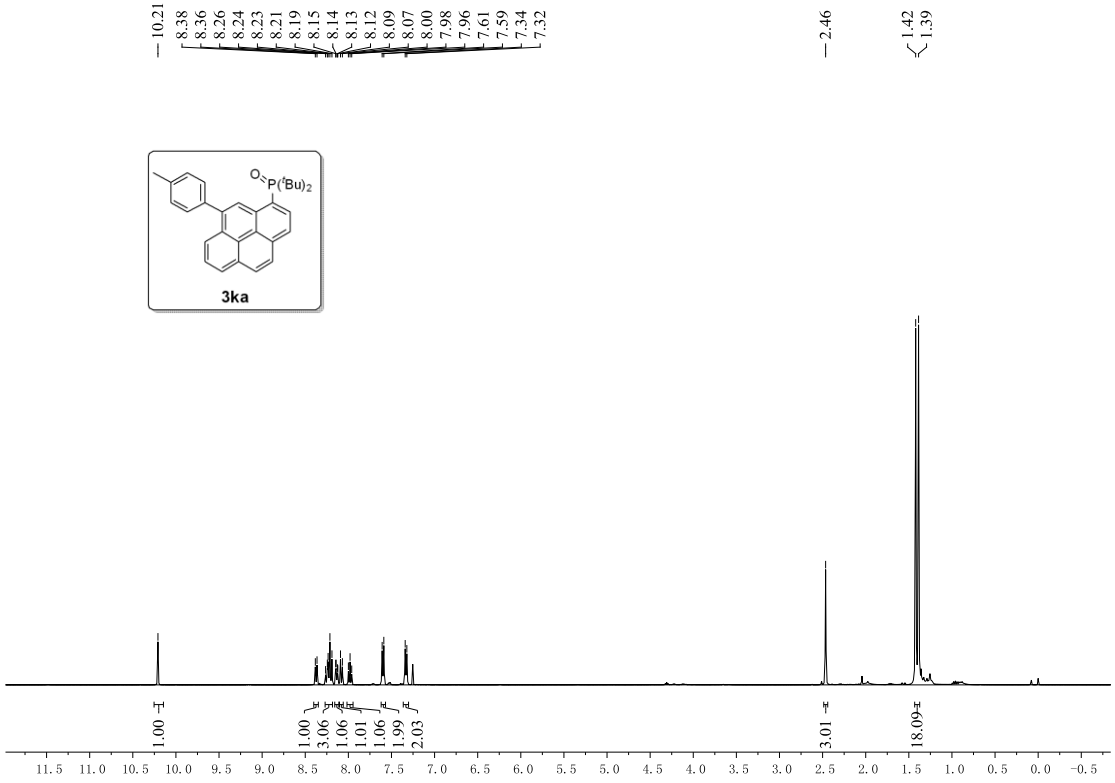
^{31}P NMR spectrum for **3ja**



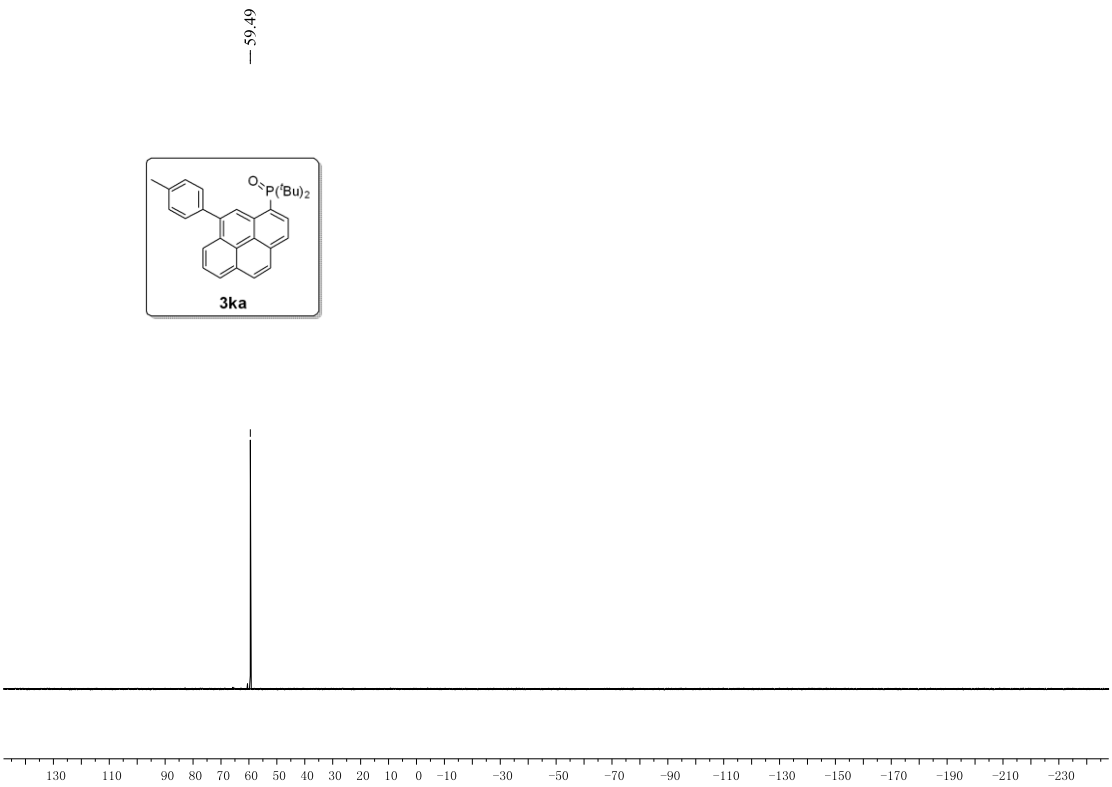
^{13}C NMR spectrum for **3ja**



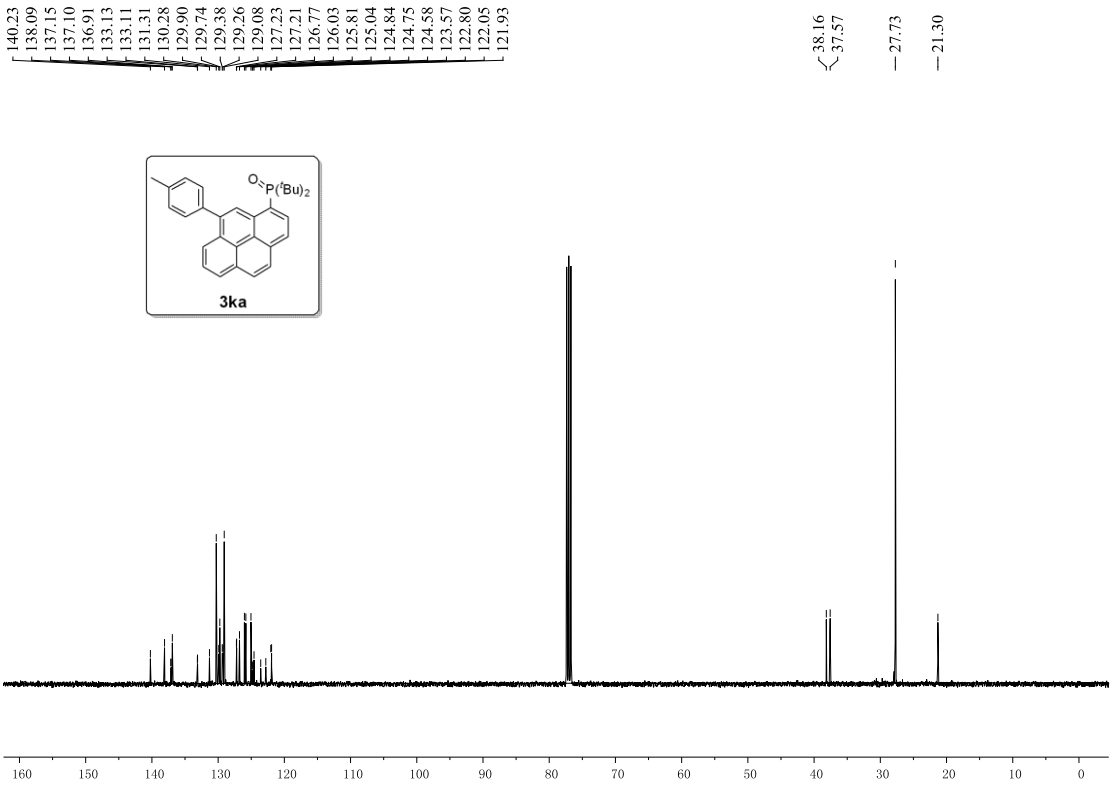
^{1}H NMR spectrum for **3ka**



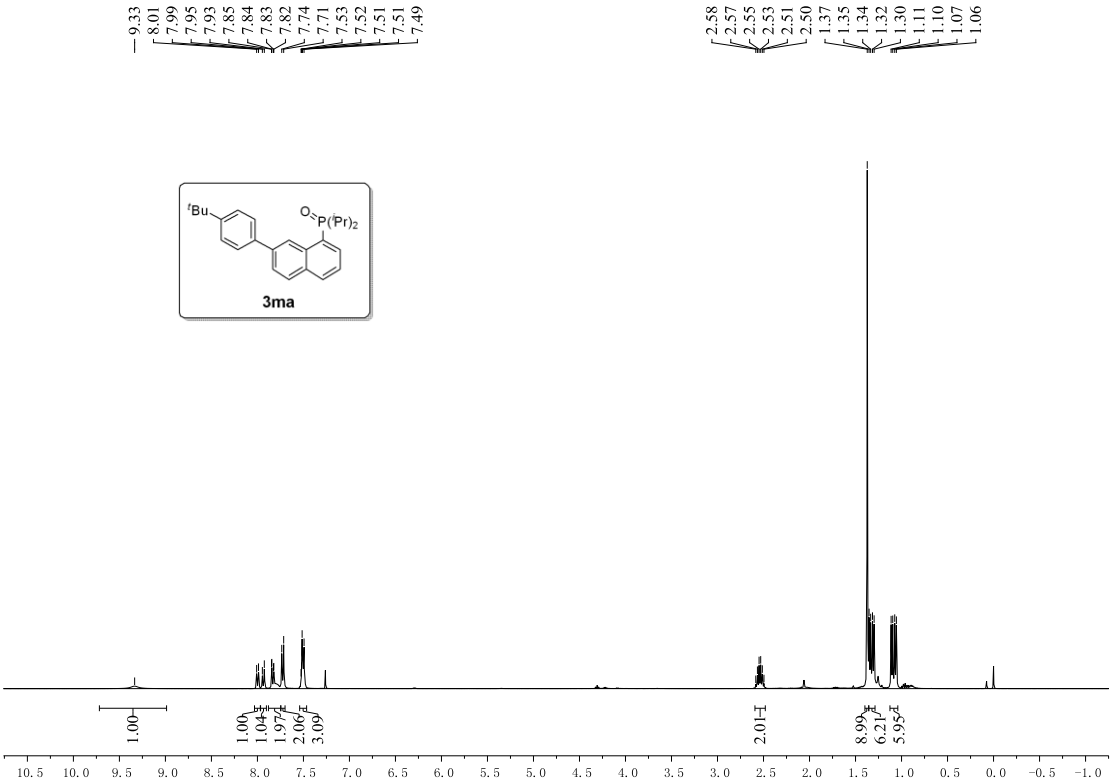
^{31}P NMR spectrum for **3ka**



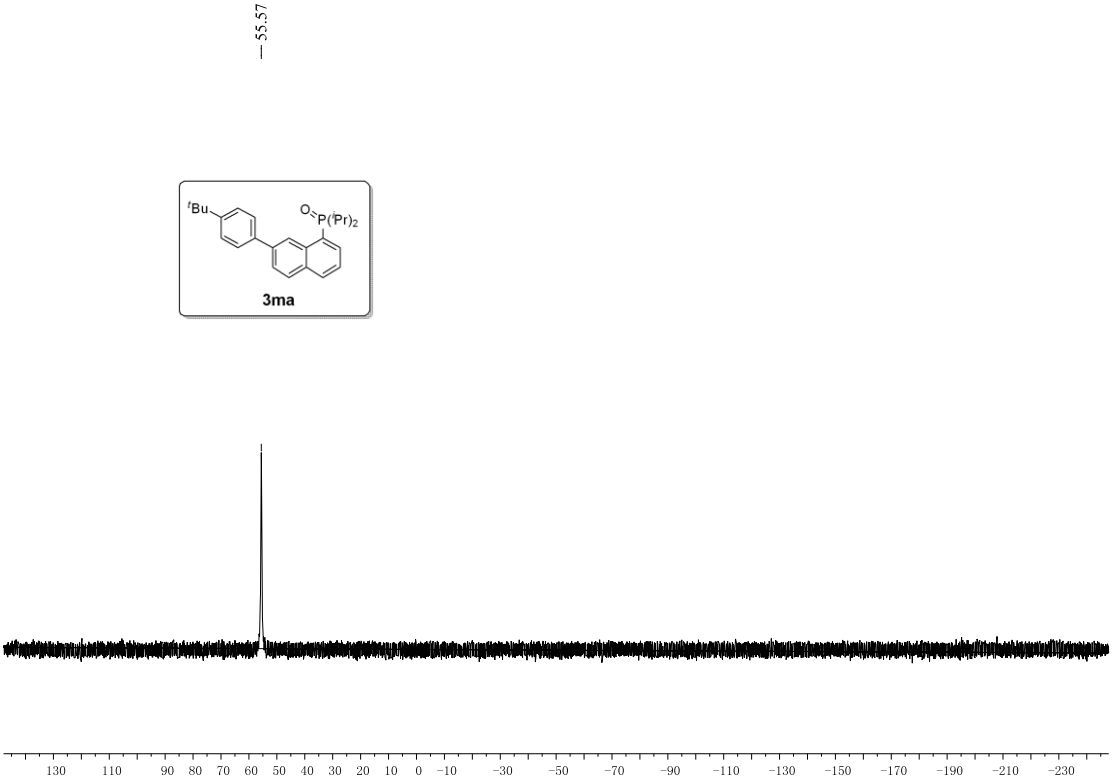
^{13}C NMR spectrum for **3ka**



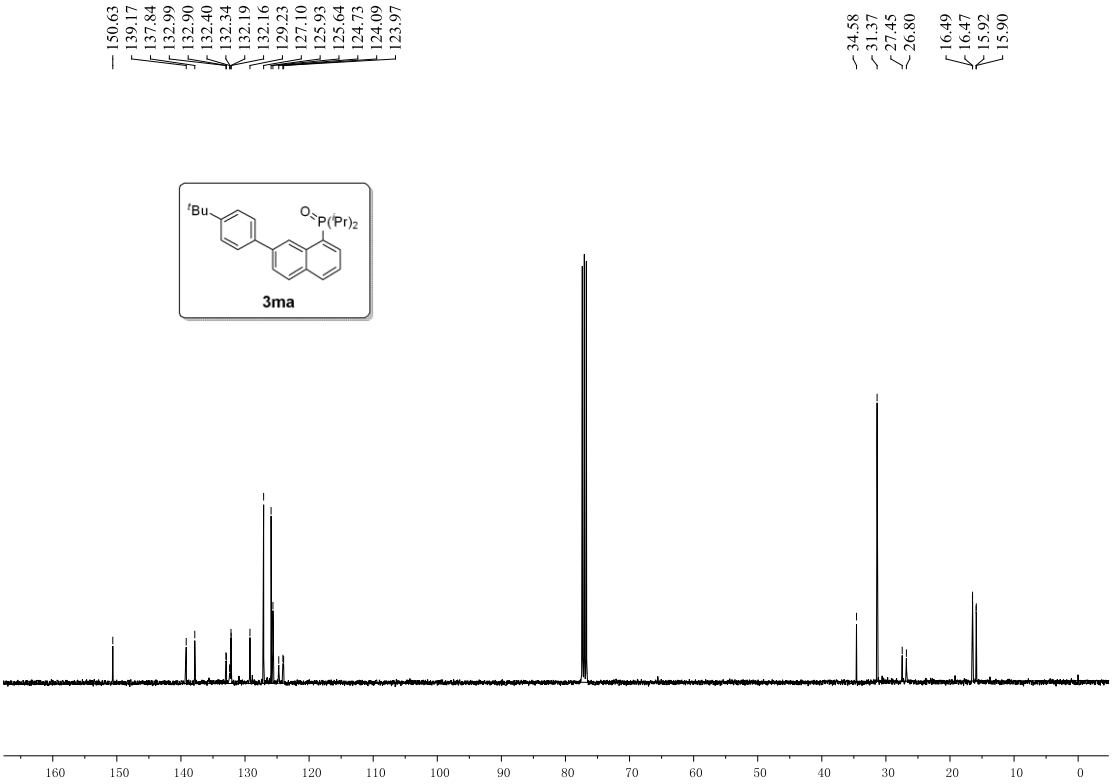
^{1}H NMR spectrum for **3ma**



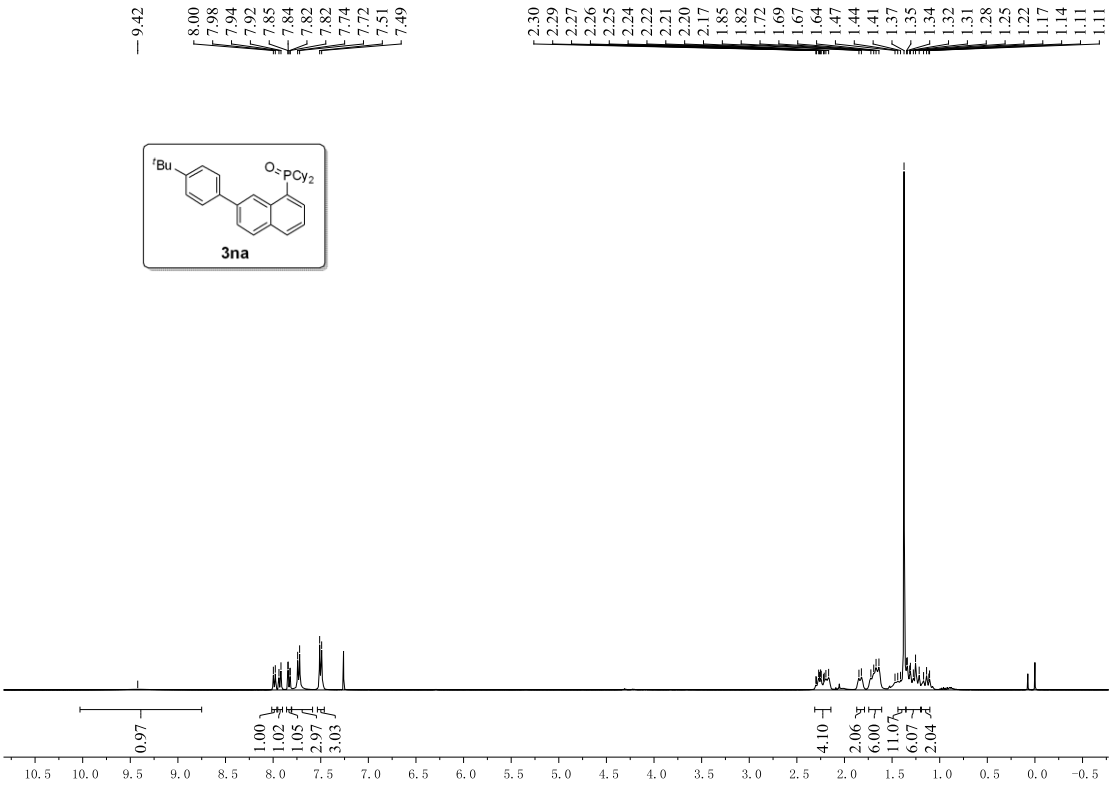
^{31}P NMR spectrum for **3ma**



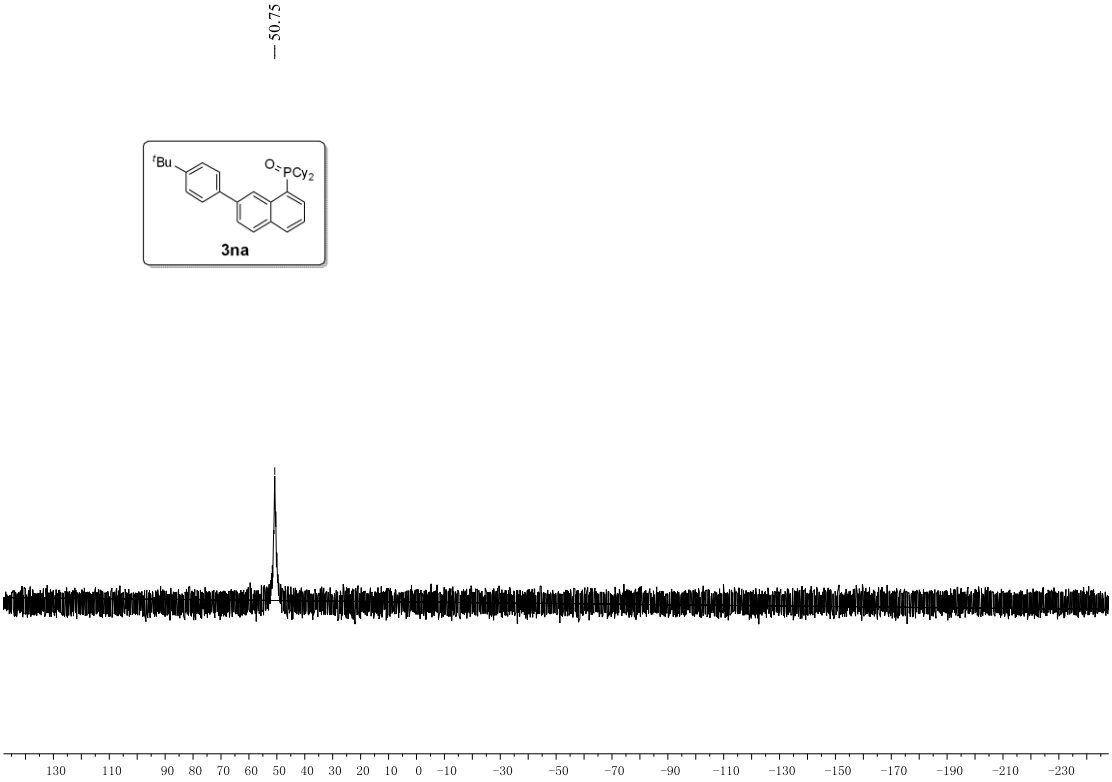
^{13}C NMR spectrum for **3ma**



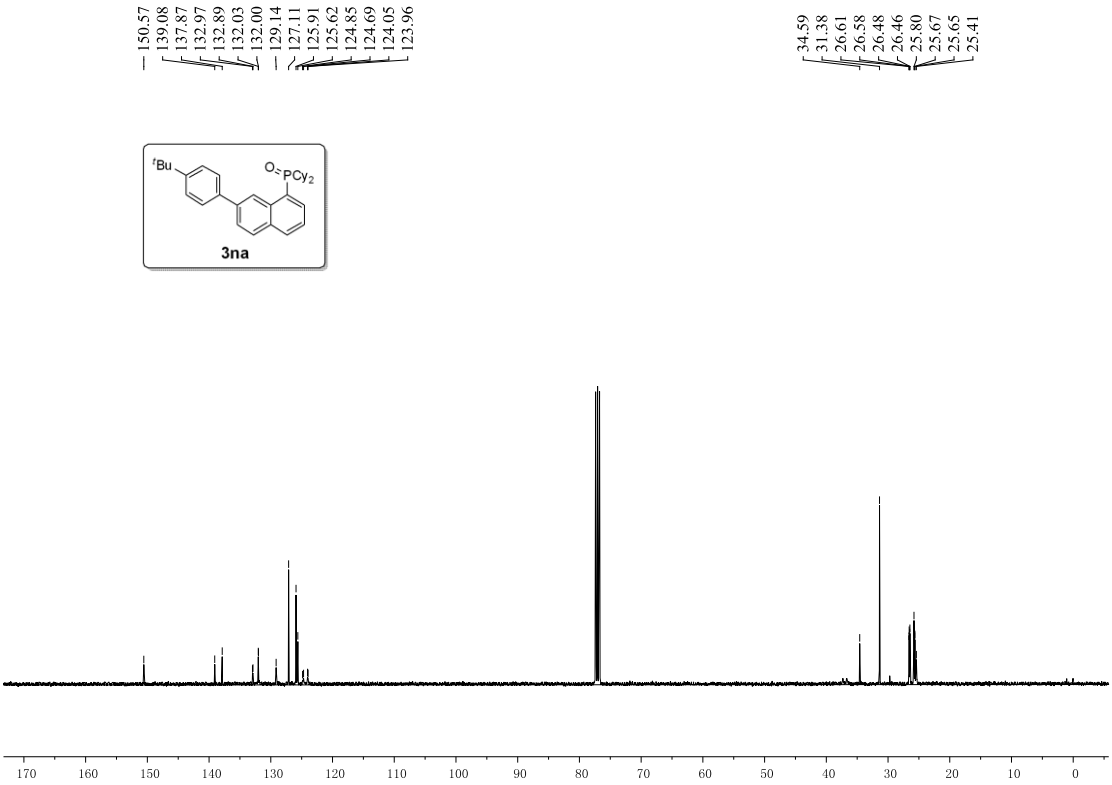
^{1}H NMR spectrum for **3na**



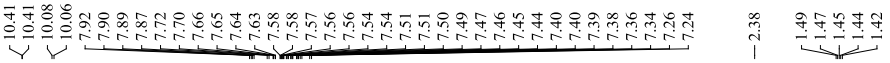
^{31}P NMR spectrum for **3na**

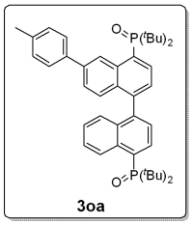


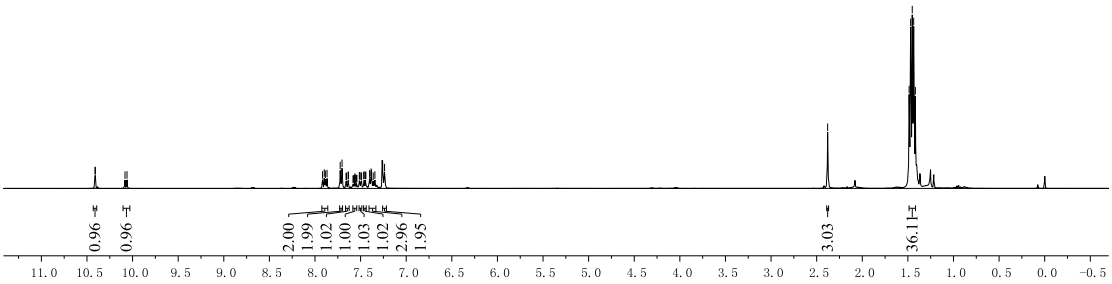
^{13}C NMR spectrum for **3na**



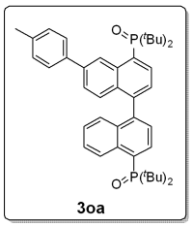
^{1}H NMR spectrum for **3oa**

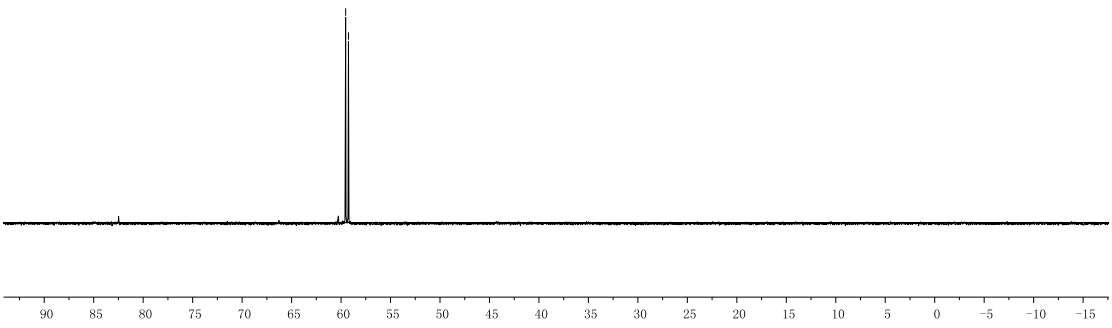




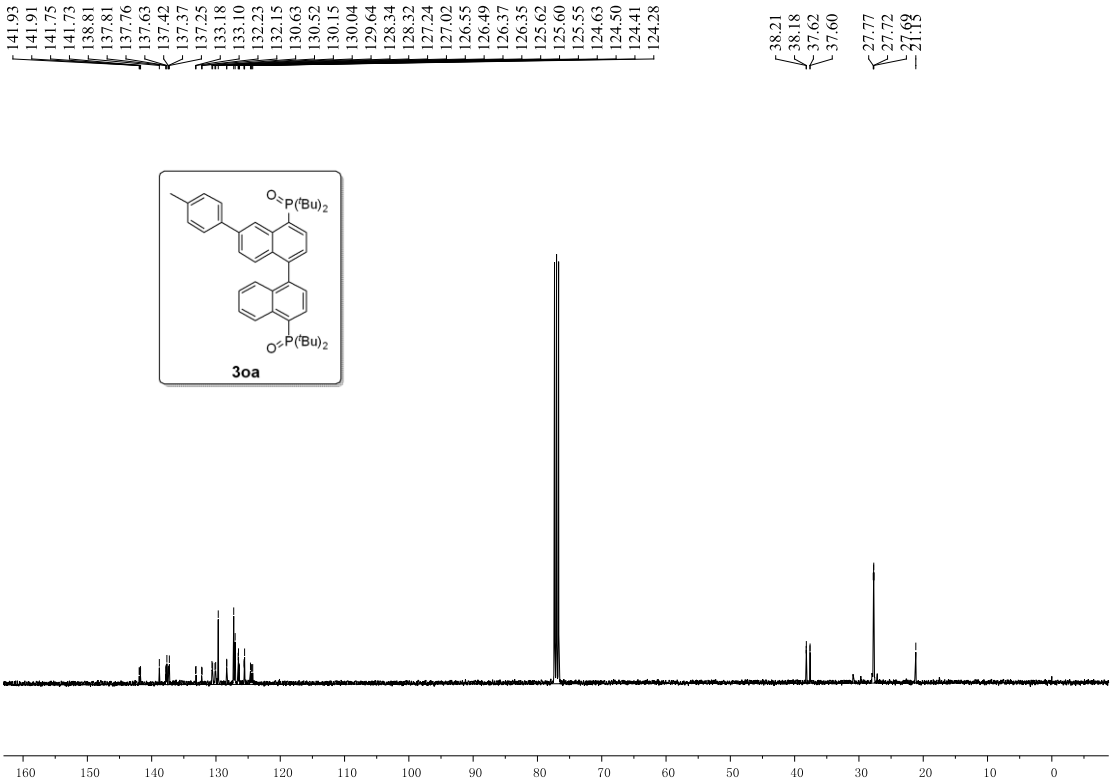


^{31}P NMR spectrum for **3oa**

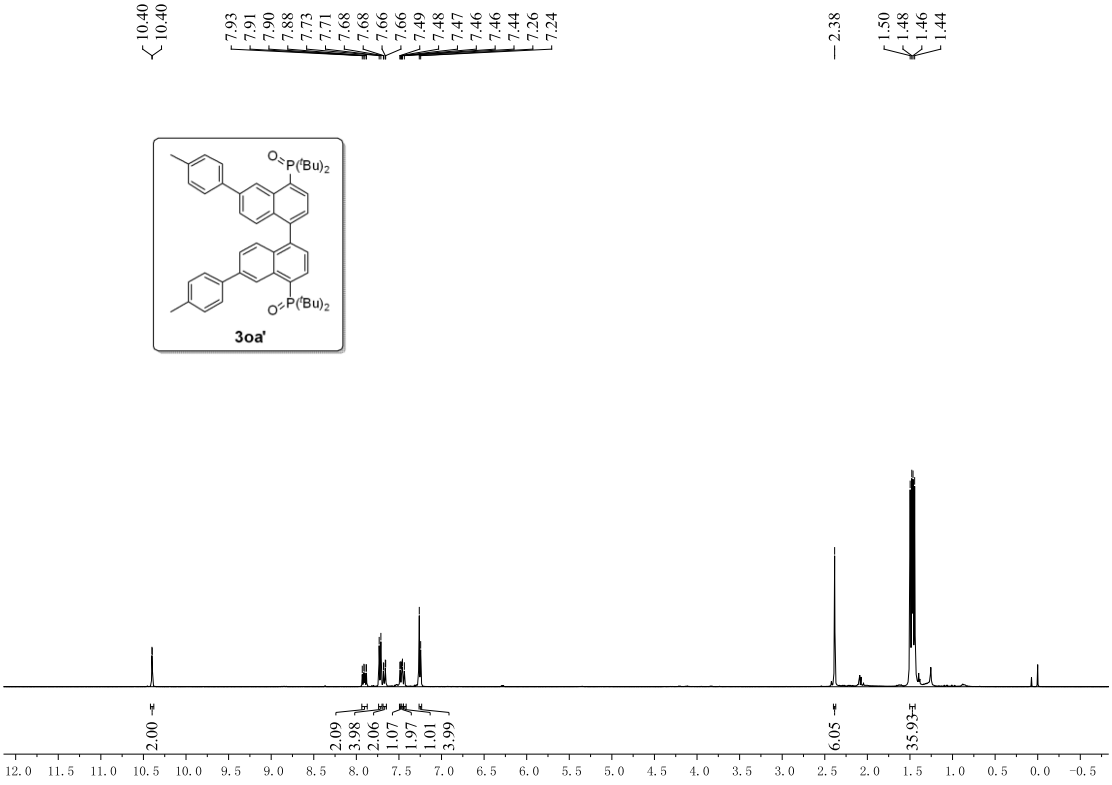




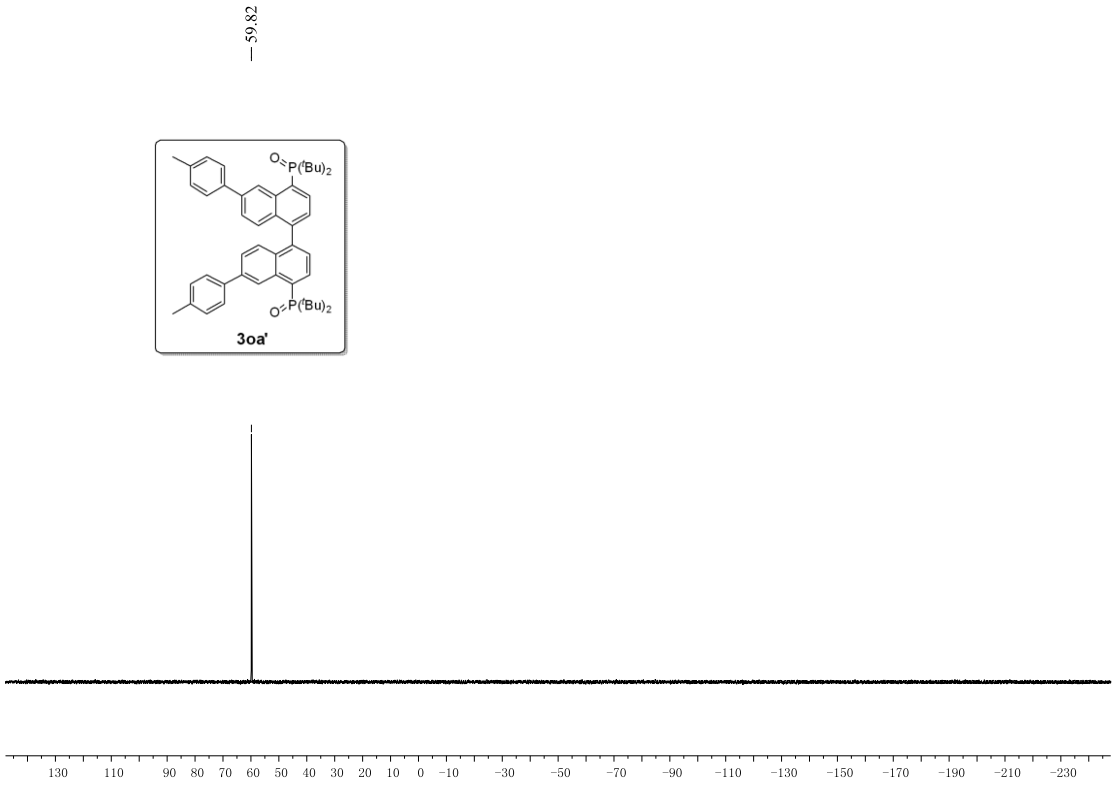
^{13}C NMR spectrum for **3oa**



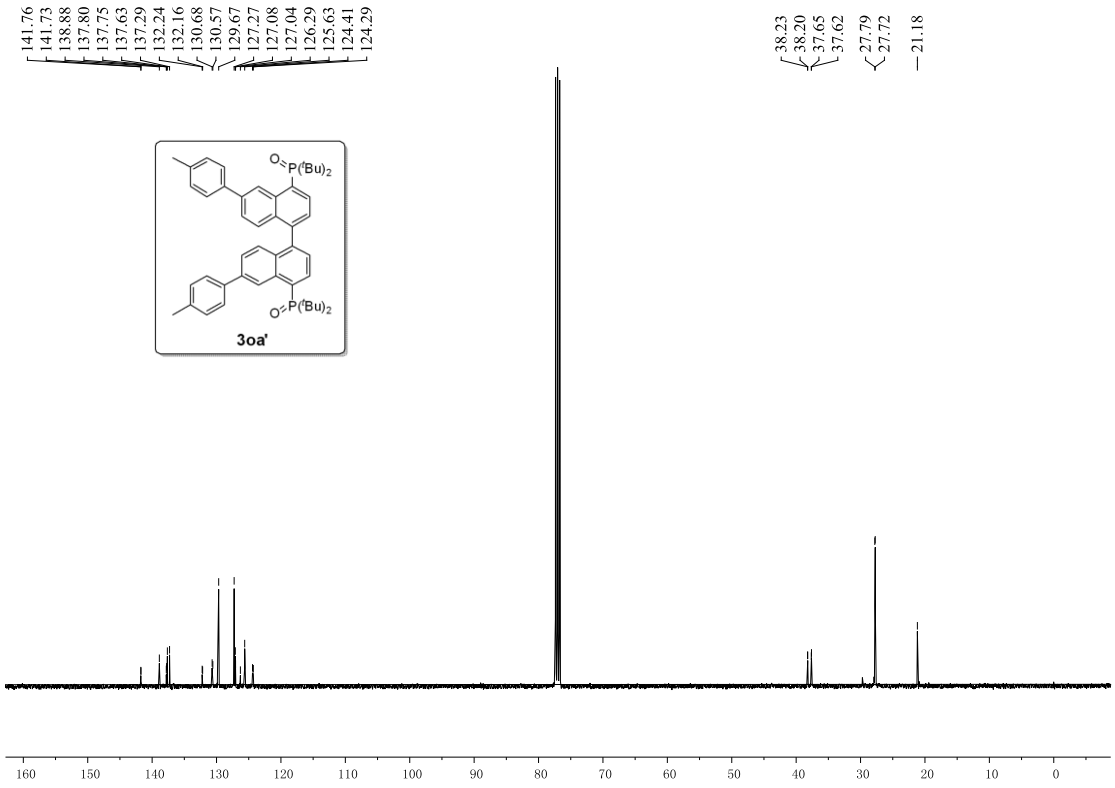
^{1}H NMR spectrum for **3oa'**



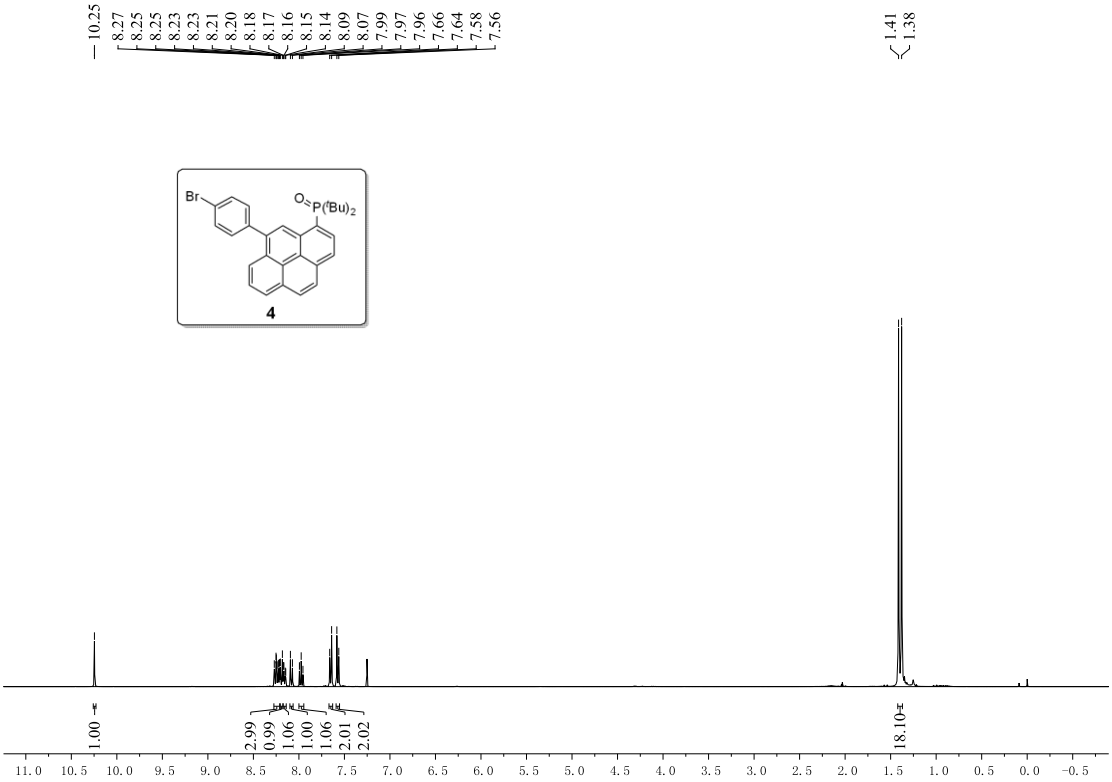
^{31}P NMR spectrum for **3oa'**



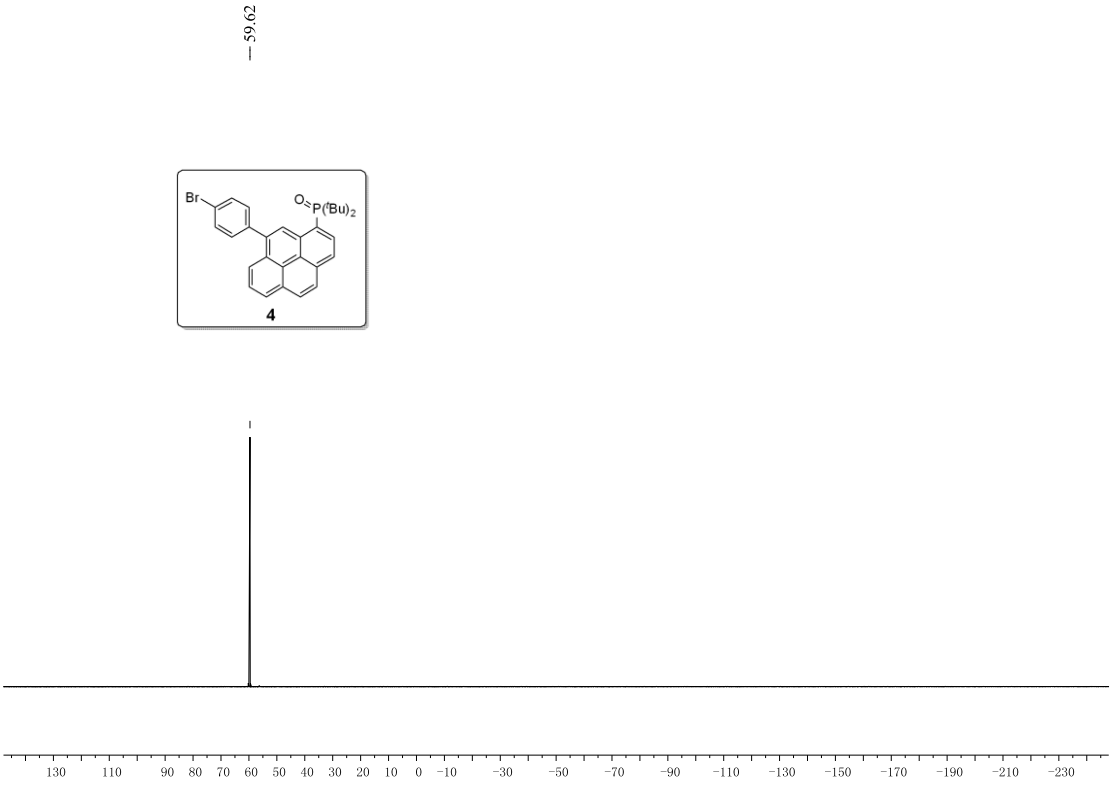
^{13}C NMR spectrum for **3oa'**



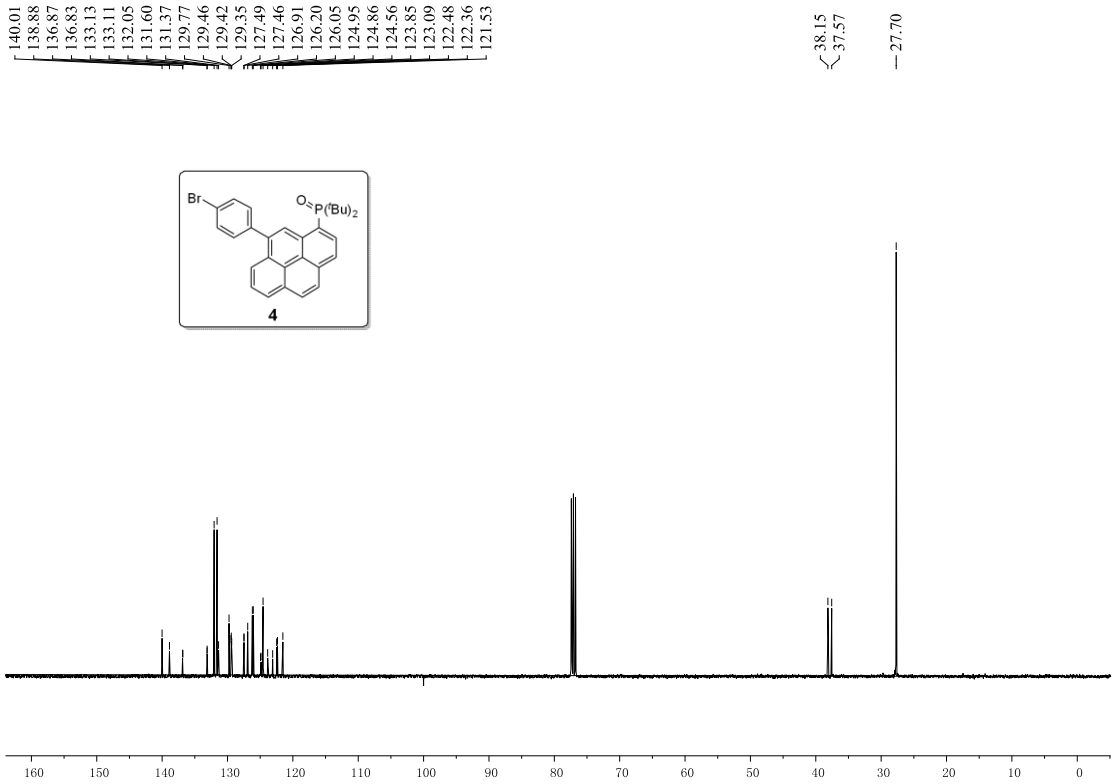
^{1}H NMR spectrum for **4**



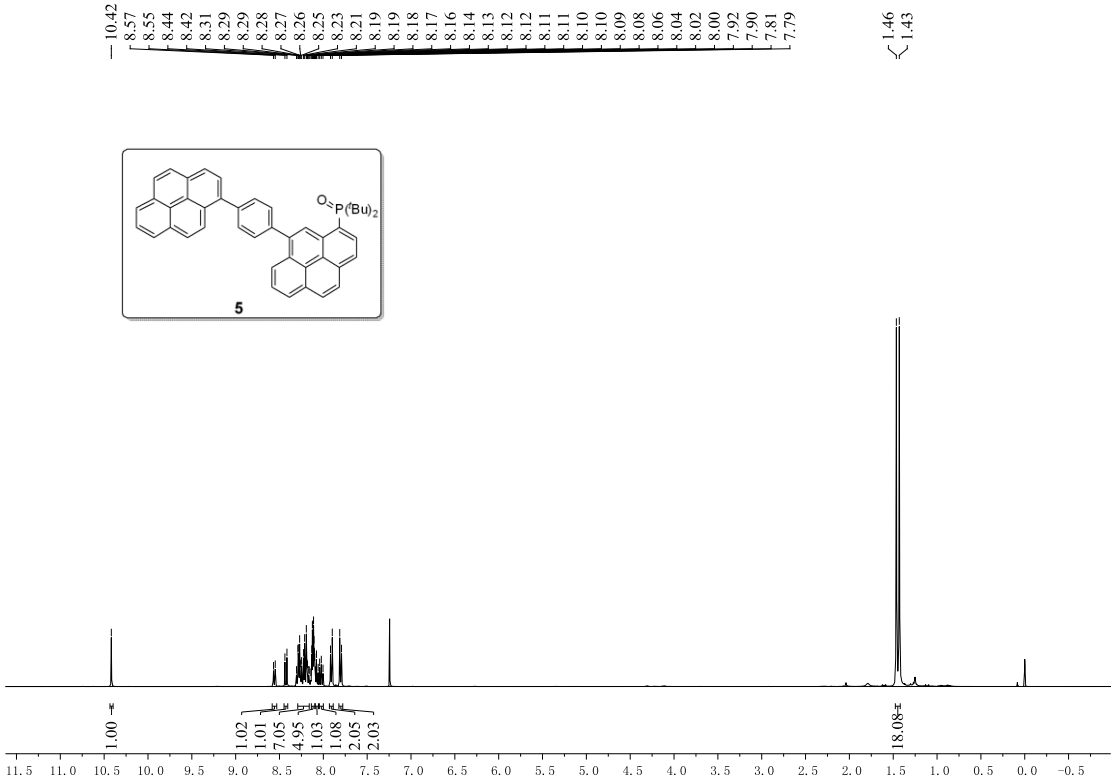
^{31}P NMR spectrum for **4**



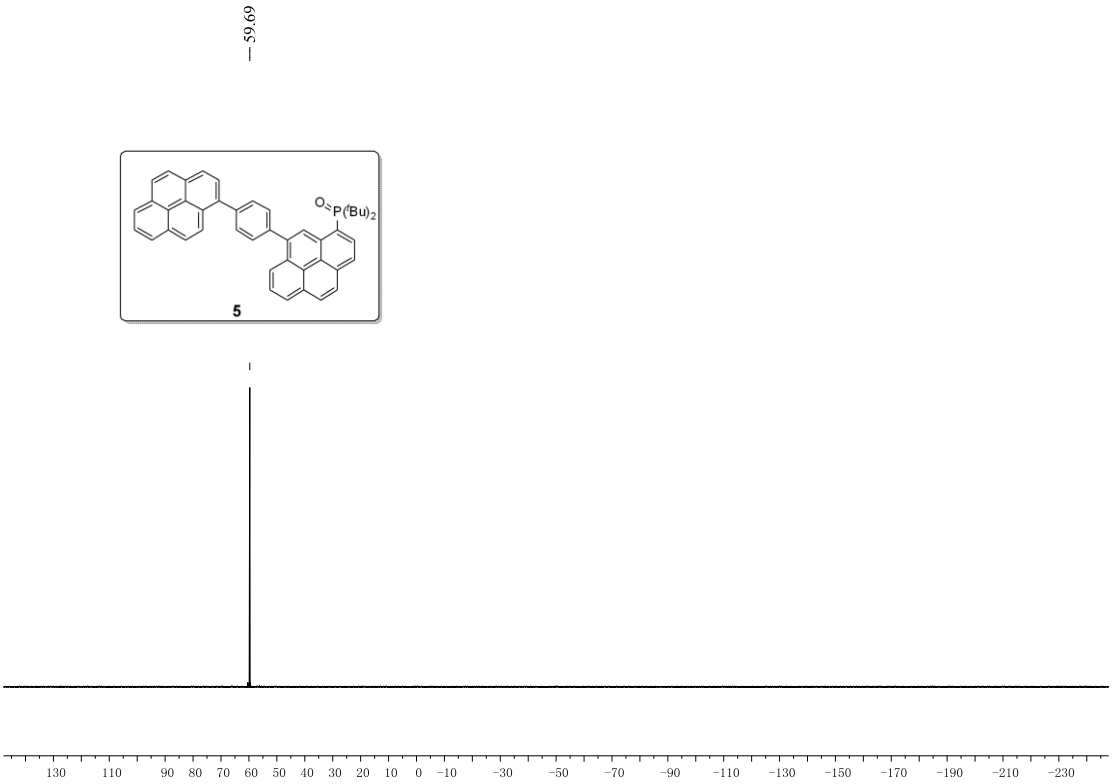
^{13}C NMR spectrum for **4**



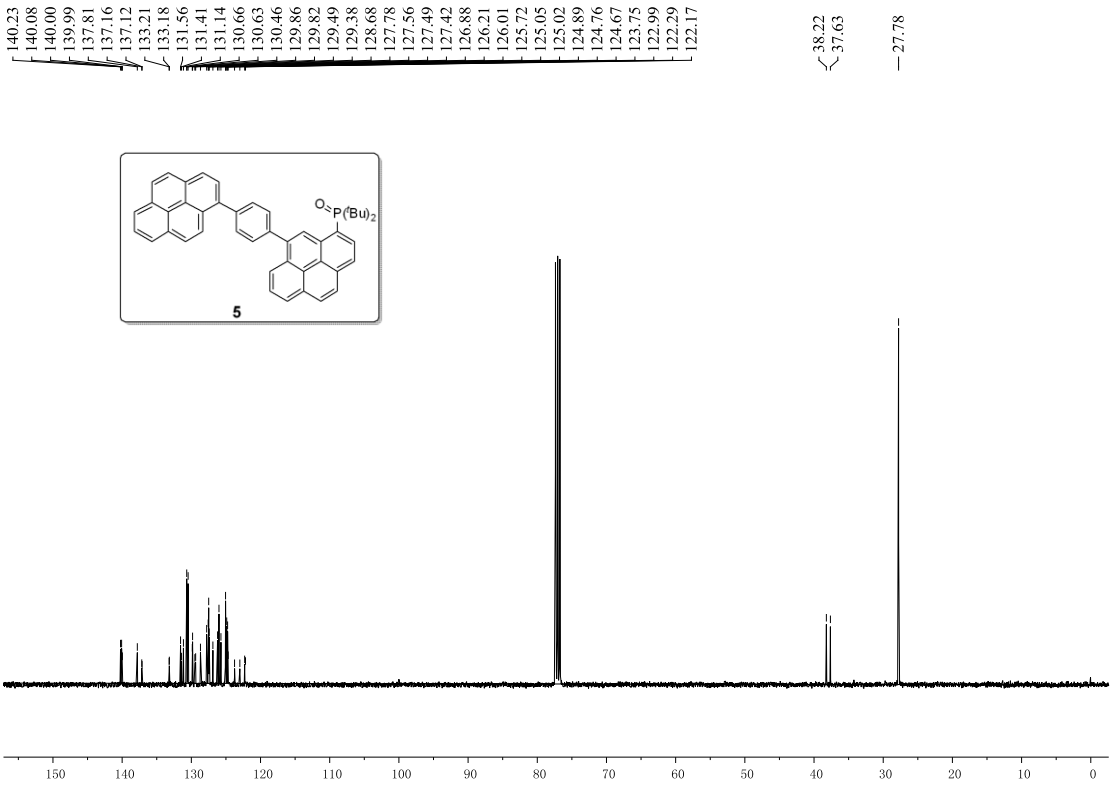
^{1}H NMR spectrum for **5**



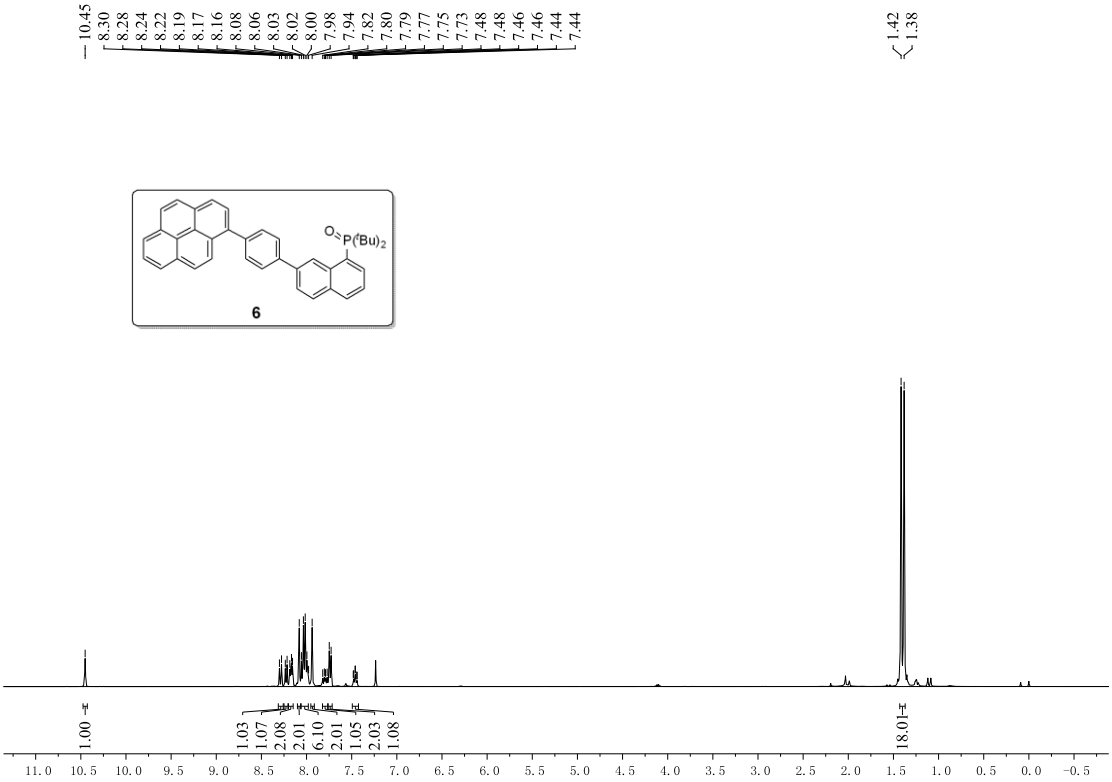
^{31}P NMR spectrum for **5**



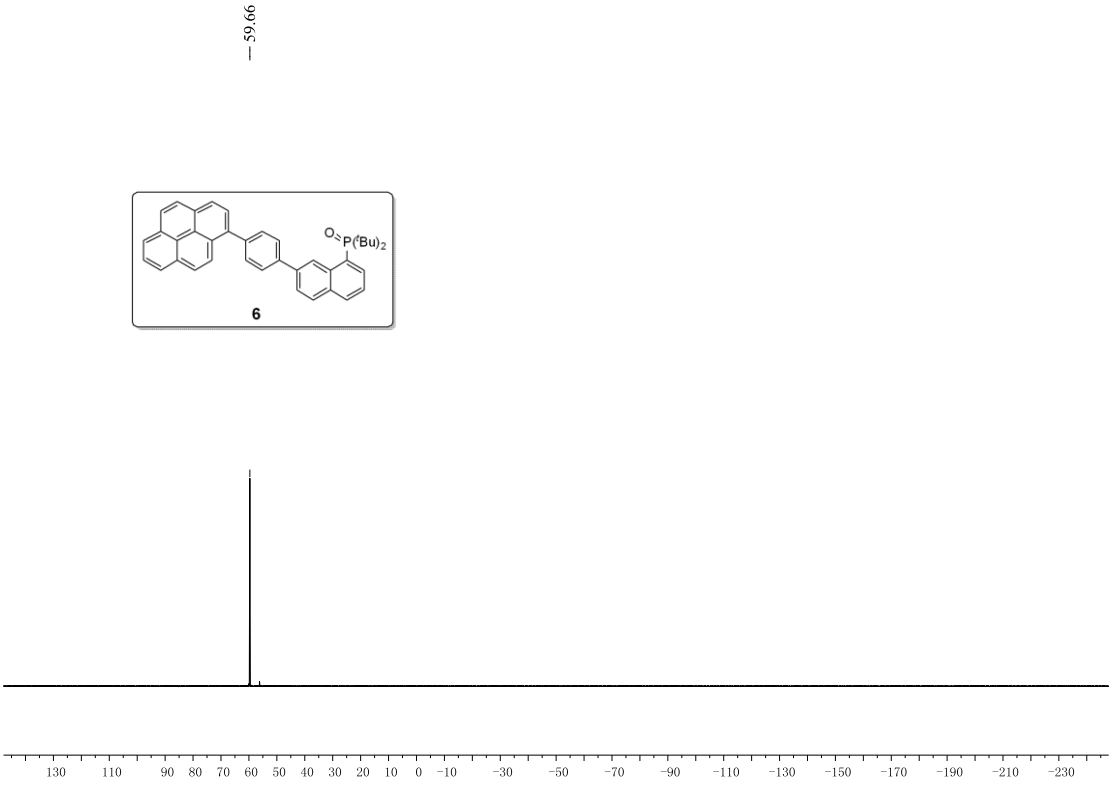
^{13}C NMR spectrum for **5**



^{1}H NMR spectrum for **6**



^{31}P NMR spectrum for **6**



^{13}C NMR spectrum for **6**