Supporting Information

Direct Air-Induced Arylphosphinoyl Radicals for Synthesis of Benzo[b]phosphole Oxides

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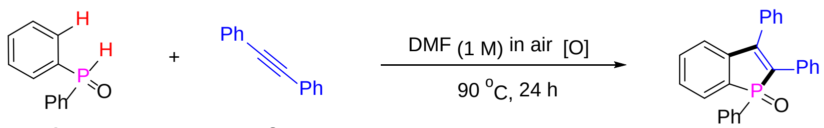
1. The Green Metrics Analysis

Table S1. Evaluation of green chemistry metrics for the synthesis of Benzo[b]phosphole oxide **3a**.



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

Chemical Formula: $C_{12}H_{11}OP$	$C_{14}H_{10}$	$C_{26}H_{19}OP$
Molecular Weight: 202.1928	178.2340	378.4108
1.4 mmol	0.5mmol	0.41 mmol (82% yield)

Reactant 1 (**1a**)	Diphenylphosphine oxide **1a**	0.28301 g	0.0014 mol	MW: 202.1928
Reactant 1 (**2a**)	Diphenyl acetylene **2a**	0.08910 g	0.0005 mol	MW: 178.2340
Solvent	*N*,*N*-Dimethylformamide (DMF)	0.5270 g	0.00721 mol	MW: 73.095
Auxiliary	Air	/	/	/
Product (**3a**)	Benzo[b]phosphole oxide **3a**	0.15515 g	0.00041 mol	MW: 378.4108

Product yield = **82%**

E-factor = {[(0.28301 + 0.08910 + 0.5270) – (0.15515)] / 0.15515} = **4.8 kg** waste/1 kg product

Atom economy = [378.4108 / (178.2340 + 202.1928*2.8)] × 100 % = **50.8%**

Atom efficiency = [47 / (24 + 25 × 2.8)] × 82% = **41%**

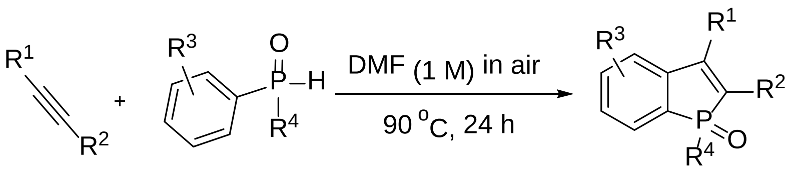
Carbon efficiency = [26 / (14 + 12 × 2.8)] × 82% = **44.8%**

Reaction mass efficiency = [0.15515 / (0.28301 + 0.08910)] × 100 % = **41.7%**

2. Materials and Instruments.

All reactions were routinely performed under an atmosphere of air by using standard Schlenk tube and dry deoxygenated solvents. Dry DMF were purchased from J&K Scientific Ltd. Silica gel (200 - 300 mesh) purchased from Qingdao Hai Yang Chemical Industry Co. Ltd. was used for chromatographic separations. NMR spectra (400 MHz/100 MHz) were recorded on an Advance DPX spectrometer (Bruker, Billerica, MA, USA) at room temperature with Chloroform-*d* as solvent. Tetramethylsilane (TMS) was used as an internal reference. High resolution mass spectrometry (HRMS) data were measured with an AB Sciex TOF 4600 instrument (Billerica, MA, USA). Data collection for X-ray crystal analysis was performed on a Bruker Smart APEX-II single S3 crystal X-ray diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 296 K.

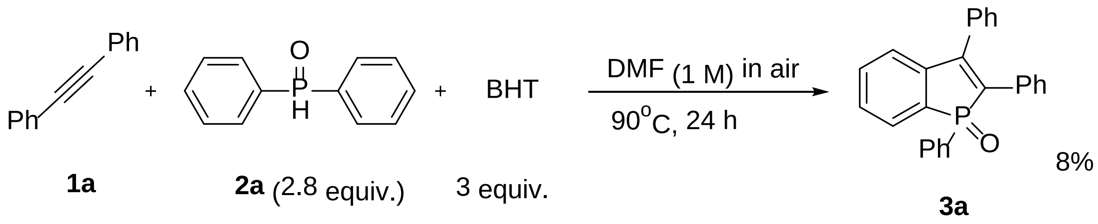
3. General procedure for the synthesis of compounds **3**.

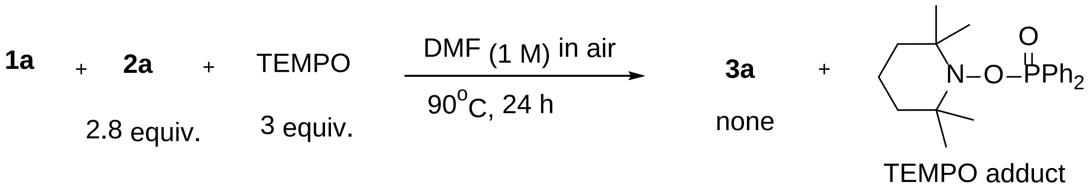


1 **2** **3**

General procedure for the synthesis of compounds **3**: The Schlenk reaction tube were added alkyne **1** (0.5 mmol) and diarylphosphine oxide **2** (2.8 mmol) with an amount of air, and DMF (0.5 mL) were added to the Schlenk reaction tube by syringe. The resulting reaction mixture was kept stirring at 90 °C in oil bath for 24 h. After required reaction time the mixture was cooled down to room temperature and exteacted by ethyl acetate (20 mL) and water (20 mL) three times. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (10 mL*2). All combined organic solutions were dried with anhydrous Na_2SO_4 and purified by flash chromatography (PE : EA=1 : 1) to afford the corresponding product **3**.

4. Radical trapping experiments and the high resolution mass spectra





The reaction was carried out according to the general procedure, except 3 equiv of TEMPO or BHT was added. At the end of the reaction, the isolated yield revealed formation of the target product **3a** decreased dramatically. The TEMPO adduct was detected by ESI-HRMS measurement of the crude reaction mixture {**HRMS (ESI)**: $C_{21}H_{29}NO_2P^+$, Calcd: 358.1930, Found: 358.1932}.

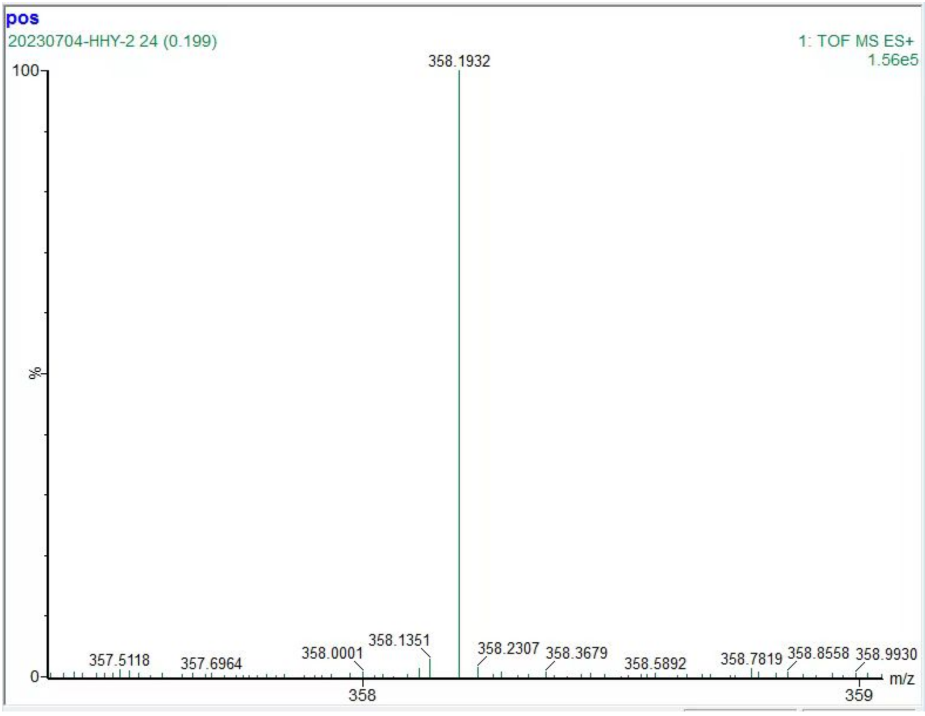


Figure s1. the high resolution mass spectra of the TEMPO adduct.

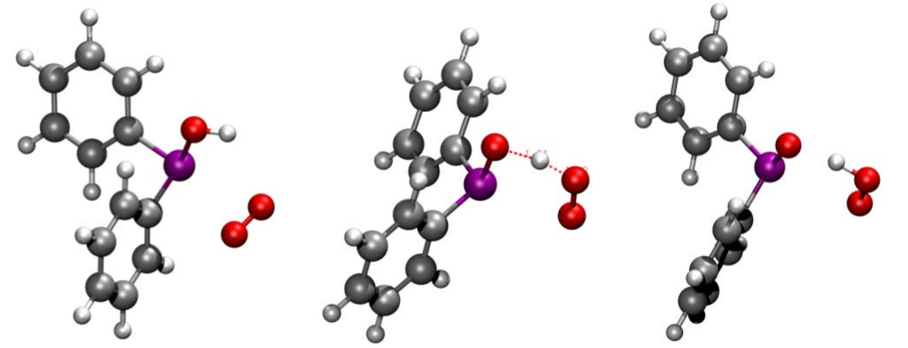
5. Computation of air-induced radical cyclization reaction.

Computational Methods:

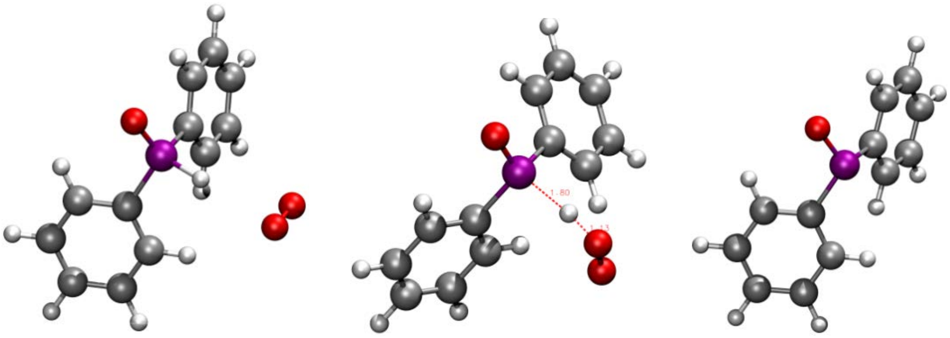
Density functional theory (DFT) investigations were performed to delineate the detailed mechanism of the h air(O_2)-induced radical cyclization. All density functional theory calculations were carried out with the Gaussian 16 programs. The geometry optimizations of the reactants, transition states, and products were performed with the B3LYP-D3 method at the 6-31G(d,p)/SMD(DMF), and energy and frequency calculations at M06-2X-D3/def-TZVP/SMD(DMF) level. The Spin Density distribution of transition state **ts-1** along its intrinsic reaction coordinate (IRC) are performed at B3LYP/6-31+G(d, p) level. The energies given in this work are M06-2X calculated Gibbs free energies in DMF solvent.

Animation of Reaction Coordinate (computational analysis) Move S1:

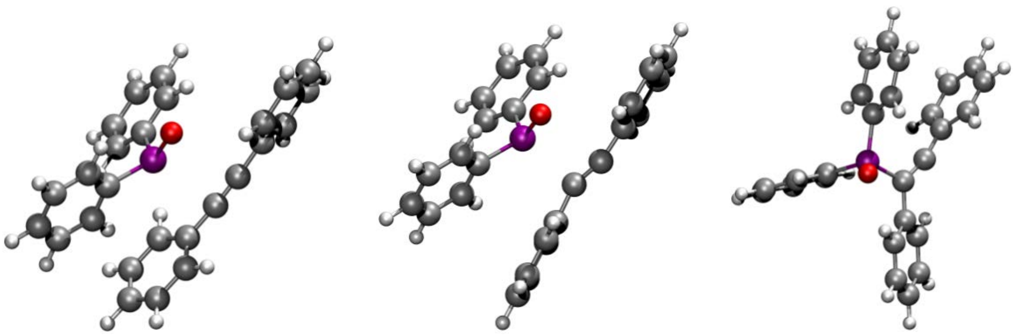
The Spin Density analysis of **ts-1**. Spin Density distribution of transition state **ts-1** along its intrinsic reaction coordinate (IRC). This video show an (P)O–H bond cleavage and new (oxygen)O–H bond formation with the spin density change. The calculated methods see supporting computational details. The video was created using Multiwfn, VMD, and Windows Movie Maker.



resonant (λ^3) **1a** with O_2 **ts-1** **int-1** with HOO·



1a with O_2 **ts-1'** **int-1**



int-1 with **2a** **ts-2** **int-2**

Figure S2. The main geometries calculated at the B3LYP-D3/6-31G(d, p) level.

Table S2. Thermal Free Energies with thermal correction (Hartree/Particle).

Intermediates or transition states	Thermal correction to Gibbs Free Energy (B3LYP-D3/6-31G(d,p))	Singlet point energies (M06-2X-D3/6-311G(d,p)/ SMD(DMF))	Thermal Free Energies with thermal correction
1a with O_2	0.151517	-1030.7155741	-1030.564057
resonant (λ^3) **1a** with O_2	0.151149	-1030.7154199	-1030.564271
int-1	0.146061	-879.7631865	-879.6171255
int-1 with HOO·	0.155288	-1030.6810103	-1030.525722
int-1 with **2a**	0.318201	-1419.1508858	-1418.832685
int-2	0.321384	-1419.1741091	-1418.852725
3a	0.318522	-1418.6499589	-1418.331437
ts-1	0.154063	-1030.6791832	-1030.52512
ts-1'	0.151149	-1030.6589971	-1030.507848
ts-2	0.319010	-1419.1381848	-1418.819175

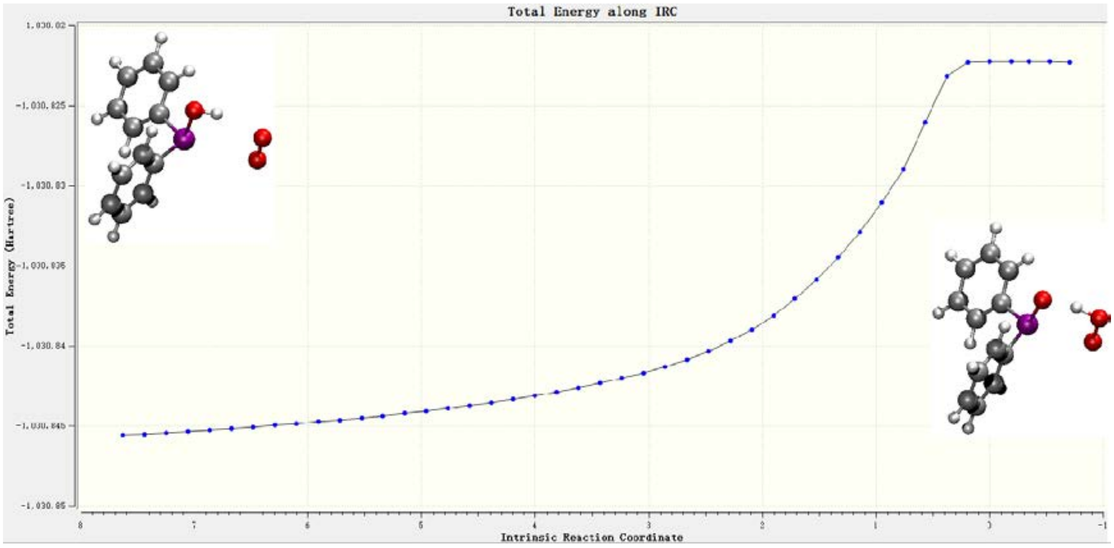


Figure S3. The intrinsic reaction coordinate (IRC) on **ts-1** at the B3LYP-D3/6-31G(d, p) level.

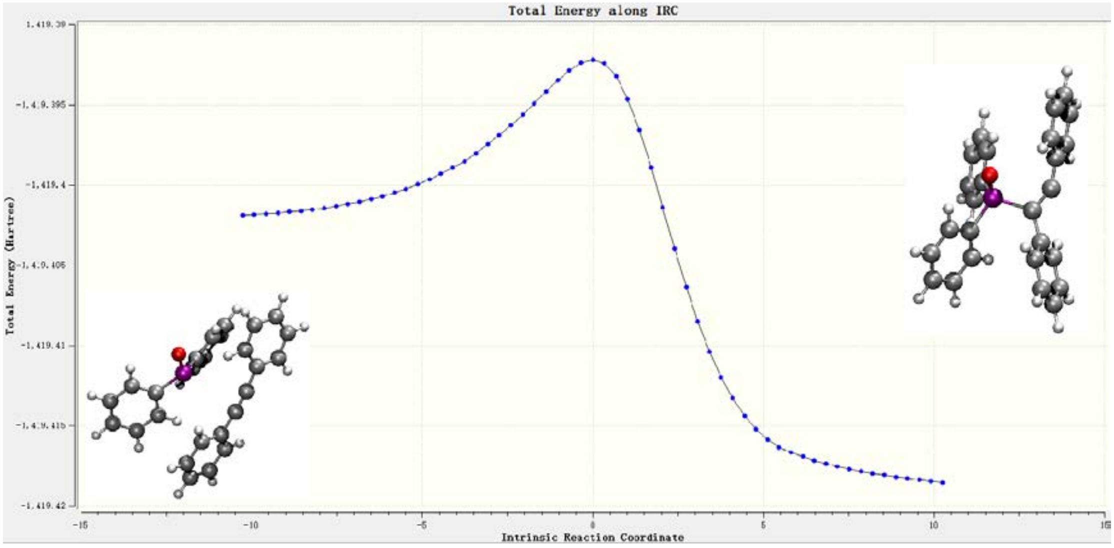
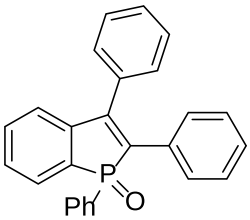


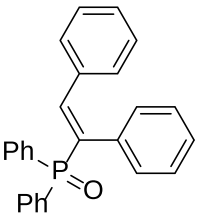
Figure S4. The intrinsic reaction coordinate (IRC) on **ts-2** at the B3LYP-D3/6-31G(d, p) level.

6. The analytical and spectral characterization data of compounds **3**.



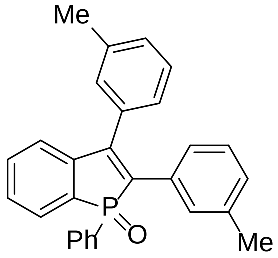
3a

3a: Reaction condition as general procedure for synthesis of compounds **3a**, the white solid **3a** was afforded (yield 82%, 155.0 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (m, 2H), 7.84 – 7.83 (m, 1H), 7.53 – 7.36 (m, 8H), 7.33 (d, *J* = 7.2 Hz, 2H), 7.26 – 7.16 (m, 3H), 7.09 (d, *J* = 5.4 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.13 (d, *J*=21.5 Hz, C), 143.88 (d, *J*=27.1 Hz, C), 134.41 (d, *J*=95.7 Hz, C), 134.37 (d, *J*=15.0 Hz, C), 133.02 (d, *J*=2.0 Hz, CH), 132.80 (d, *J*=9.8 Hz, C), 132.29 (d, *J*=2.9 Hz, CH),132.18 (d, *J*=105.9 Hz, C), 131.08 (d, *J*=10.6 Hz, 2CH), 130.05 (d, *J*=99.7 Hz, C), 129.22 (d, *J*=13.7 Hz, CH), 129.21 (d, *J*=2.3 Hz, 2CH), 129.15 (s, 3CH), 129.08 (s, 2CH), 129.05 (s, CH), 128.86 (d, *J*=12.2 Hz, 2CH), 128.37 (s, 2CH), 127.95 (s, CH), 124.17 (d, *J*=10.9 Hz, CH); ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.11; HRMS Calcd. For $C_{26}H_{20}OP^{+}$ [M + H^{+}]$^{+}$, 379.1246. Found: 379.1239.



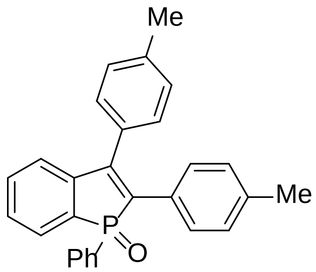
3a′

3a': ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (s, 1H), 7.60 – 7.55 (m, 6H), 7.30 (d, *J*=7.2 Hz, 2H), 7.20 (d, *J*=7.2 Hz, 2H), 7.16 – 7.11 (m, 7H), 7.06 (d, *J*=5.5 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.00 (d, J_{C-P} =6.9 Hz, CH), 141.47 (d, J_{C-P} =10.5 Hz, C), 136.89 (d, J_{C-P} =91.7 Hz, C), 135.40 (d, J_{C-P} =5.8 Hz, C), 134.15 (s, C), 133.12 (s, C), 131.47 (s, 2CH), 131.38 (s, 2CH), 130.92 (d, J_{C-P} =2.9 Hz, 2CH), 130.08 (d, J_{C-P} =1.4 Hz, 2CH), 128.77 (d, J_{C-P} =4.5 Hz, 2CH), 128.60 (s, CH), 128.11 (s, 2CH), 128.04 (s, 2CH), 127.86 (d, J_{C-P} =12.3 Hz, 4CH), 127.12 (s, CH); ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.94; HRMS Calcd. For $C_{26}H_{22}OP^+$ [M + H$^+$]$^+$, 381.1403. Found: 381.1403.



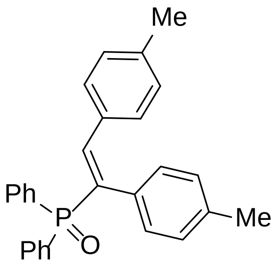
3b

3b: Reaction condition as general procedure for synthesis of compounds **3a**, the white solid **3b** was afforded (yield 70%, 142.2 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.74 (m, 2H), 7.77 – 7.68 (m, 1H), 7.50 – 7.42 (m, 2H), 7.36 – 7.29 (m, 3H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.23 – 7.18 (m, 2H), 7.14 (s, 1H), 7.10 (d, *J* = 6.6 Hz, 1H), 7.06 – 6.83 (m, 4H), 2.36 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.15 (d, J_{C-P} = 21.4 Hz, C), 144.08 (d, J_{C-P} = 27.1 Hz, C), 138.69(s, C), 137.77(s, C), 134.48 (d, J_{C-P} = 15.1 Hz, C), 134.15 (d, J_{C-P} = 95.8 Hz, C), 132.94 (d, J_{C-P} = 2.0 Hz, CH), 132.76 (d, J_{C-P} = 2.9 Hz, C), 132.19 (d, J_{C-P} = 2.9 Hz, CH), 132.19 (d, J_{C-P} = 98.8 Hz, C), 131.09 (d, J_{C-P} = 10.5 Hz, 2CH), 130.32 (d, J_{C-P} = 99.4 Hz, C), 129.74 (d, J_{C-P} = 5.6 Hz, CH), 129.46 (d, J_{C-P} = 2.4 Hz, 2CH), 129.09 (d, *J*=10.6 Hz, CH), 129.05 (d, *J*=10.2 Hz, CH), 129.00(s, CH), 128.94(s, CH), 128.87(s, CH), 128.75 (s, CH), 128.12 (s, CH), 126.34 (d, J_{C-P} = 5.9 Hz, CH), 126.22 (s, CH), 124.16 (d, J_{C-P} = 10.8 Hz, CH), 21.60 (s, CH_3), 21.46 (s, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.13; HRMS Calcd. For $C_{28}H_{24}OP^+$ [M + H$^+$]$^+$, 407.1559. Found: 407.1559.



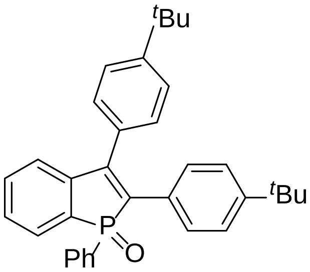
3c

3c: Reaction condition as general procedure for synthesis of compounds **3a**, the white solid **3c** was afforded (yield 73%, 148.2 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.71 (m, 2H), 7.71 – 7.65 (m, 1H), 7.47 – 7.41 (m, 5H), 7.27 – 7.18 (m, 5H), 7.15 (d, *J* = 7.9 Hz, 2H), 6.90 (d, *J* = 7.9 Hz, 2H), 2.40 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.50 (d, J_{C-P} = 21.6 Hz, C), 144.17 (d, J_{C-P} = 27.2 Hz, C), 138.59 (s, C), 137.76 (s, C), 133.84 (d, J_{C-P} = 95.7 Hz, C), 132.90 (d, J_{C-P} = 2.1 Hz, CH), 132.20 (d, J_{C-P} = 105.6 Hz, C), 132.15 (d, J_{C-P} = 2.9 Hz, CH), 131.52 (d, J_{C-P} = 15.2 Hz, C), 131.06 (d, J_{C-P} = 10.6 Hz, 2CH), 130.42 (d, J_{C-P} = 79.9 Hz, C), 129.88 (d, J_{C-P} = 9.4 Hz, C), 129.78 (s, 2CH), 129.11 (s, 2CH), 129.04 (s, 3CH), 128.98 (d, J_{C-P} = 2.2 Hz, 2CH), 128.97 (s, CH), 128.93 (d, J_{C-P} = 1.6 Hz, CH), 128.85 (s, CH), 124.01 (d, J_{C-P} = 10.9 Hz, CH), 21.53 (s, CH_3), 21.32 (s, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.17; HRMS Calcd. For $C_{28}H_{24}OP^+$ [M + H$^+$]$^+$, 407.1559. Found:407.1548.



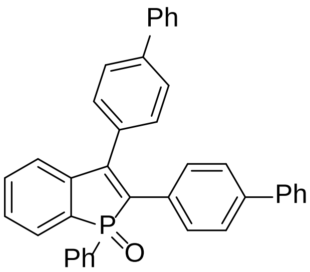
3c'

3c': [1]H NMR (400 MHz, Chloroform-*d*) δ 7.53 (dd, *J*=11.6, 7.9 Hz, 4H), 7.38 – 7.30 (m, 4H), 7.27 – 7.21 m 4H), 6.85 – 6.82 (m, 2H), 6.78 (d, *J*=2.5 Hz, 3H), 6.68 (d, *J*=7.6 Hz, 2H), 2.12 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.27 (d, $J_{C\text{-}P}$ =10.5 Hz, CH), 138.19(s, C), 136.50 (d, $J_{C\text{-}P}$ =2.5 Hz, C), 132.76 (d, $J_{C\text{-}P}$ =95.7 Hz, C), 131.40 (d, $J_{C\text{-}P}$ =9.5 Hz, 4CH), 131.19 (d, $J_{C\text{-}P}$ =18.1 Hz, C), 130.85 (d, $J_{C\text{-}P}$ =2.8 Hz, 2CH), 130.84 (s, C), 129.98 (d, $J_{C\text{-}P}$ =103.5 Hz, 2C), 129.32 (s, 2CH), 128.90 (d, $J_{C\text{-}P}$ =4.4 Hz, 2CH), 128.53 (d, $J_{C\text{-}P}$ =1.8 Hz, 2CH), 127.95 (s, 2CH), 127.29 (d, $J_{C\text{-}P}$ =12.0 Hz, 4CH), 20.28 (s, CH_3), 20.27 (s, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.92; HRMS Calcd. For $C_{28}H_{26}OP^+$ [M + H^+]$^+$, 409.1716. Found: 409.1720.



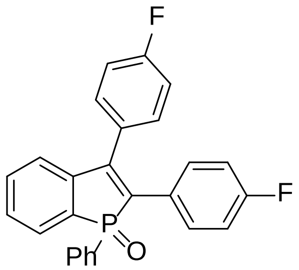
3d

3d: Reaction condition as general procedure for synthesis of compounds **3a**, the yellow solid **3d** was afforded (yield 79%, 193.7 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.75 (m, 2H), 7.69 – 7.63 (m, 1H), 7.53 – 7.44 (m, 3H), 7.44 – 7.35 (m, 3H), 7.34 – 7.30(m, 1H), 7.29 – 7.25 (m, 2H), 7.18 (dd, *J* = 7.6, 2.8 Hz, 1H), 7.15 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 1.38 (s, 9H), 1.19 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 151.85 (s, C), 150.85 (s, C), 149.43 (d, $J_{C\text{-}P}$ = 21.5 Hz, C), 144.37 (d, $J_{C\text{-}P}$ = 27.2 Hz, C), 133.69 (d, $J_{C\text{-}P}$ = 96.1 Hz, C), 132.90 (d, $J_{C\text{-}P}$ = 2.2 Hz, CH), 132.28 (d, *J*=126.3 Hz, C), 132.13 (d, *J*=2.9 Hz, CH), 131.81 (s, C), 131.13 (d, *J*=10.6 Hz, 2CH), 130.79 (d, *J*=98.7 Hz, C),129.84 (d, $J_{C\text{-}P}$ = 10.1 Hz, C), 129.05 (s, CH), 128.98 (s, CH), 128.89 (s, 2CH), 128.88 (d, $J_{C\text{-}P}$ = 9.2 Hz, 2CH), 128.81 (s, 2CH), 126.00 (s, 2CH), 125.31 (s, 2CH), 124.13 (d, $J_{C\text{-}P}$ = 11.0 Hz, CH), 34.92 (s, C), 34.64 (s, C), 31.48 (s, $3CH_3$), 31.24 (s, $3CH_3$); ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.18; HRMS Calcd. For $C_{34}H_{36}OP^+$ [M + H^+]$^+$, 491.2498. Found: 491.2495.



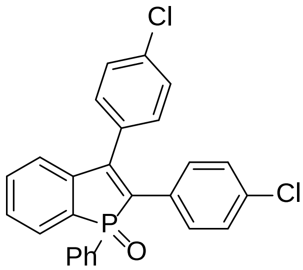
3e

3e: Reaction condition as general procedure for synthesis of compounds **3a**, the white solid **3e** was afforded (yield 75%, 198.8 mg); [1]H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.80 (m, 2H), 7.78 – 7.64 (m, 6H), 7.64 – 7.58 (m, 1H), 7.50 – 7.47 (m, 5H), 7.46 – 7.44 (m, 2H), 7.43 – 7.40 (m, 2H), 7.37 (s, 7H), 7.32 – 7.28 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.69 (d, J_{C-P} = 21.4 Hz, C), 143.95 (d, J_{C-P} = 27.0 Hz, C), 141.62 (s, C), 140.55 (s, C), 140.44 (s, C), 140.38 (s, C), 134.13 (d, J_{C-P} = 95.3 Hz, C), 133.44 (d, J_{C-P} = 15.0 Hz, C), 133.11 (d, J_{C-P} = 1.6 Hz, CH), 132.63 (d, J_{C-P} = 90.4 Hz, C), 132.36 (d, J_{C-P} = 2.9 Hz, CH), 132.01 (d, J_{C-P} =33.6 Hz, C), 131.26 (d, J_{C-P} = 106.8 Hz, C), 131.21 (s, CH), 131.11 (s, CH), 129.74 (s, 2CH), 129.63 (d, *J*=5.9 Hz, 2CH), 129.33 (d, J_{C-P} = 4.6 Hz, CH), 129.23 (d, J_{C-P} = 3.7 Hz, CH), 129.13 (s, CH), 129.06 (s, 2CH), 129.01 (s, CH), 128.84 (s, 2CH), 127.80 (s, 2CH), 127.71 (d, J_{C-P} = 35.2 Hz, 2CH), 127.19 (s, 2CH), 127.08 (s, 2CH), 126.99 (s, 2CH), 124.21 (d, J_{C-P} = 10.7 Hz, CH); ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.15; HRMS Calcd. For $C_{38}H_{28}OP^+$ $[M + H^+]^+$, 531.1872. Found: 531.1880.



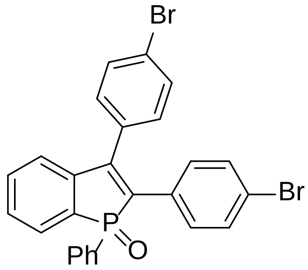
3f

3f: Reaction condition as general procedure for synthesis of compounds **3a**, the yellow solid **3f** was afforded (yield 55%, 113.9 mg); [1]H NMR (400 MHz, Chloroform-d) δ 7.76 – 7.70 (m, 3H), 7.48 (t, *J* = 6.7 Hz, 2H), 7.42 – 7.37 m, 3H), 7.31 – 7.28 (m, 2H), 7.20 (t, *J* = 6.6 Hz, 3H), 7.14 (t, *J* = 8.4 Hz, 2H), 6.81 (t, *J* = 8.5 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.01 (d, J_{C-F} = 249.3 Hz, C), 162.45 (d, J_{C-F} = 249.1 Hz, C), 148.99 (d, J_{C-F} = 22.1 Hz, C), 143.64 (d, *J* = 26.8 Hz, C), 134.08 (d, J_{C-P} = 96.2 Hz, C), 133.22 (d, *J* = 2.0 Hz, CH), 132.52 (d, *J* = 2.9 Hz, CH), 131.92 (d, J_{C-P} = 106.0 Hz, C), 131.14 (d, *J* = 8.2 Hz, 2CH), 131.07 (d, *J* = 10.6 Hz, 2CH), 130.98 (dd, *J* = 8.2, 5.5 Hz, 2CH), 130.67 (d, *J* = 103.2 Hz, C), 130.00 (dd, *J* = 15.3, 3.7 Hz, C), 129.46 (d, *J* = 17.1 Hz, CH), 129.46 (d, *J* = 3.3 Hz, CH), 129.10 (d, *J* = 12.3 Hz, 2CH), 128.72 (dd, *J* = 10.1, 3.4 Hz, C), 124.01 (d, *J* = 10.9 Hz, CH), 116.46 (d, *J* = 21.6 Hz, 2CH), 115.70 (d, *J* = 21.6 Hz, 2CH); ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.81; HRMS Calcd. For $C_{26}H_{18}F_2OP^+$ $[M + H^+]^+$, 415.1058. Found: 415.1057.



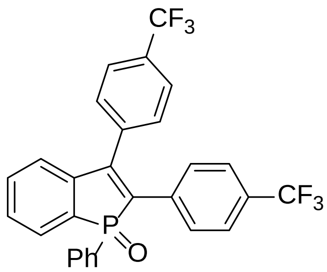
3g

3g: Reaction condition as general procedure for synthesis of compounds **3a**, the white solid **3g** was afforded (56%, 124.9 mg);[1]H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.69 (m, 3H), 7.49 (q, *J*=7.1 Hz, 2H), 7.44 – 7.40 (m, 5H), 7.28 – 7.24 (m, 2H), 7.22 – 7.13 (m, 3H), 7.09 (d, *J*=8.3 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.19 (d, J_{C-P} = 21.7 Hz, C), 143.29 (d, J_{C-P} = 26.5 Hz, C), 135.11 (s, C), 134.21 (s, 2C), 134.05 (d, J_{C-P} = 95.6 Hz, C), 133.26 (d, J_{C-P} = 2.0 Hz, 2CH), 132.59 (d, J_{C-P} = 2.9 Hz, CH), 132.39 (d, J_{C-P} = 15.0 Hz, C), 131.91 (d, J_{C-P} = 106.0 Hz, C), 131.04 (d, J_{C-P} = 10.8 Hz, 2CH), 130.57 (s, 2CH), 130.35 (d, J_{C-P} = 5.5 Hz, 2CH), 129.65 (d, J_{C-P} = 10.7 Hz, CH), 129.63 (s, 2CH), 129.48 (d, J_{C-P} = 9.8 Hz, CH), 129.39 (d, J_{C-P} = 99.8 Hz, C), 129.13 (d, J_{C-P}=12.4 Hz, 2CH), 128.89 (s, CH), 124.06 (d, J_{C-P} = 10.6 Hz, CH); ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.92; HRMS Calcd. For $C_{26}H_{18}Cl_2OP^+$ [M + H$^+$]$^+$, 447.0467. Found: 447.0462.



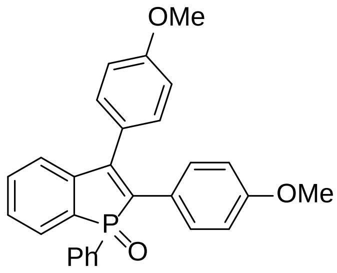
3h

3h: Reaction condition as general procedure for synthesis of compounds **3a**, the yellow solid **3h** was afforded (yield 62%, 165.5 mg); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.76 – 7.67(m, 3H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.49 (q, *J* = 7.0 Hz, 2H), 7.42 – 7.36 (m, 3H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 3H), 7.10 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.22 (d, J_{C-P} = 21.7 Hz, C), 143.23 (d, J_{C-P} = 26.5 Hz, C), 134.17 (d, J_{C-P} = 95.3 Hz, C), 133.26 (d, J_{C-P} = 1.9 Hz, CH), 132.89 (d, J_{C-P} = 14.9 Hz, C), 132.59 (d, J_{C-P} = 2.9 Hz, 3CH), 132.02 (d, J_{C-P} = 90.8 Hz, C), 131.84 (s, 2CH), 131.44 (d, J_{C-P} = 5.3 Hz, C), 131.09 (s, CH), 130.98 (s, CH), 130.80 (s, 2CH), 130.60 (d, J_{C-P} = 5.5 Hz, 2CH), 129.67 (d, J_{C-P} = 10.7 Hz, CH), 129.48 (d, J_{C-P} = 9.7 Hz, CH), 129.40 (d, J_{C-P} = 100.5 Hz, C), 129.13 (d, J_{C-P} = 12.4 Hz, 2CH), 124.07 (d, J_{C-P} = 10.8 Hz, CH), 123.33 (s, C), 122.59 (s, C); ^{31}P NMR (162 MHz, CDCl3) δ 38.78; HRMS Calcd. For $C_{26}H_{18}Br_2OP^+$ [M + H$^+$]$^+$, 536.9436. Found: 536.9430.



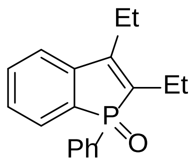
3i

3i: Reaction condition as general procedure for synthesis of compounds **3a**, the yellow solid **3i** was afforded (yield 48%, 123.4 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.69 (m, 4H), 7.60 – 7.49 (m, 2H), 7.45 (t, *J* = 7.2 Hz, 3H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.37 (s, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.26 (s, 1H), 7.17 (dd, *J* = 7.6, 3.0 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.03 (d, J_{C-P} = 21.6 Hz, C), 142.91 (d, J_{C-P} = 26.1 Hz, C), 137.64 (d, J_{C-P} = 14.6 Hz, C), 136.09 (d, J_{C-P} = 9.8 Hz, C), 134.86 (d, J_{C-P} = 94.6 Hz, C), 133.44 (d, J_{C-P} = 2.0 Hz, CH), 132.81 (d, J_{C-P} = 3.0 Hz, CH), 131.96 (d, J_{C-P} = 106.4 Hz, C), 131.37 (d, J_{C-F} = 33.0 Hz, C), 131.07 (d, J_{C-P} = 10.7 Hz, 2CH), 130.2 (d, J_{C-F} = 33.0 Hz, C), 130.10 (d, J_{C-P} = 10.8 Hz, CH), 129.71 (d, J_{C-P} = 9.6 Hz, CH), 129.64(s,2CH),129.32 (s, 2CH), 129.23 (d, J_{C-P} = 7.8 Hz, 2CH), 129.04 (d, J_{C-P} = 100.8 Hz, C), 126.35 (d, J_{C-P} = 3.8 Hz, 2CH), 125.61 (dd, J_{C-P} = 7.7, 3.9 Hz, 2CH), 124.30 (d, J_{C-P} = 10.8 Hz, CH), 123.96 (q, J_{C-F} = 273.2 Hz, C), 123.94 (q, J_{C-F} = 273.1 Hz, C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.89; HRMS Calcd. For $C_{28}H_{18}F_6OP^+$ [M + H$^+$]$^+$, 515.0994. Found: 515.0997.



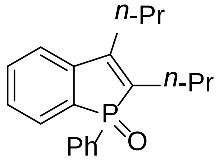
3j

3j: Reaction condition as general procedure for synthesis of compounds **3a**, the yellow solid **3j** was afforded (yield 80%, 175.3 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.68 (m, 2H), 7.66 – 7.61 (m, 1H), 7.50 – 7.42 (m, 2H), 7.36 – 7.29 (m, 3H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.23 – 7.18 (m, 2H), 7.14 (s, 1H), 7.10 (d, *J* = 6.6 Hz, 1H), 7.06 – 6.83 (m, 4H), 2.36 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.85 (s, C), 159.15 (s, C), 148.24 (d, $J_{C\text{-}P}$ = 22.2 Hz, C), 144.32 (d, $J_{C\text{-}P}$ = 27.4 Hz, C), 133.20 (d, $J_{C\text{-}P}$ = 96.2 Hz, C), 132.92 (s, CH), 132.16 (d, $J_{C\text{-}P}$ = 2.9 Hz, CH), 132.09 (d, $J_{C\text{-}P}$ = 106.3 Hz, C), 131.06 (d, $J_{C\text{-}P}$ = 10.6 Hz, 2CH), 130.59 (s, CH), 130.54 (d, $J_{C\text{-}P}$ = 6.0 Hz, 2CH), 130.42 (d, $J_{C\text{-}P}$ = 99.5 Hz, C),128.99 (s, CH), 128.92 (d, *J*=11.8 Hz, CH), 128.92 (d, *J*=30.1 Hz, CH), 128.88 (s, CH), 126.65 (d, $J_{C\text{-}P}$ = 15.3 Hz, C), 125.42 (d, $J_{C\text{-}P}$ = 10.4 Hz, C), 123.81 (d, $J_{C\text{-}P}$ = 10.9 Hz, 2CH), 114.59 (s, 2CH), 113.90 (s, 2CH), 55.41 (s, CH_3), 55.19(s, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.15; HRMS Calcd. For $C_{28}H_{24}O_3P^+$ $[M + H^+]^+$, 439.1458. Found: 439.1459.



3k

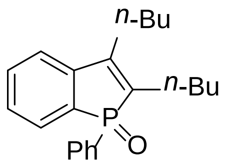
3k: Reaction condition as general procedure for synthesis of compounds **3a**, the white solid **3k** was afforded (yield 57%, 80.4 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.52 (m, 2H), 7.48 – 7.43 (m, 1H), 7.42 – 7.37 (m, 2H), 7.32 – 7.26 (m, 3H), 7.20 – 7.15 (m, 1H), 2.52 (t, *J* = 7.8 Hz, 2H), 2.48 – 2.35 (m, 1H), 2.24 – 2.14 (m, 1H), 1.55 – 1.46 (m, 2H), 1.43 – 1.36 (m, 2H), 1.34 – 1.23 (m, 2H), 1.19 – 1.12 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.69 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.59 (d, $J_{C\text{-}P}$ = 19.8 Hz, C), 143.31 (d, $J_{C\text{-}P}$ = 29.1 Hz, C), 135.26 (d, $J_{C\text{-}P}$ = 96.5 Hz, C), 132.87 (d, $J_{C\text{-}P}$ = 2.1 Hz, CH), 132.39 (d, $J_{C\text{-}P}$ = 105.2 Hz, C), 131.94 (d, $J_{C\text{-}P}$ = 2.8 Hz, CH), 130.99 (d, $J_{C\text{-}P}$ = 10.6 Hz, 2CH), 130.35 (d, $J_{C\text{-}P}$ = 96.8 Hz, C), 128.75 (d, $J_{C\text{-}P}$ = 12.0 Hz, 2CH), 128.68 (d, $J_{C\text{-}P}$ = 9.7 Hz, CH), 128.31 (d, $J_{C\text{-}P}$ = 10.6 Hz, CH), 121.29 (d, $J_{C\text{-}P}$ = 11.3 Hz, CH), 19.66 (d, $J_{C\text{-}P}$ = 13.6 Hz, CH_2), 19.06 (d, $J_{C\text{-}P}$ = 11.0 Hz, CH_2), 14.00 (d, $J_{C\text{-}P}$ = 2.1 Hz, CH_3), 13.17 (d, $J_{C\text{-}P}$ = 2.2 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.66; HRMS Calcd. For $C_{18}H_{20}OP^+$ $[M + H^+]^+$, 283.1246. Found: 283.1241.



3l

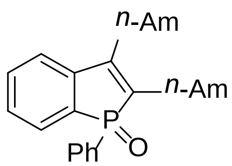
3l: Reaction condition as general procedure for synthesis of compounds **3a**, the white solid **3l** was afforded (yield 67%, 103.9 mg)); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.58 (m, 2H), 7.55 (dd, *J*

= 9.8, 7.2 Hz, 1H), 7.52 – 7.42 (m, 2H), 7.41 – 7.34(m, 3H), 7.29 – 7.24 (m, 1H), 2.59 (t, *J* = 7.8 Hz, 2H), 2.5 – 2.4 (m, 1H), 2.30 – 2.20 (m, 1H), 1.68 – 1.59(m, 2H), 1.46 – 1.36 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H), 0.83 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.95 (d, J_{C-P} = 20.2 Hz, C), 143.65 (d, J_{C-P} = 29.5 Hz, C), 134.23 (d, J_{C-P} = 96.6 Hz, C), 133.07 (d, J_{C-P} = 2.1 Hz, CH), 132.17 (d, J_{C-P} = 2.9 Hz, CH), 131.79 (d, J_{C-P} = 105.9 Hz, C), 131.01 (d, J_{C-P} = 10.7 Hz, 2CH), 129.73 (d, J_{C-P} = 97.8 Hz, C), 128.89 (d, J_{C-P} = 12.3 Hz, 2CH), 128.81 (d, J_{C-P} = 9.7 Hz, CH), 128.48 (d, J_{C-P} = 10.5 Hz, CH), 121.57 (d, J_{C-P} = 11.4 Hz, CH), 28.67 (d, J_{C-P} = 13.4 Hz, CH_2), 28.30 (d, J_{C-P} = 10.8 Hz, CH_2), 22.37 (d, J_{C-P} = 1.9 Hz, CH_2), 21.92 (d, J_{C-P} = 1.9 Hz, CH_2), 14.50 (s, CH_3), 14.43 (s, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.46; HRMS Calcd. For $C_{20}H_{24}OP^+$ [M + H$^+$]$^+$, 311,1559. Found: 311,1555.



3m

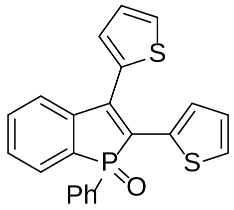
3m: Reaction condition as general procedure for synthesis of compounds **3a**, the white solid **3m** was afforded (yield 65%, 109.9 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.52 (m, 2H), 7.46 (dd, *J* = 9.7, 7.2 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.32 – 7.26 (m, 3H), 7.20 – 7.15(m, 1H), 2.52 (t, *J* = 7.8 Hz, 2H), 2.48 – 2.35 (m, 1H), 2.24 – 2.14 (m, 1H), 1.55 – 1.46 (m, 2H), 1.43 – 1.36 (m, 2H), 1.34 – 1.23 (m, 2H), 1.19 – 1.12 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.69 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.48 (d, J_{C-P} = 19.8 Hz, C), 143.66 (d, J_{C-P} = 29.2 Hz, C), 134.55 (d, J_{C-P} = 96.4 Hz, C), 132.80 (d, J_{C-P} = 2.2 Hz, CH), 132.23 (d, J_{C-P} = 105.2 Hz, C), 131.87 (d, J_{C-P} = 2.9 Hz, CH), 130.94 (d, J_{C-P} = 10.6 Hz, 2CH), 130.33 (d, J_{C-P} = 96.9 Hz, C), 128.68 (d, J_{C-P} = 12.1 Hz, 2CH), 128.61 (d, J_{C-P} = 9.7 Hz, CH), 128.22 (d, J_{C-P} = 10.4 Hz, CH), 121.34 (d, J_{C-P} = 11.4 Hz, CH), 30.98 (d, J_{C-P} = 1.8 Hz, CH_2), 30.62 (d, J_{C-P} = 1.9 Hz, CH_2), 26.33 (d, J_{C-P} = 13.4 Hz, CH_2), 25.84 (d, J_{C-P} = 10.8 Hz, CH_2), 23.08 (s, CH_2), 22.85 (s, CH_2), 13.94 (s, CH_3), 13.65 (s, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.91; HRMS Calcd. For $C_{22}H_{28}OP^+$ [M + H$^+$]$^+$, 339.1872. Found: 339.1866.



3n

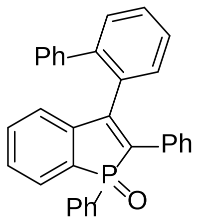
3n: Reaction condition as general procedure for synthesis of compounds **3a**, the white solid **3n** was afforded (yield 62%, 113.5 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (dd, *J* = 12.4, 7.5 Hz, 2H), 7.55 (dd, *J* = 9.7, 7.2 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.41 – 7.34 (m, 3H), 7.29 – 7.34(m, 1H), 2.60 (t, *J* = 7.8 Hz, 2H), 2.54 – 2.43 (m, 1H), 2.33 – 2.21 (m, 1H), 1.66 – 1.55 (m, 2H), 1.45 – 1.33 (m, 6H), 1.24 – 1.12 (m, 4H), 0.92 (t, *J* = 6.9 Hz, 3H), 0.80 – 0.72 (m, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.64 (d, J_{C-P} = 20.1 Hz, C), 143.71 (d, J_{C-P} = 29.3 Hz, C), 134.52 (d, J_{C-P} = 96.4 Hz, C), 132.91 (d, J_{C-P} = 2.0 Hz, CH), 132.10 (d, J_{C-P} = 105.4 Hz, C), 131.98 (d, J_{C-P} = 2.8 Hz, CH), 131.00 (d, J_{C-P} = 10.7 Hz, 2CH), 130.20 (d, J_{C-P} = 97.4 Hz, C), 128.74 (d, J_{C-P} = 12.1 Hz, 2CH), 128.69 (d, J_{C-P} = 9.7 Hz, CH), 128.30 (d, J_{C-P} = 10.5 Hz, CH), 121.41 (d, J_{C-P} = 11.4 Hz, CH), 32.17 (s, CH_2), 31.96 (s, CH_2), 28.62 (d, J_{C-P} = 1.8 Hz, CH_2), 28.22 (d, J_{C-P} = 2.0 Hz, CH_2), 26.63 (d, J_{C-P} = 13.3 Hz, CH_2), 26.11 (d, J_{C-P} = 10.9

Hz, CH_2), 22.55 (s, CH_2), 22.28 (s, CH_2), 14.05 (s, CH_3), 13.93 (s, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 40.28; HRMS Calcd. For $C_{24}H_{32}OP^+$ [M + H^+]$^+$, 367.2185. Found: 367.2184.



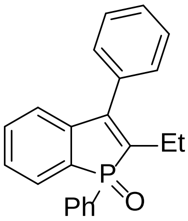
3o

3o: Reaction condition as general procedure for synthesis of compounds **3a**, the white solid **3p** was afforded (yield 55%, 108.1 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (dd, *J* = 12.9, 7.5 Hz, 2H), 7.66 (dd, *J* = 15.3, 6.0 Hz, 2H), 7.51 (q, *J* = 6.0, 4.4 Hz, 1H), 7.47 – 7.42 (m, 4H), 7.34 (td, *J* = 7.4, 4.0 Hz, 1H), 7.27 (d, *J* = 4.2 Hz, 1H), 7.18 (q, *J* = 3.8, 2.8 Hz, 3H), 6.88 (t, *J* = 4.6 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.66 (d, J_{C-P} = 25.0 Hz, C), 139.20 (d, J_{C-P} = 23.1 Hz, C), 135.10 (d, J_{C-P} = 14.3 Hz, C), 133.53 (d, J_{C-P} = 2.4 Hz, CH), 133.08 (d, J_{C-P} = 63.1 Hz, C), 132.56 (d, J_{C-P} = 2.9, Hz, CH), 131.58 (d, J_{C-P} = 49.5 Hz, C), 131.06 (d, J_{C-P} = 10.9 Hz, 2CH), 130.44 (d, J_{C-P} = 33.5 Hz, C), 130.14 (d, J_{C-P} = 4.5 Hz, CH), 129.35(d, J_{C-P} = 52.3 Hz, C), 129.19 (d, J_{C-P} = 3.5 Hz, 2CH), 129.09 (s, CH), 129.02 (d, J_{C-P} = 21.3 Hz, CH), 129.01 (s, CH), 128.68 (s, CH), 128.57 (s, CH), 128.39 (s, CH), 127.07 (s, CH), 123.80 (d, J_{C-P} = 10.9 Hz, CH); ^{31}P NMR (162 MHz, $CDCl_3$) δ 37.91; HRMS Calcd. For $C_{22}H_{16}OPS_2^+$ [M + H^+]$^+$, 391.0375. Found: 391.0371.



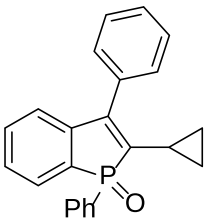
3p

3p: Reaction condition as general procedure for synthesis of compounds **3a**, the brown solid **3o** was afforded (yield 66%, 149.9 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (t, *J* = 8.5, 1H), 7.58 – 7.46(m, 6H), 7.46 – 7.36 (m, 4H), 7.36 – 7.27 (m, 2H), 7.23 (d, *J* = 7.0, 1H), 7.20 – 7.10 (m, 8H), 7.06 – 7.02 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.91 (d, J_{C-P} = 22.0 Hz, C), 144.44 (d, J_{C-P} = 26.9 Hz, C), 141.39 (s, C), 141.21 (s, C), 135.09 (d, J_{C-P} = 95.7 Hz, C), 133.17 (d, J_{C-P} = 75.5 Hz, C), 132.92 (d, J_{C-P} = 2.4 Hz, CH), 132.92 (d, J_{C-P} = 96.6 Hz, C), 132.25 (d, J_{C-P} = 2.9 Hz, CH), 131.25 (d, J_{C-P} = 11.0 Hz, 2CH), 131.08 (d, J_{C-P} = 62.2 Hz, C), 130.90 (s, CH), 130.03 (s, CH), 129.16 (d, J_{C-P} = 124.7 Hz, C), 129.08 (s, 2CH), 128.86 (s, 2CH), 128.83 (d, J_{C-P} = 27.0 Hz, CH), 128.80 (s, CH), 128.73 (s, CH), 128.55 (s, 2CH), 128.35 (s, 2CH), 128.25 (s, 2CH), 128.16 (d, J_{C-P} = 30.6 Hz, 2CH), 127.26 (s, CH), 124.38 (d, J_{C-P} = 10.7 Hz, CH); ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.81; HRMS Calcd. For $C_{32}H_{24}OP^+$ [M + H^+]$^+$, 455.1559. Found: 455.1558.



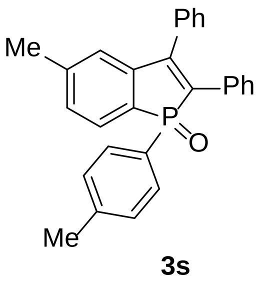
3q

3q: Reaction condition as general procedure for synthesis of compounds **3a**, the white solid **3q** was afforded (yield 59%, 97.4 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.72 (m, 2H), 7.65 – 7.59 (m, 1H), 7.56 – 7.49 (m, 3H), 7.48 – 7.41 (m, 3H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.08 – 6.97 (dd, *J* = 7.6, 3.0 Hz, 1H), 2.55 – 2.39 (m, 1H), 2.33 – 2.19 (m, 1H), 0.96 (t, *J*=7.6 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.22 (d, $J_{C\text{-}P}$ =22.2 Hz, C), 144.36 (d, $J_{C\text{-}P}$ =28.0 Hz, C), 138.00 (d, $J_{C\text{-}P}$ =93.9 Hz, C), 134.03 (d, $J_{C\text{-}P}$ =15.9 Hz, C), 132.92 (d, $J_{C\text{-}P}$ =2.2 Hz, CH), 132.22 (d, $J_{C\text{-}P}$ =2.9 Hz, CH), 132.01 (d, $J_{C\text{-}P}$ =105.3 Hz, C), 131.08 (d, $J_{C\text{-}P}$ =10.7 Hz, 2CH), 130.21 (d, $J_{C\text{-}P}$ =97.6 Hz, C), 129.03 (s, CH), 128.91 (s, 2CH), 128.84 (d, $J_{C\text{-}P}$ =28.6 Hz, CH), 128.64 (s, CH),128.73 (d, $J_{C\text{-}P}$ =30.1 Hz, 2CH), 128.58 (s, 2CH), 123.38 (d, $J_{C\text{-}P}$ =11.0 Hz, CH), 20.10 (d, $J_{C\text{-}P}$ =10.3 Hz, CH_2), 13.97 (d, $J_{C\text{-}P}$ =2.1 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.82; HRMS Calcd. For $C_{22}H_{20}OP^+$ $[M + H^+]^+$, 331.1246. Found: 331.1248.



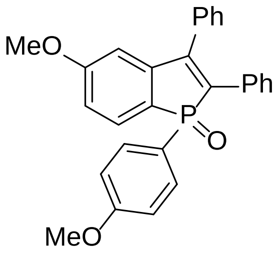
3r

3r: Reaction condition as general procedure for synthesis of compounds **3a**, the white solid **3r** was afforded (yield 56%, 95.8 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.72 (m, 2H), 7.56 – 7.49 (m, 4H), 7.48 – 7.41 (m, 5H), 7.39 – 7.34 (m, 1H), 7.26 – 7.20 (m, 1H), 7.07 – 7.01 (m, 1H), 1.70 – 1.57 (m, 1H), 1.29 – 1.22 (m, 1H), 0.81 – 0.72 (m, 1H), 0.55 (q, *J* = 7.4 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.14 (d, $J_{C\text{-}P}$ = 22.1 Hz, C), 143.77 (d, $J_{C\text{-}P}$ = 26.6 Hz, C), 137.51 (d, $J_{C\text{-}P}$ = 96.8 Hz, C), 134.30 (d, $J_{C\text{-}P}$ = 15.1 Hz, C), 132.86 (d, $J_{C\text{-}P}$ = 1.8 Hz, CH), 132.17 (d, $J_{C\text{-}P}$ = 2.9 Hz, CH), 131.94 (d, $J_{C\text{-}P}$ = 106.6 Hz, C), 130.96 (d, $J_{C\text{-}P}$ = 10.7 Hz, 2CH), 130.70 (d, $J_{C\text{-}P}$ = 97.3 Hz, C), 129.08 (s, 3CH), 128.95 (s, CH), 128.84 (s, 2CH), 128.68 (d, $J_{C\text{-}P}$ = 9.8 Hz, CH), 128.57 (s, CH), 128.36 (d, $J_{C\text{-}P}$ = 10.8 Hz, CH), 122.66 (d, $J_{C\text{-}P}$ = 10.8 Hz, CH), 11.06 (d, $J_{C\text{-}P}$ = 9.4 Hz, CH), 7.44 (d, $J_{C\text{-}P}$ = 3.2 Hz, CH_2), 7.12 (d, $J_{C\text{-}P}$ = 2.3 Hz, CH_2); ^{31}P NMR (162 MHz, $CDCl_3$) δ 37.56; HRMS Calcd. For $C_{23}H_{20}OP^+$ $[M + H^+]^+$, 343.1246. Found: 343.1249.



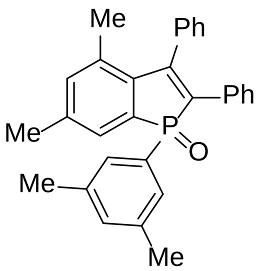
3s

3s: Reaction condition as general procedure for synthesis of compounds **3a**, the white solid **3s** was afforded (yield 71%, 144.2 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (dd, *J* = 12.3, 7.8 Hz, 2H), 7.50 (d, *J* = 10.1 Hz, 1H), 7.44 – 7.38 (d, *J* = 6.6 Hz, 3H), 7.34 – 7.29 (m, 2H), 7.24 – 7.18 (m, 5H), 7.10 – 7.05 (m, 4H), 2.33 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.08 (d, J_{C-P} = 21.5 Hz, C), 142.74 (d, J_{C-P} = 3.0 Hz, C), 141.17 (d, J_{C-P} = 26.8 Hz, C), 139.51 (d, J_{C-P} = 10.4 Hz, C), 134.62 (d, J_{C-P} = 15.1 Hz, C), 133.41 (d, J_{C-P} = 97.0 Hz, C), 133.33 (d, J_{C-P} = 2.1 Hz, CH), 133.07 (s, C), 132.50 (d, J_{C-P} = 96.1 Hz, C), 131.08 (d, J_{C-P} = 11.0 Hz, 2CH), 129.82 (d, J_{C-P} = 9.6 Hz, CH), 129.77 (d, J_{C-P} = 12.7 Hz, 2CH), 129.13 (d, J_{C-P} = 5.9 Hz, 2CH), 129.13 (s, 2CH), 129.00 (s, 2CH), 128.67 (s, CH), 128.28 (s, 2CH), 127.70 (s, CH), 126.72 (d, J_{C-P} = 101.9 Hz, C), 123.96 (d, J_{C-P} = 11.4 Hz, CH), 21.72 (s, CH_3), 21.35 (s, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.50; HRMS Calcd. For $C_{28}H_{24}OP^+$ $[M + H^+]^+$, 407.1559. Found: 407.1555.



3t

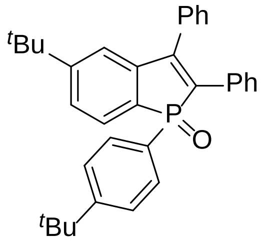
3t: Reaction condition as general procedure for synthesis of compounds **3a**, the yellow solid **3t** was afforded (yield 75%, 164.3 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 11.9, 8.4 Hz, 2H), 7.27 (d, *J* = 6.6 Hz, 3H), 7.20 – 7.13 (m, 2H), 7.13 – 7.10 (m, 1H), 7.09 – 7.01 (m, 2H), 6.99 – 6.88 (m, 4H), 6.82 – 6.68 (m, 3H), 3.66 (d, *J* = 2.7 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.82 (d, J_{C-P} = 2.8, C), 160.73 (d, J_{C-P} = 13.4 Hz, C), 149.79 (d, J_{C-P} = 21.2 Hz, C), 136.07 (d, J_{C-P} = 26.9 Hz, C), 134.62 (d, J_{C-P} = 15.3 Hz, C), 134.48 (d, J_{C-P} = 104.9 Hz, C), 133.05 (d, J_{C-P} = 10.1 Hz, C), 132.87 (d, J_{C-P} = 12.1 Hz, 2CH), 130.40 (d, J_{C-P} = 284.5 Hz, C), 129.02 (s, 2CH), 128.97 (d, J_{C-P} = 5.6 Hz, 2CH), 128.89 (s, 2CH), 128.57 (s, CH), 128.19 (s, 2CH), 127.45 (s, CH), 125.20 (d, J_{C-P} = 12.7 Hz, CH), 120.66 (d, J_{C-P} = 105.5 Hz, C), 117.85 (s, CH), 114.59 (d, J_{C-P} = 13.3 Hz, 2CH), 114.56 (d, J_{C-P} = 10.8 Hz, CH), 55.70 (s, CH_3), 55.28 (s, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.99; HRMS Calcd. For $C_{28}H_{24}O_3P^+$ $[M + H^+]^+$, 439.1458. Found: 439.1457.



3u

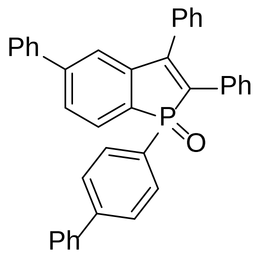
3u: Reaction condition as general procedure for synthesis of compounds **3a**, the white solid **3u** was afforded (yield 73%, 158.5 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.30 (m, 7H), 7.23 – 7.18 (m, 1H), 7.15 – 7.07 (m, 3H), 7.06 – 7.00 (m, 3H), 6.98 (s, 1H), 2.28 (s, 9H), 1.73 (d, *J* = 1.8 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.67 (d, J_{C-P} = 21.4 Hz, C), 139.32 (d, J_{C-P} = 11.6 Hz, C), 138.57 (d, J_{C-P} = 12.9 Hz, 2C), 137.94 (d, J_{C-P} = 15.2 Hz, C), 137.80 (d, J_{C-P} = 26.2 Hz, C), 137.77 (d, J_{C-P} = 2.1 Hz, CH), 134.71 (d, J_{C-P} = 109.9 Hz, C), 134.14 (d, J_{C-P} = 203.2 Hz, 2C), 134.13(d, J_{C-P} = 18.4

Hz, C), 134.05 (d, J_{C-P} = 3.0 Hz, CH), 131.71 (d, J_{C-P} = 302.3 Hz, C), 129.27 (s, CH), 129.17 (d, J_{C-P} = 5.5 Hz, 2CH), 128.80 (s, CH), 128.69 (s, CH), 128.65 (s, CH),128.60 (d, J_{C-P} = 2.5 Hz, 2CH), 128.20 (s, CH), 128.08 (s, 2CH), 128.01 (d, J_{C-P} = 9.7 Hz, CH), 127.41 (s, CH), 21.42 (s, $3CH_3$), 21.02 (s, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.39; HRMS Calcd. For $C_{30}H_{28}OP^+$ $[M + H^+]^+$, 435.1872. Found: 435.1875.



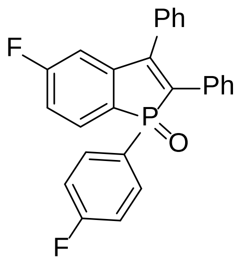
3v

3v: Reaction condition as general procedure for synthesis of compounds **3a**, the white solid **3v** was afforded (yield 79%, 193.6 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.61 (m, 1H), 7.59 – 7.53 (m, 2H), 7.34 – 7.25 (m, 6H), 7.19 – 7.15 (m, 2H), 7.13 – 7.09 (m, 2H), 7.00 – 6.94 (m, 4H), 1.16 (s, 9H), 1.15 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.61 (d, J_{C-P} = 2.9 Hz, C), 152.81 (d, J_{C-P} = 9.7 Hz, C), 149.79 (d, J_{C-P} = 21.5 Hz, C), 141.26 (d, J_{C-P} = 27.2 Hz, C), 134.74 (d, J_{C-P} = 15.0 Hz, C), 134.00 (d, J_{C-P} = 96.2 Hz, C), 133.22 (d, J_{C-P} = 9.9 Hz, C), 132.27 (d, J_{C-P} = 105.5 Hz, C), 131.01 (d, J_{C-P} = 10.9 Hz, 2CH), 129.79 (d, J_{C-P} = 2.0 Hz, CH), 129.23 (d, J_{C-P} = 5.6 Hz, 2CH), 129.15 (s, 2CH), 128.99 (s, 2CH), 128.63 (s, CH), 128.30 (s, 2CH), 127.70 (s, CH), 126.95 (d, J_{C-P} = 101.8 Hz, C), 126.30 (d, J_{C-P} = 9.9 Hz, CH), 126.02 (d, J_{C-P} = 12.5 Hz, 2CH), 123.80 (d, J_{C-P} = 11.5 Hz, CH), 35.20 (s, C), 35.11 (s, C), 31.35 (s, $3CH_3$), 31.20 (s, $3CH_3$); ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.73; HRMS Calcd. For $C_{34}H_{36}OP^+$ $[M + H^+]^+$, 491.2498. Found: 491.2496.



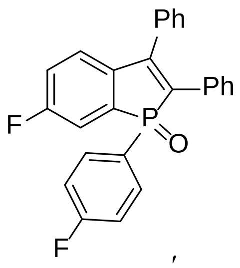
3w

3w: Reaction condition as general procedure for synthesis of compounds **3a**, the white solid **3w** was afforded (yield 78%, 206.8 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 10.4 Hz, 1H), 7.87 (dd, *J* = 12.2, 7.9 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.58 (m, 3H), 7.54 (d, *J* = 7.7 Hz, 2H), 7.51 – 7.33 (m, 12H), 7.31 – 7.27 (m, 3H), 7.15 – 7.08 (m, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.69 (d, J_{C-P} = 21.4 Hz, C), 143.95 (d, J_{C-P} = 27.0 Hz, C), 141.62 (s, C), 140.55 (s, C), 140.41 (d, J_{C-P} = 5.8 Hz, 2C), 134.13 (d, J_{C-P} = 95.3 Hz, C), 133.44 (d, J_{C-P} = 15.0 Hz, C), 133.11 (s, CH), 132.51 (d, J_{C-P} = 66.6 Hz, C), 132.36 (d, J_{C-P} = 2.9 Hz, CH), 131.90 (d, J_{C-P} = 10.0 Hz, C), 131.26 (d, J_{C-P}= 106.8 Hz, C), 131.21 (s, CH), 131.11 (s, CH), 129.74 (s, 2CH), 129.63 (d, J_{C-P} = 5.9 Hz, 2CH), 129.33 (d, J_{C-P} = 4.6 Hz, CH), 129.23 (d, J_{C-P} = 3.7 Hz, CH), 129.13 (s, CH), 129.06 (s, 2CH), 129.01 (s, CH), 128.84 (s, 2CH), 127.80 (s, 2CH), 127.71 (d, J_{C-P} = 35.2 Hz, 2CH), 127.19 (s, 2CH), 127.08 (s, 2CH), 126.99 (s, 2CH), 124.21 (d, J_{C-P} = 10.7 Hz, CH); ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.64; HRMS Calcd. For $C_{38}H_{28}OP^+$ $[M + H^+]^+$, 531.1872. Found: 531.1874



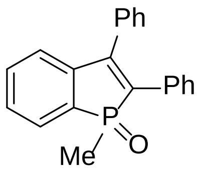
3x

3x: Reaction condition as general procedure for synthesis of compounds **3a**, the yellow solid **3x** was afforded (yield 46%, 95.2 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.71 (m, 2H), 7.69 – 7.63 (m, 1H), 7.46 – 7.39 (m, 3H), 7.32 – 7.27 (m, 2H), 7.24 – 7.20 (m, 2H), 7.11 – 6.99 (m, 6H), 6.92 (dd, J = 9.4, 2.4 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.38 (dd, $J_{C\text{-}F}$ = 254.5 Hz, $J_{C\text{-}P}$ = 2.3 Hz, C), 165.50 (dd, $J_{C\text{-}F}$ = 254.7 Hz, $J_{C\text{-}P}$ = 3.4 Hz, C), 148.64 (dd, J_1 = 20.3 Hz, J_2 = 1.9 Hz, C), 147.08 (dd, J_1 = 29.5 Hz, J_2 = 8.8 Hz, C), 136.22 (d, $J_{C\text{-}P}$ = 95.8 Hz, C), 136.60 (d, $J_{C\text{-}P}$ = 16.6 Hz, C), 133.53 (dd, J_1 = 12.0 Hz, J_2 = 9.1 Hz, 2CH), 132.25 (d, $J_{C\text{-}P}$ = 9.7 Hz, C), 131.06 (dd, J_1 = 10.6 Hz, J_2 = 10.2 Hz, CH), 129.12 (d, $J_{C\text{-}P}$ = 30.3 Hz, 3CH), 129.07 (d, $J_{C\text{-}P}$ = 14.9 Hz, 2CH), 129.05 (s, CH), 128.47 (s, 2CH), 128.37 (s, CH), 127.94 (d, $J_{C\text{-}P}$ = 7.8 Hz, CH), 127.22 (dd, $J_{C\text{-}P}$ = 109.7 Hz, $J_{C\text{-}F}$ = 3.3 Hz, C), 125.38 (dd, $J_{C\text{-}P}$ = 104.1 Hz, $J_{C\text{-}F}$ = 3.2 Hz, C), 116.51 (dd, J_1 = 21.6 Hz, J_2 = 13.6 Hz, 2CH), 115.92 (dd, J_1 = 22.4 Hz, J_2 = 11.8 Hz, CH), 112.28 (dd, J_1 = 24.2 Hz, J_2 = 12.4 Hz, CH); δ 36.63; HRMS Calcd. For $C_{26}H_{18}F_2OP^+$ [M + H$^+$]$^+$, 415.1058. Found: 415.1063.



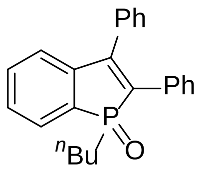
3x′

3x': ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.72 (m, 2H), 7.47 – 7.37 (m, 4H), 7.34 – 7.28 (m, 2H), 7.19 (q, J = 5.5 Hz, 3H), 7.14 – 7.07 (m, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.65 (dd, $J_{C\text{-}F}$ = 254.7 Hz, $J_{C\text{-}P}$ = 3.23 Hz, C), 163.55 (dd, $J_{C\text{-}F}$ = 253.2 Hz, $J_{C\text{-}P}$ = 15.3 Hz, C), 149.58 (d, J = 20.8 Hz, C), 139.61 (dd, J_1 = 27.0 Hz, J_2 = 3.1 Hz, C), 134.72 (dd, $J_{C\text{-}P}$ = 105.2 Hz, $J_{C\text{-}F}$ =6.8 Hz, C), 134.45 (d, $J_{C\text{-}F}$ = 4.0 Hz, C), 134.03 (d, J = 15.5 Hz, C), 133.59 (dd, J_1 = 12.1 Hz, J_2 = 8.9 Hz, 2CH), 132.44 (d, J = 9.9 Hz, C), 129.25 (s, 2CH), 129.11 (s, CH), 129.06 (s, 3CH), 129.01 (s, CH), 128.52 (s, 2CH), 128.19 (s, CH), 125.94 (dd, J_1 = 12.8 Hz, J_2 = 7.7 Hz, CH), 125.16 (dd, $J_{C\text{-}P}$ = 103.2 Hz, $J_{C\text{-}F}$ = 3.3 Hz, C), 119.68 (d, J = 22.4 Hz, CH), 116.97 (dd, J_1 = 20.1 Hz, J_2 = 10.5 Hz, CH), 116.65 (dd, J_1 = 21.5 Hz, J_2 = 13.7 Hz, 2CH); ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.98, 36.94; HRMS Calcd. For $C_{26}H_{18}F_2OP^+$ [M + H$^+$]$^+$, 415.1058. Found: 415.1055.



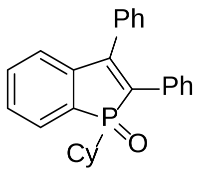
3y

3y: Reaction condition as general procedure for synthesis of compounds **3a**, the white solid **3y** was afforded (yield 52%, 82.2 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.15 (m, 7H), 1.76 (d, *J* = 13.0 Hz, 3H), 7.90 – 7.82 (m, 1H), 7.48 – 7.39 (m, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.23 (d, $J_{C\text{-}P}$ = 21.3 Hz, C), 142.89 (d, $J_{C\text{-}P}$ = 27.1 Hz, C), 134.33 (d, $J_{C\text{-}P}$ = 14.9 Hz, C), 134.24 (d, $J_{C\text{-}P}$ = 93.8 Hz, C), 133.00 (d, $J_{C\text{-}P}$ = 10.2 Hz, C), 132.88 (d, $J_{C\text{-}P}$ = 1.9 Hz, CH), 131.79 (d, $J_{C\text{-}P}$ = 103.1 Hz, C), 129.19 (s, 2CH), 129.12 (s, CH), 129.06 (s, 2CH), 128.98 (d, $J_{C\text{-}P}$ = 10.6 Hz, 2CH), 128.73 (s, CH), 128.61 (s, 2CH), 128.35 (d, $J_{C\text{-}P}$ = 9.7 Hz, CH), 128.16 (s, CH), 124.12 (d, $J_{C\text{-}P}$ = 10.6 Hz, CH), 14.93 (d, $J_{C\text{-}P}$ = 69.2 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 45.28; HRMS Calcd. For $C_{21}H_{18}OP^+$ [M + H^+]$^+$, 317.1090. Found: 317.1088.



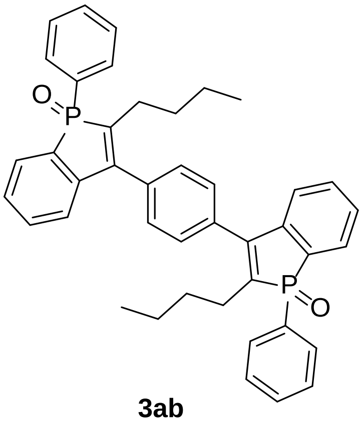
3z

3z: Reaction condition as general procedure for synthesis of compounds **3a**, the white solid **3z** was afforded (yield 55%, 98.5 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (t, *J* = 7.9 Hz, 1H), 7.33 – 7.24 (m, 6H), 7.18 – 6.95 (m, 7H), 1.86 – 1.72 (m, 2H), 1.37 – 1.24 (m, 2H), 1.21 – 1.11 (m, 3H), 0.66 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.99 (d, $J_{C\text{-}P}$ = 20.0 Hz, C), 143.45 (d, $J_{C\text{-}P}$ = 25.5 Hz, C), 134.39 (d, $J_{C\text{-}P}$ = 14.4 Hz, C), 133.35 (d, $J_{C\text{-}P}$ = 91.2 Hz, C), 133.32 (d, $J_{C\text{-}P}$ = 9.9 Hz, C), 132.80 (d, $J_{C\text{-}P}$ = 1.9 Hz, CH), 130.78 (d, $J_{C\text{-}P}$ = 100. 0 Hz, C), 129.18 (s, CH), 129.08 (d, $J_{C\text{-}P}$ = 5.5 Hz, 2CH), 129.05 (s, CH), 129.03 (s, 2CH), 128.88 (s, CH), 128.73 (d, $J_{C\text{-}P}$ = 11.3 Hz, 2CH), 128.56 (s, 2CH), 128.08 (s, CH), 124.05 (d, $J_{C\text{-}P}$ = 10.3 Hz, CH), 28.37 (d, $J_{C\text{-}P}$ = 67.5 Hz, CH_2), 24.05 (d, $J_{C\text{-}P}$ = 1.9 Hz, CH_2), 23.96 (d, $J_{C\text{-}P}$ = 15.3 Hz, CH_2), 13.60 (s, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 50.53; HRMS Calcd. For $C_{24}H_{24}OP^+$ [M + H^+]$^+$, 359.1559. Found: 359.1555.



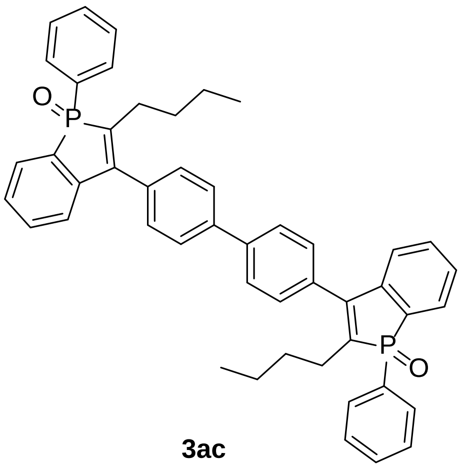
3aa

3aa: Reaction condition as general procedure for synthesis of compounds **3a**, the white solid **3aa** was afforded (yield 60%, 115.2 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (t, *J* = 7.6 Hz, 1H), 7.74 – 7.33 (m, 7H), 7.33 – 6.97 (m, 6H), 2.16 – 2.02 (m, 2H), 1.93 – 1.74 (m, 2H), 1.68 (d, *J* = 10.3 Hz, 1H), 1.58 – 0.98 (m, 5H), 0.99 – 0.84(m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.76 (d, $J_{C\text{-}P}$ = 19.4 Hz, C), 143.99 (d, $J_{C\text{-}P}$ = 24.7 Hz, C), 134.46 (d, $J_{C\text{-}P}$ = 14.0 Hz, C), 133.85 (d, $J_{C\text{-}P}$ = 9.7 Hz, C), 132.66 (d, $J_{C\text{-}P}$ = 1.8 Hz, CH), 132.44 (d, $J_{C\text{-}P}$ = 88.0 Hz, C), 129.86 (d, $J_{C\text{-}P}$ = 97.1 Hz, C), 129.33 (d, $J_{C\text{-}P}$ = 8.7 Hz, 2CH), 129.18 (s, CH), 129.12 (d, $J_{C\text{-}P}$ = 5.3 Hz, 2CH), 128.97 (s, 2CH), 128.68 (s, CH), 128.63 (d, $J_{C\text{-}P}$ = 9.8 Hz, CH), 128.58 (s, CH), 128.49 (s, 2CH), 123.94 (d, $J_{C\text{-}P}$ = 10.0 Hz, CH), 37.61 (d, $J_{C\text{-}P}$ = 68.4 Hz, CH), 26.37 (dd, $J_{C\text{-}P}$ = 16.9, 13.8 Hz, $2CH_2$), 25.93 (s, CH_2), 25.35 (d, $J_{C\text{-}P}$ = 2.9 Hz, $2CH_2$); ^{31}P NMR (162 MHz, $CDCl_3$) δ 53.66; HRMS Calcd. For $C_{26}H_{26}OP^+$ [M + H^+]$^+$, 385.1716. Found: 385.1711.



3ab

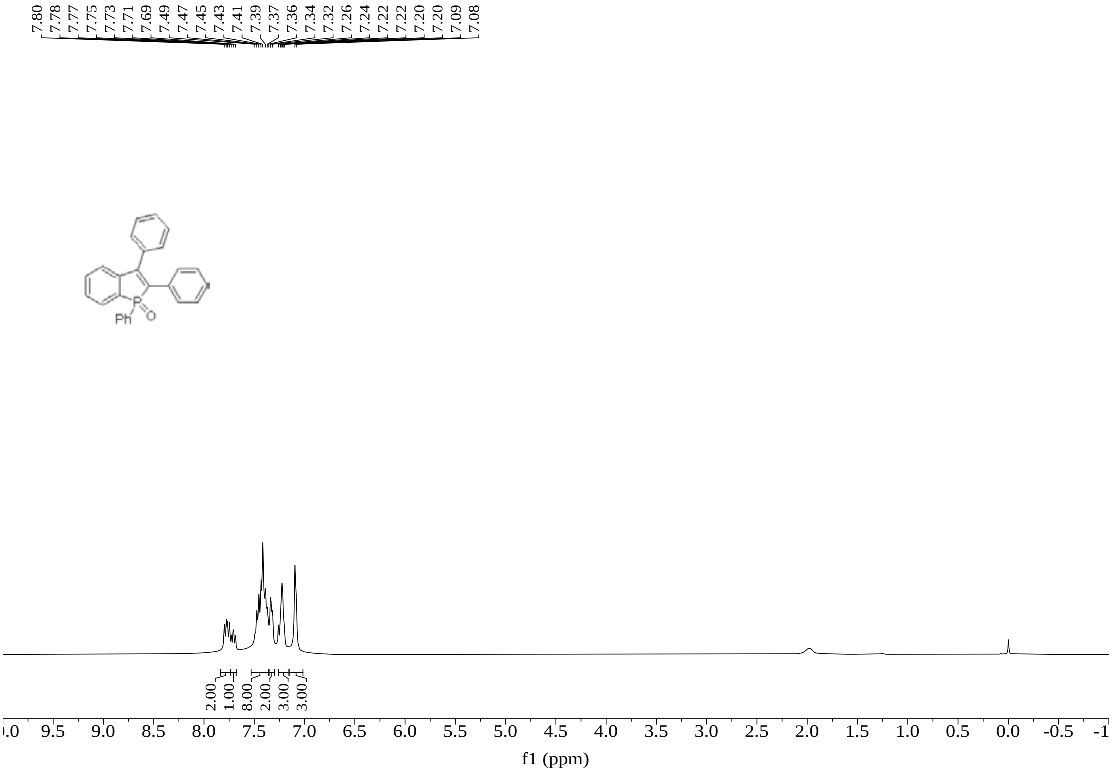
3ab: Reaction condition as general procedure for synthesis of compounds **3a**, the white solid **3ab** was afforded (yield 21%, 67.0 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.73 (m, 3H), 7.67 – 7.61(m, 2H), 7.54 (t, *J* = 7.4, 2H), 7.50 – 7.43 (m, 9H), 7.36 – 7.31 (m, 2H), 7.13 – 7.06 (m, 2H), 2.54 – 2.42 (m, 2H), 2.31 – 2.19 (m, 2H), 1.41 – 1.32 (m, 4H), 1.19 – 1.08 (m, 4H), 0.73 – 0.56 (m, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.78 (d, $J_{C\text{-}P}$ = 22.3 Hz, 2C), 144.15 (d, $J_{C\text{-}P}$ = 28.0 Hz, 2C), 137.72 (d, $J_{C\text{-}P}$ = 93.1 Hz, 2C), 134.42 (d, $J_{C\text{-}P}$ = 16.7 Hz, 2C), 133.05 (s, 2CH), 132.37 (s, 2CH), 131.94 (d, $J_{C\text{-}P}$ = 105.0 Hz, 2C), 131.10 (d, $J_{C\text{-}P}$ = 10.7 Hz, 4CH), 130.00 (d, $J_{C\text{-}P}$ = 98.1 Hz, 2C), 129.16 (s, 6CH), 129.07 (s, 2CH), 128.95 (s, 2CH), 128.85 (d, $J_{C\text{-}P}$ = 10.7 Hz, 2CH), 123.21 (d, $J_{C\text{-}P}$ = 10.7 Hz, 2CH), 30.93 (d, $J_{C\text{-}P}$ = 1.4 Hz, 2CH$_2$), 26.48 (d, $J_{C\text{-}P}$ = 9.5 Hz, 2CH$_2$), 22.71 (s, 2CH$_2$), 13.54 (s, 2CH$_3$); ^{31}P NMR (162 MHz, CDCl$_3$) δ 39.76; HRMS Calcd. For $C_{42}H_{41}O_2P_2^+$ [M + H$^+$]$^+$, 639.2576. Found: 639.2579.



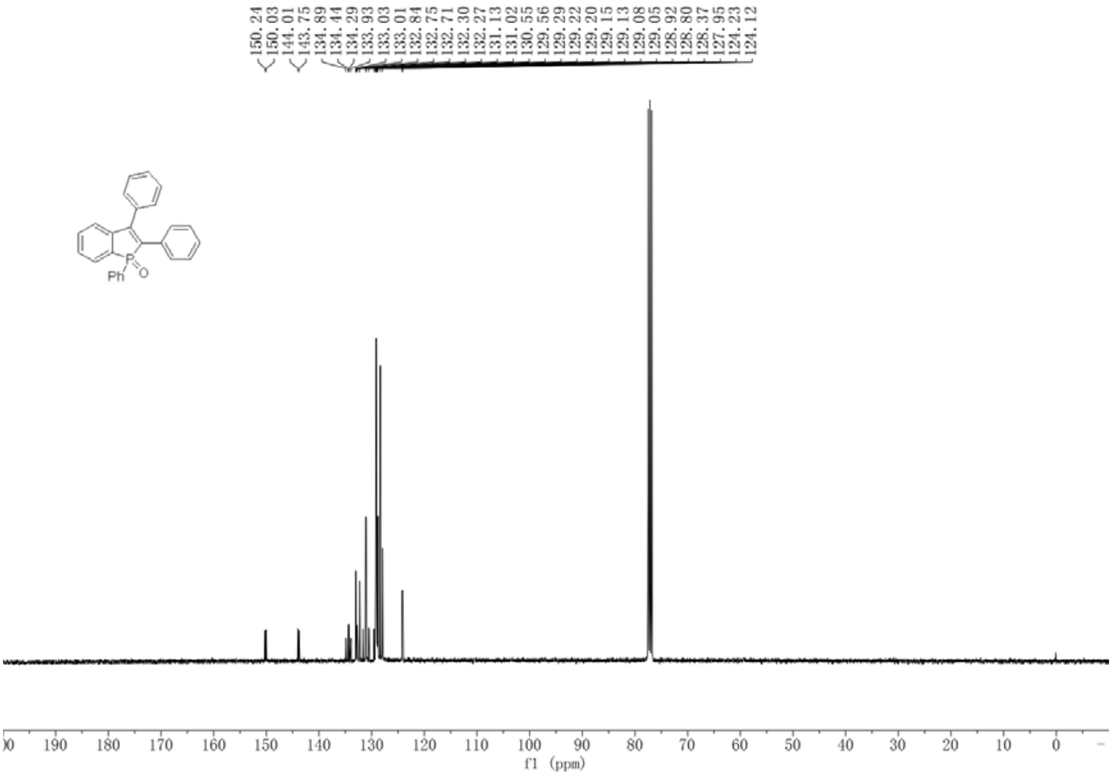
3ac

3ac: Reaction condition as general procedure for synthesis of compounds **3a**, the white solid **3ac** was afforded (yield 26%, 92.9 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.75 (m, 7H), 7.67 – 7.61 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.51 – 7.37 (m, 10H), 7.36 – 7.30 (m, 2H), 7.15 – 7.06 (m, 2H), 2.58 – 2.44 (m, 2H), 2.32 – 2.21 (m, 2H), 1.43 – 1.31 (m, 4H), 1.21 – 1.09 (m, 4H), 0.68 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.03 (d, $J_{C\text{-}P}$ = 22.4 Hz, 2C), 144.36 (d, $J_{C\text{-}P}$ = 27.8 Hz, 2C), 140.63 (s, 2C), 137.37 (d, $J_{C\text{-}P}$ = 93.5 Hz, 2C), 133.50 (d, $J_{C\text{-}P}$ = 16.1 Hz, 2C), 133.02 (d, $J_{C\text{-}P}$ = 1.8 Hz, 2CH), 132.30 (d, $J_{C\text{-}P}$ = 2.9 Hz, 2CH), 132.01 (d, $J_{C\text{-}P}$ = 105.0 Hz, 2C), 131.14 (d, $J_{C\text{-}P}$ = 10.6 Hz, 4CH), 130.18 (d, $J_{C\text{-}P}$ = 97.7 Hz, 2C), 129.35 (s, 4CH), 129.09 (d, $J_{C\text{-}P}$ = 8.3 Hz, 2CH), 1298.99 (d, $J_{C\text{-}P}$ = 12.1 Hz, 4CH), 128.75 (d, $J_{C\text{-}P}$ = 10.5 Hz, 2CH), 127.52 (s, 4CH), 123.33 (d, $J_{C\text{-}P}$ = 10.9 Hz, 2CH), 31.04 (s, 2CH$_2$), 26.69 (d, $J_{C\text{-}P}$ = 10.0 Hz, 2CH$_2$), 22.84 (s, 2CH$_2$), 13.65 (s, 2CH$_3$); ^{31}P NMR (162 MHz, CDCl$_3$) δ 39.99; HRMS Calcd. For $C_{48}H_{45}O_2P_2^+$ [M + H$^+$]$^+$, 715.2889. Found: 715.2880.

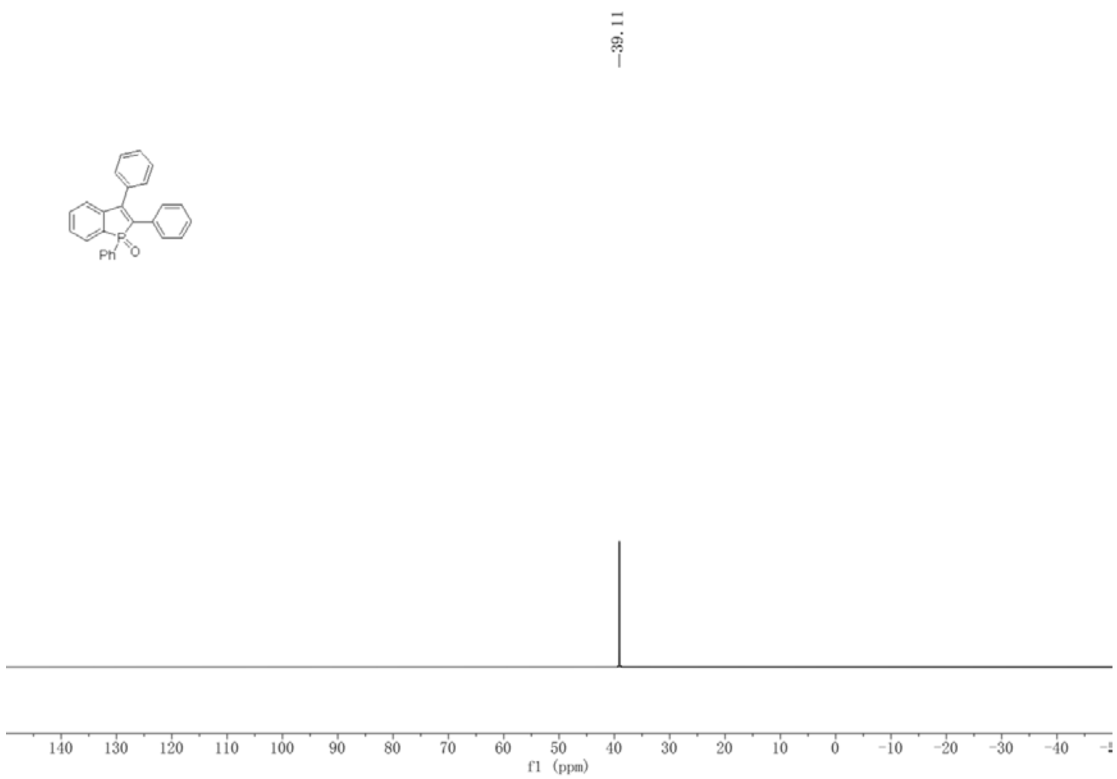
7. Copies of ^{1}H NMR, ^{13}C NMR, ^{31}P NMR Spectra of compounds **3**.



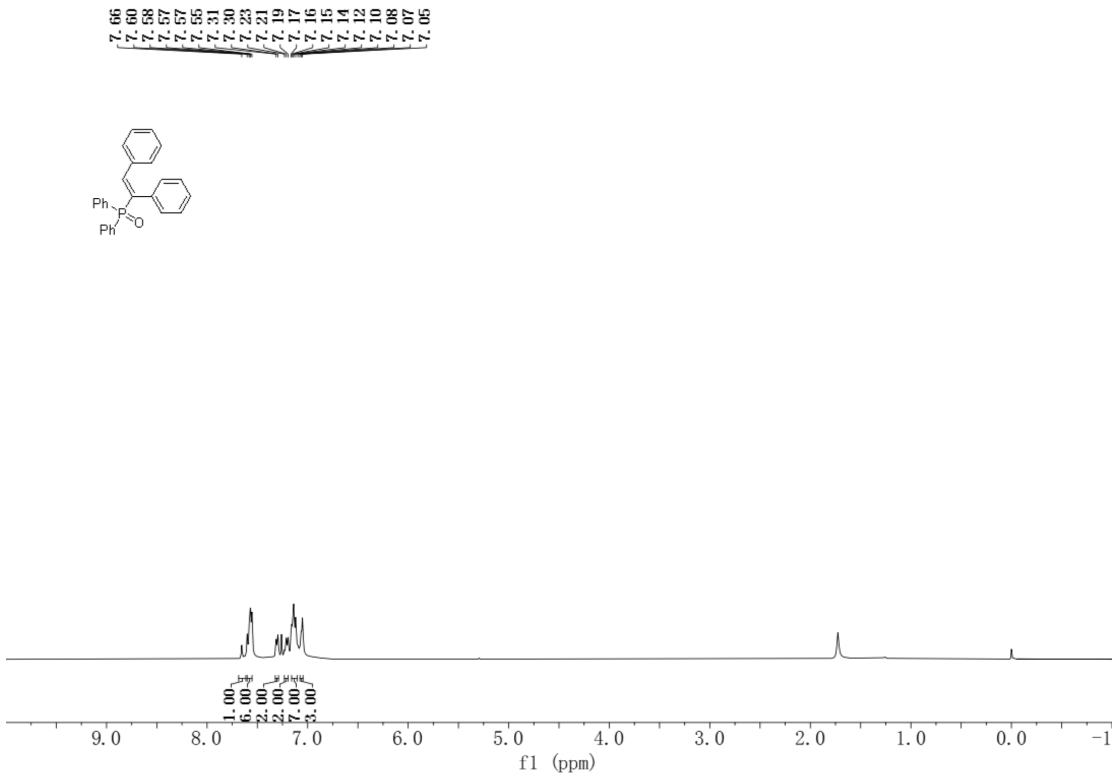
^{1}H NMR (CDCl$_3$-*d*) of **3a**



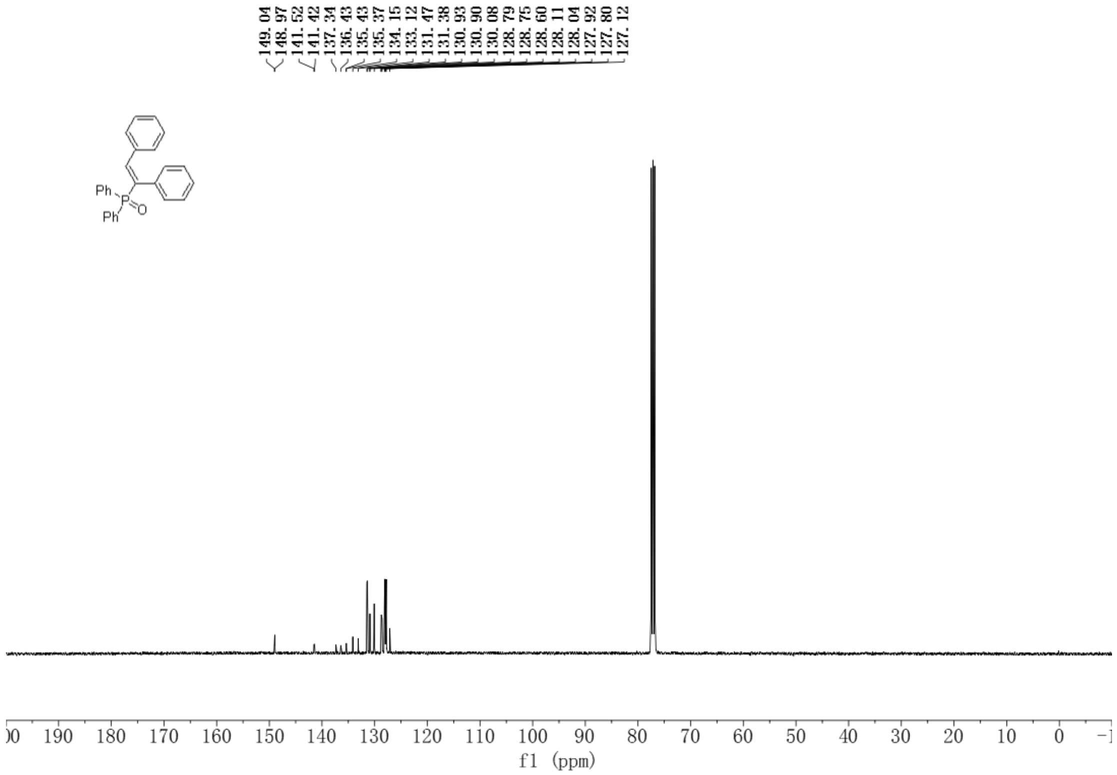
^{13}C NMR (CDCl$_3$-*d*) of **3a**



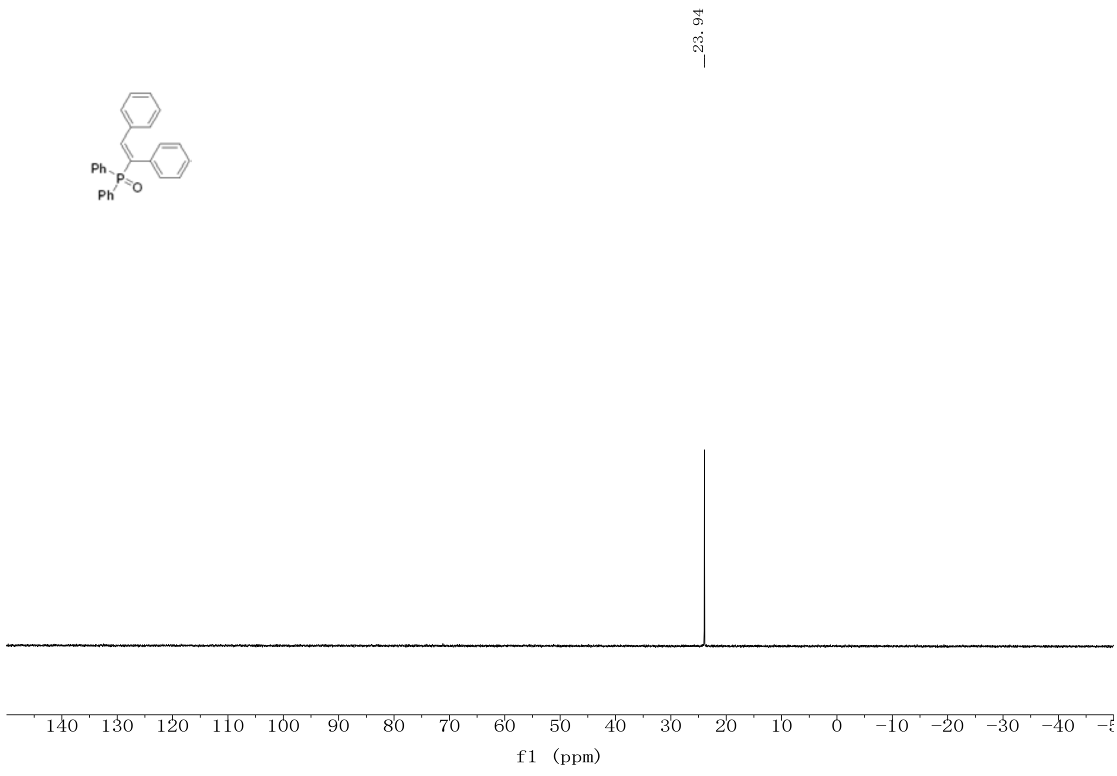
^{31}P NMR ($CDCl_3$-*d*) of **3a**



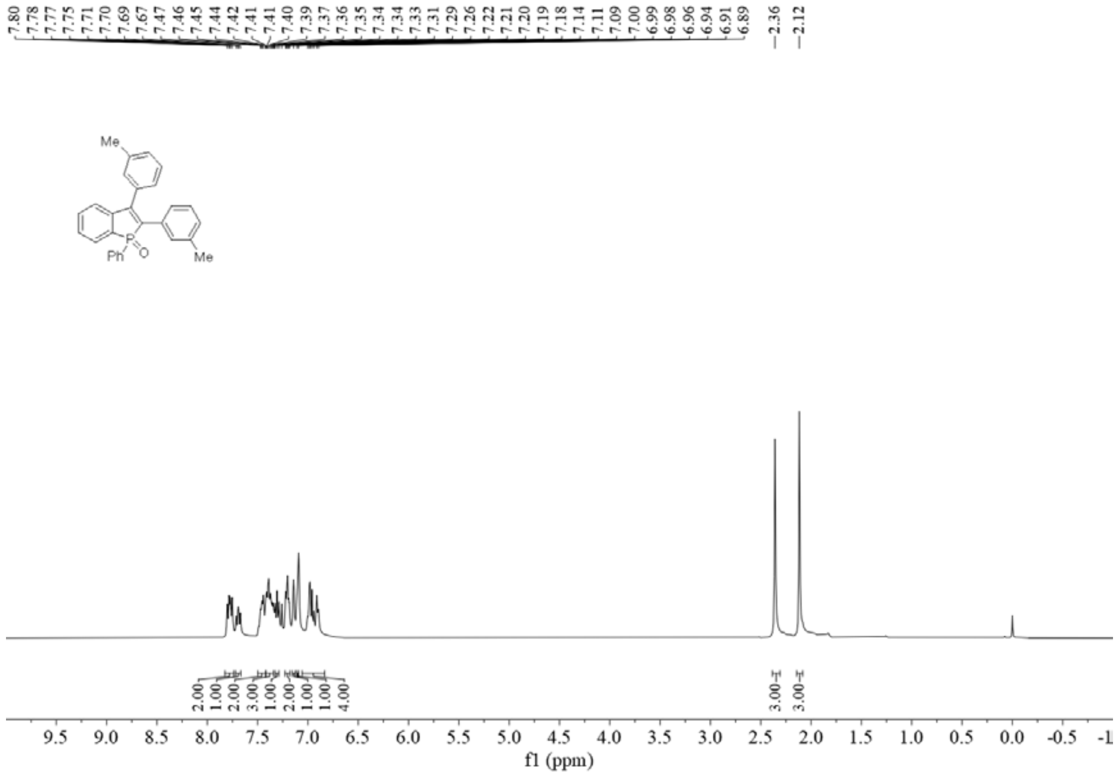
^{1}H NMR ($CDCl_3$-*d*) of **3a'**



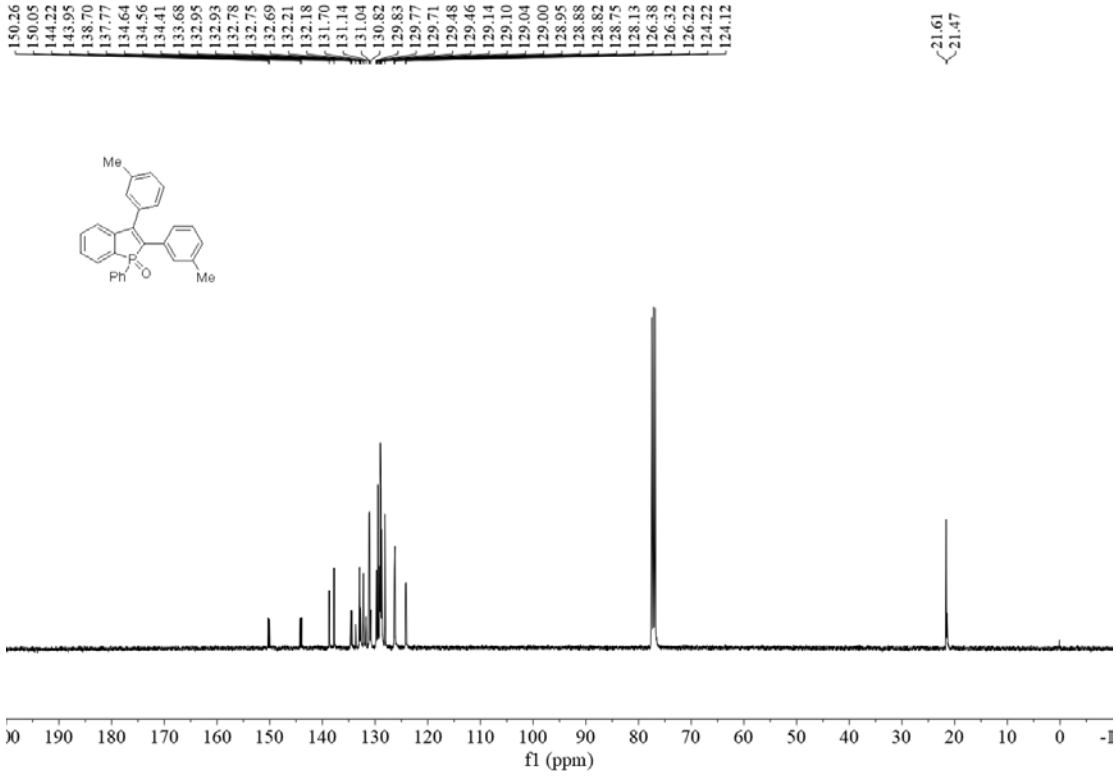
^{13}C NMR ($CDCl_3$-*d*) of **3a'**



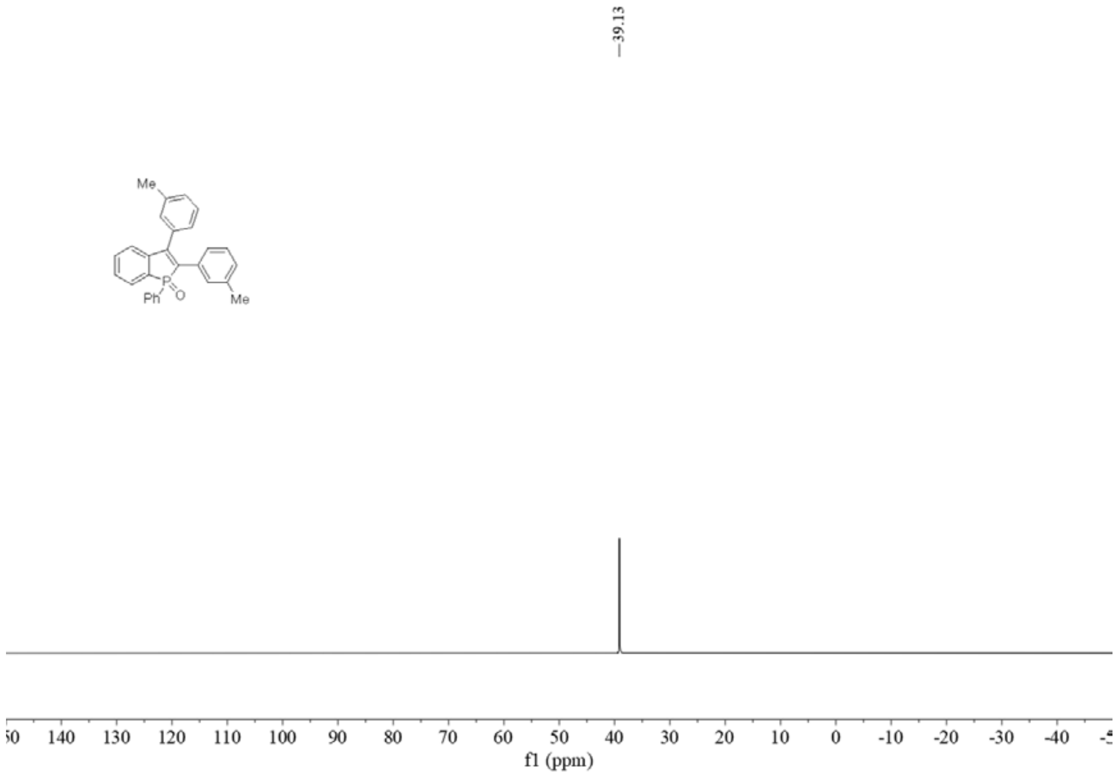
^{31}P NMR ($CDCl_3$-*d*) of **3a'**



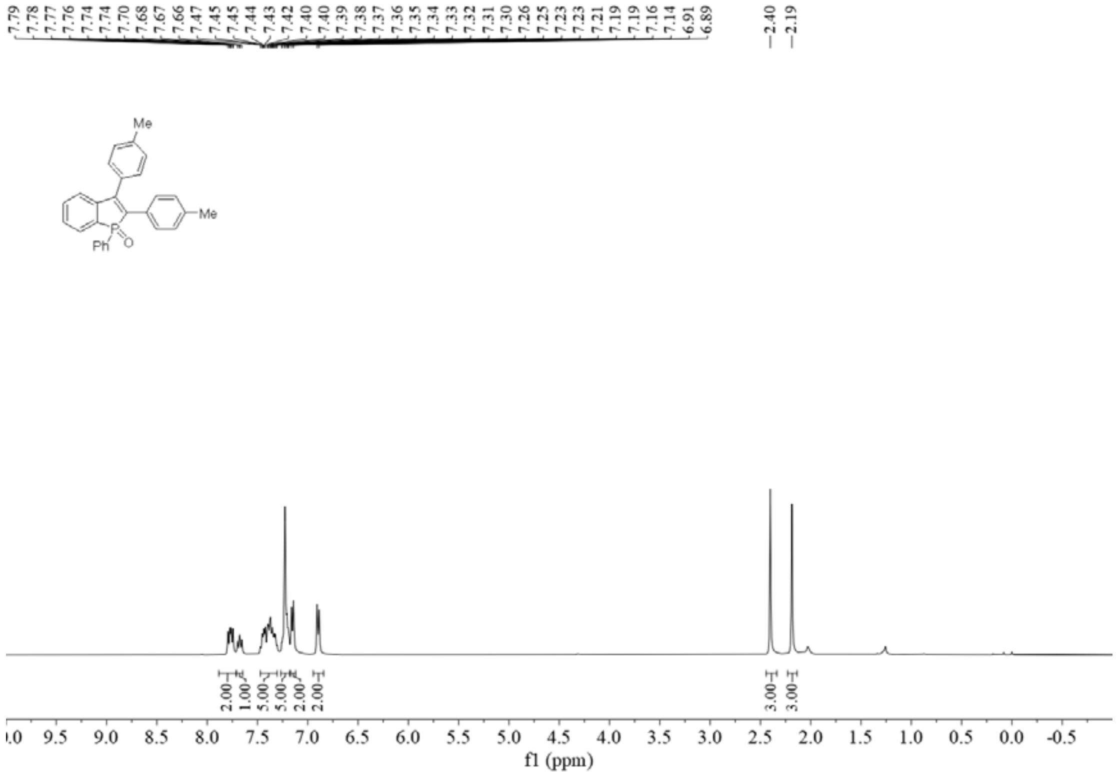
^{1}H NMR (CDCl$_3$-*d*) of **3b**



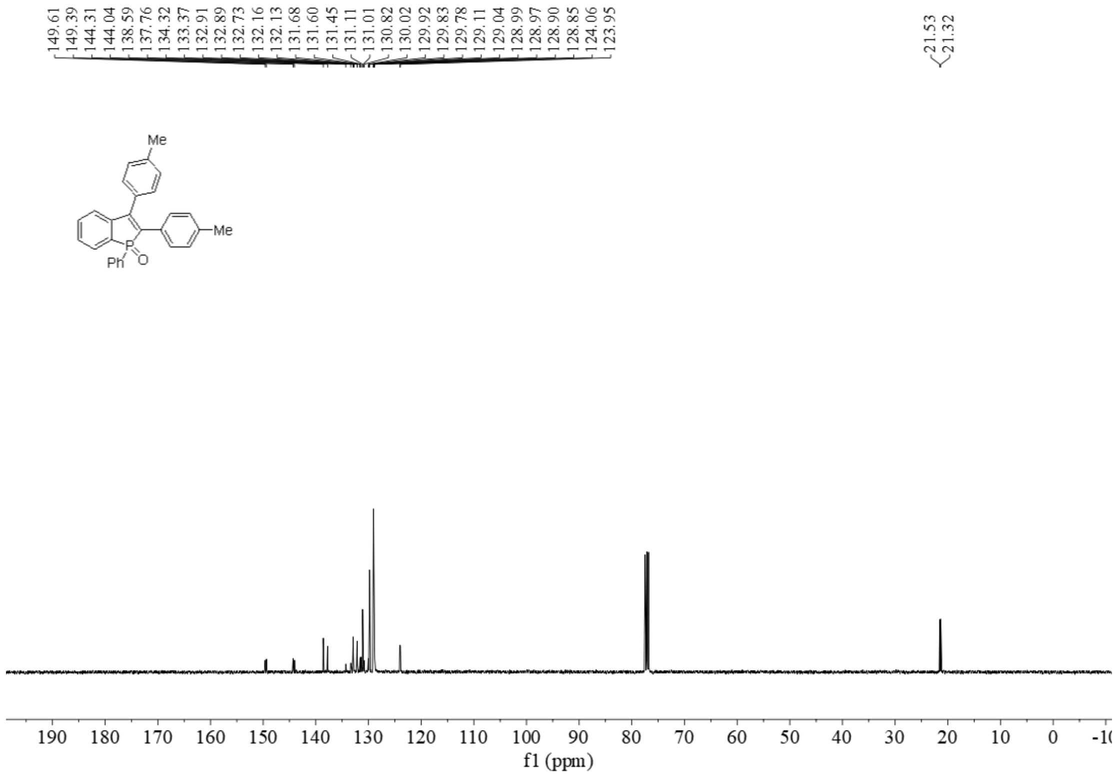
^{13}C NMR (CDCl$_3$-*d*) of **3b**



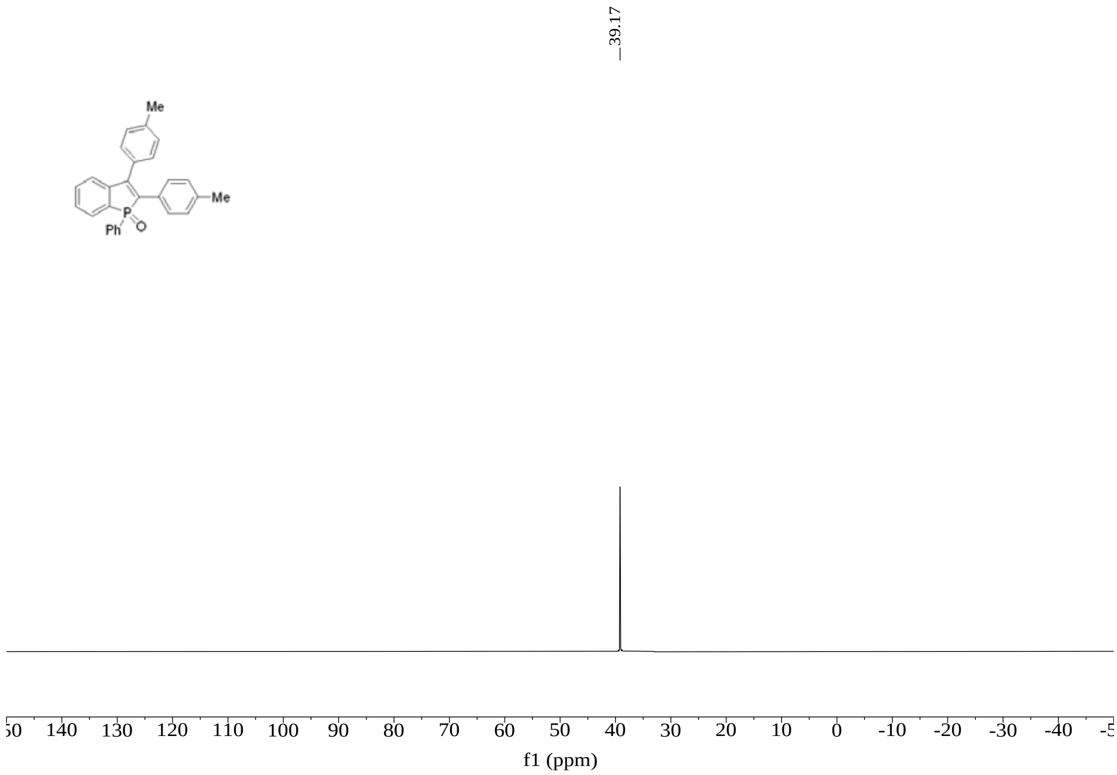
^{31}P NMR ($CDCl_3$-*d*) of **3b**



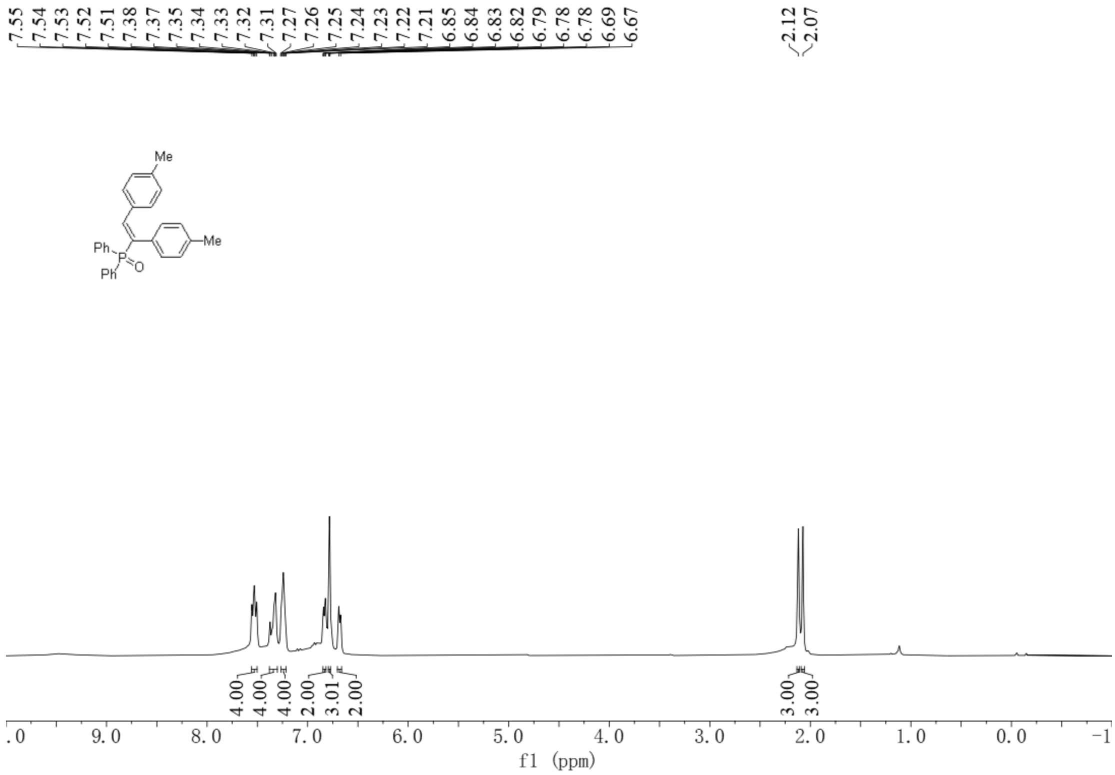
^{1}H NMR ($CDCl_3$-*d*) of **3c**



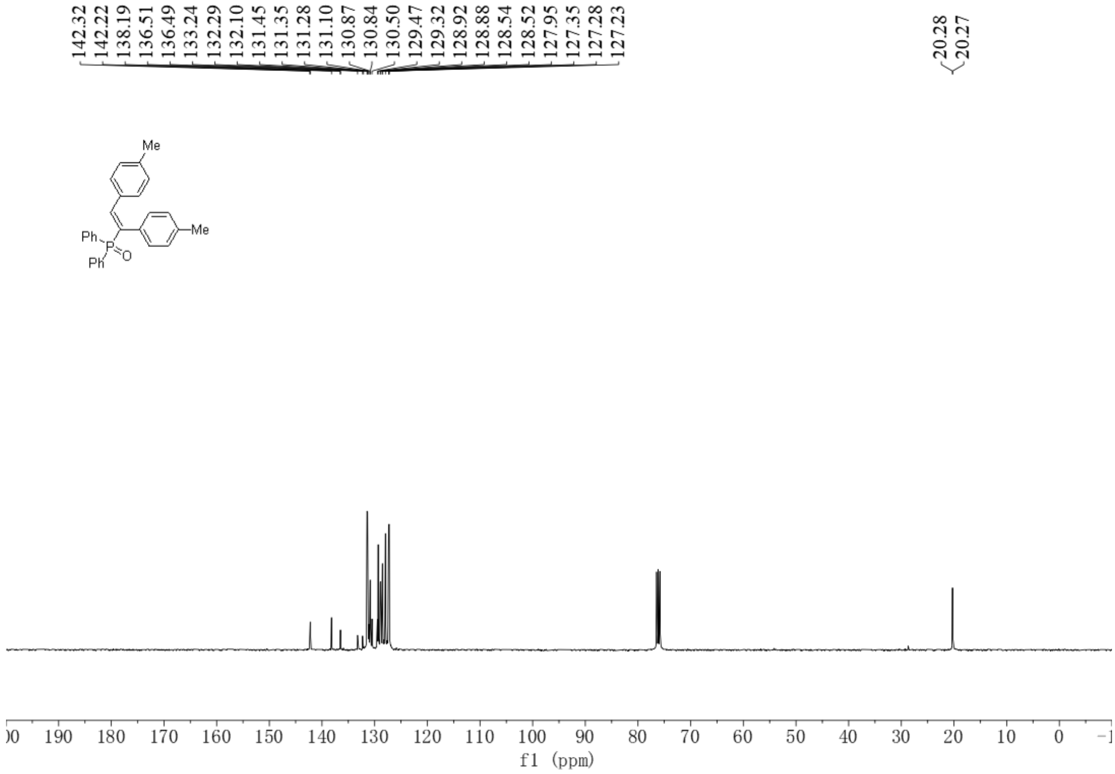
^{13}C NMR ($CDCl_3$-*d*) of **3c**



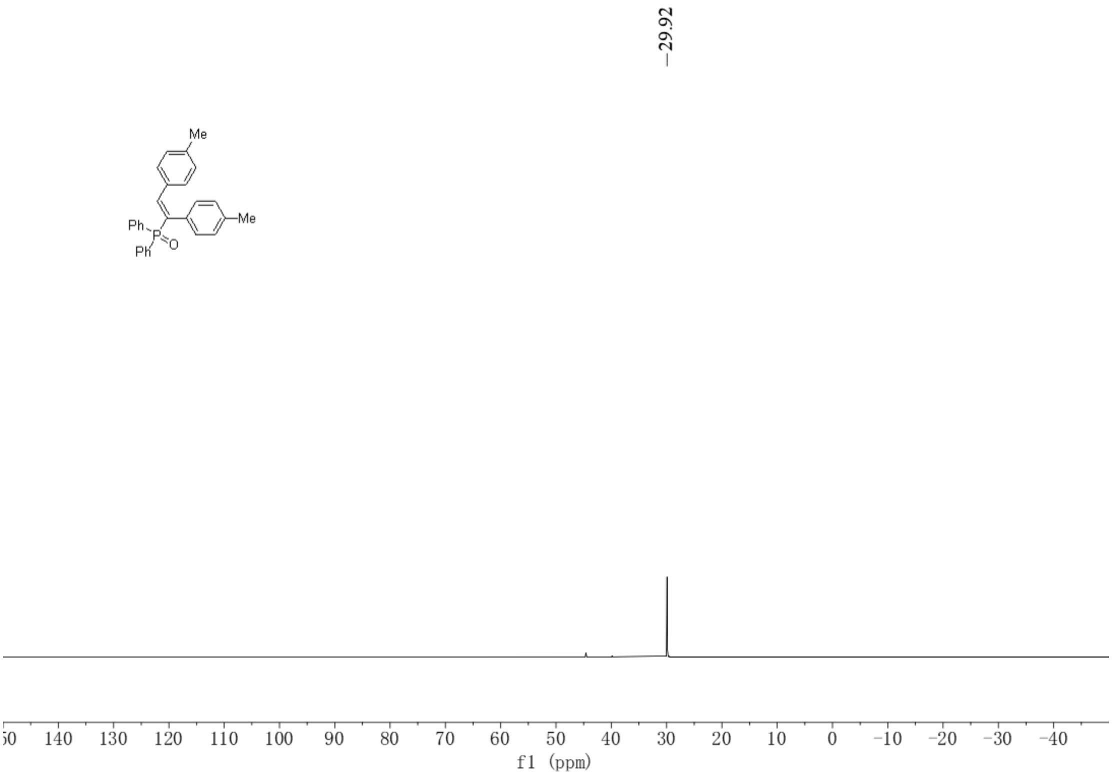
^{31}P NMR ($CDCl_3$-*d*) of **3c**



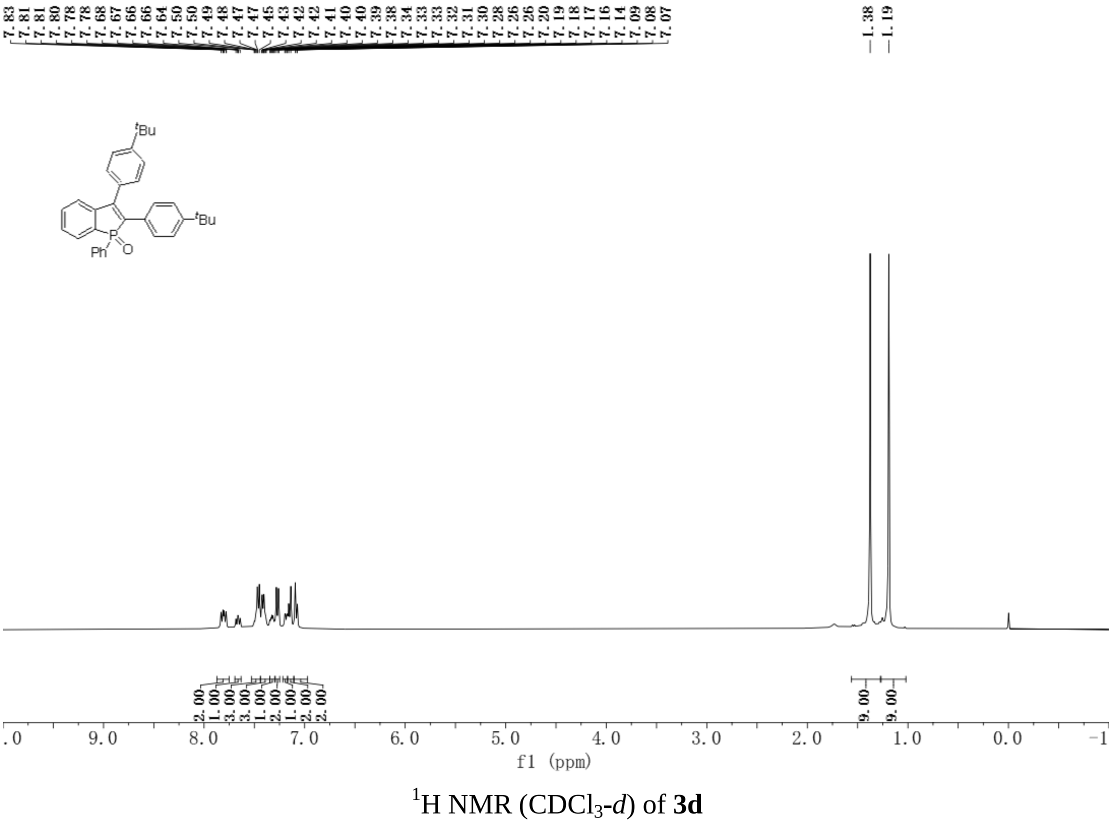
^{1}H NMR ($CDCl_3$-*d*) of 3**c'**



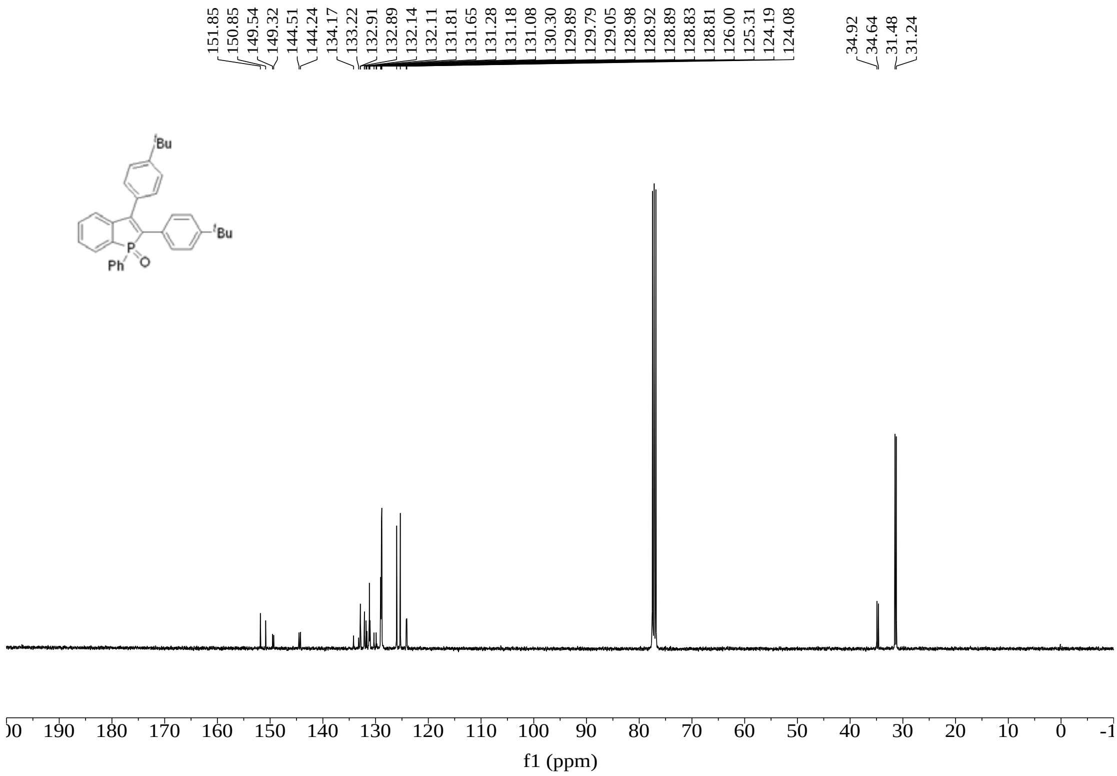
^{13}C NMR ($CDCl_3$-*d*) of **3c'**



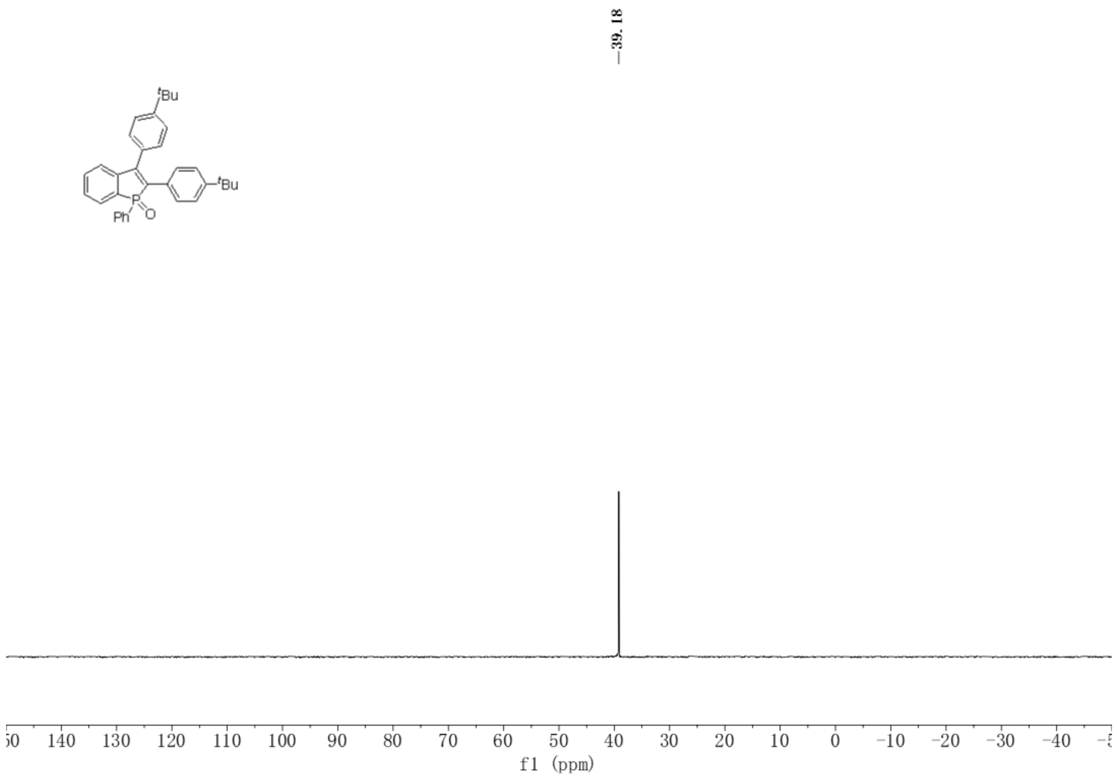
^{31}P NMR ($CDCl_3$-*d*) of **3c'**



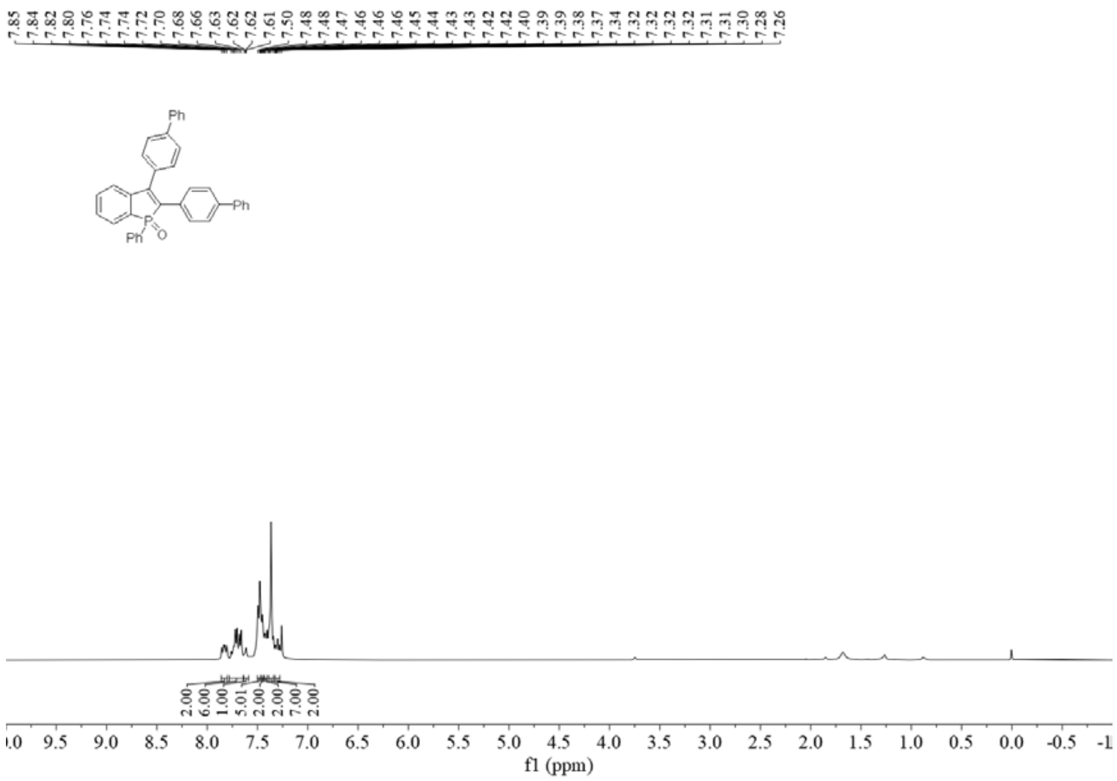
^{1}H NMR ($CDCl_3$-*d*) of **3d**



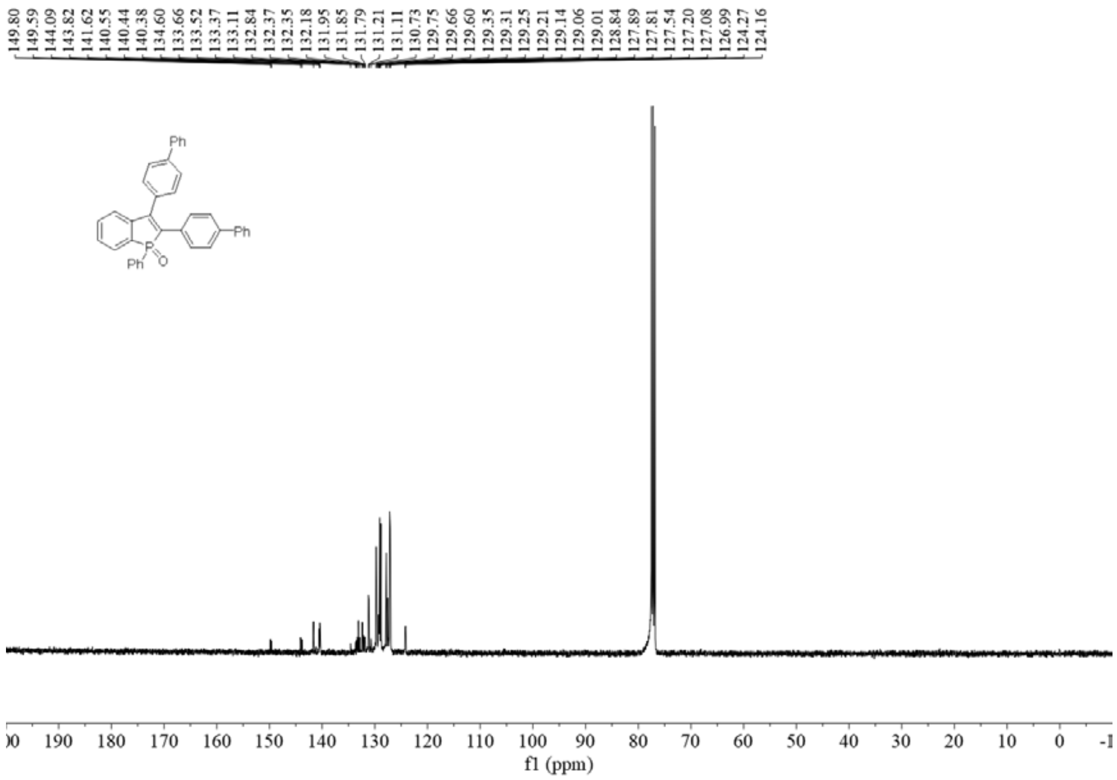
^{13}C NMR ($CDCl_3$-*d*) of **3d**



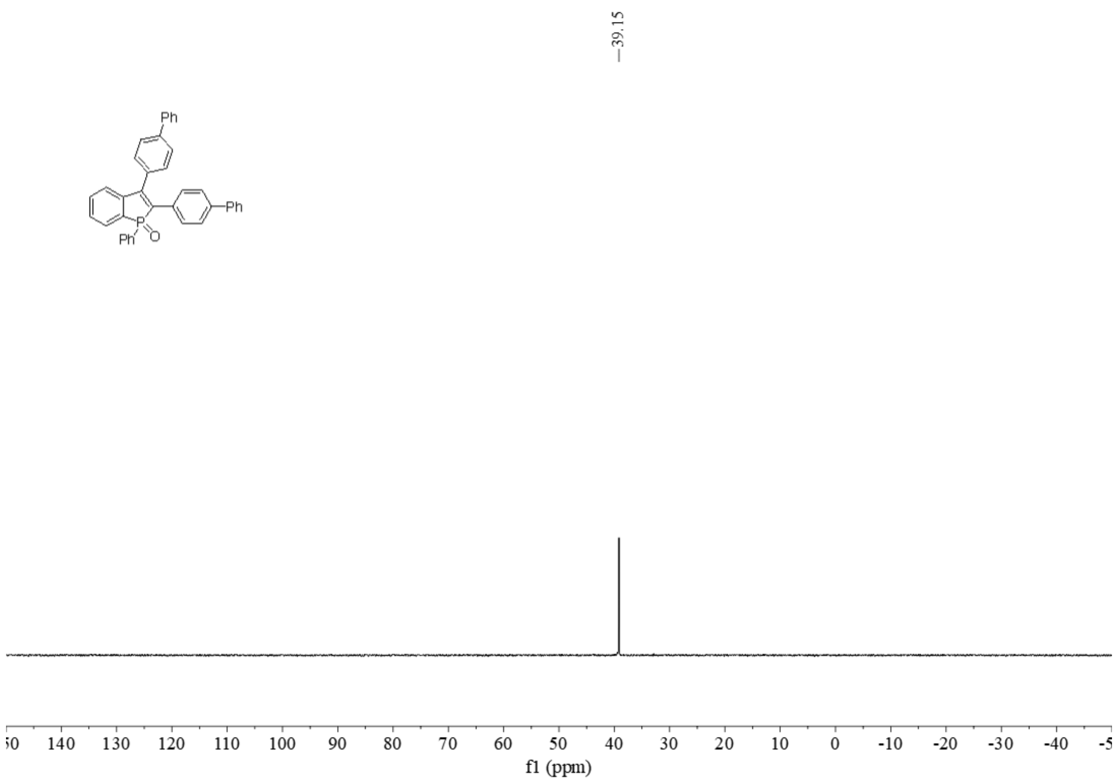
^{31}P NMR ($CDCl_3$-*d*) of **3d**



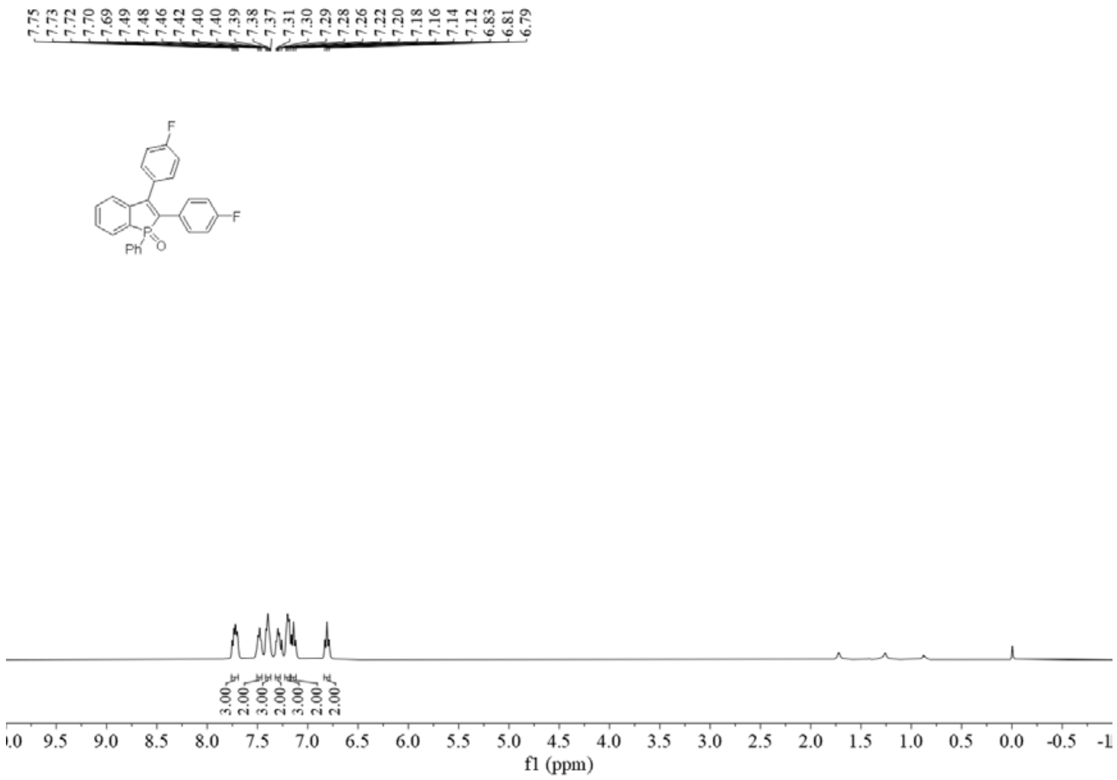
^{1}H NMR (CDCl$_3$-*d*) of **3e**



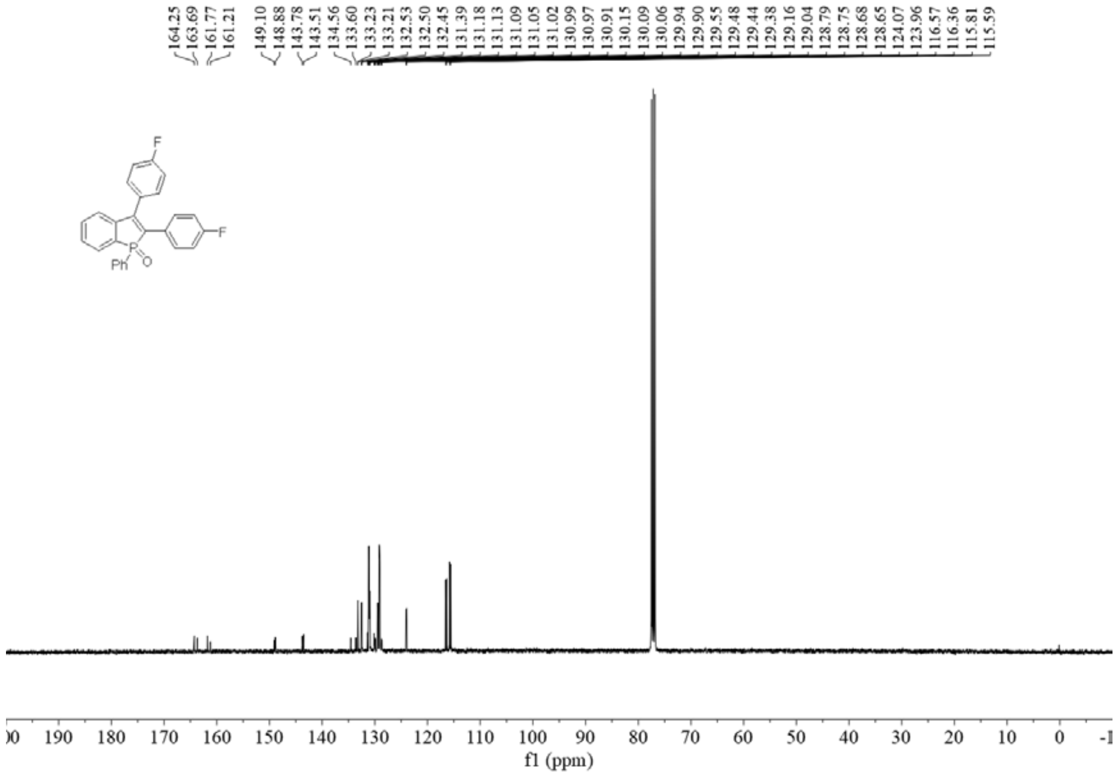
^{13}C NMR (CDCl$_3$-*d*) of **3e**



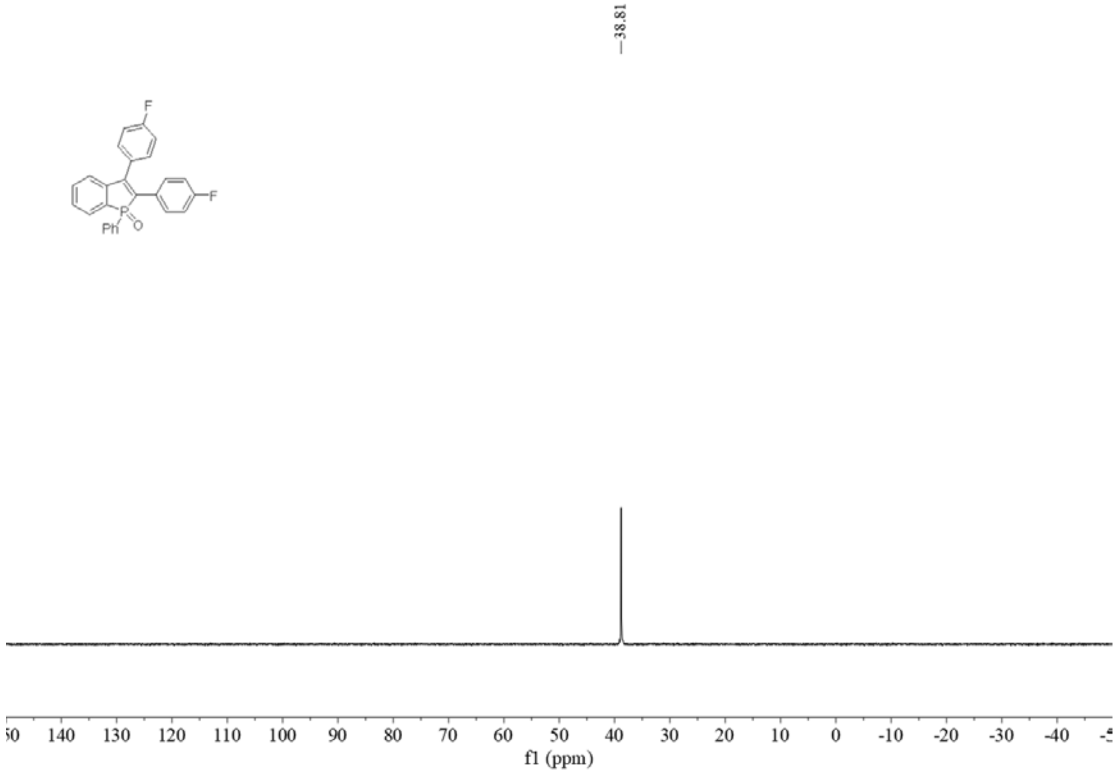
^{31}P NMR ($CDCl_3$-*d*) of **3e**



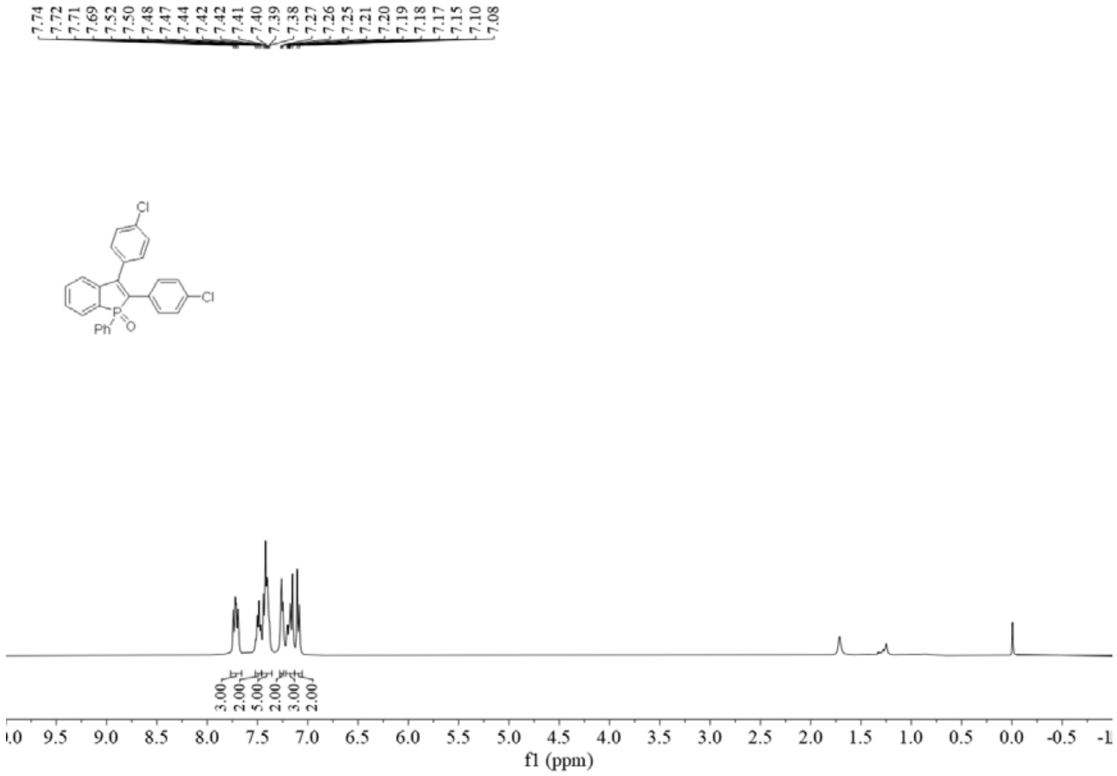
^{1}H NMR ($CDCl_3$-*d*) of **3f**



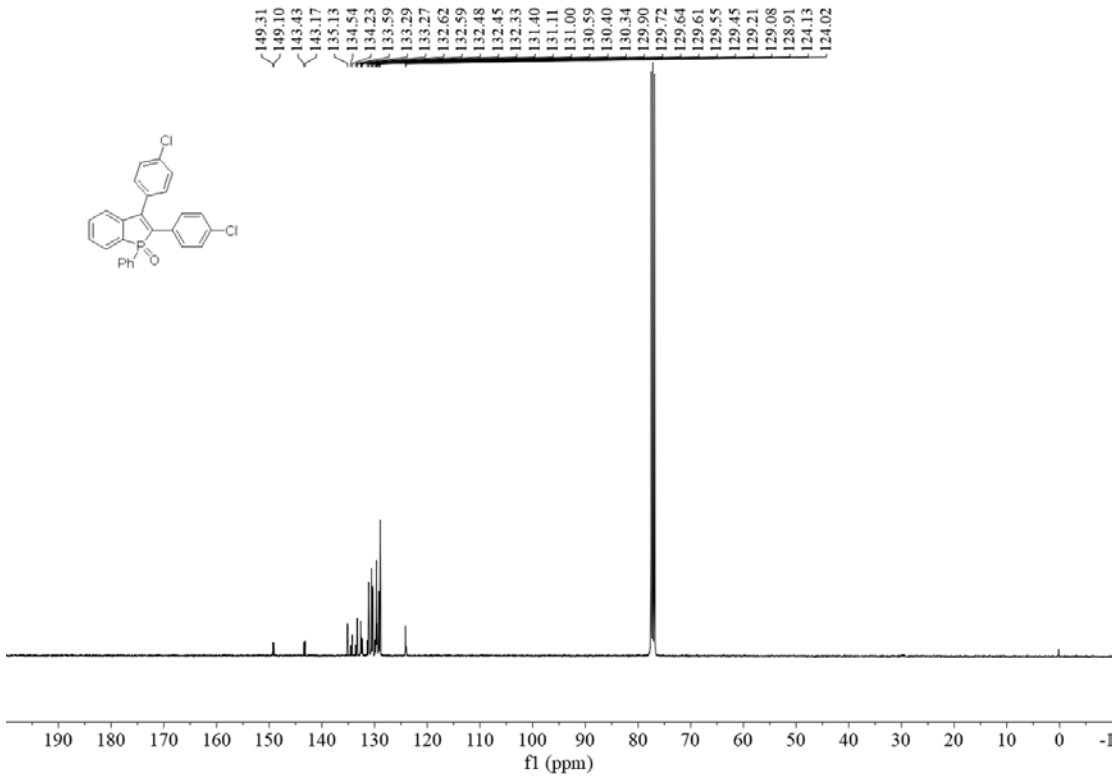
^{13}C NMR ($CDCl_3$-*d*) of **3f**



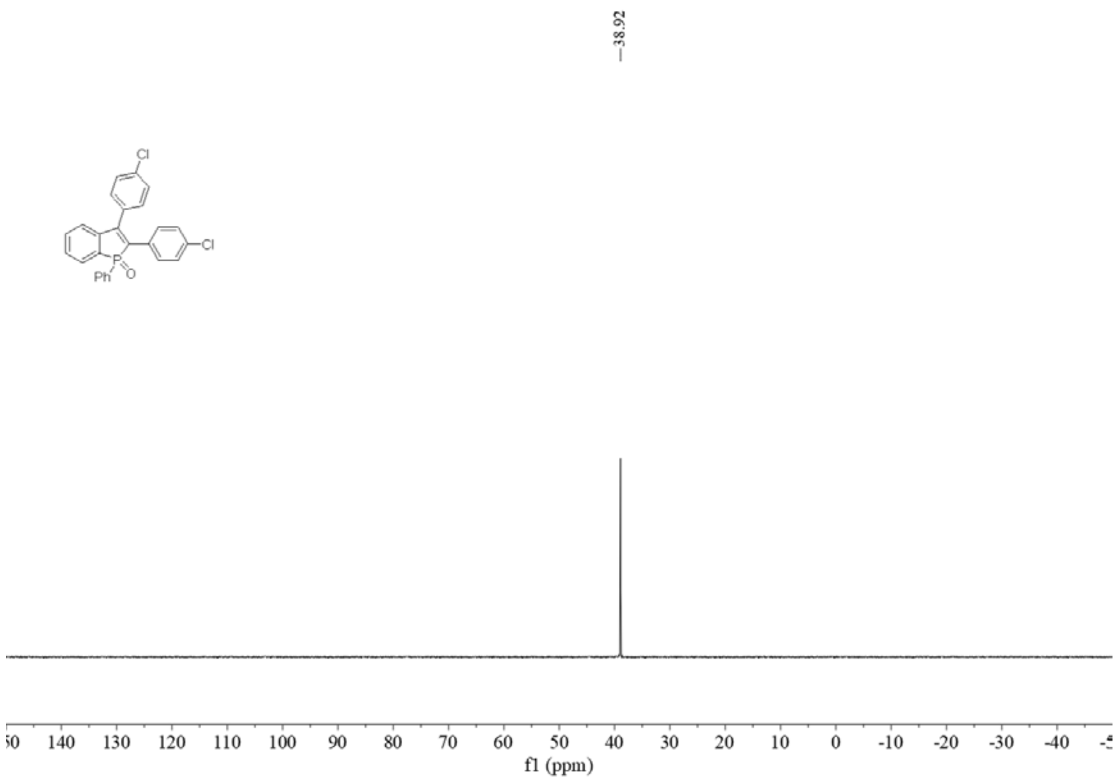
^{31}P NMR ($CDCl_3$-*d*) of **3f**



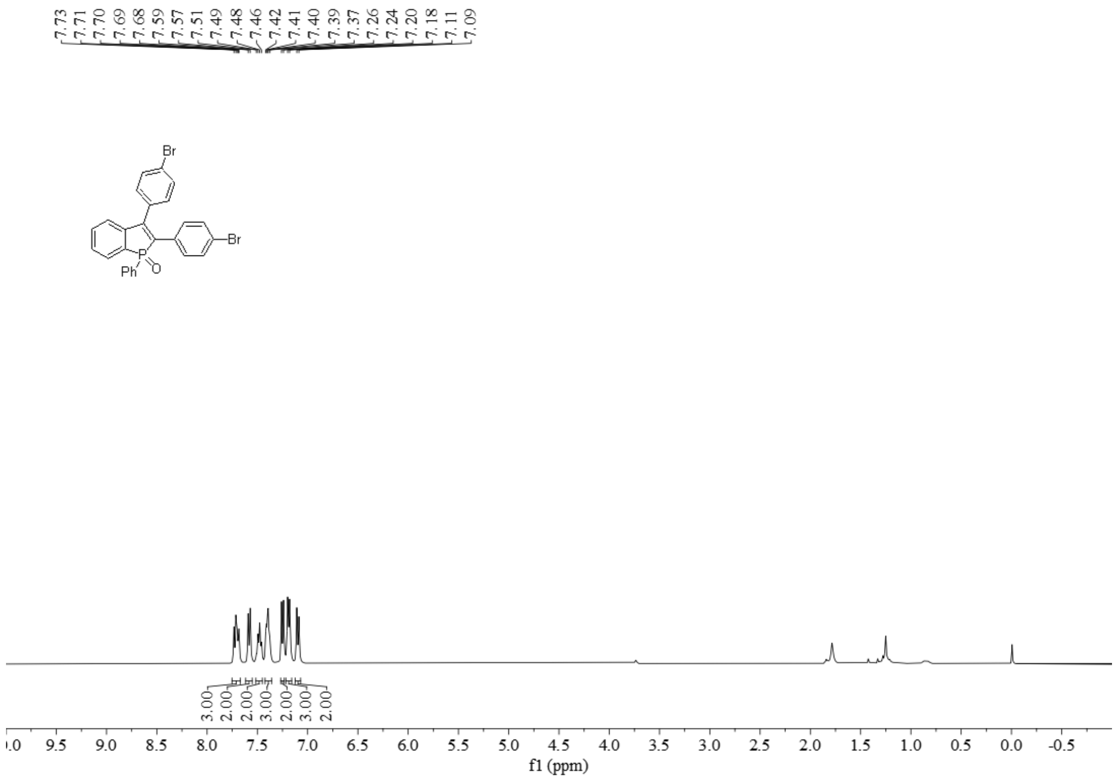
^{1}H NMR (CDCl$_3$-*d*) of **3g**



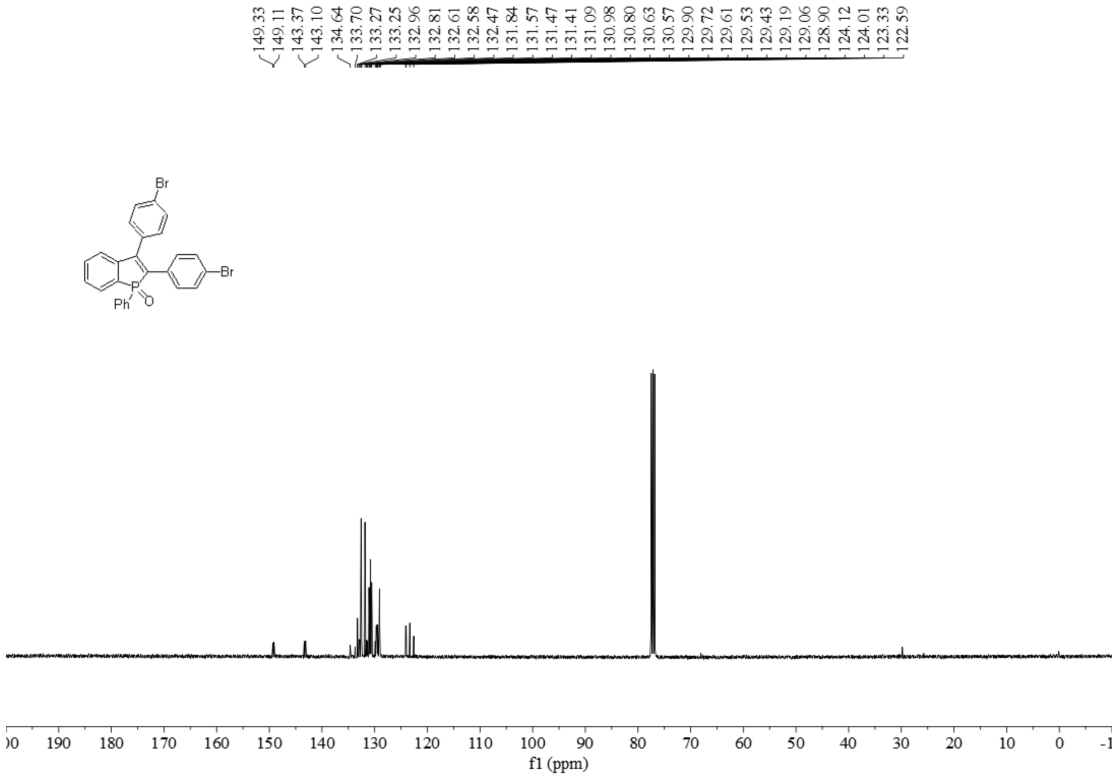
^{13}C NMR (CDCl$_3$-*d*) of **3g**



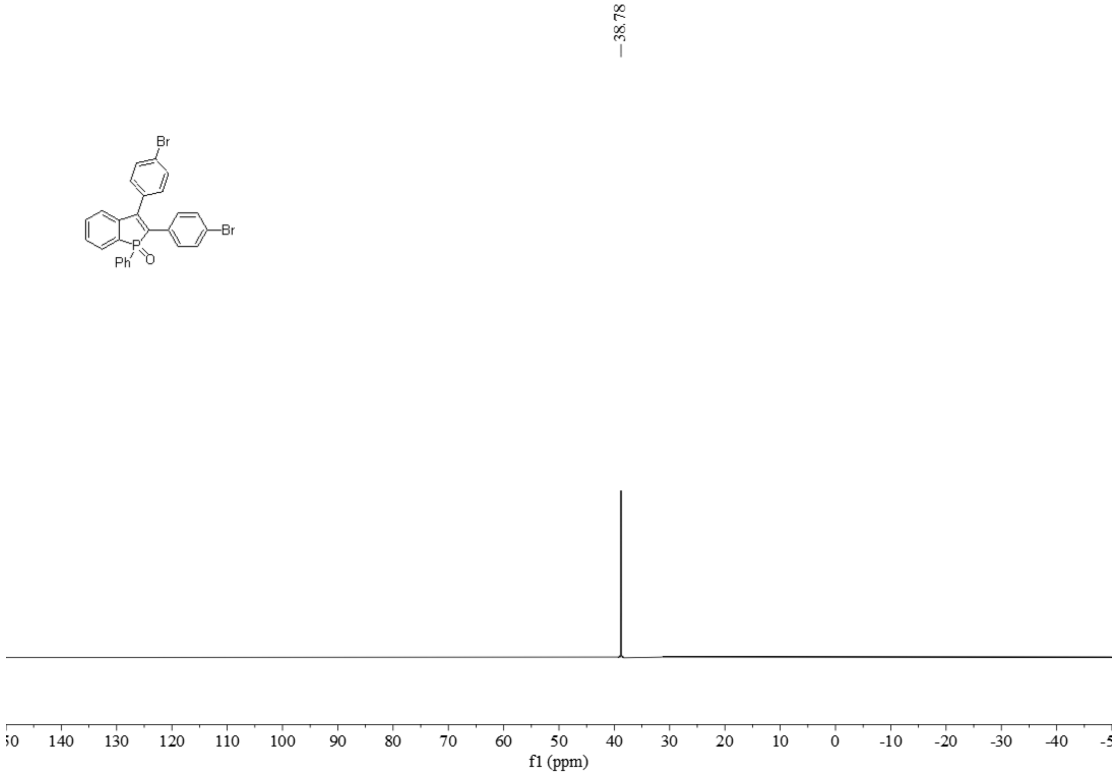
^{31}P NMR ($CDCl_3$-*d*) of **3g**



^{1}H NMR ($CDCl_3$-*d*) of **3h**



^{13}C NMR ($CDCl_3$-*d*) of **3h**



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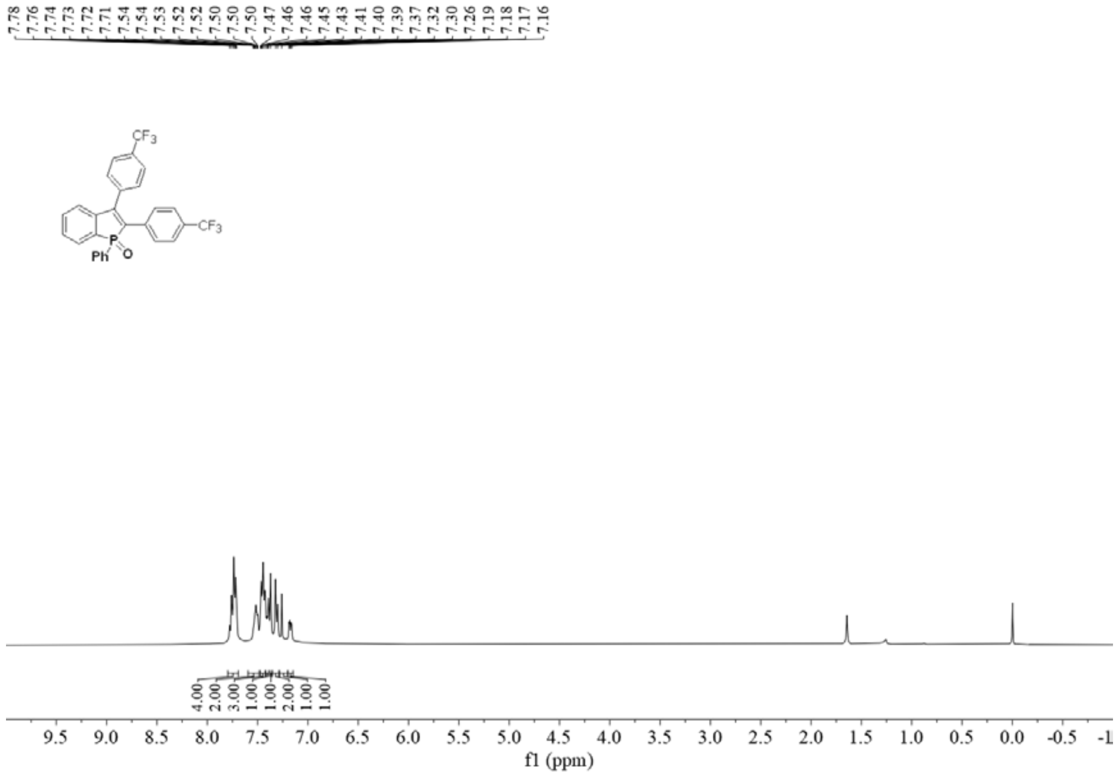
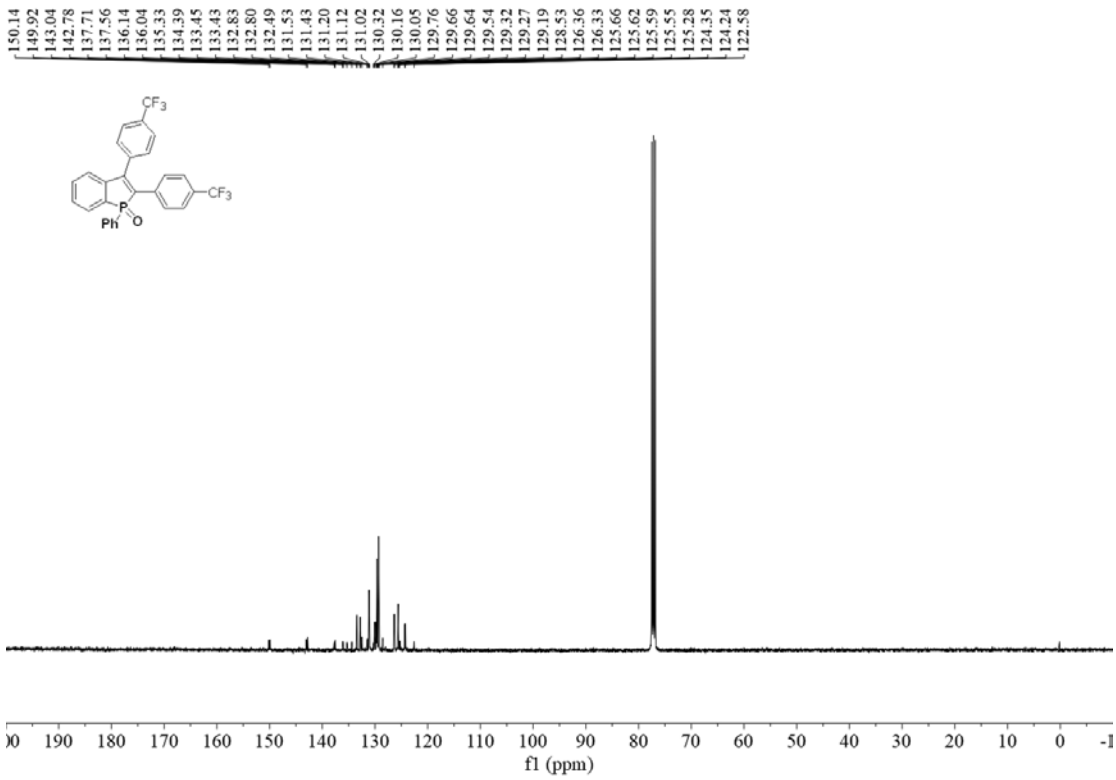
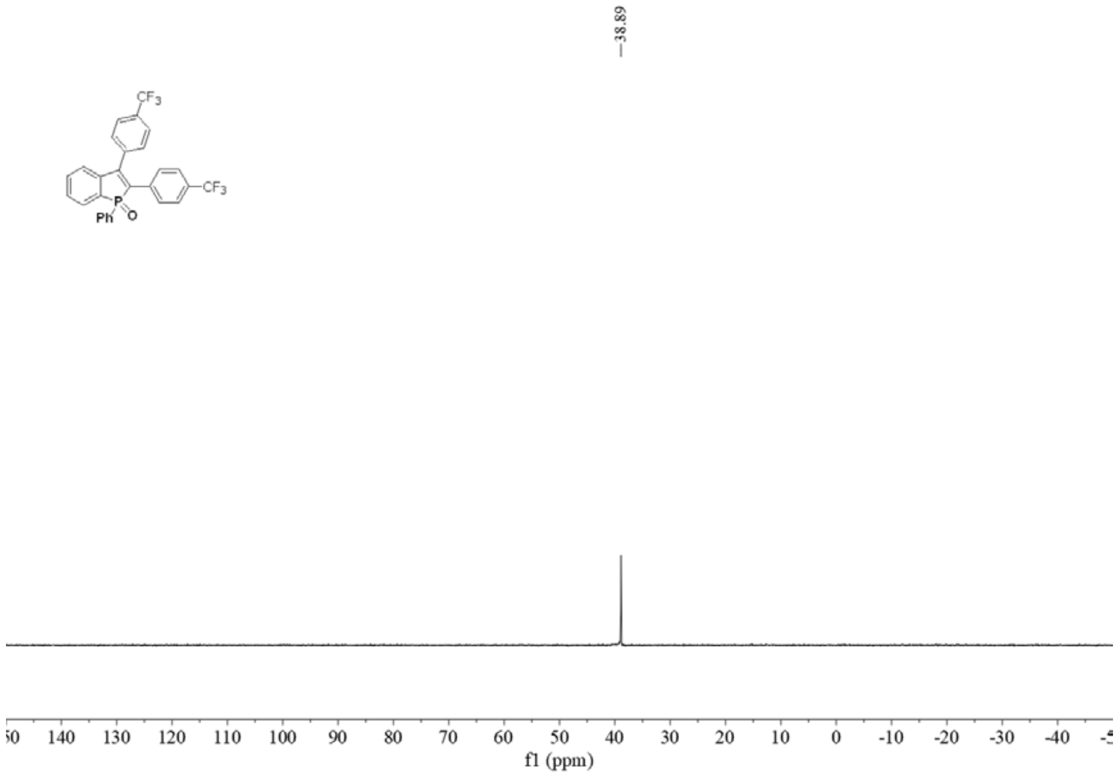


^{1}H NMR ($CDCl_3$-*d*) of **3i**



^{13}C NMR ($CDCl_3$-*d*) of **3i**



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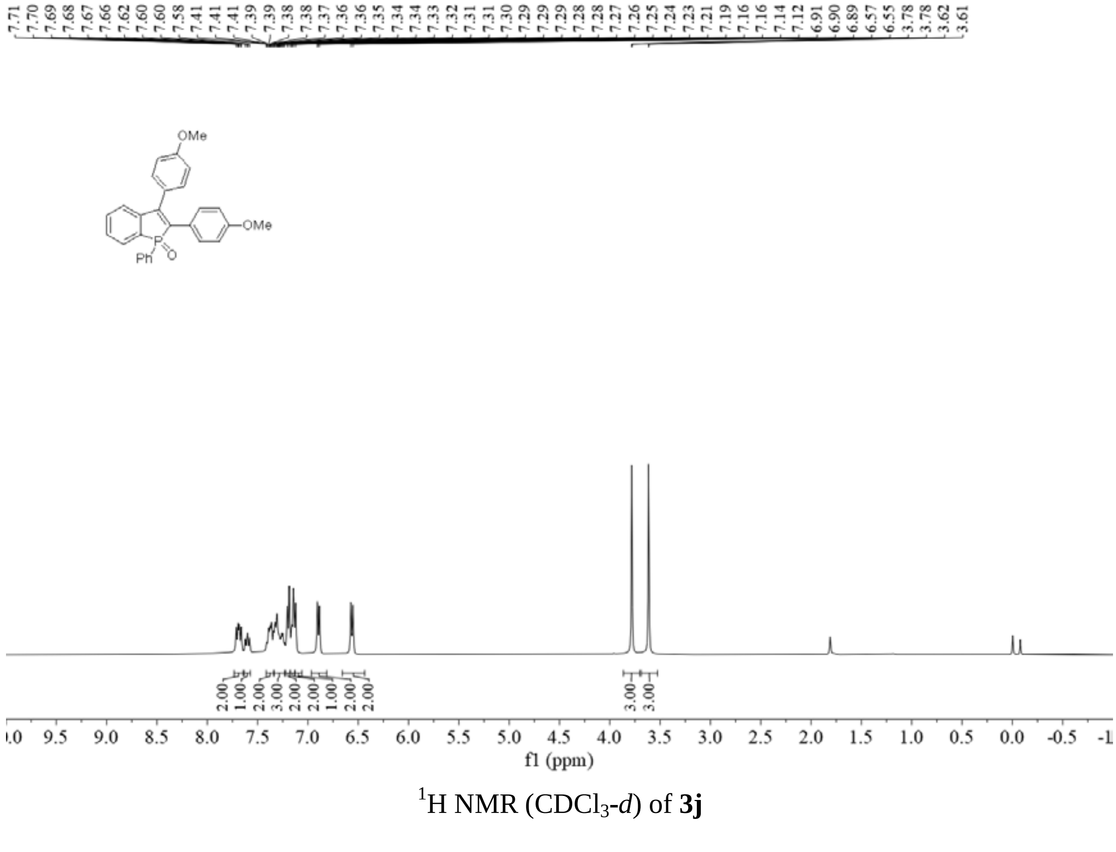

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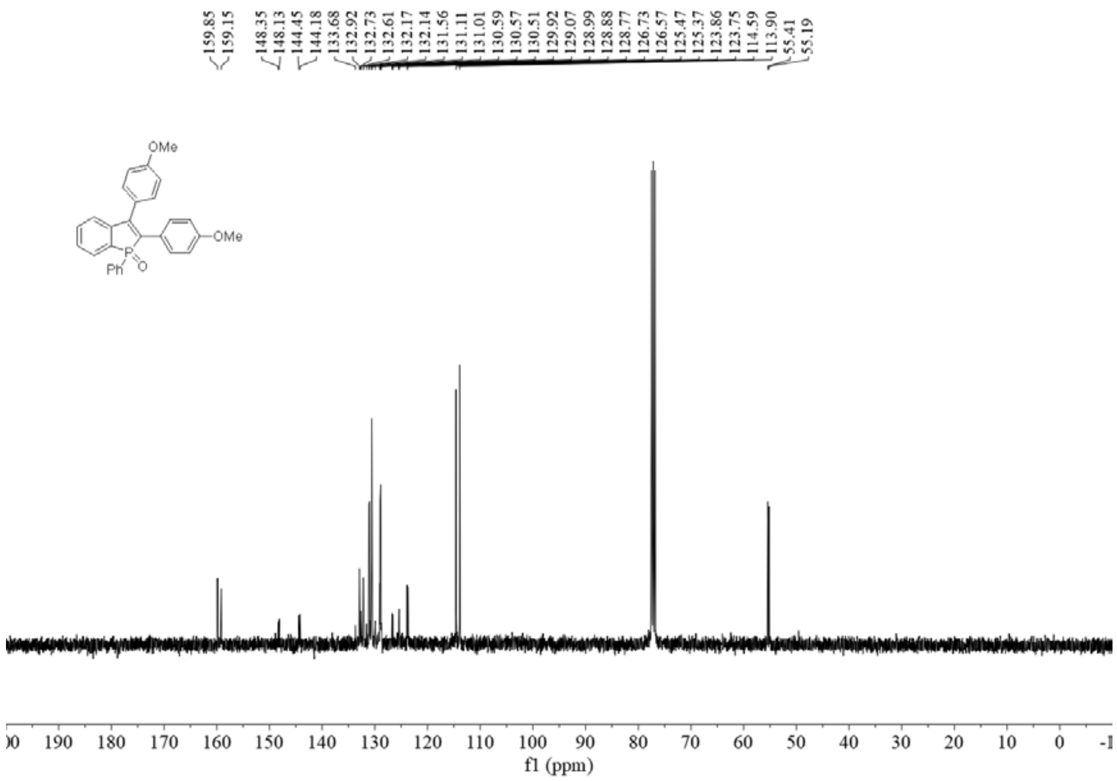
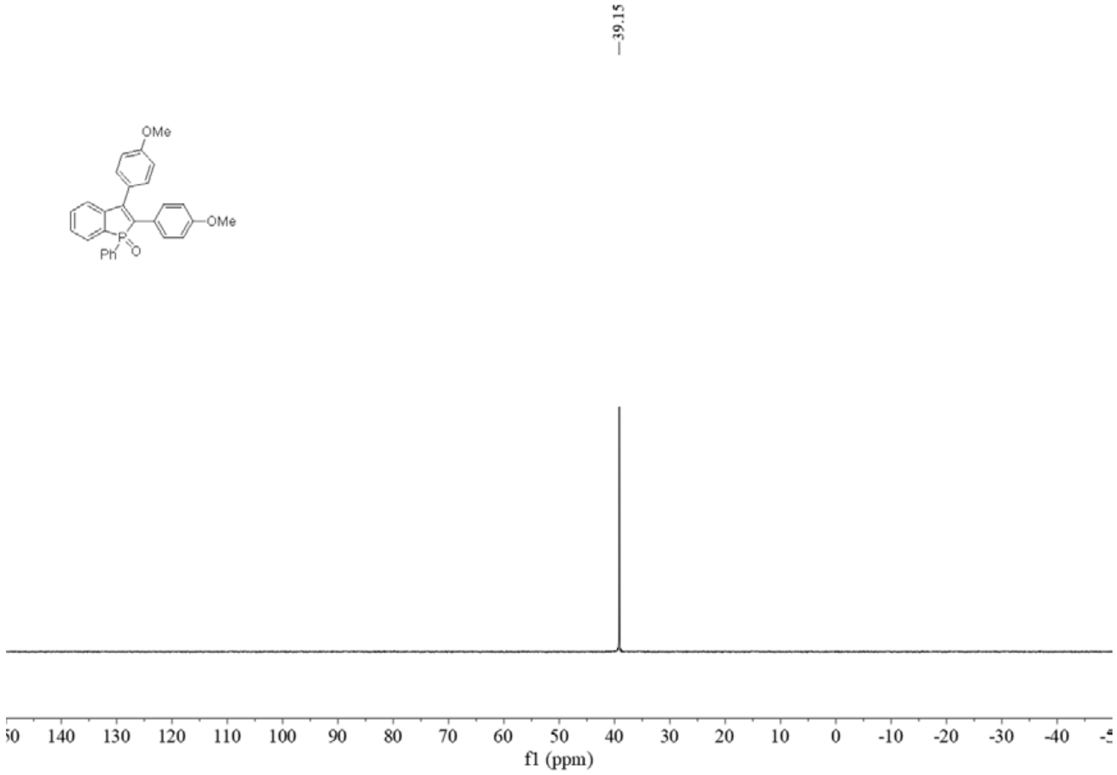
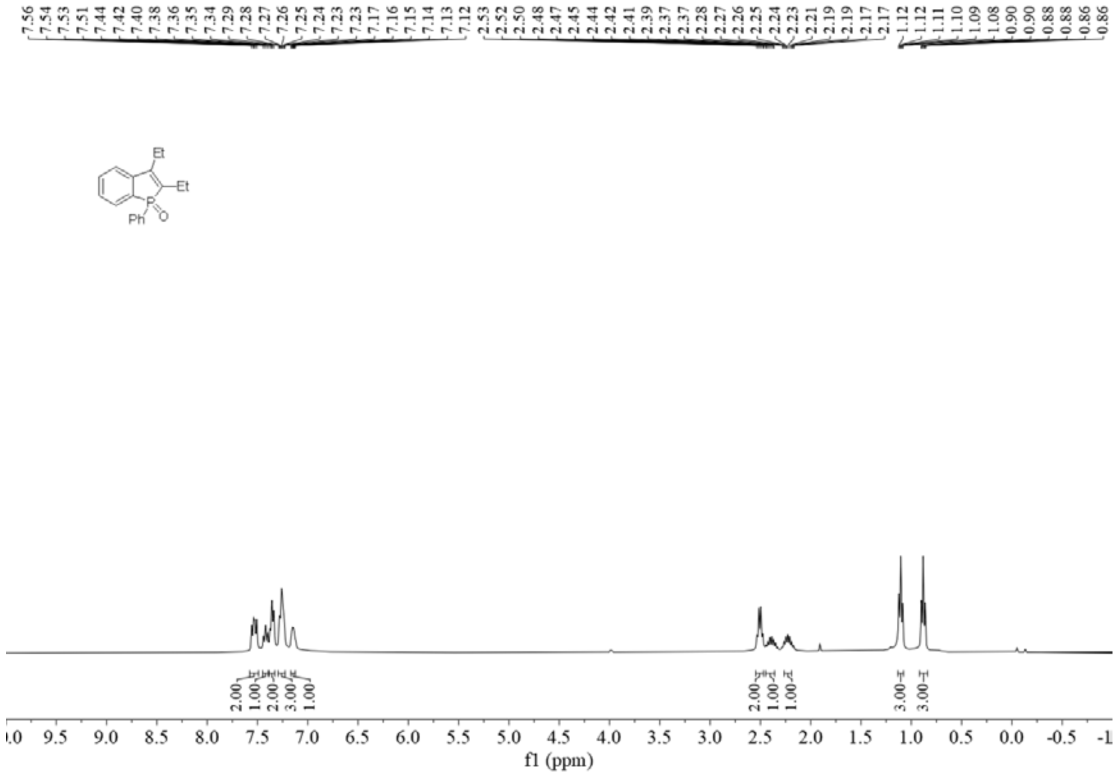


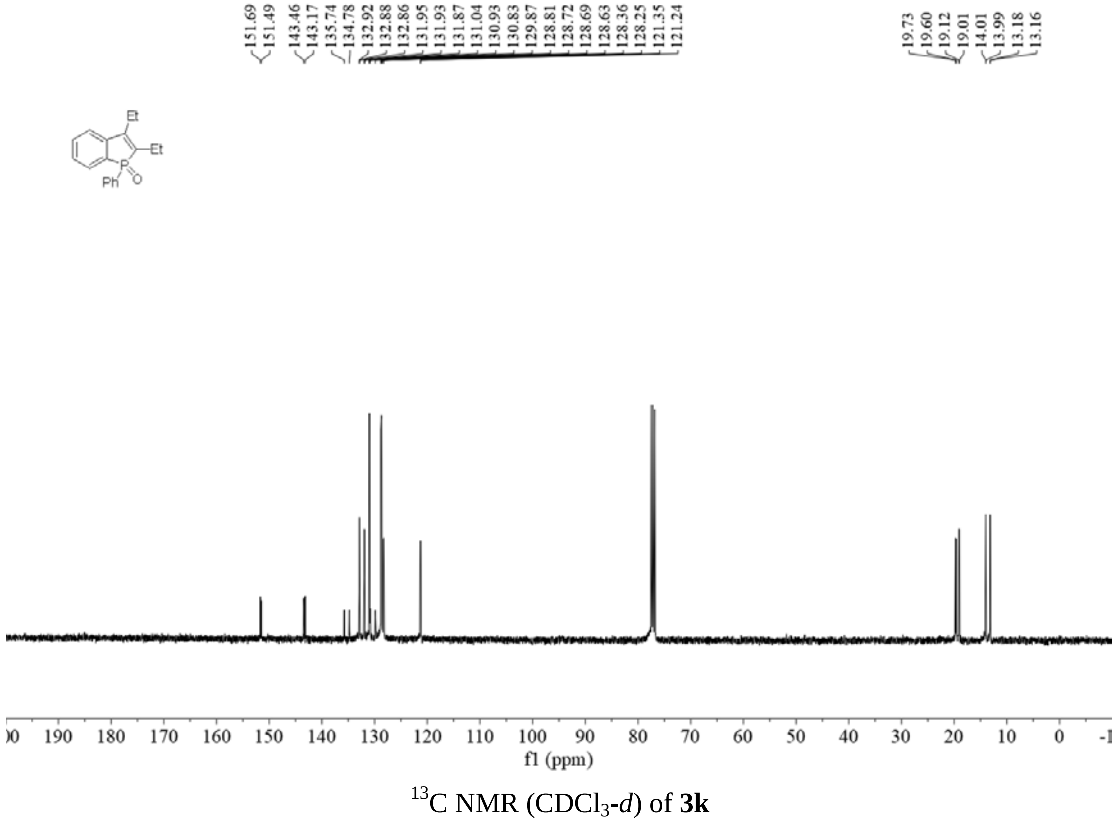
^{13}C NMR ($CDCl_3$-*d*) of **3j**



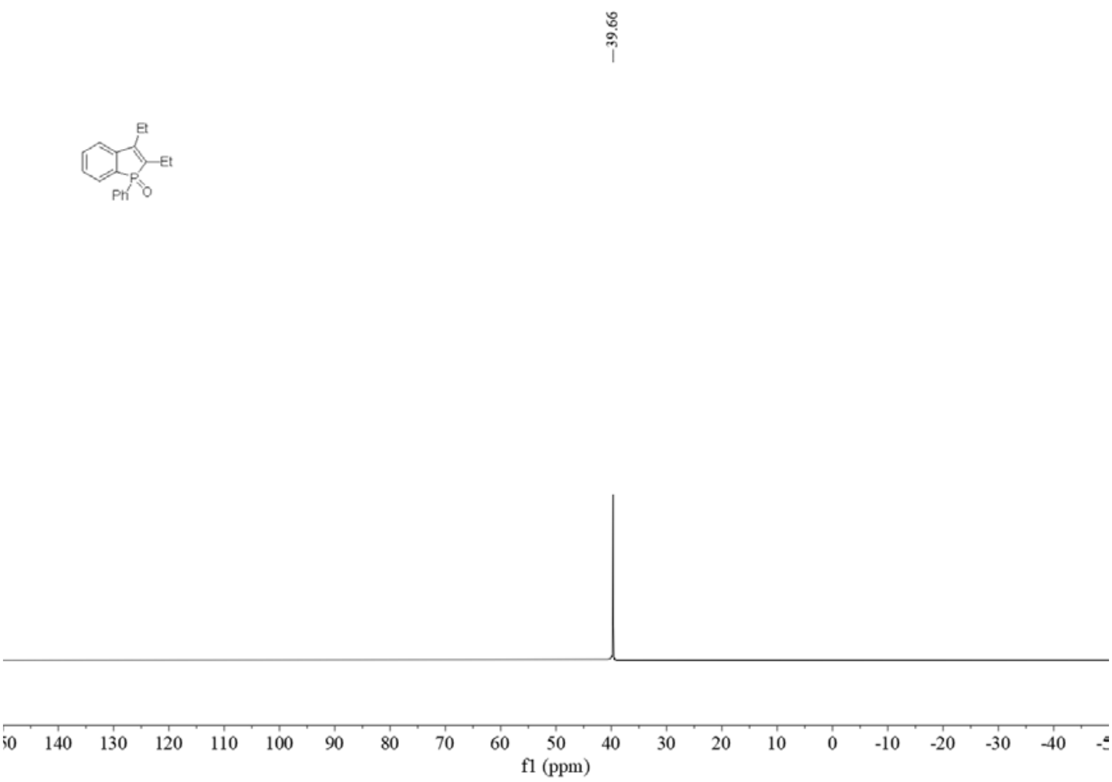
^{31}P NMR ($CDCl_3$-*d*) of **3j**



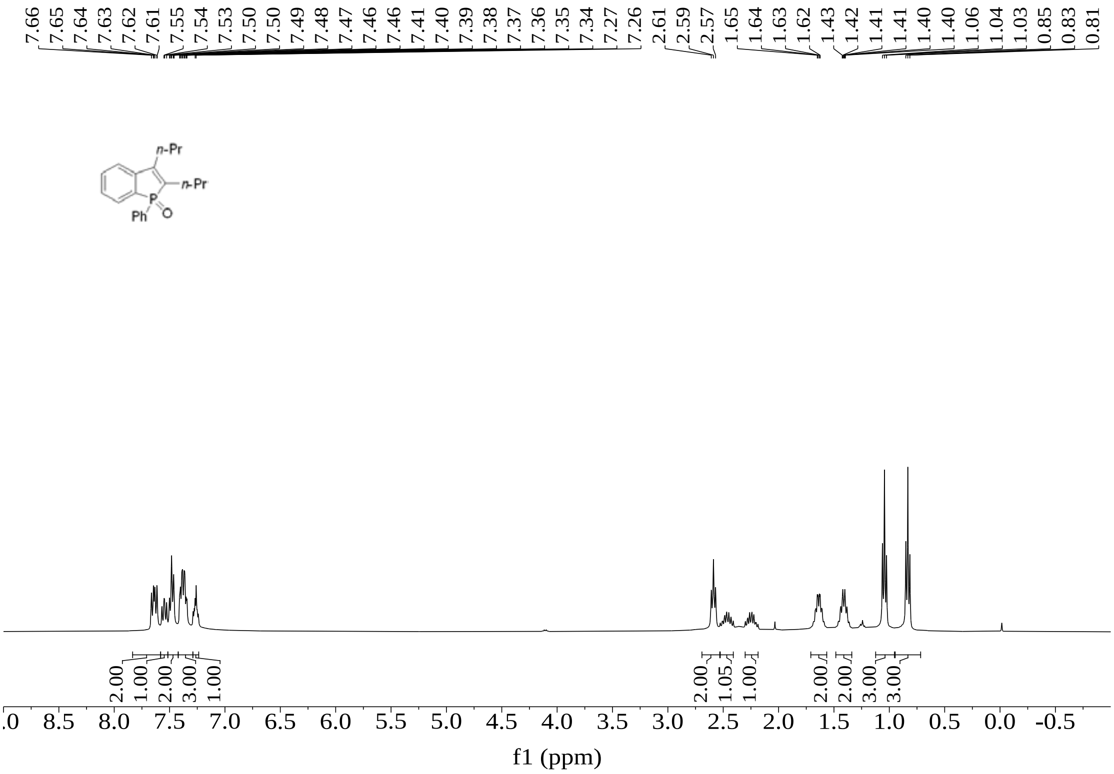
[1]H NMR ($CDCl_3$-*d*) of **3k**



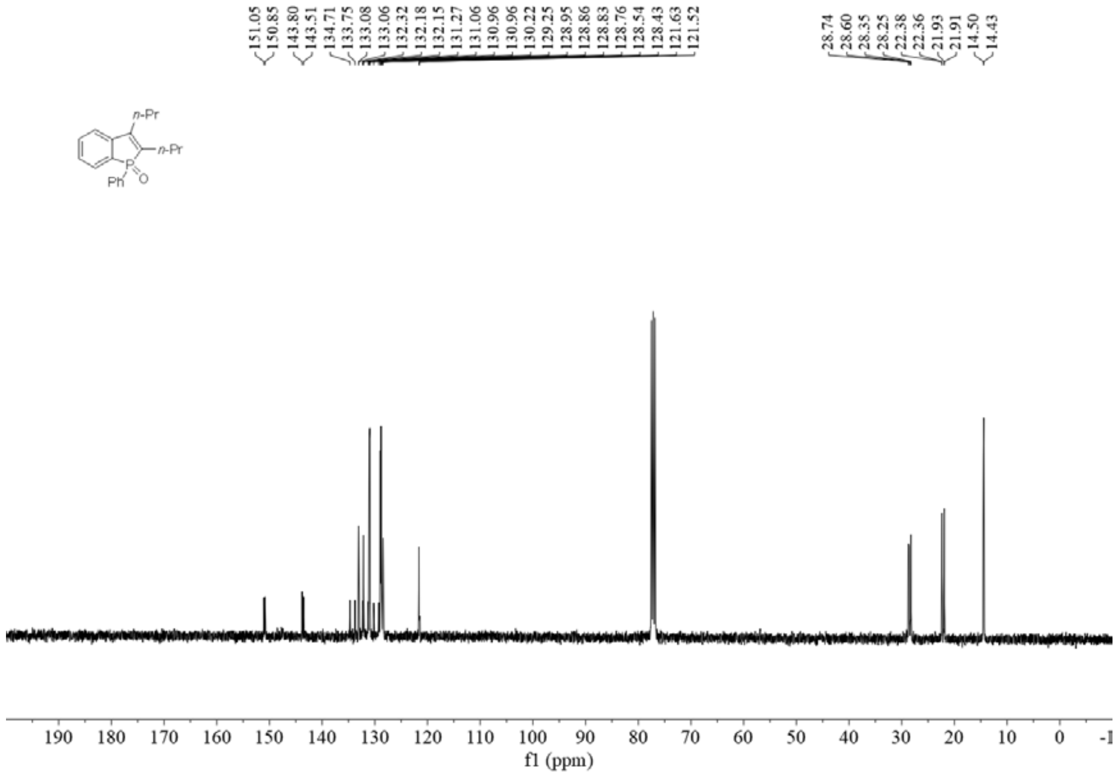
[13]C NMR ($CDCl_3$-*d*) of **3k**



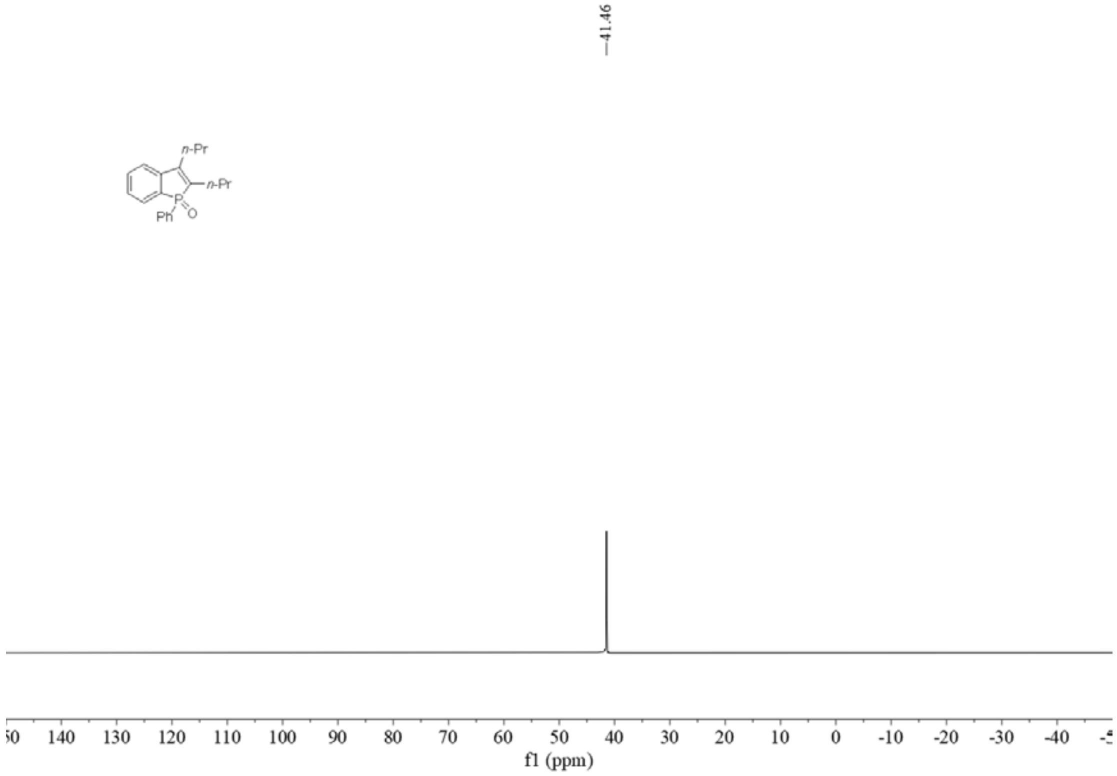
^{31}P NMR (CDCl$_3$-*d*) of **3k**



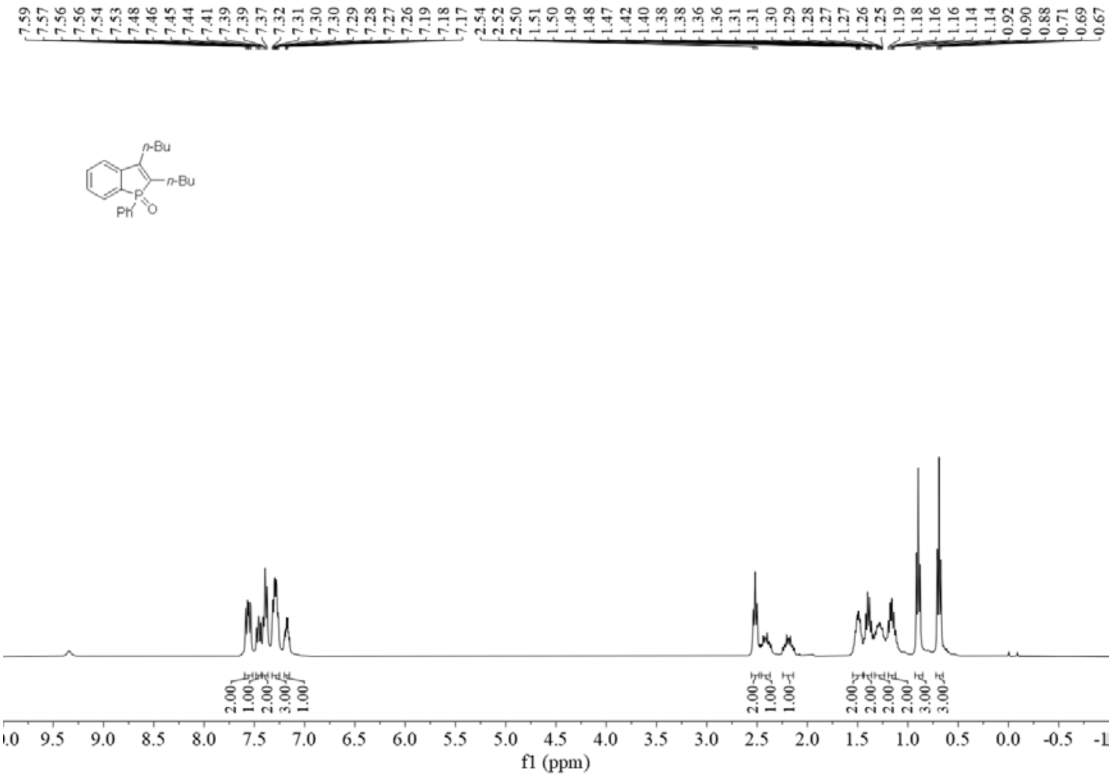
^{1}H NMR (CDCl$_3$-*d*) of **3l**



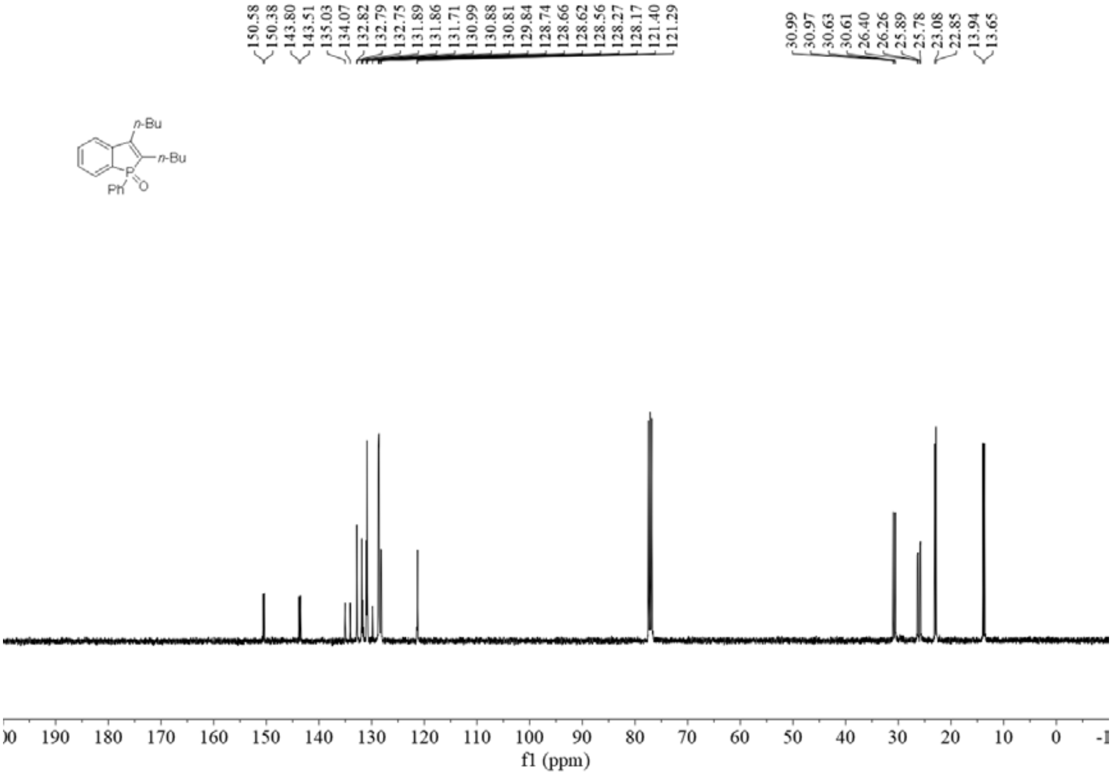
^{13}C NMR (CDCl$_3$-*d*) of **3l**



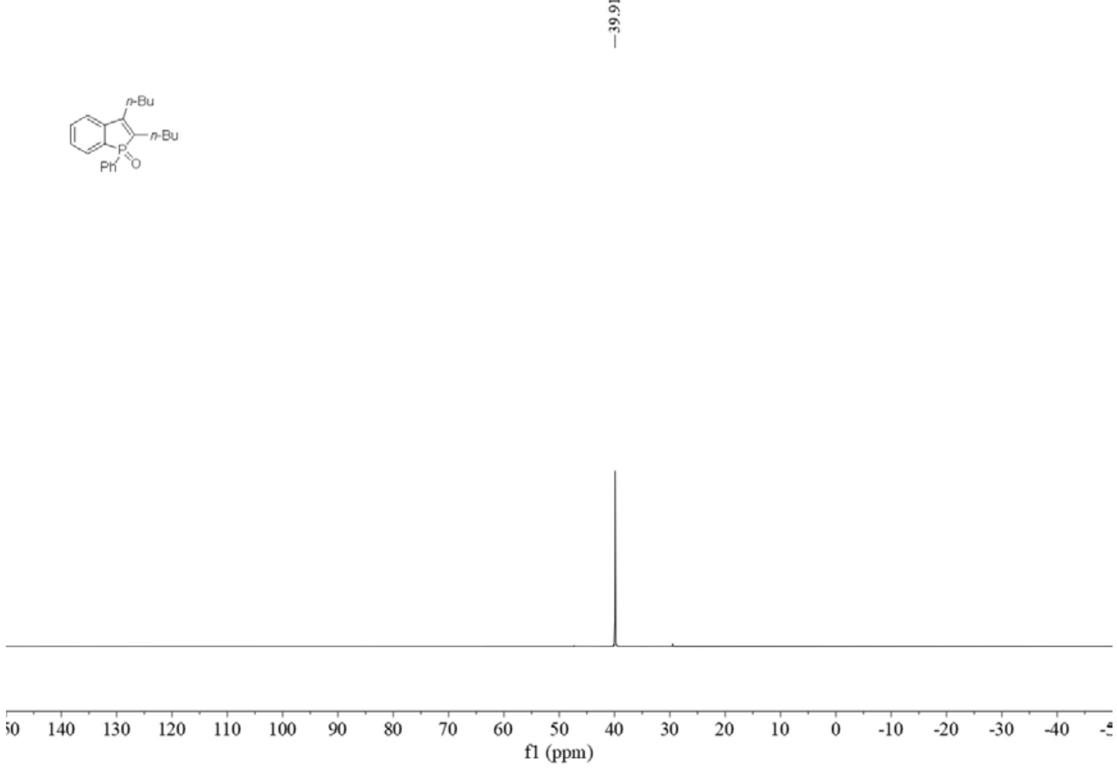
^{31}P NMR (CDCl$_3$-*d*) of **3l**



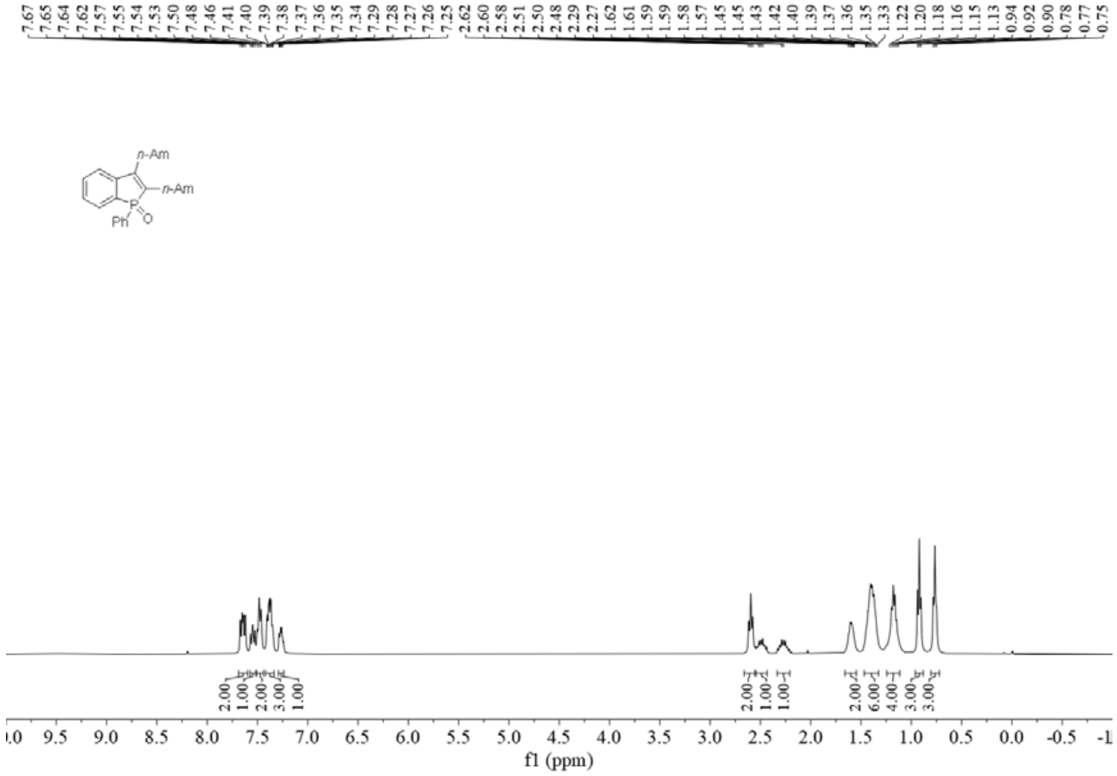
^{1}H NMR ($CDCl_3$-*d*) of **3m**



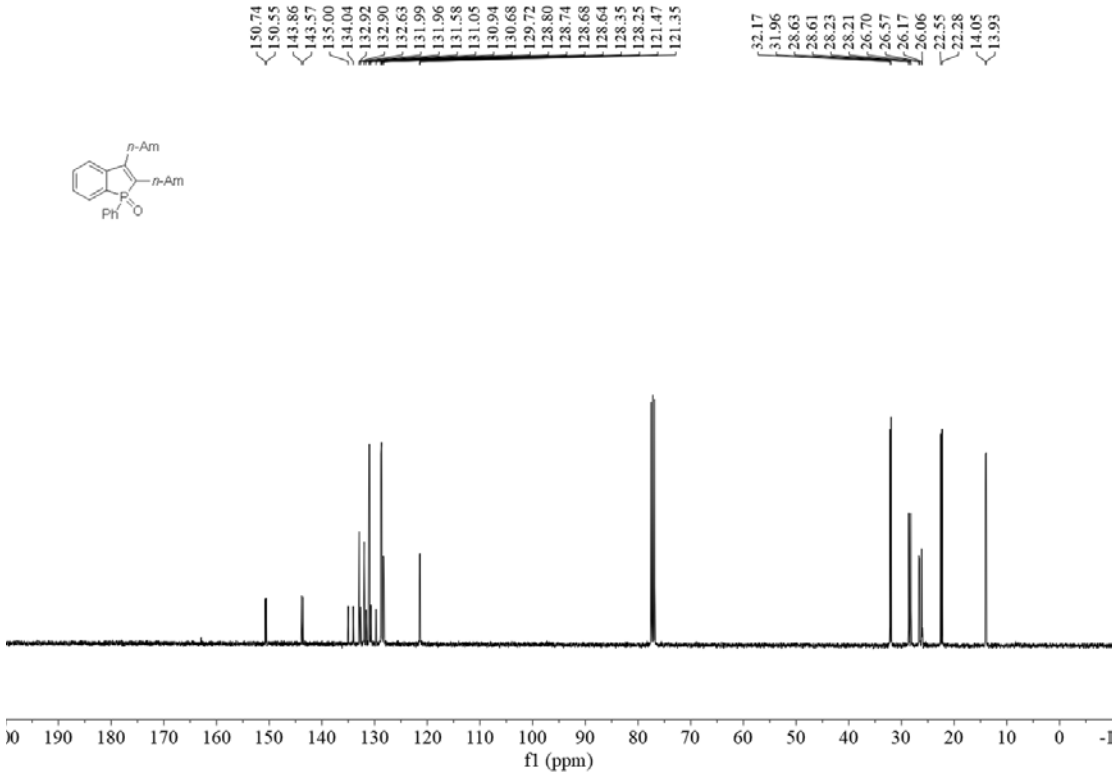
^{13}C NMR ($CDCl_3$-*d*) of **3m**



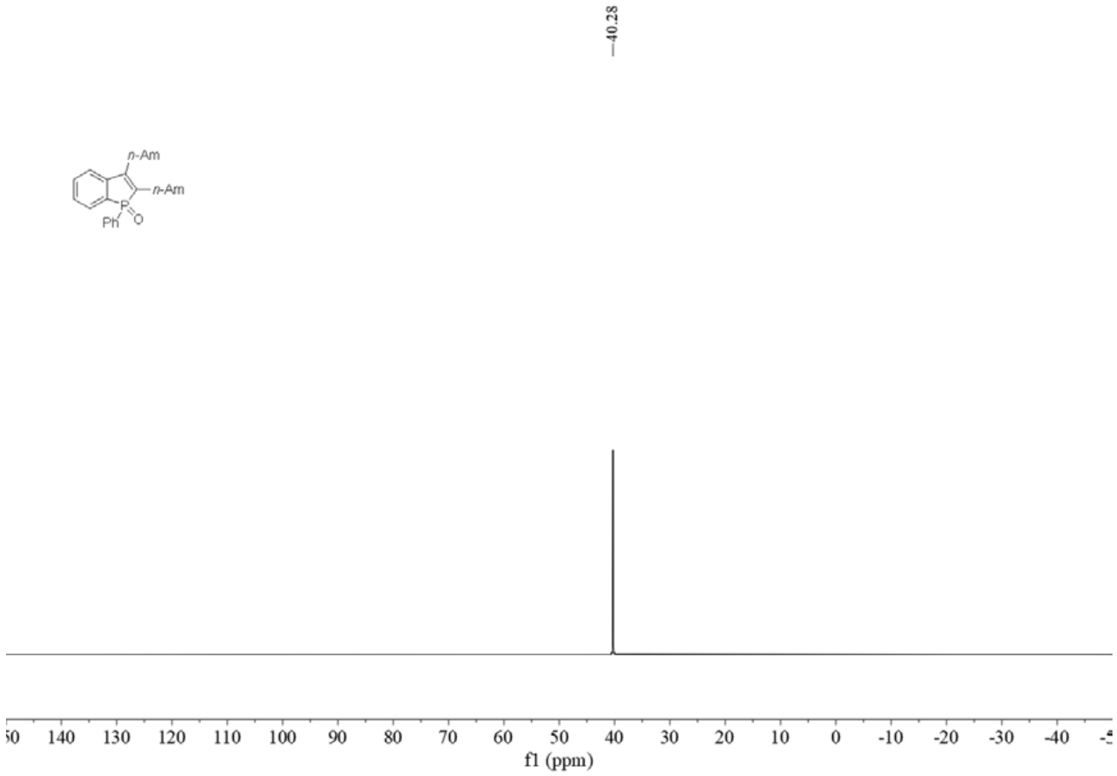
^{31}P NMR ($CDCl_3$-*d*) of **3m**



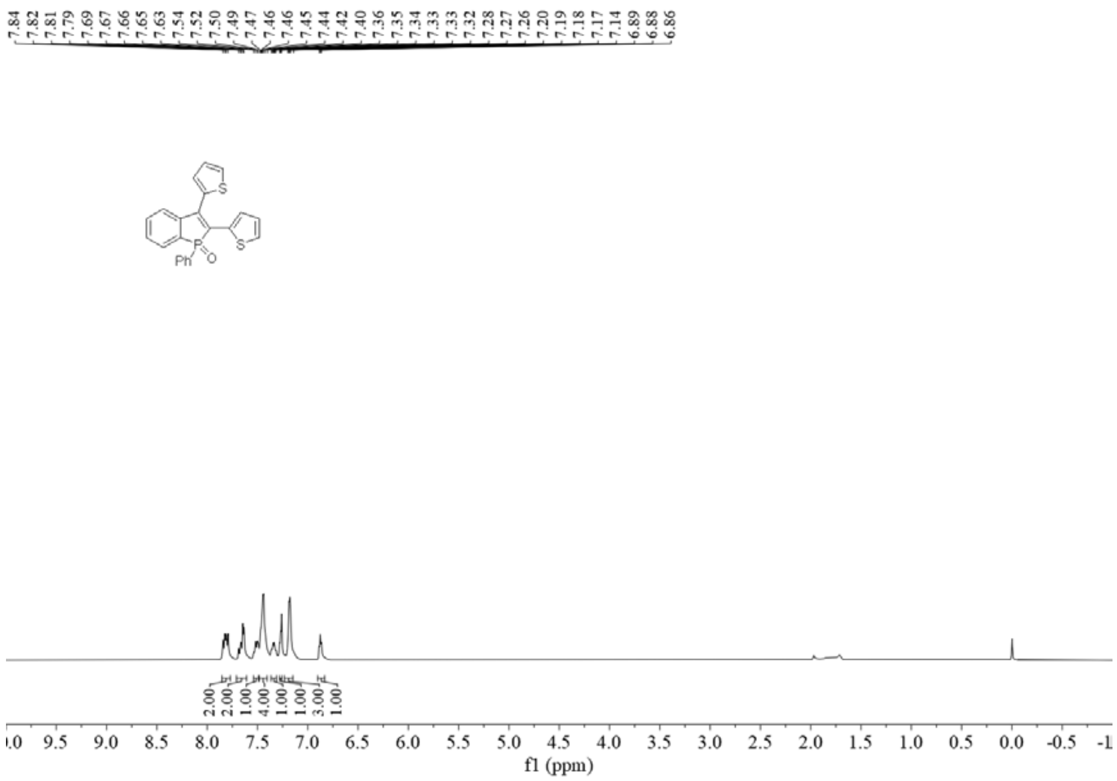
^{1}H NMR ($CDCl_3$-*d*) of **3n**



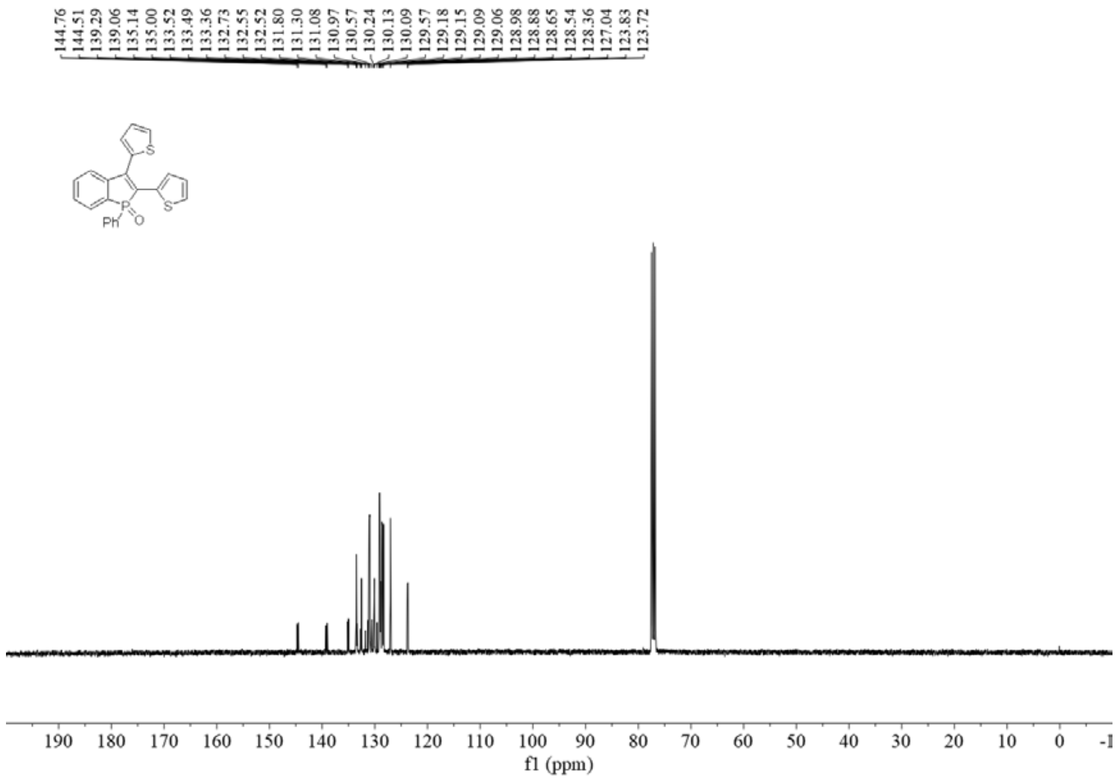
^{13}C NMR ($CDCl_3$-*d*) of **3n**



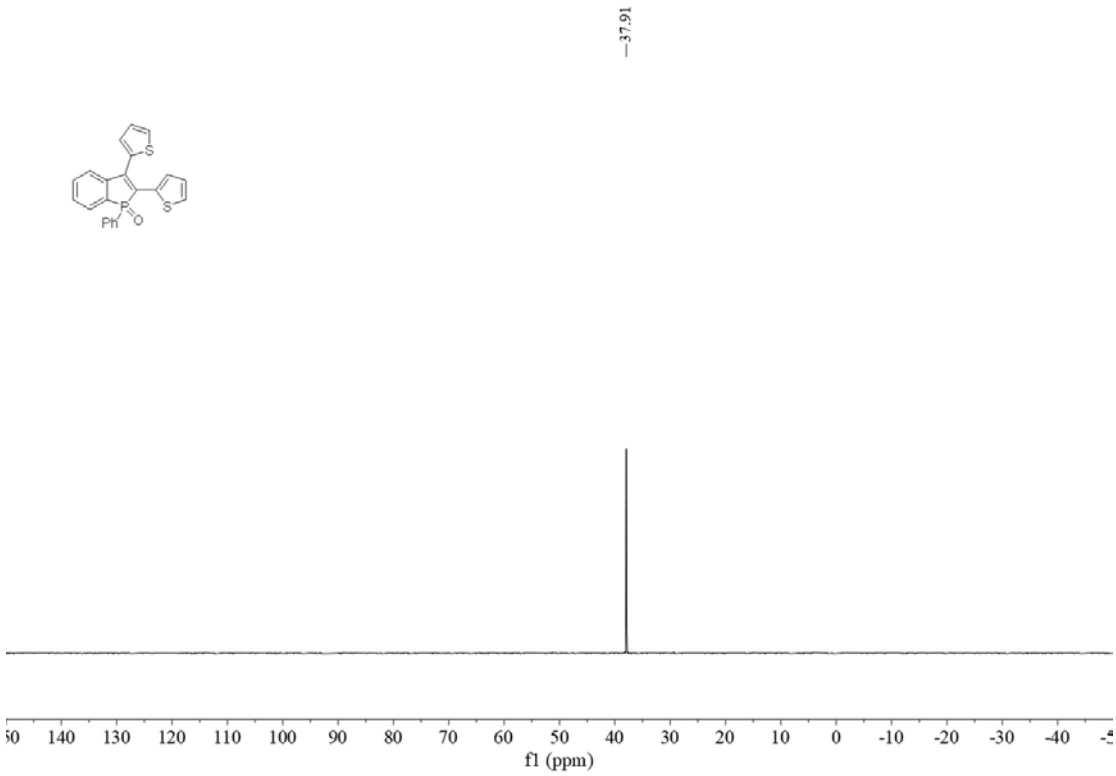
^{31}P NMR ($CDCl_3$-*d*) of **3n**



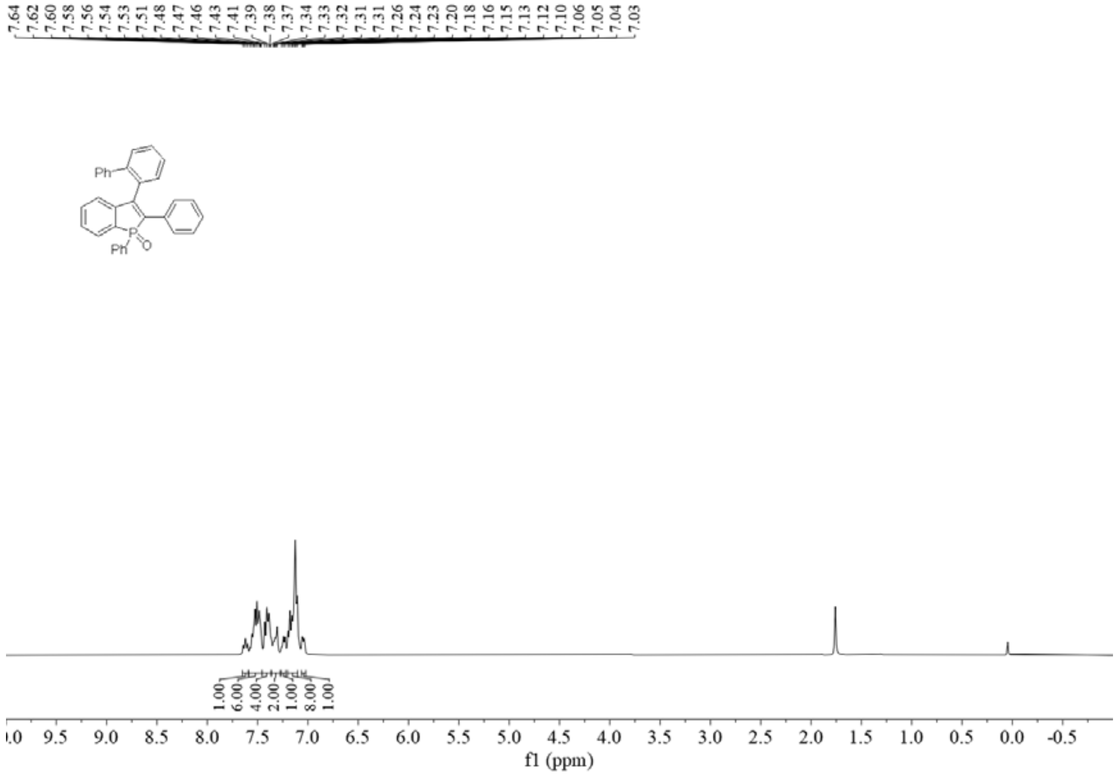
^{1}H NMR ($CDCl_3$-*d*) of **3o**



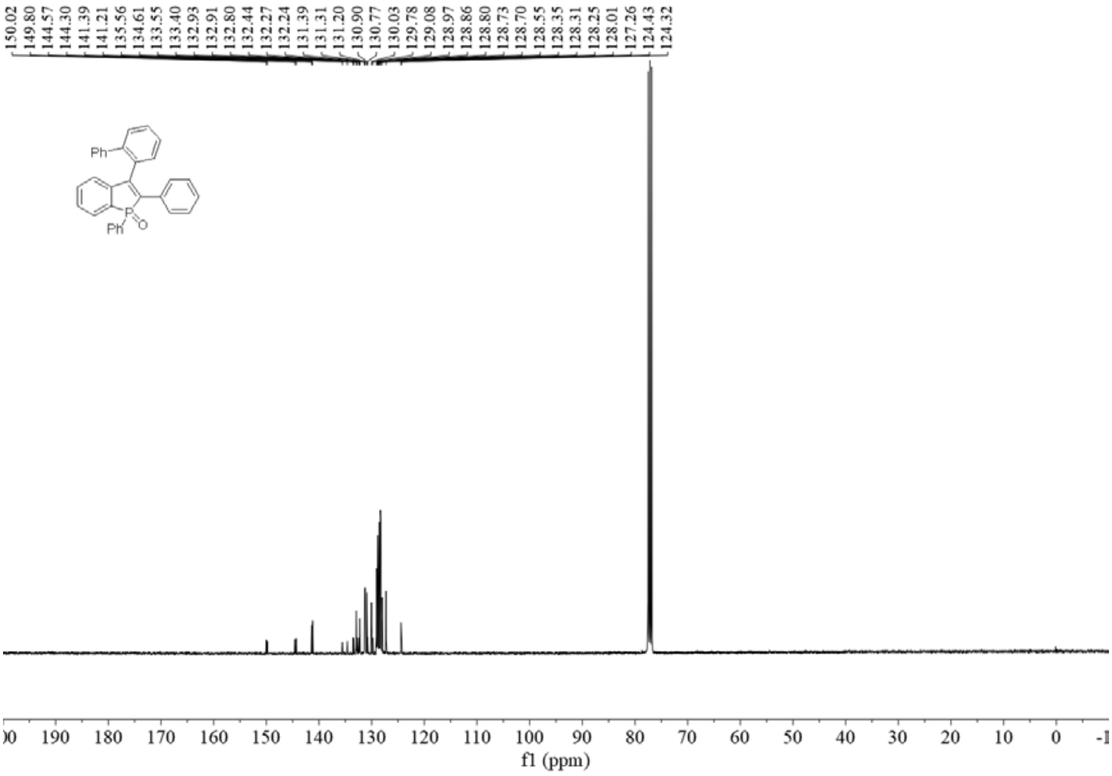
^{13}C NMR ($CDCl_3$-*d*) of **3o**



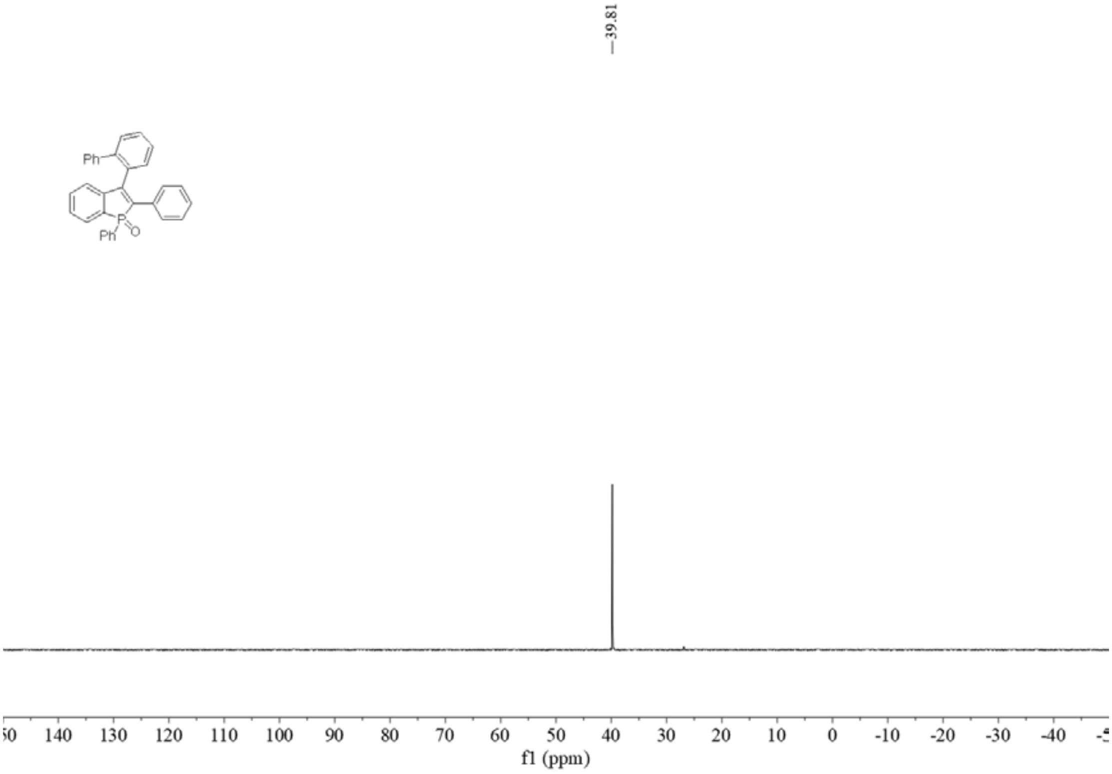
^{31}P NMR ($CDCl_3$-*d*) of **3o**



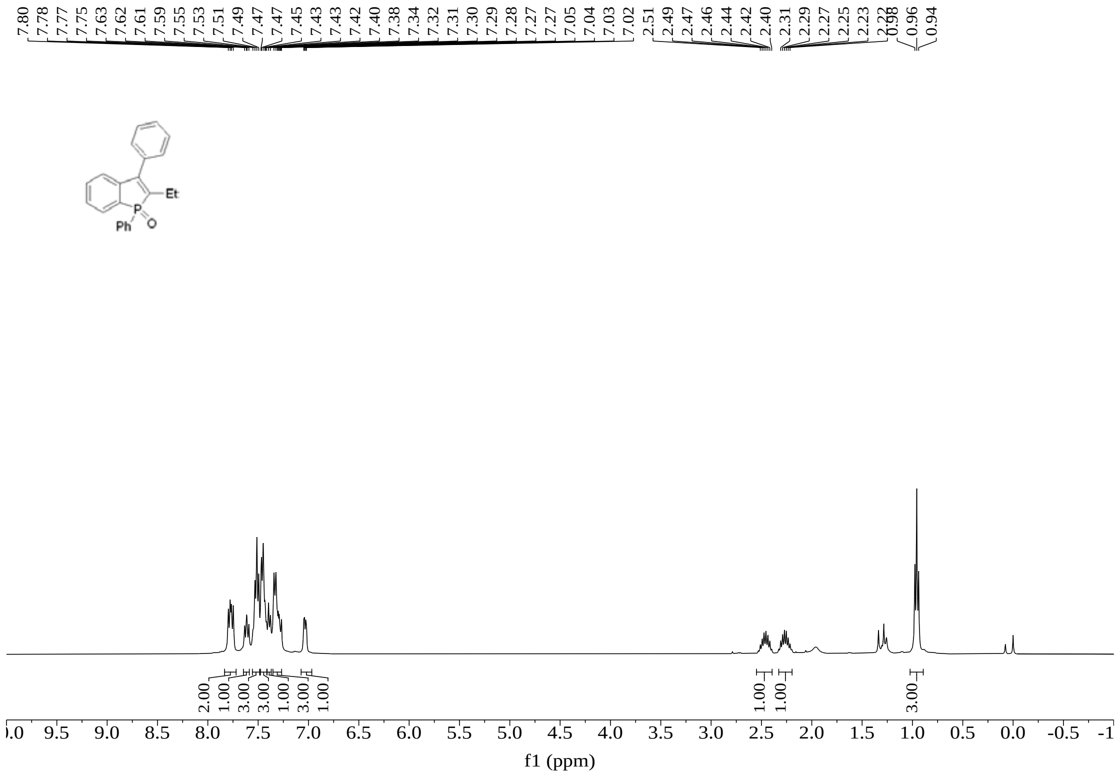
^{1}H NMR ($CDCl_3$-*d*) of **3p**



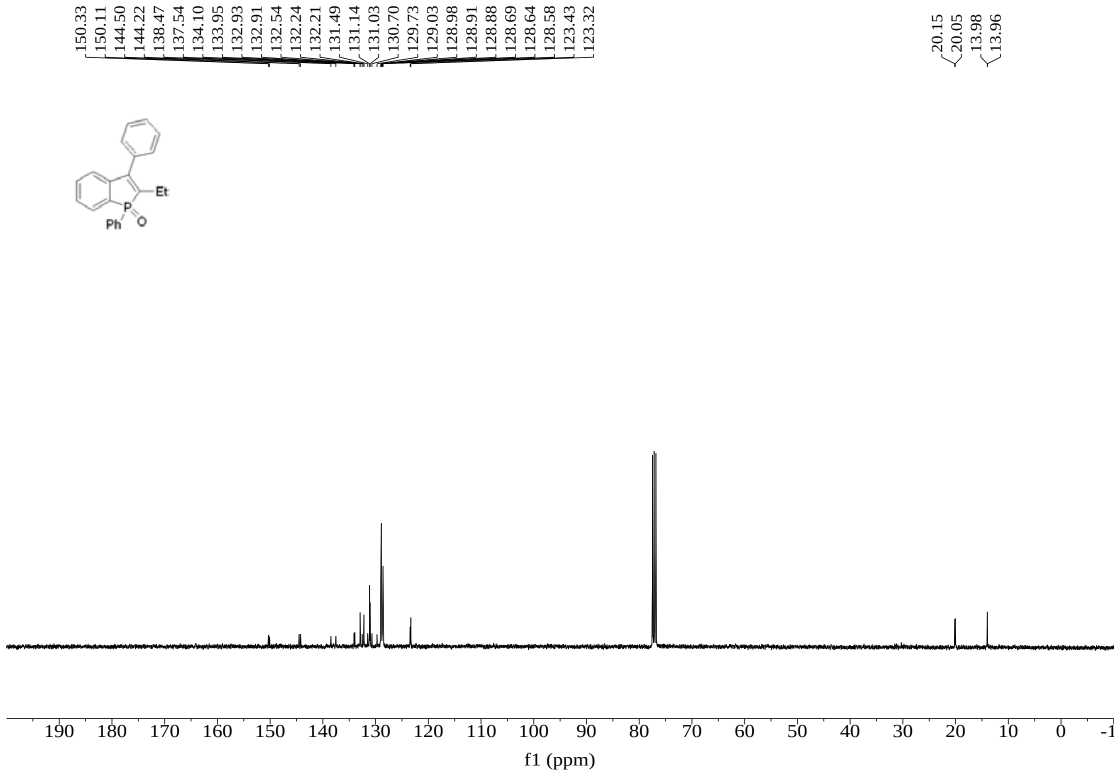
^{13}C NMR ($CDCl_3$-*d*) of **3p**



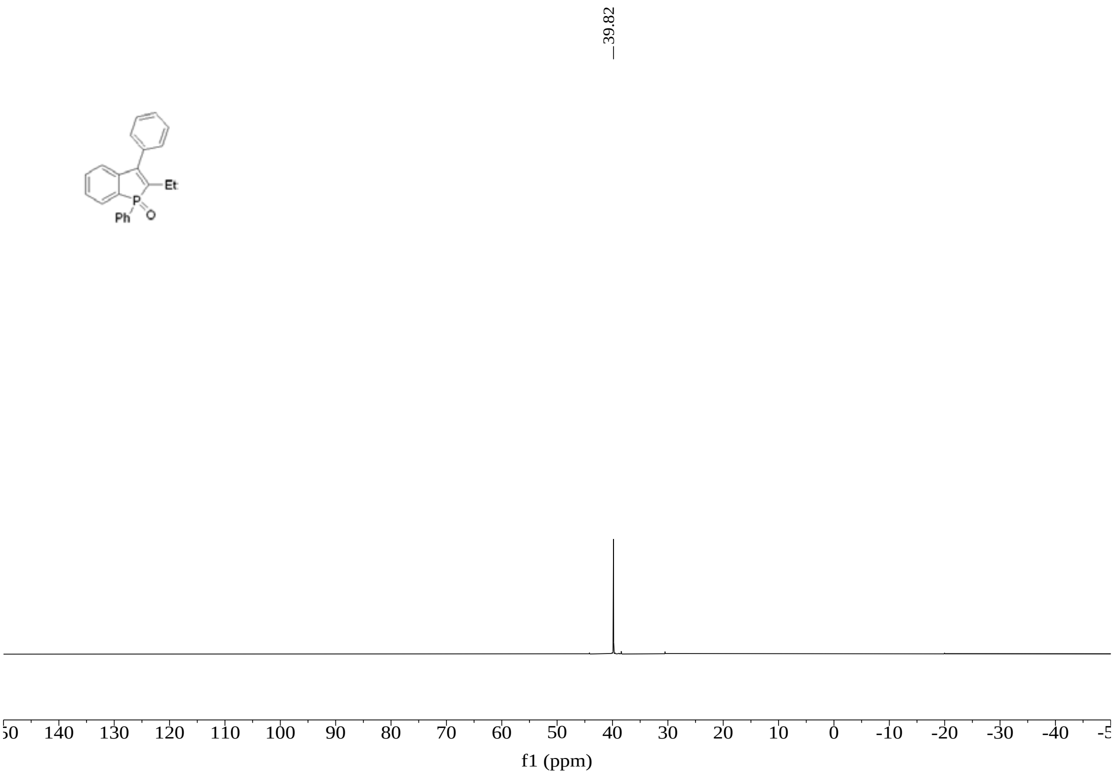
^{31}P NMR ($CDCl_3$-*d*) of **3p**



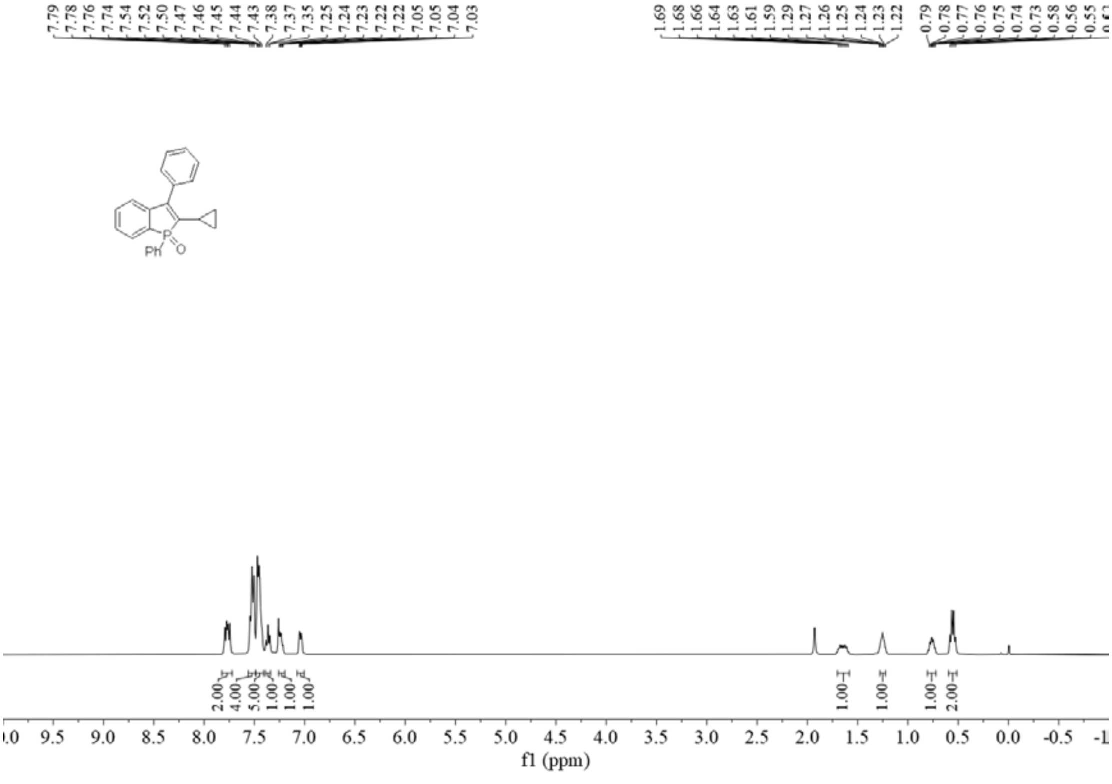
^{1}H NMR ($CDCl_3$-*d*) of **3q**



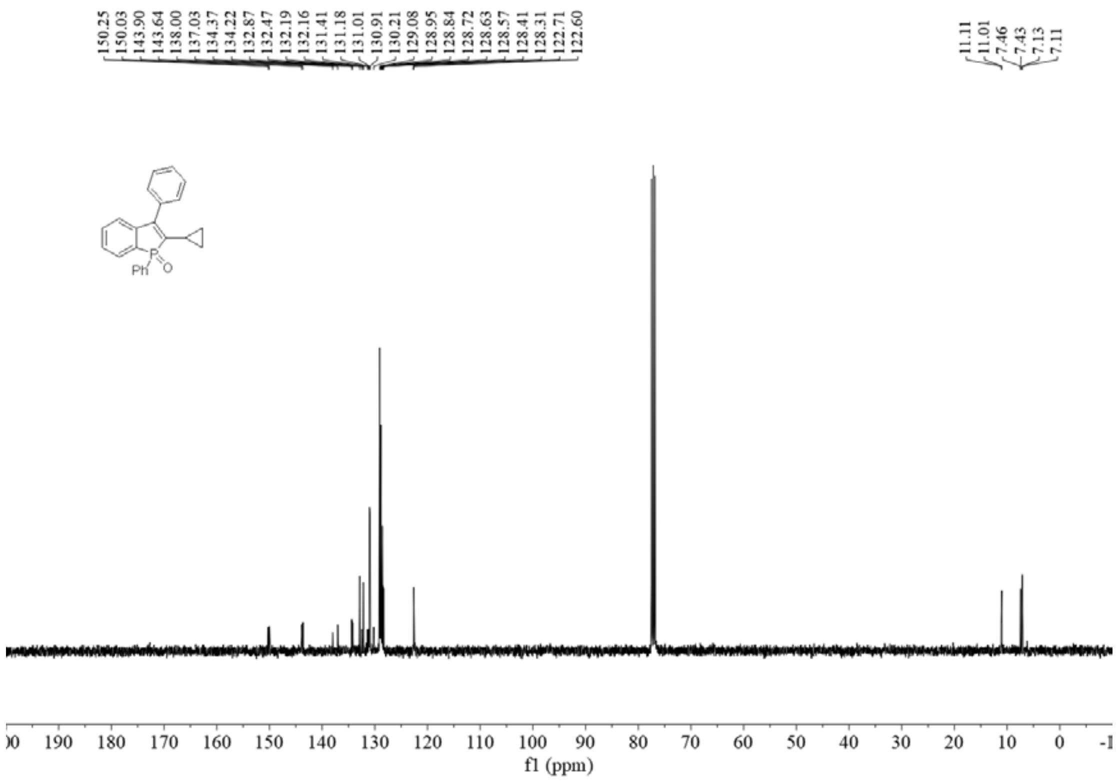
^{13}C NMR ($CDCl_3$-*d*) of **3q**



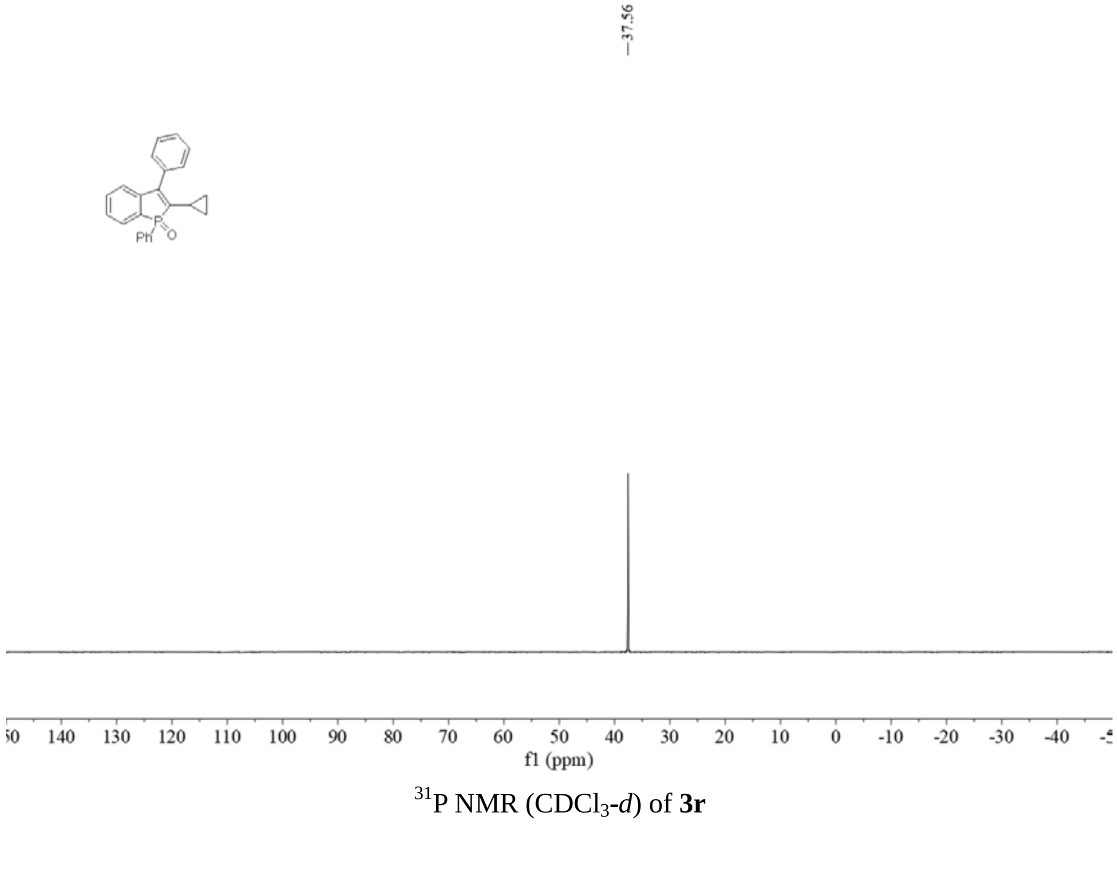
^{31}P NMR ($CDCl_3$-*d*) of **3q**



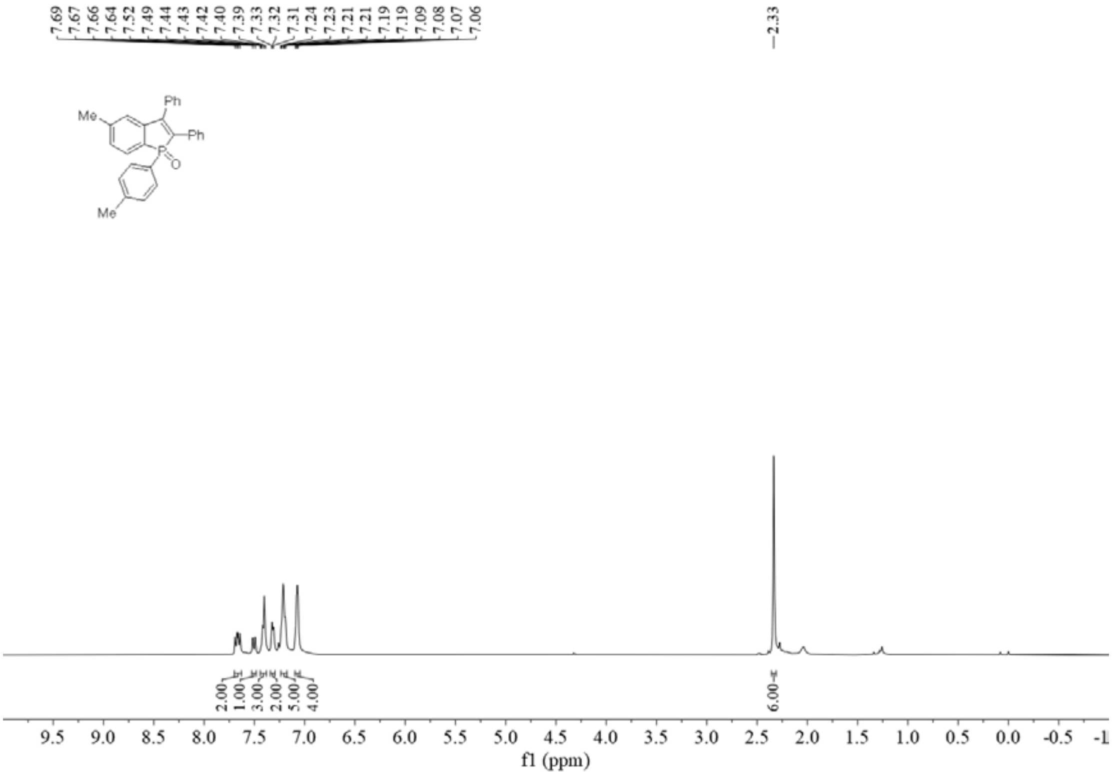
^{1}H NMR ($CDCl_3$-*d*) of **3r**



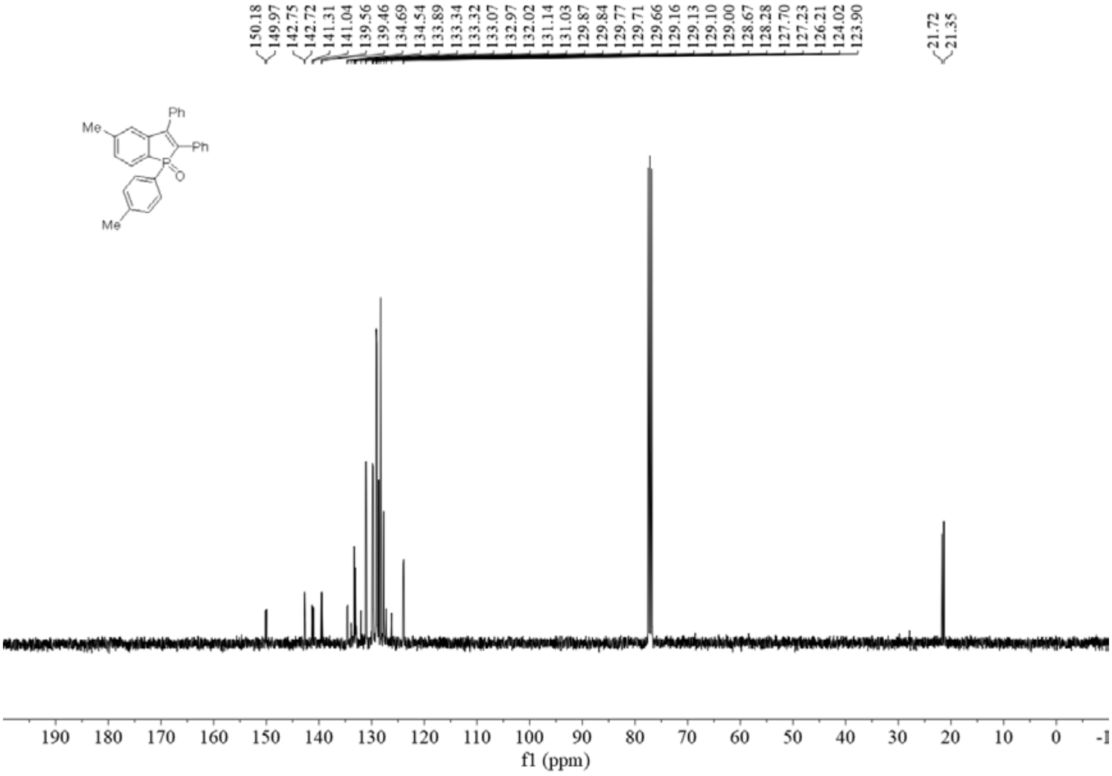
^{13}C NMR ($CDCl_3$-*d*) of **3r**



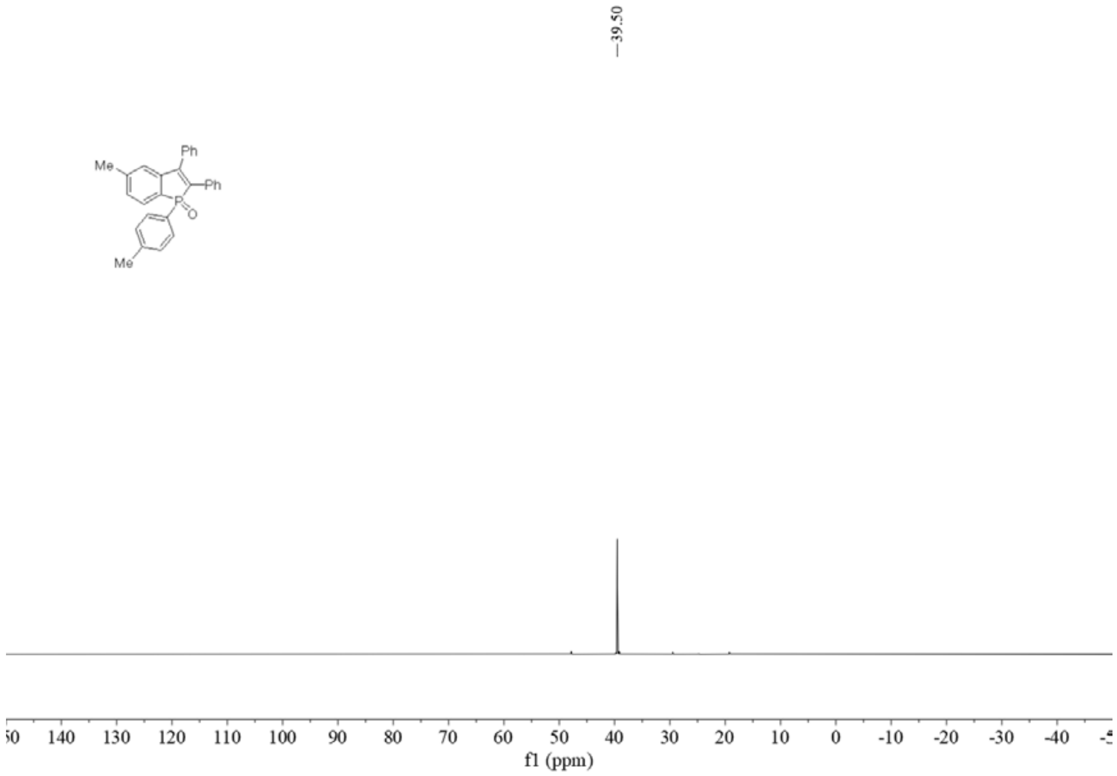
^{31}P NMR ($CDCl_3$-*d*) of **3r**



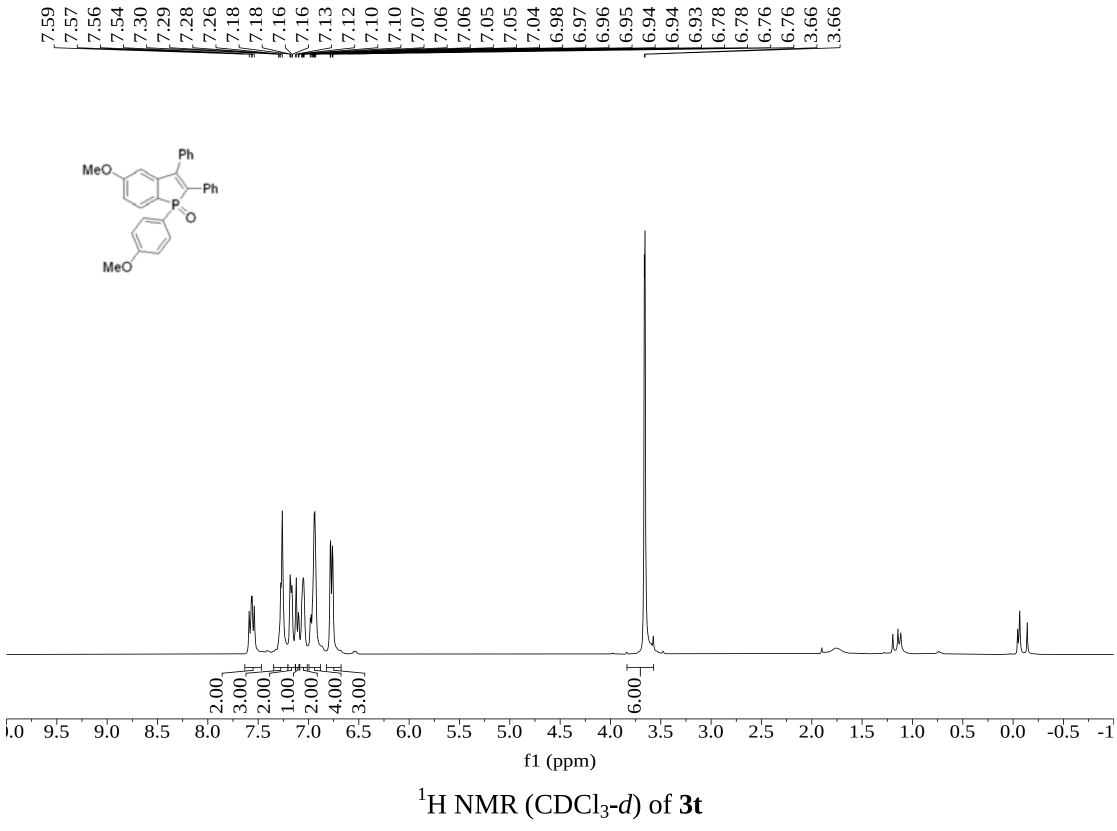
^{1}H NMR (CDCl$_3$-*d*) of **3s**



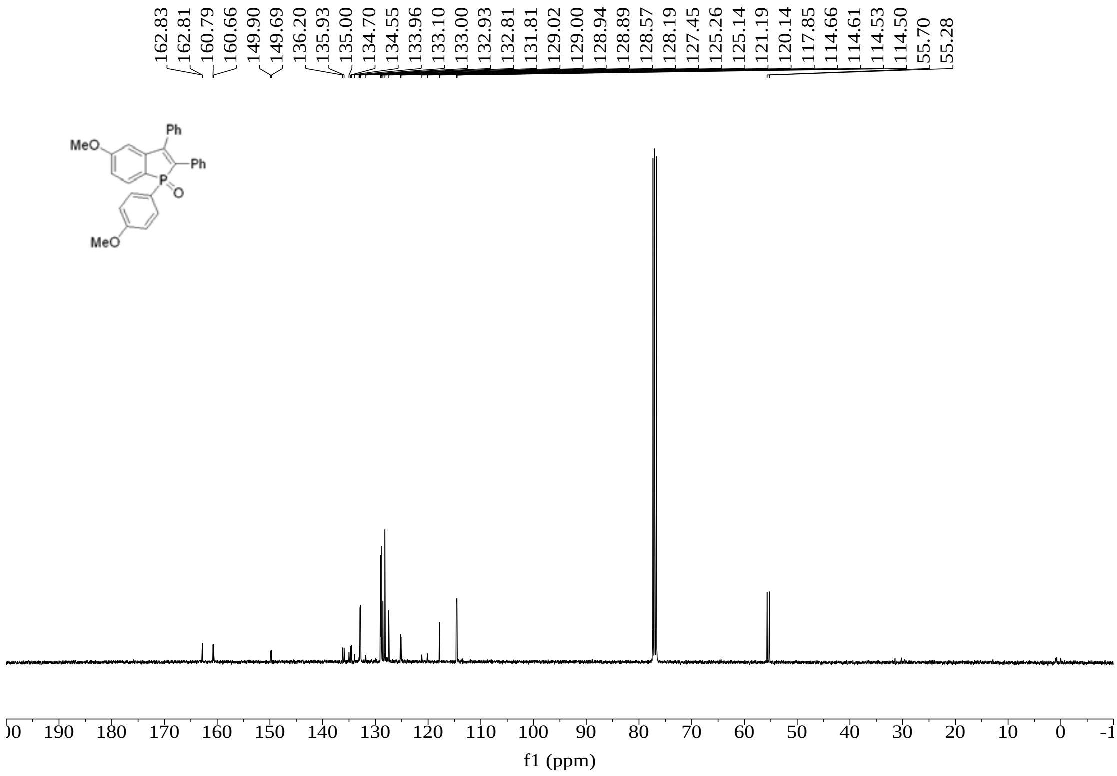
^{13}C NMR (CDCl$_3$-*d*) of **3s**



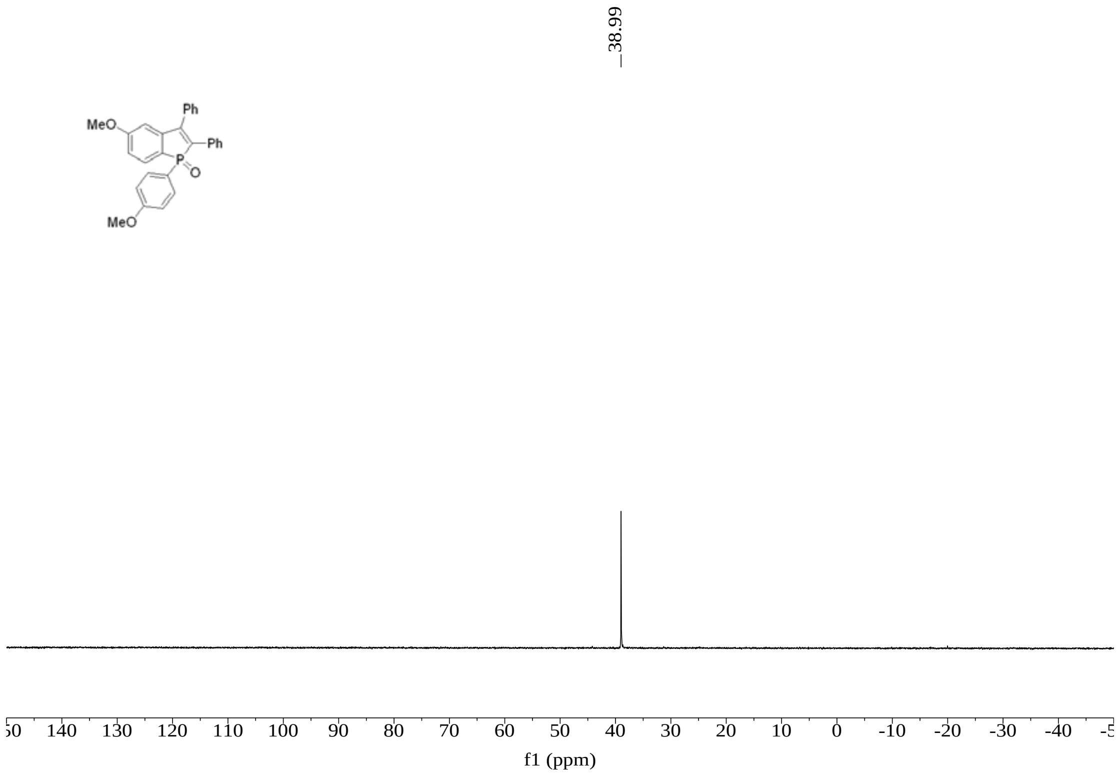
^{31}P NMR ($CDCl_3$-*d*) of **3s**



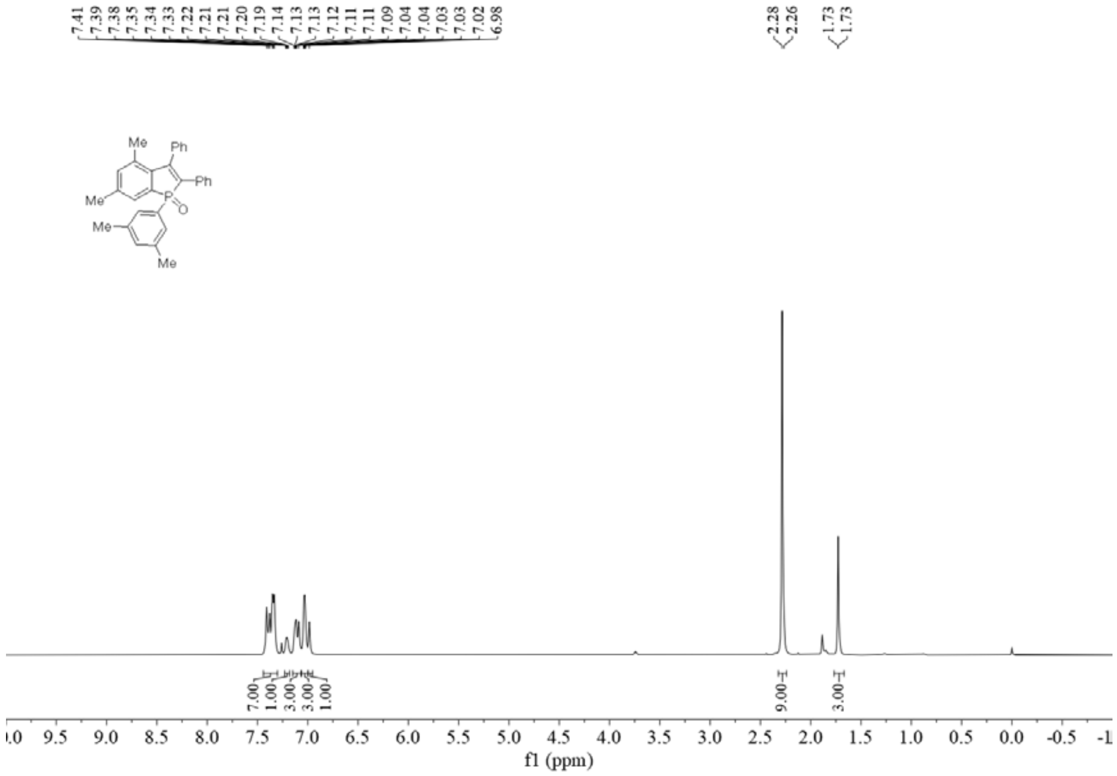
^{1}H NMR ($CDCl_3$-*d*) of **3t**



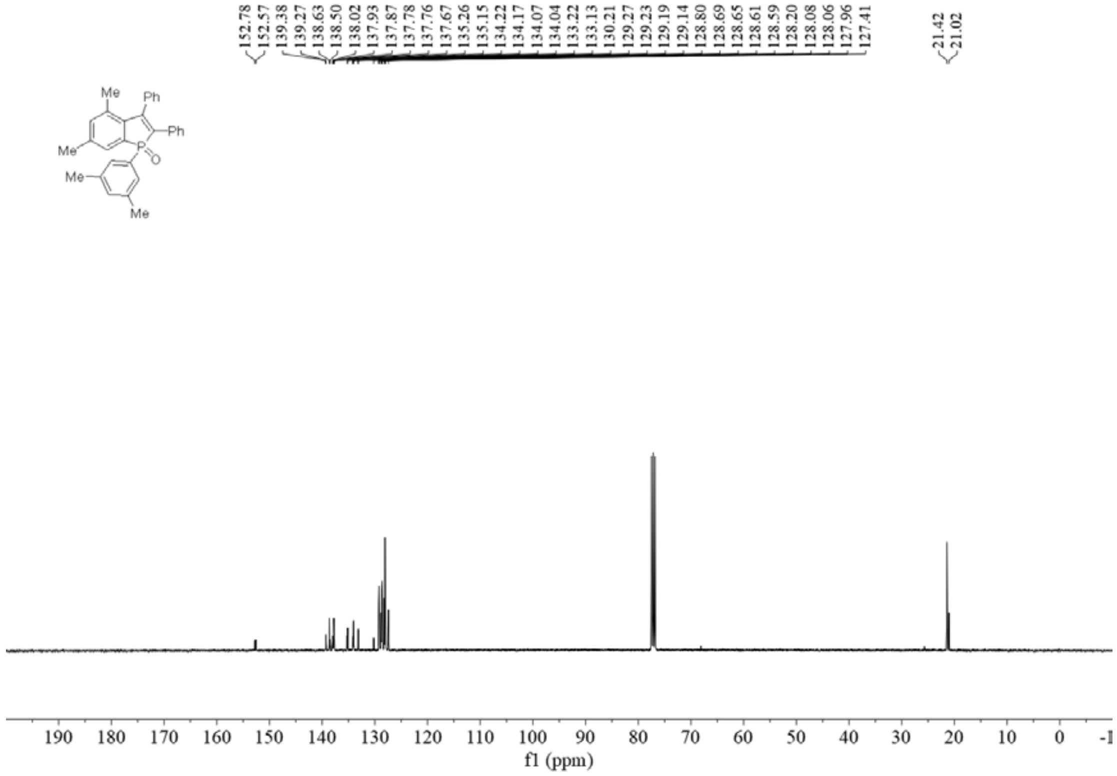
^{13}C NMR ($CDCl_3$-*d*) of **3t**



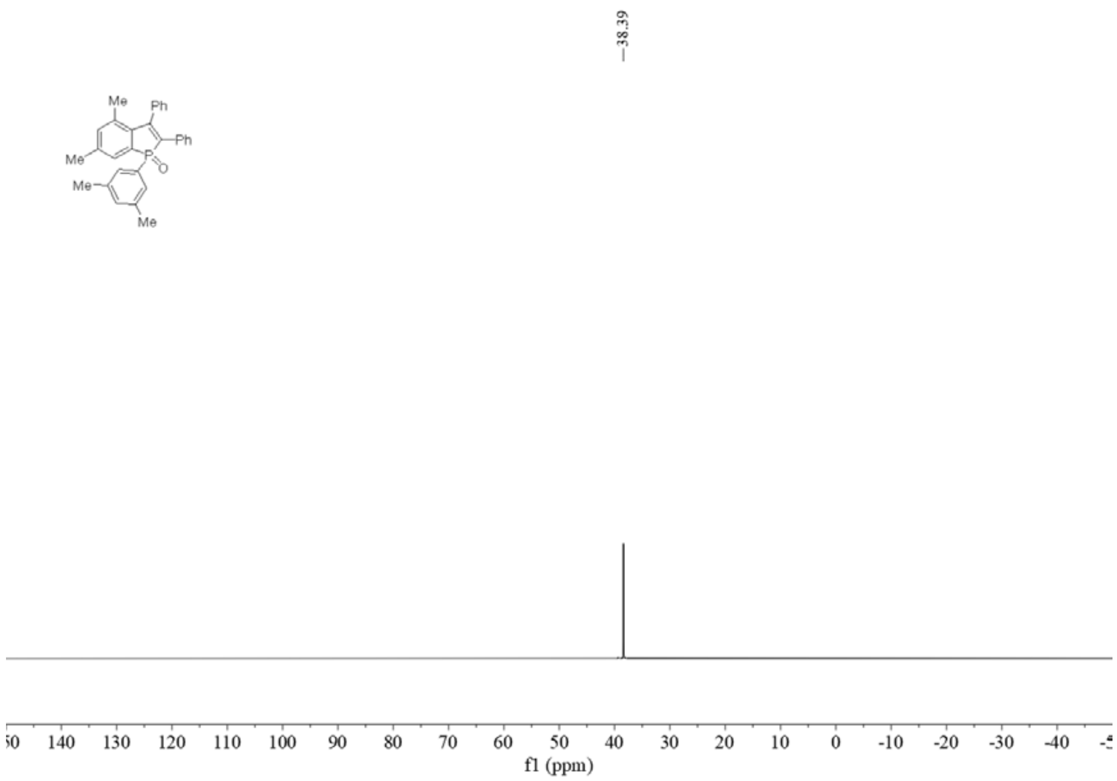
^{31}P NMR ($CDCl_3$-*d*) of **3t**



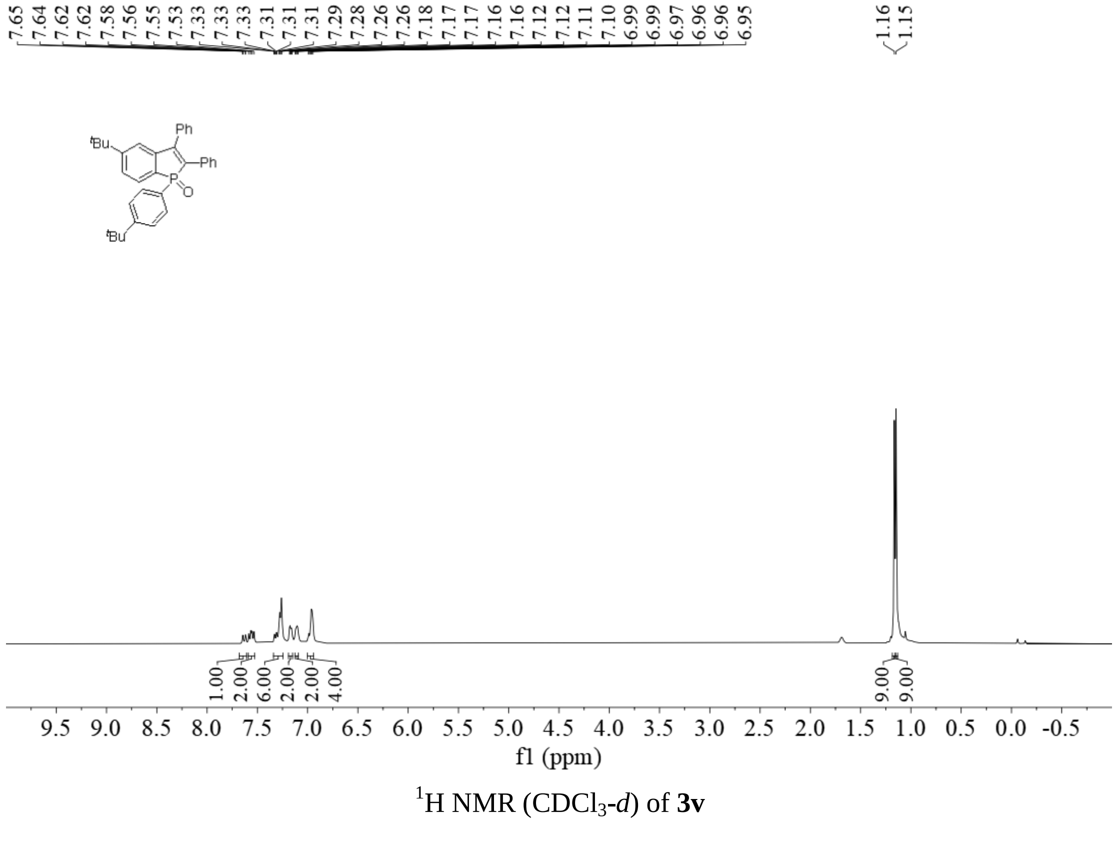
[1]H NMR ($CDCl_3$-*d*) of **3u**



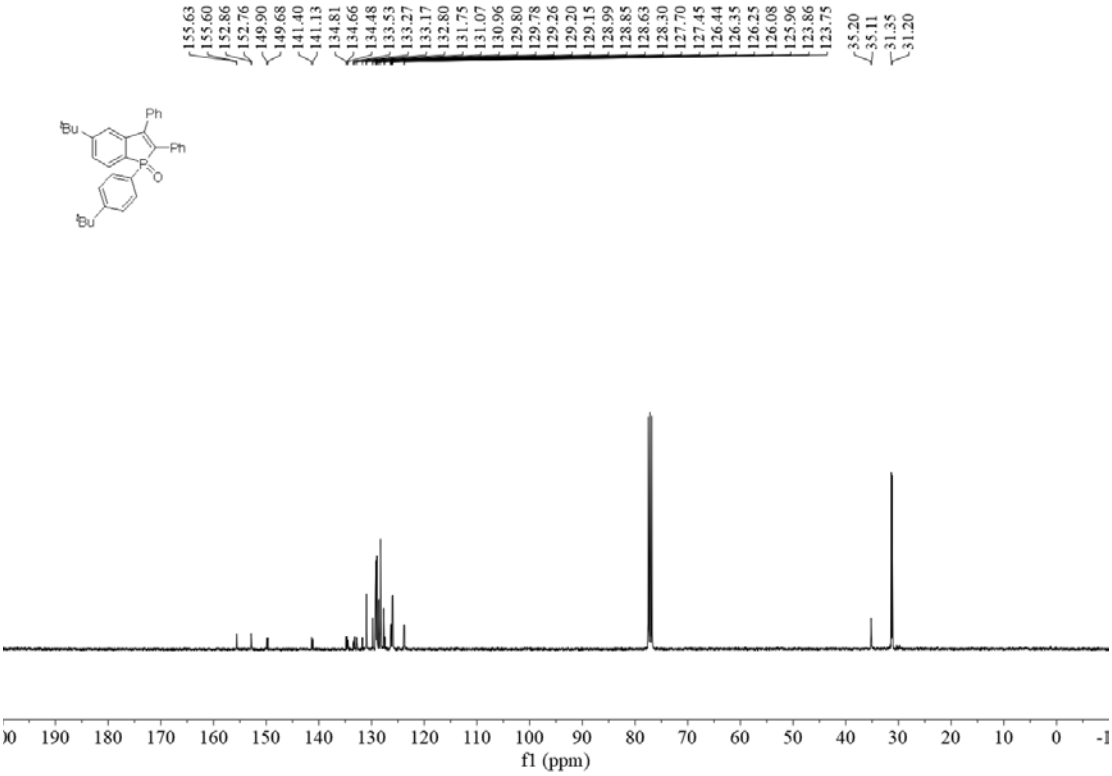
[13]C NMR ($CDCl_3$-*d*) of **3u**



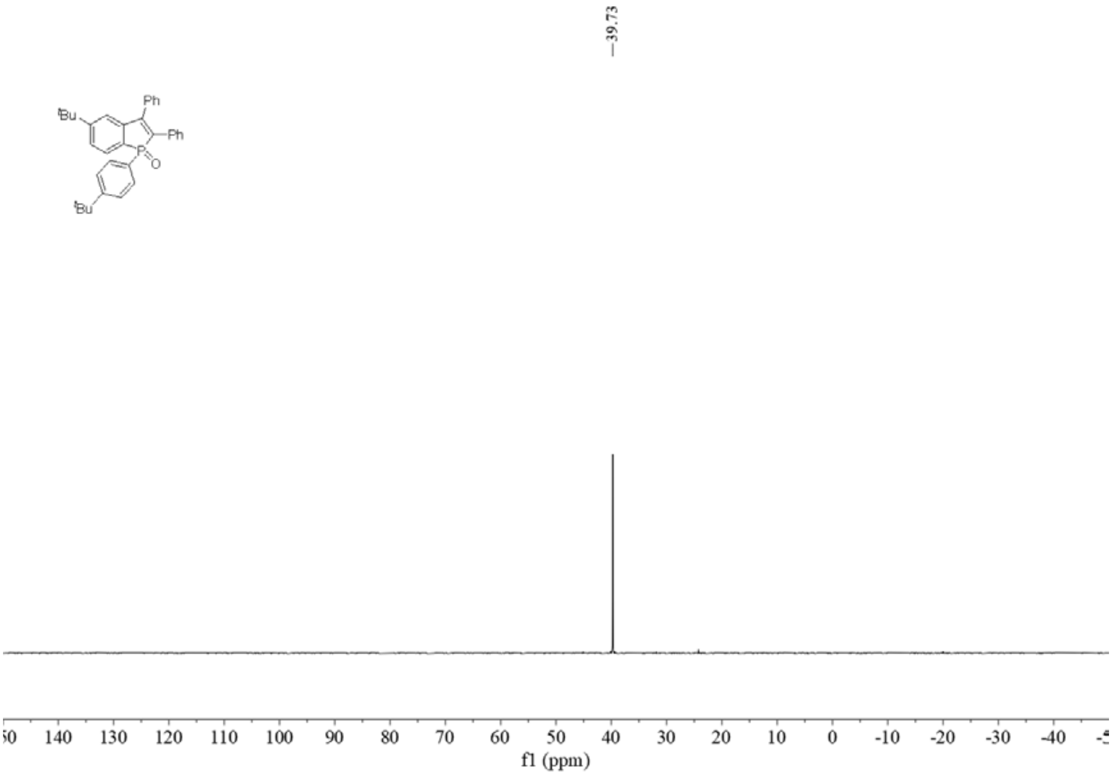
^{31}P NMR ($CDCl_3$-*d*) of **3u**



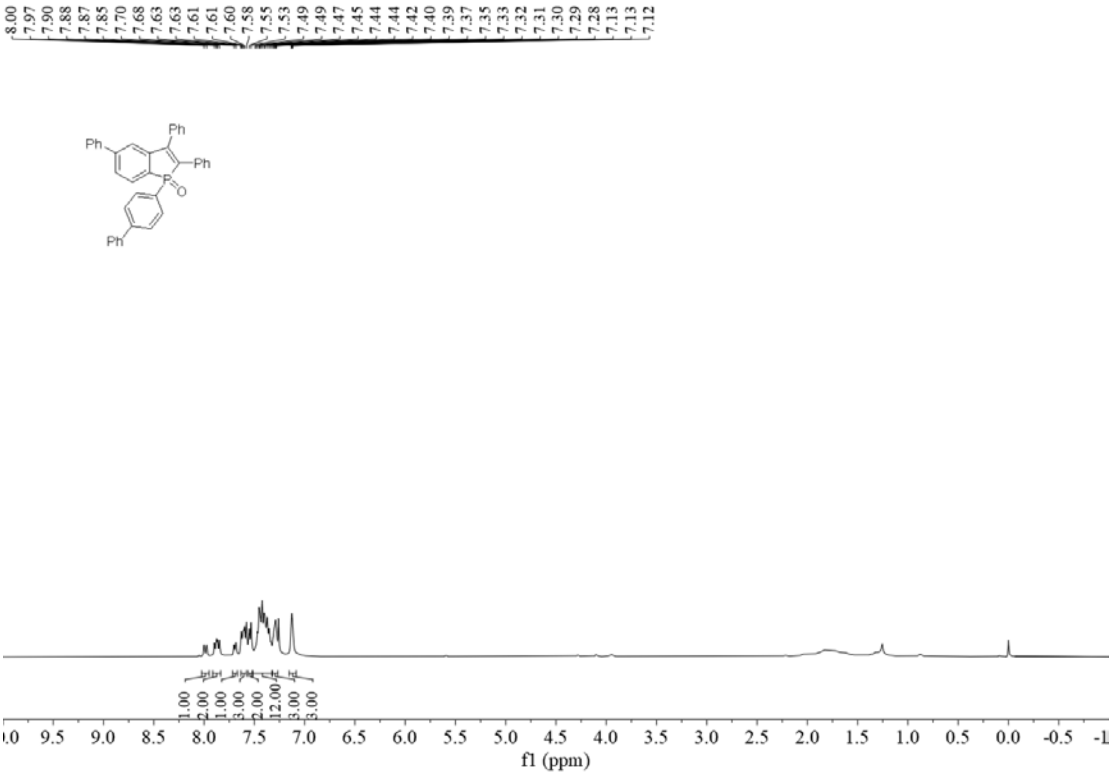
^{1}H NMR ($CDCl_3$-*d*) of **3v**



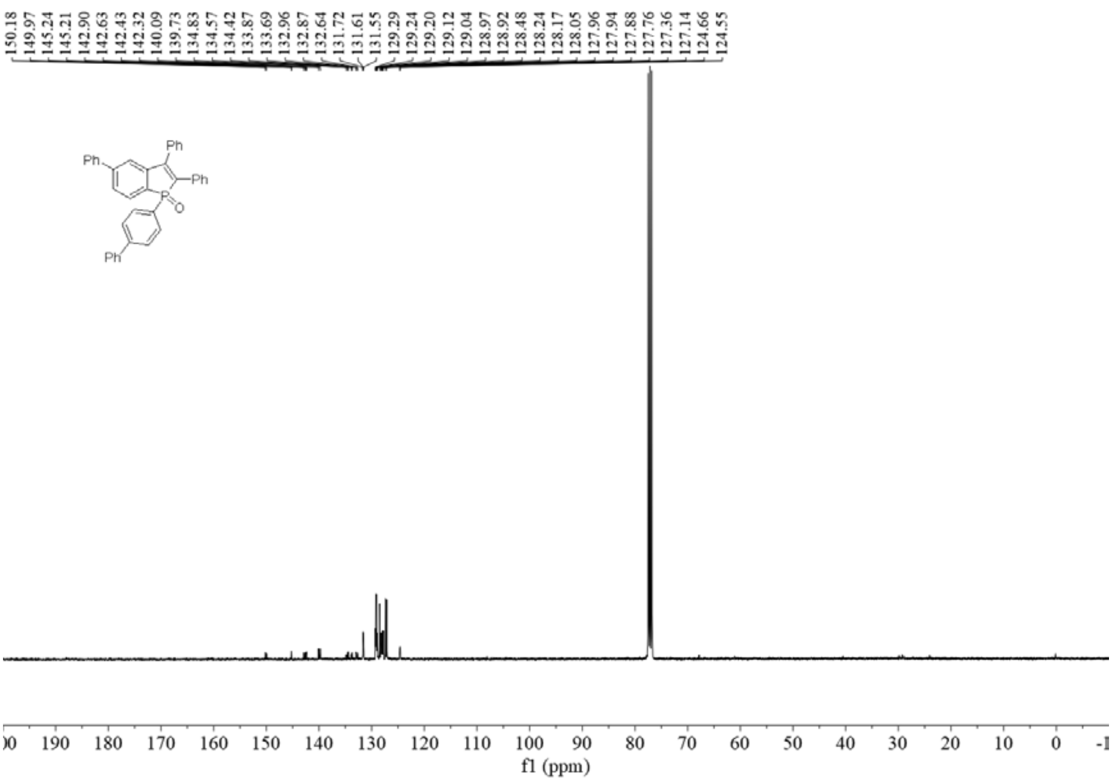
^{13}C NMR ($CDCl_3$-*d*) of **3v**



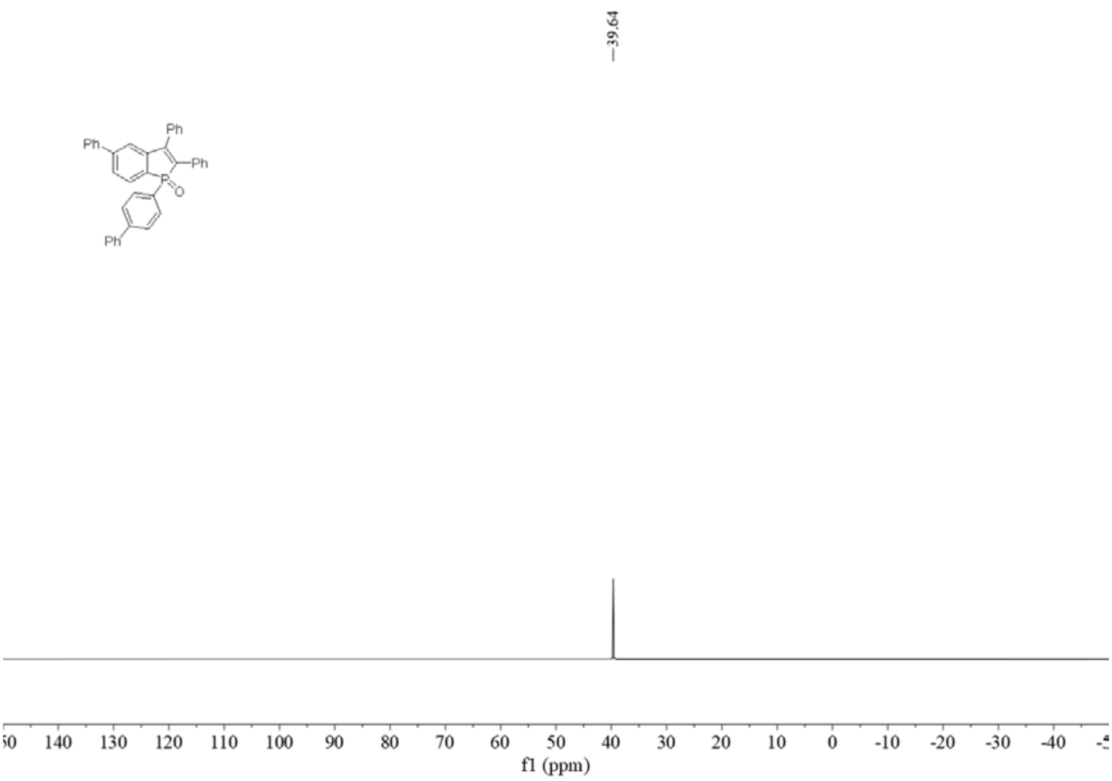
^{31}P NMR ($CDCl_3$-*d*) of **3v**



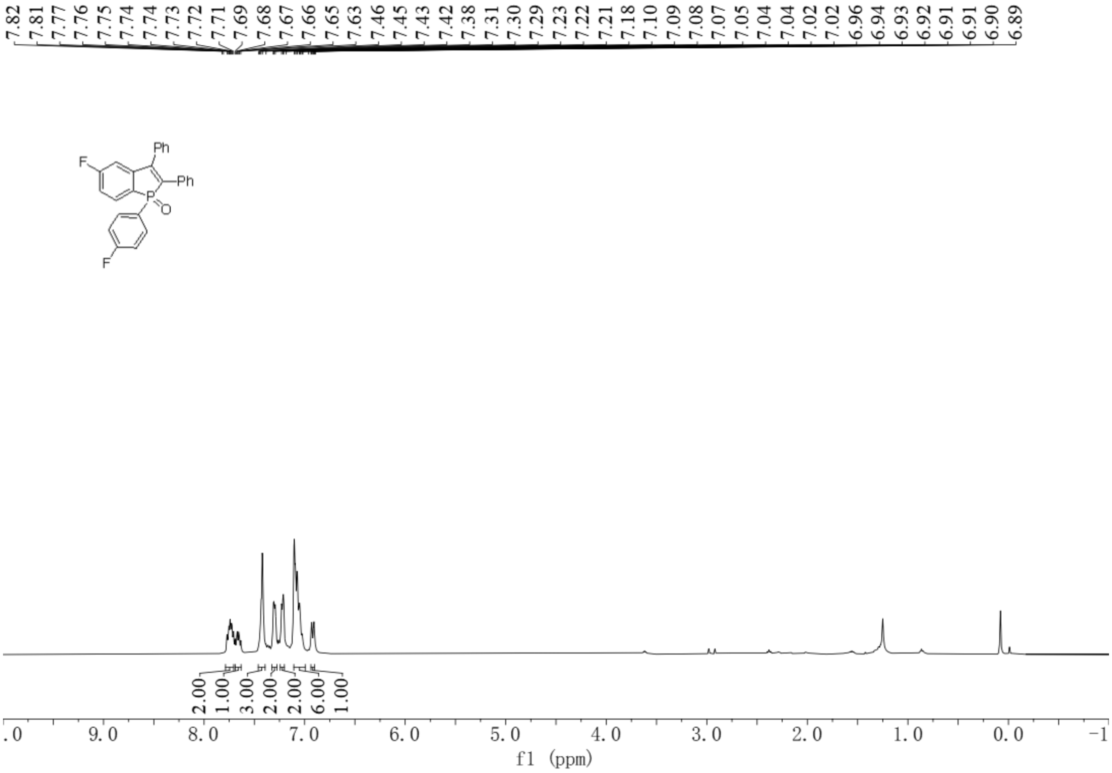
[1]H NMR ($CDCl_3$-*d*) of **3w**



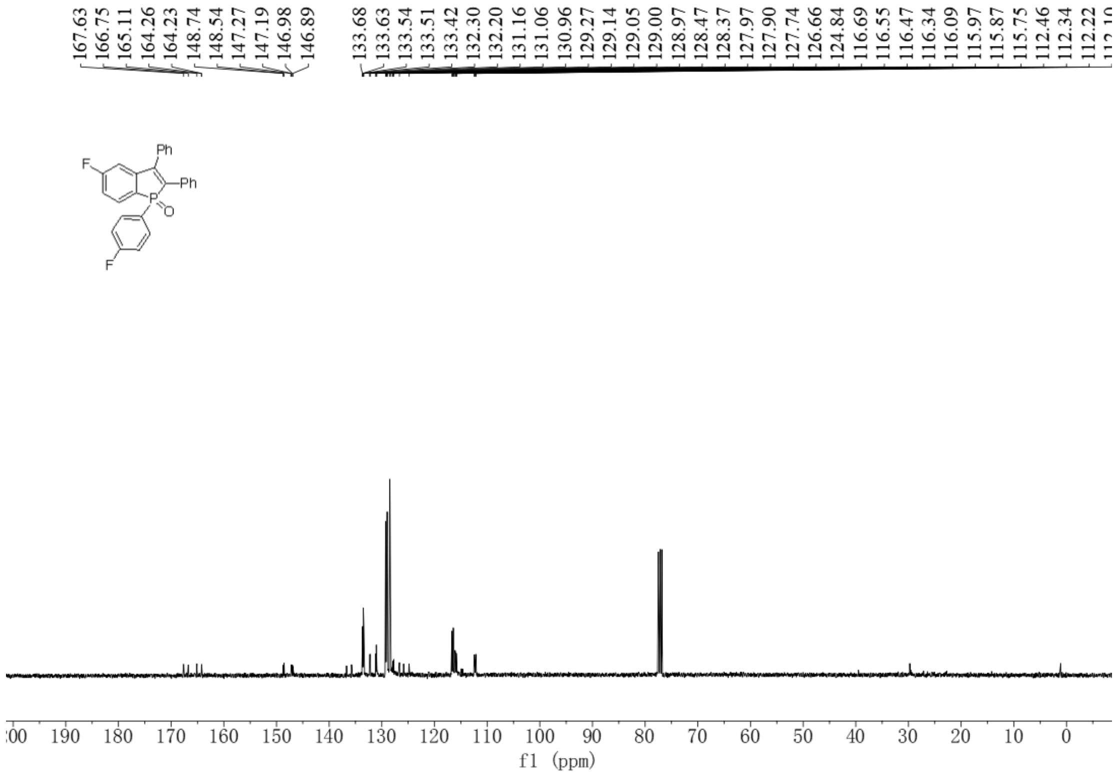
[13]C NMR ($CDCl_3$-*d*) of **3w**



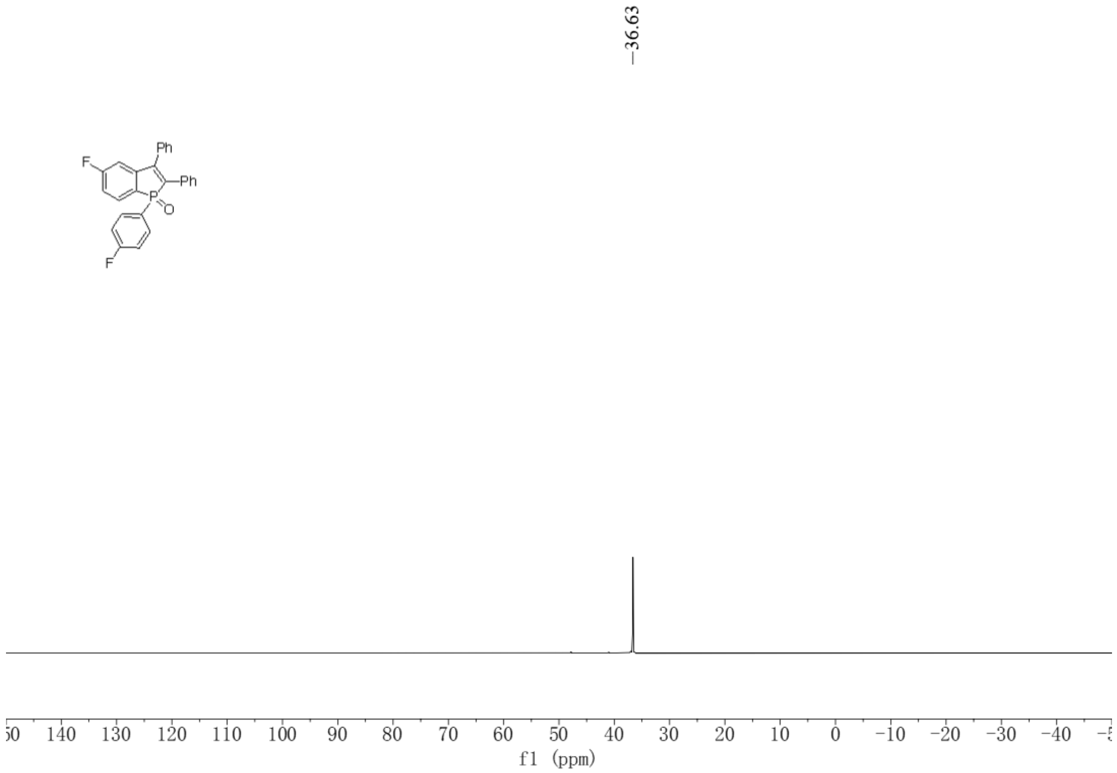
^{31}P NMR ($CDCl_3$-*d*) of **3w**



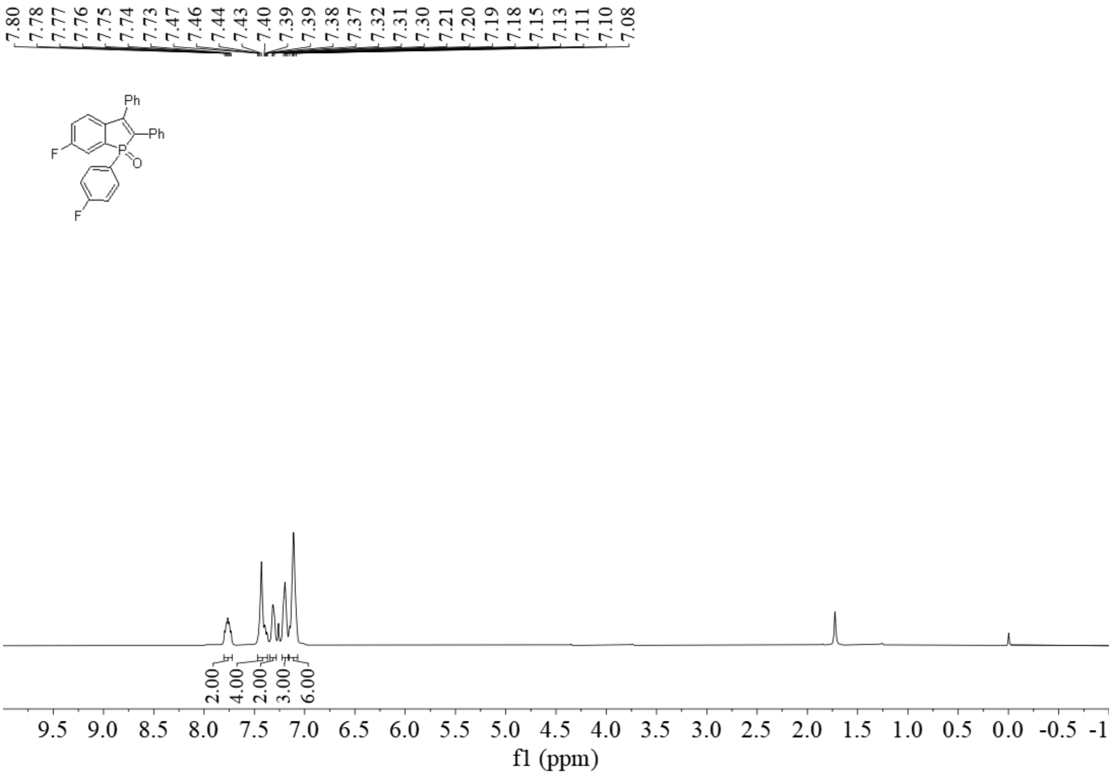
^{1}H NMR ($CDCl_3$-*d*) of **3x**



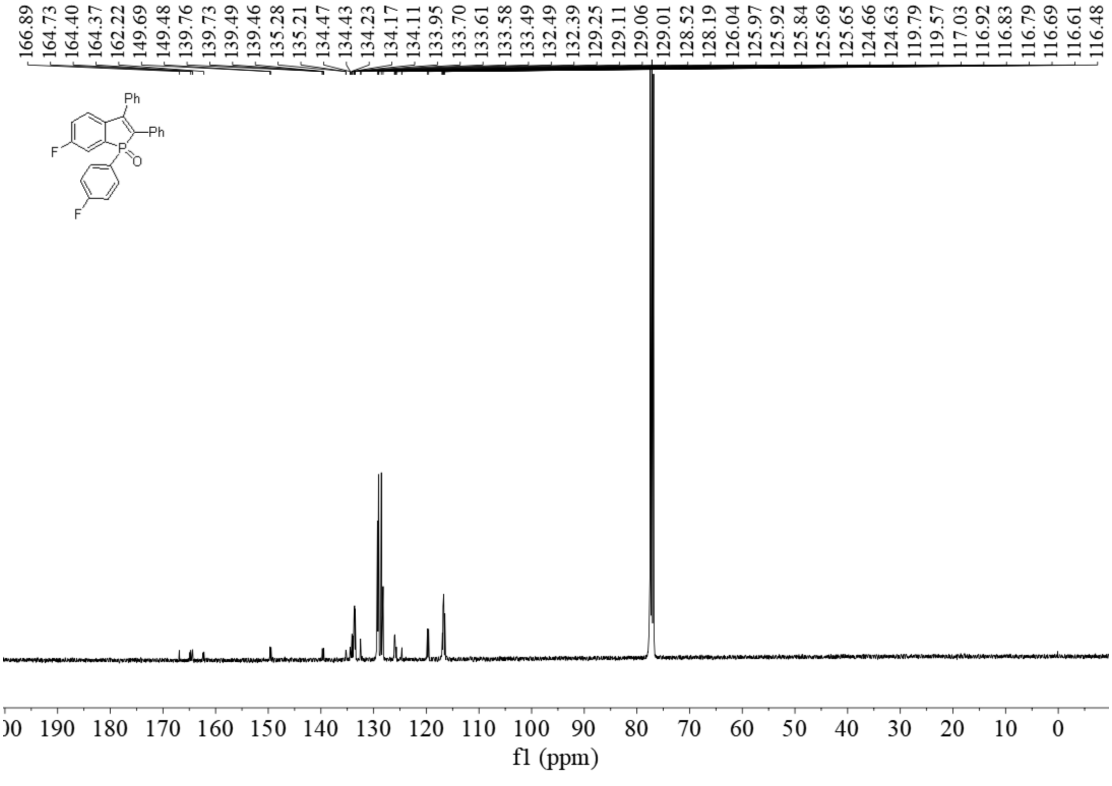
^{13}C NMR (CDCl$_3$-*d*) of **3x**



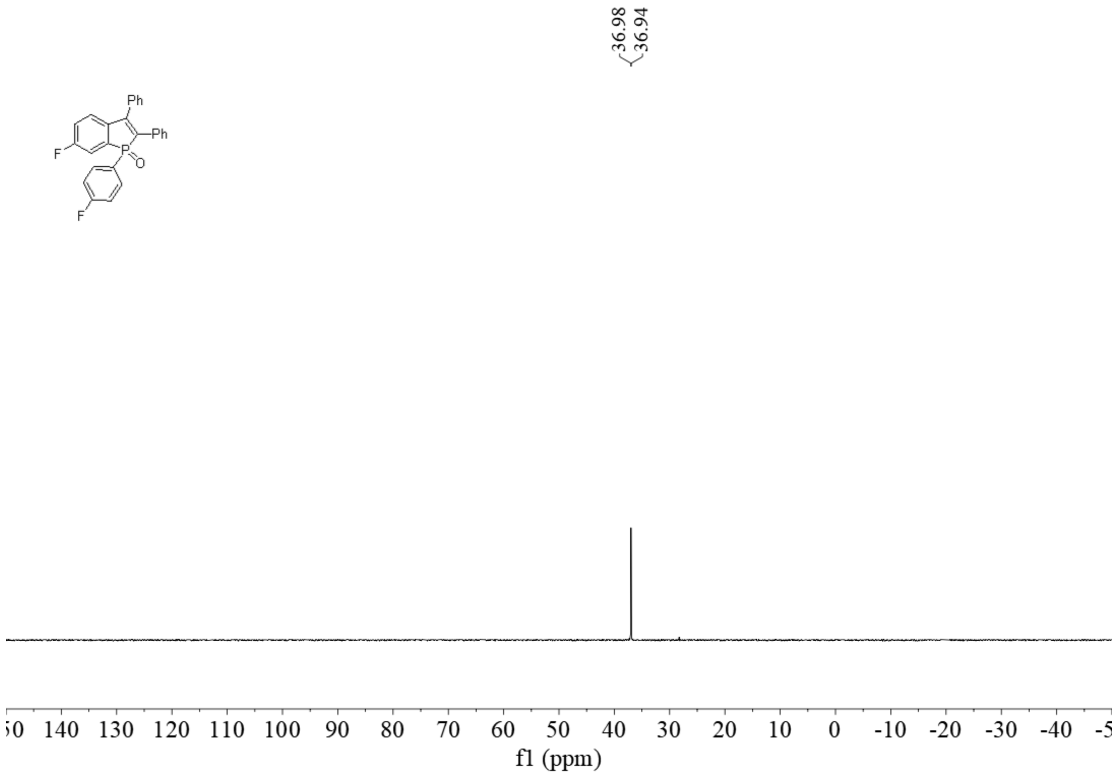
^{31}P NMR (CDCl$_3$-*d*) of **3x**



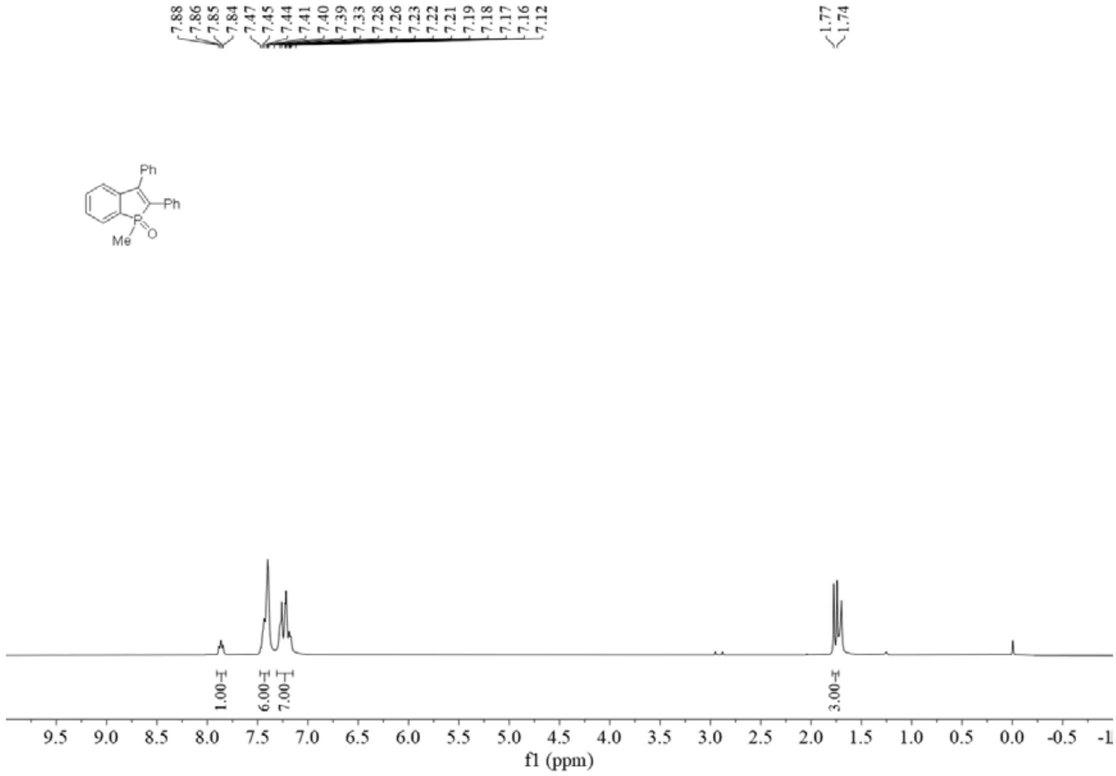
[1]H NMR ($CDCl_3$-*d*) of **3x'**



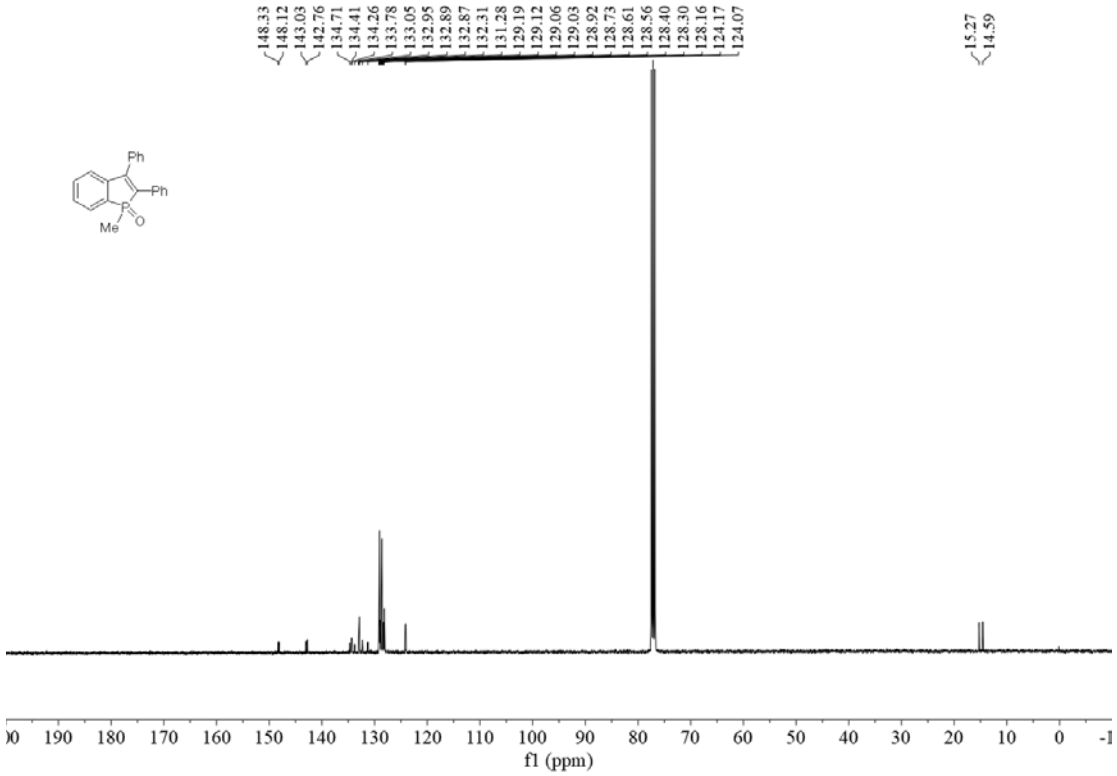
[13]C NMR ($CDCl_3$-*d*) of **3x'**



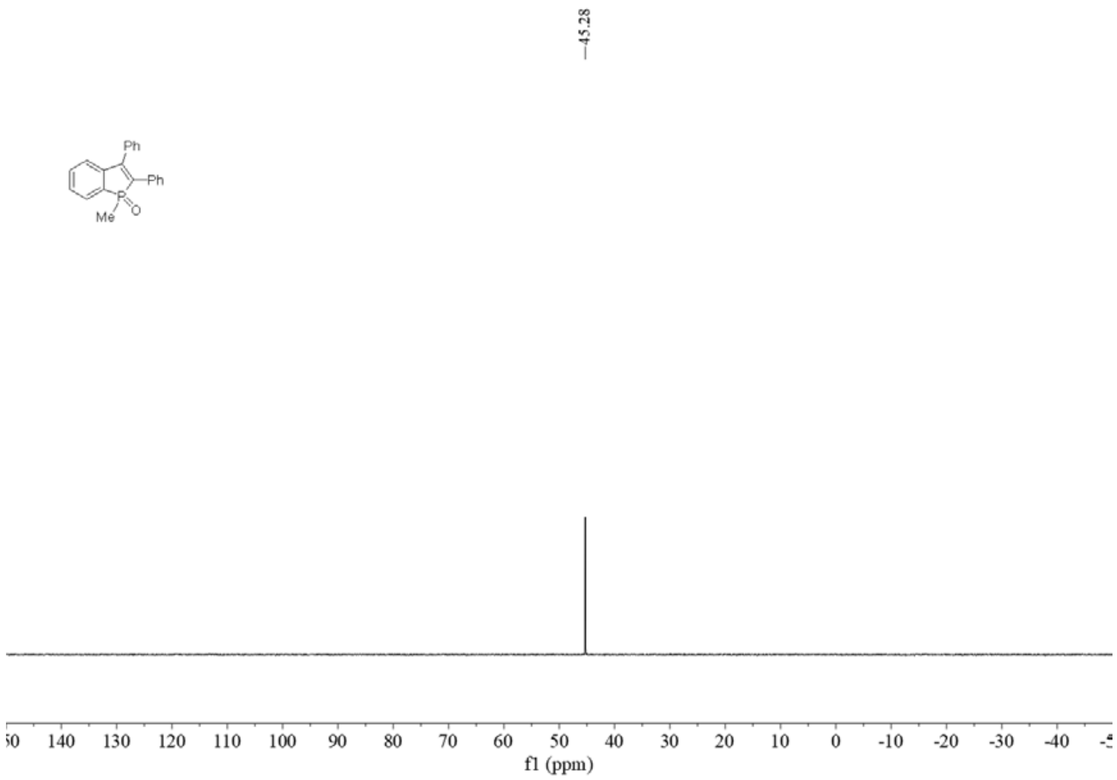
^{31}P NMR ($CDCl_3$-*d*) of **3x'**



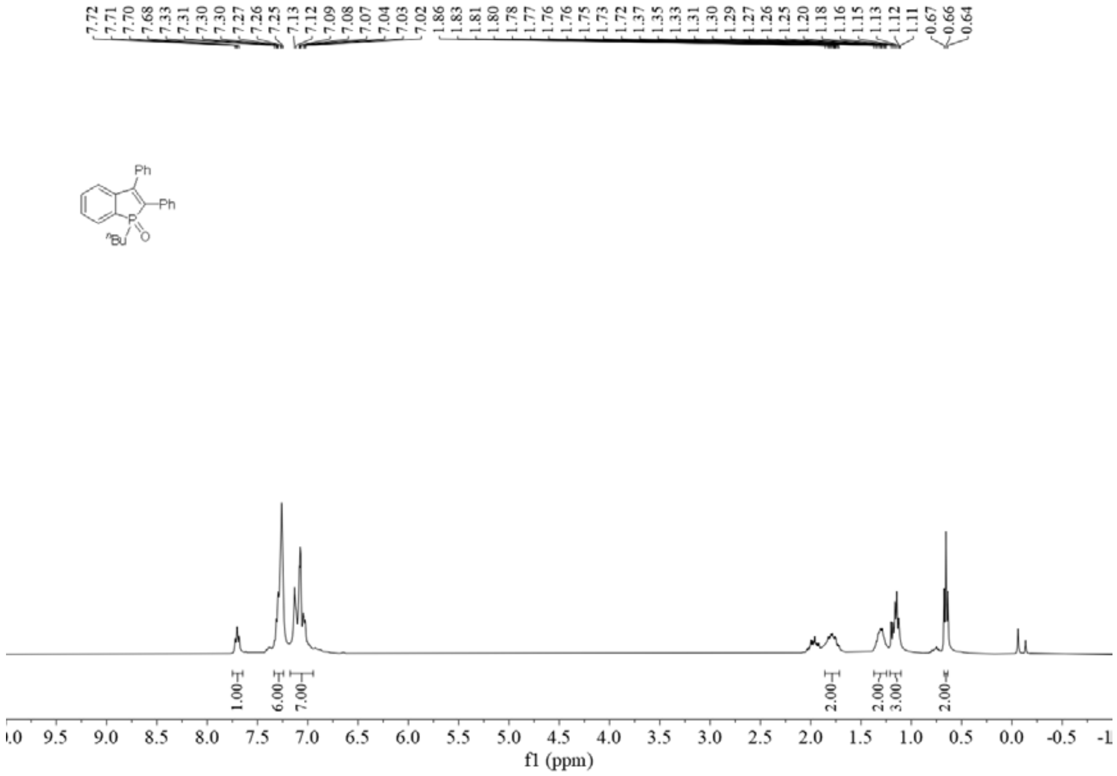
^{1}H NMR ($CDCl_3$-*d*) of **3y**



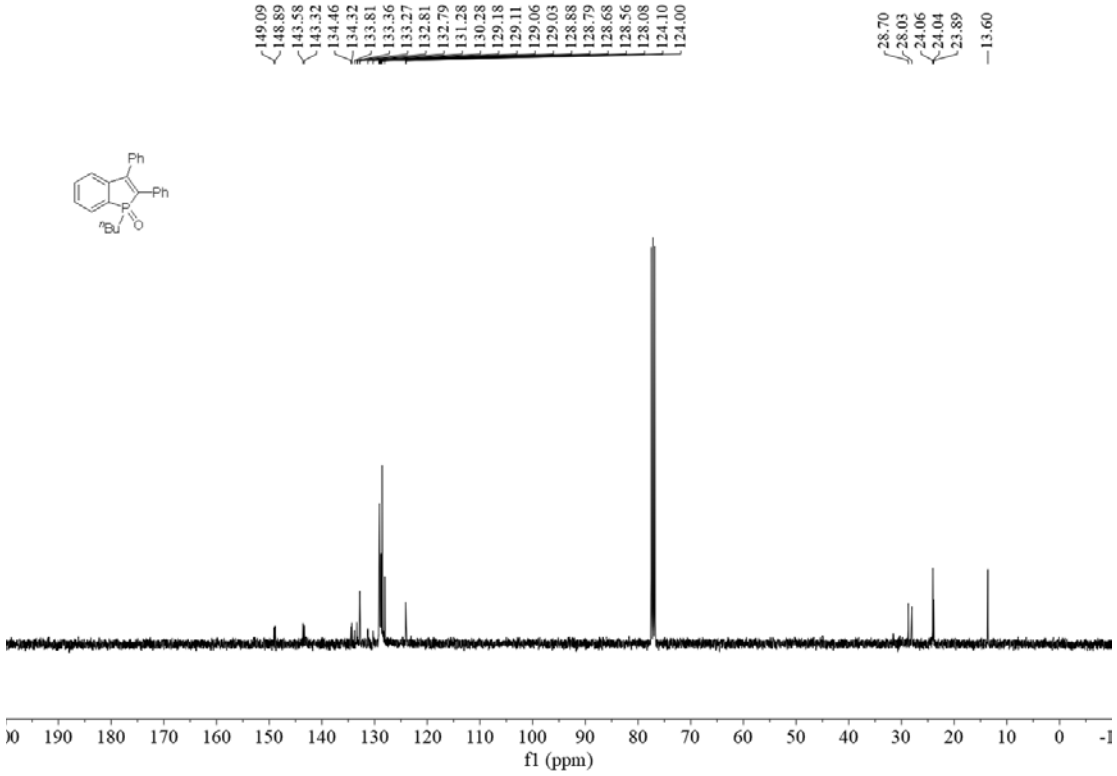
^{13}C NMR ($CDCl_3$-*d*) of **3y**



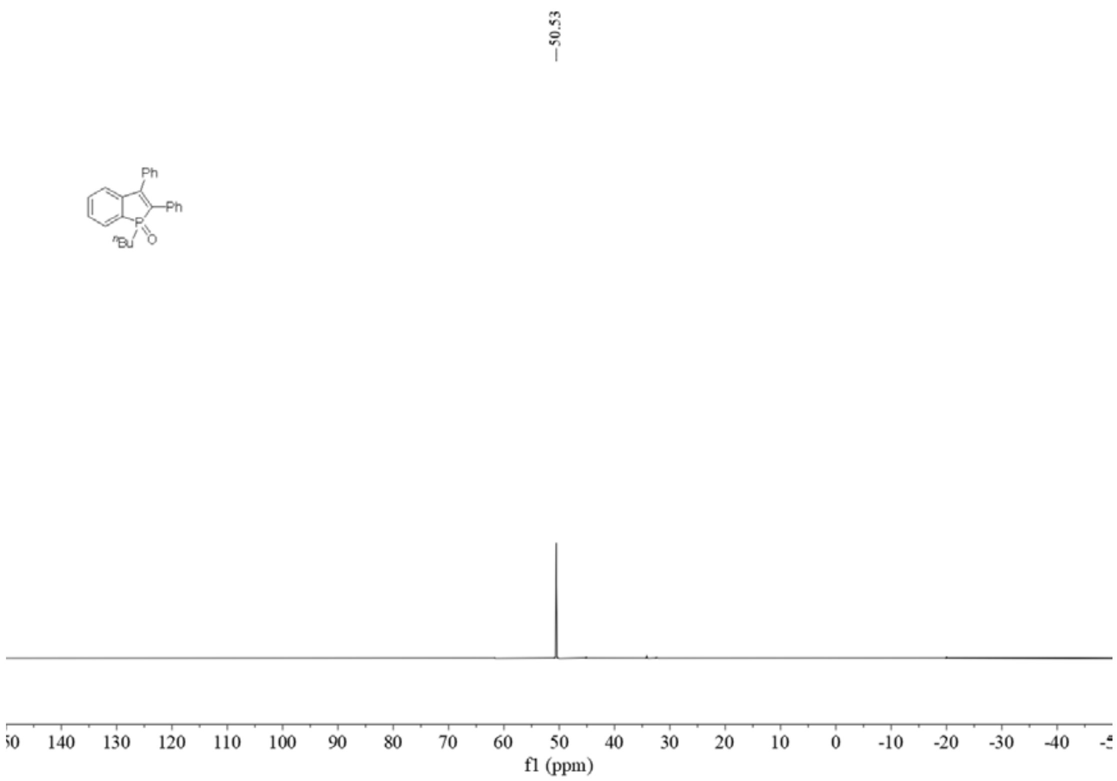
^{31}P NMR ($CDCl_3$-*d*) of **3y**



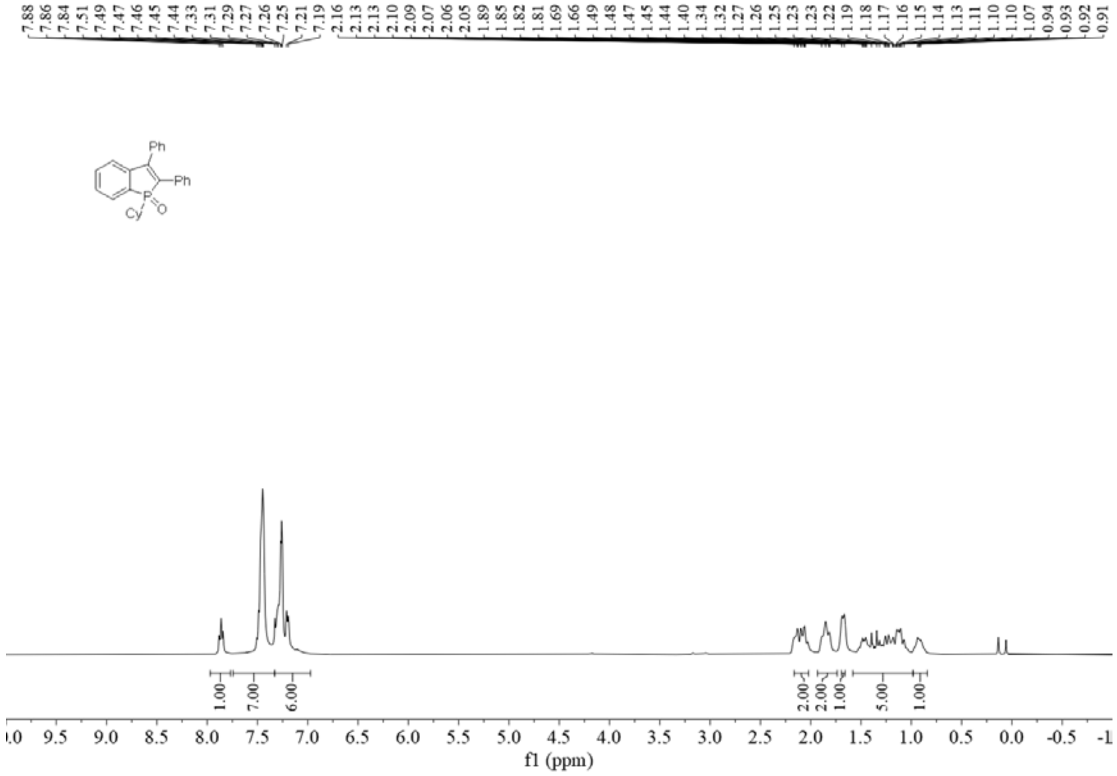
^{1}H NMR (CDCl$_3$-*d*) of **3z**



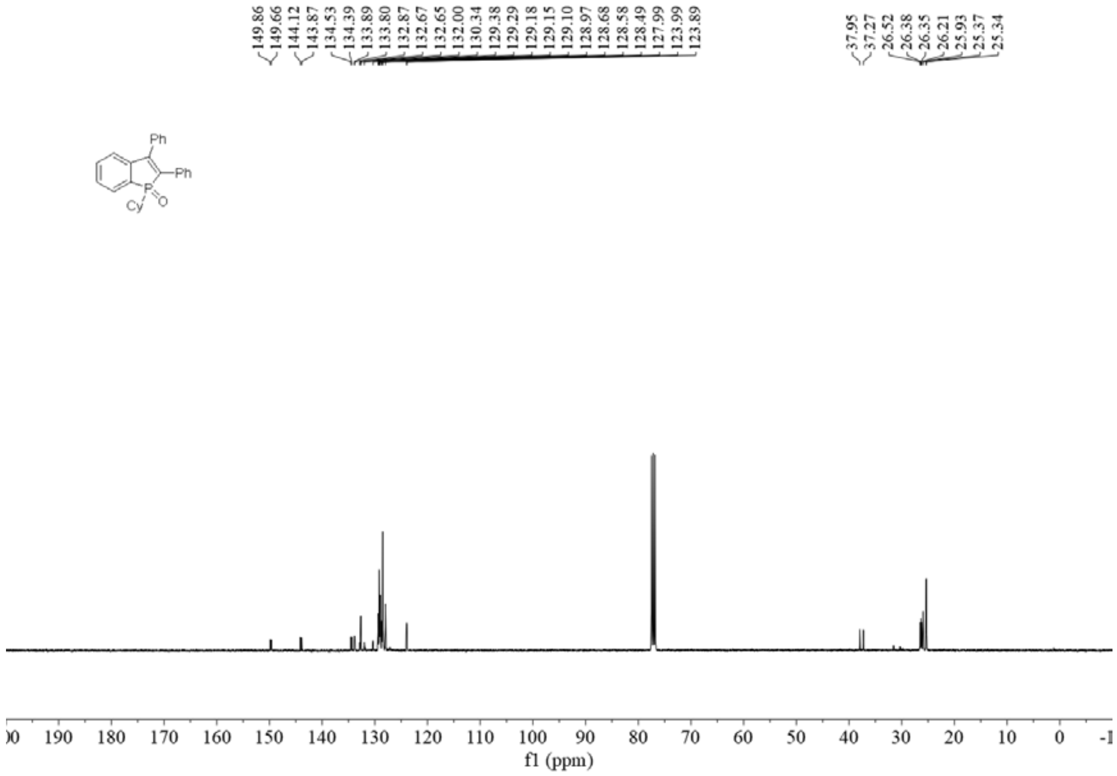
^{13}C NMR (CDCl$_3$-*d*) of **3z**



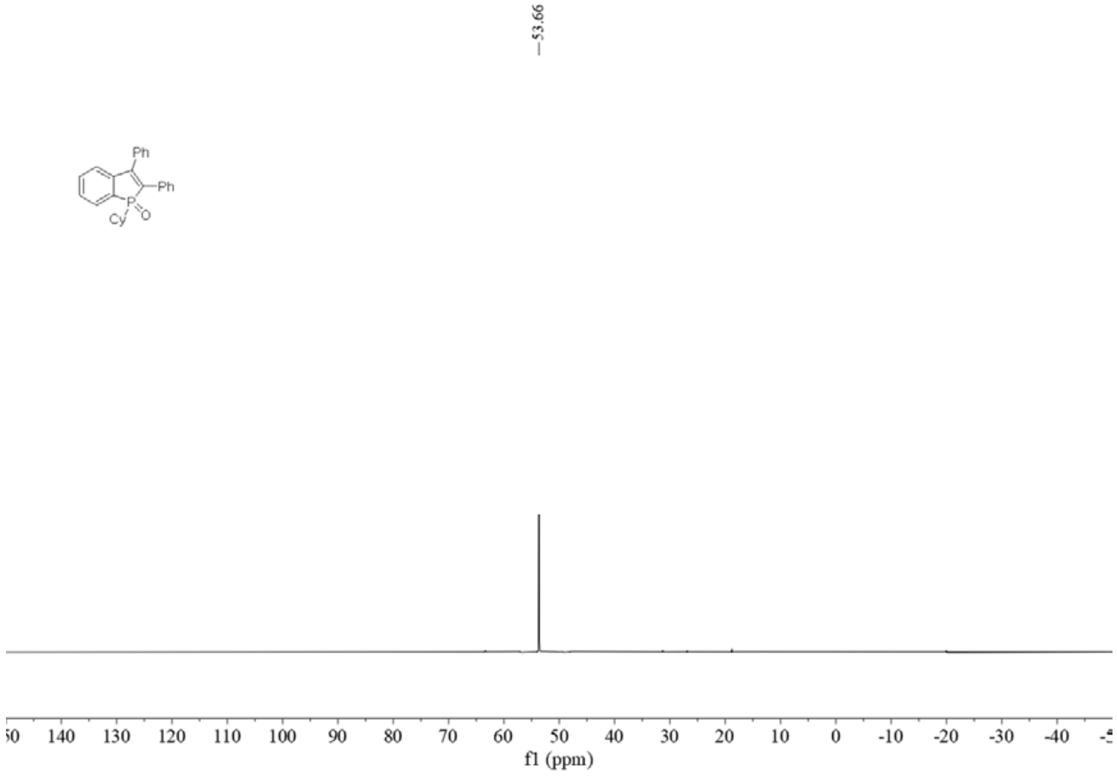
^{31}P NMR (CDCl$_3$-*d*) of **3z**



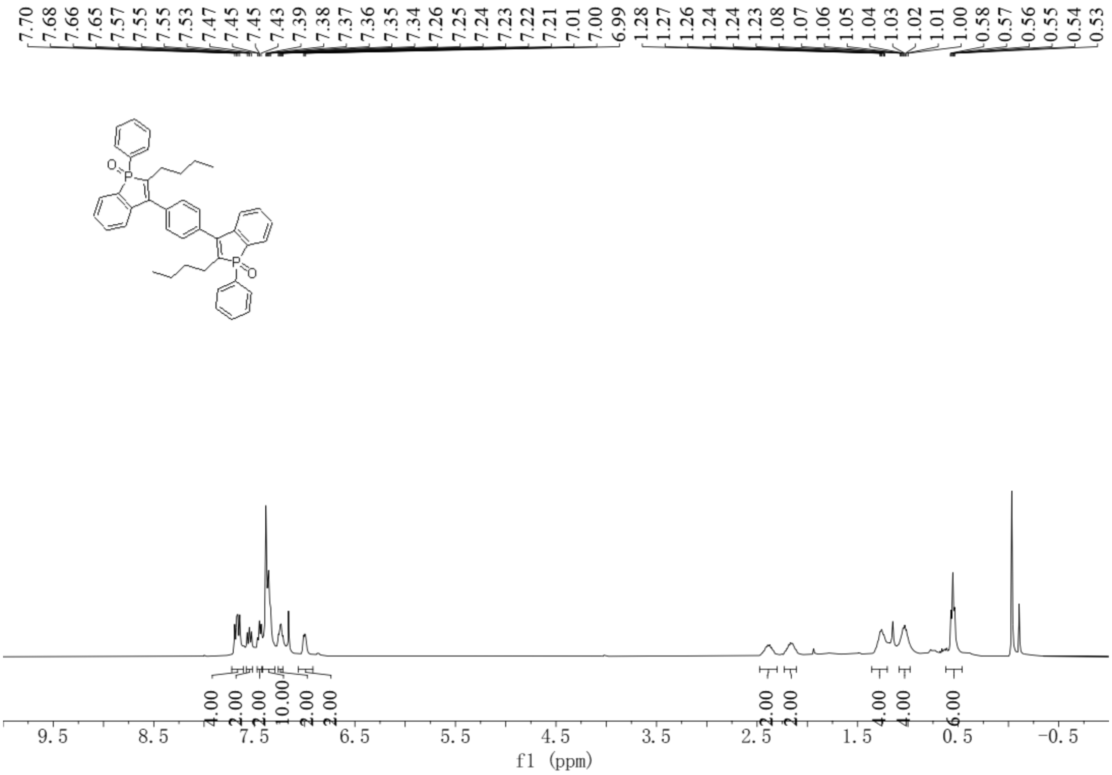
^{1}H NMR (CDCl$_3$-*d*) of **3aa**



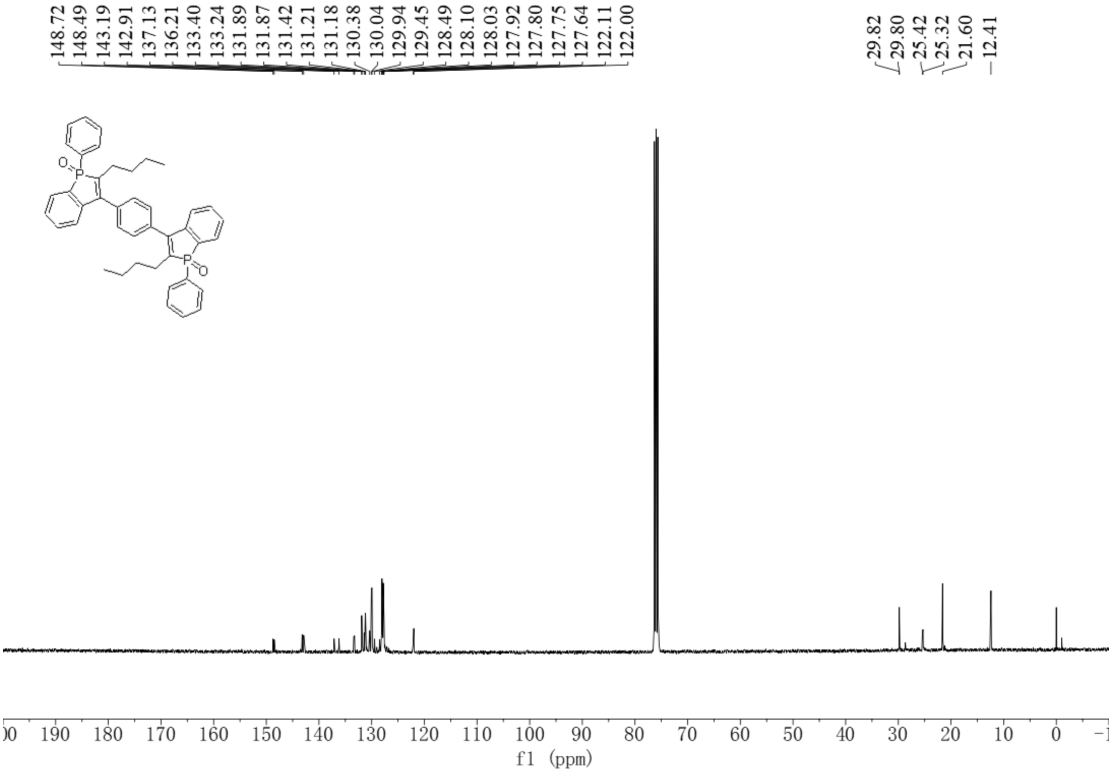
^{13}C NMR (CDCl$_3$-*d*) of **3aa**



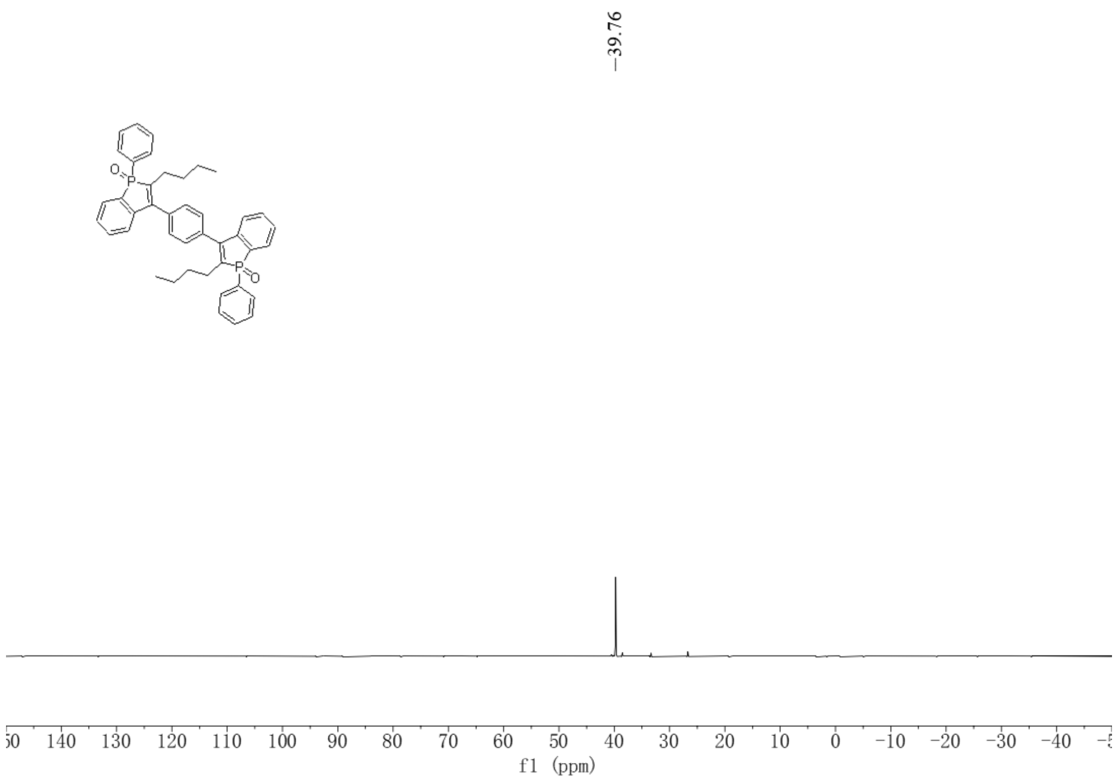
^{31}P NMR (CDCl$_3$-*d*) of **3aa**



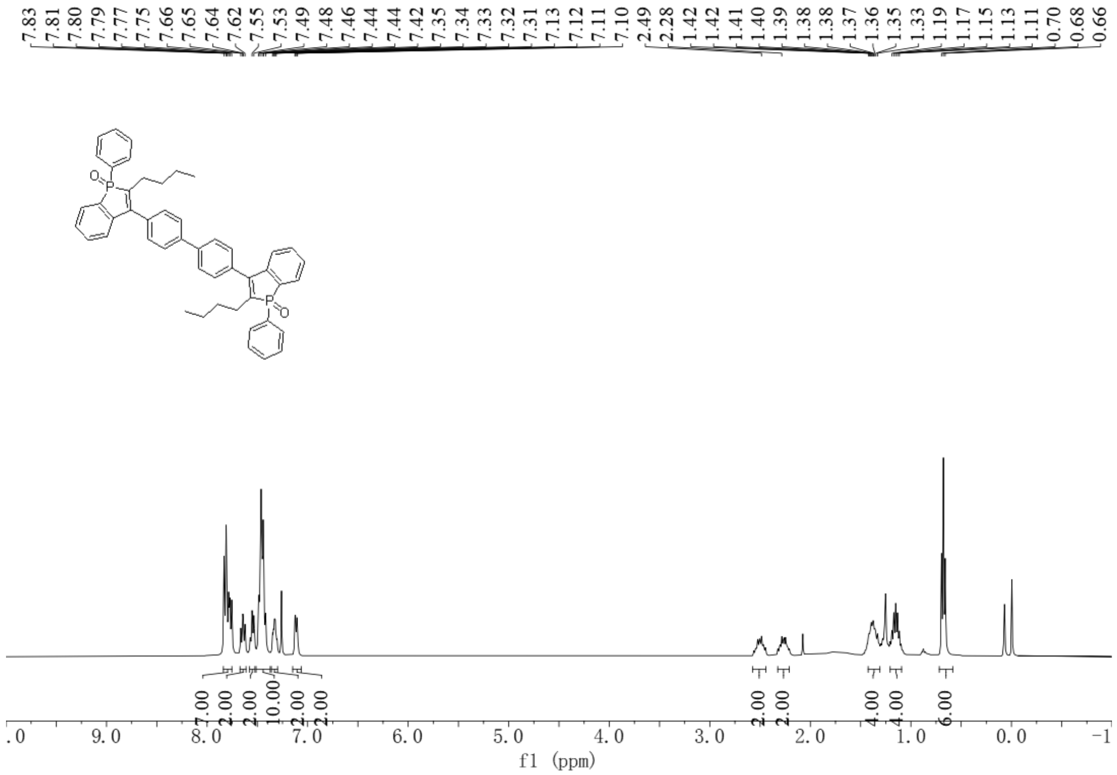
[1]H NMR ($CDCl_3$-*d*) of **3ab**



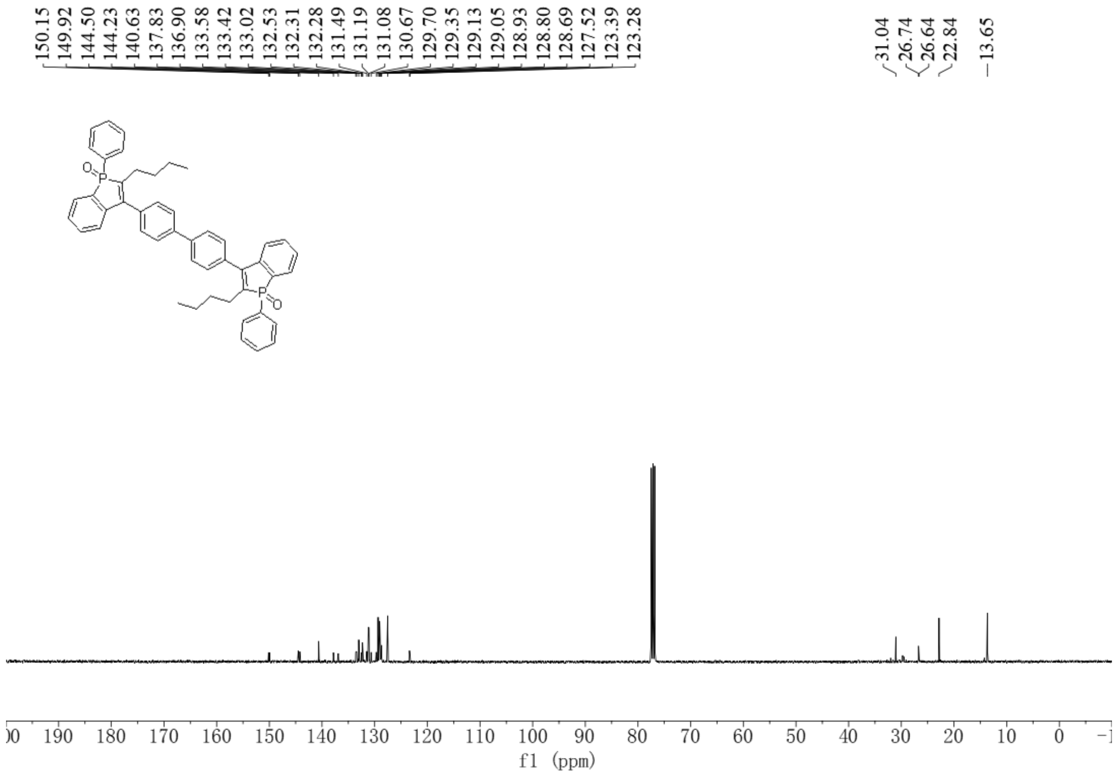
[13]C NMR ($CDCl_3$-*d*) of **3ab**



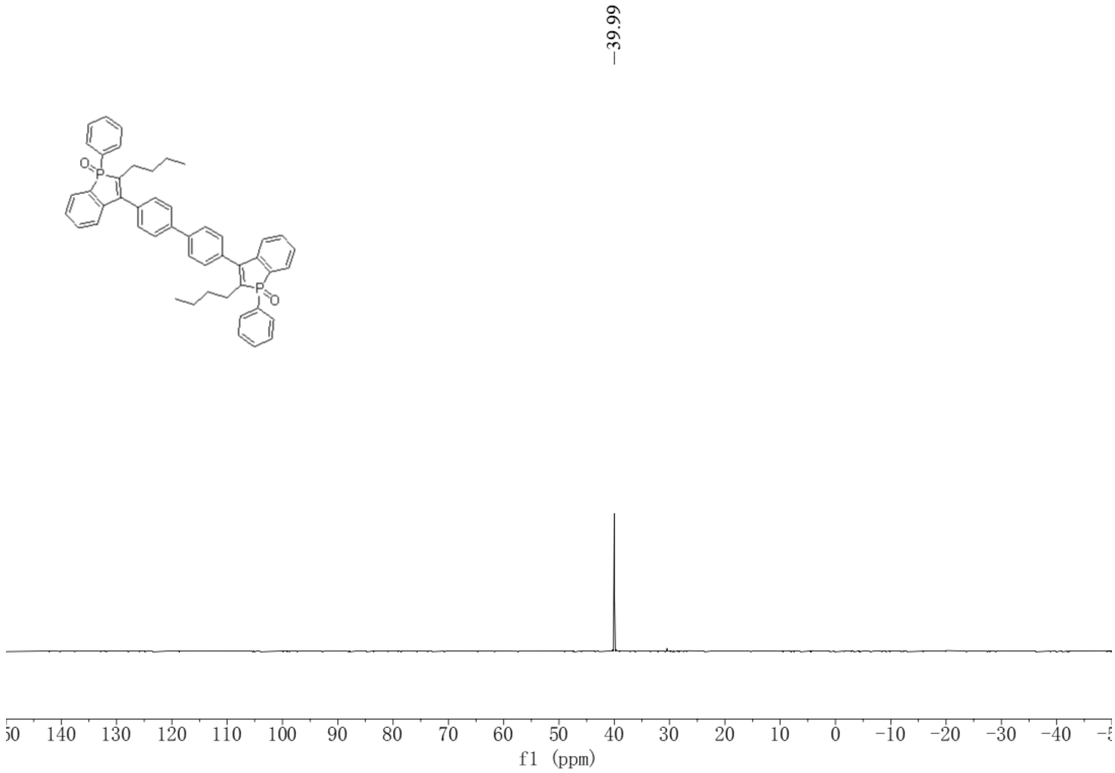
^{31}P NMR ($CDCl_3$-*d*) of **3ab**



^{1}H NMR ($CDCl_3$-*d*) of **3ac**



^{13}C NMR ($CDCl_3$-*d*) of **3ac**



^{31}P NMR ($CDCl_3$-*d*) of **3ac**

8. X-ray crystal structures of **3c′** and **3j**.

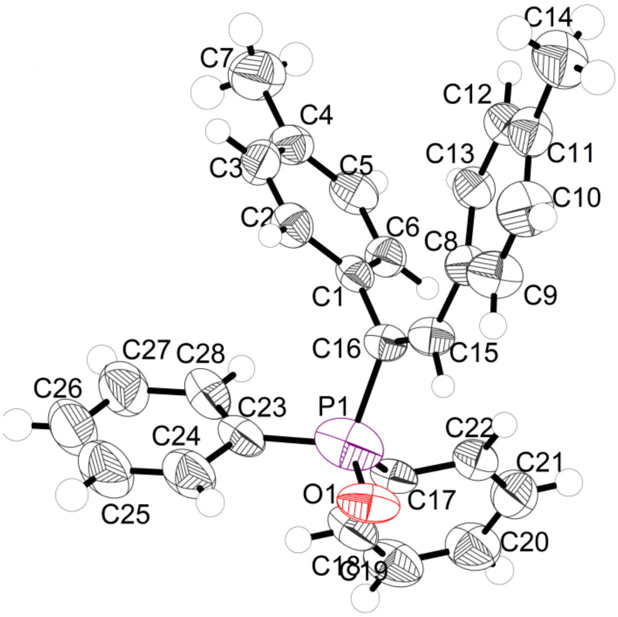


Figure s5. Crystal plot of compound **3c′** (The ellipsoid probability =50%). The single-crystal was obtained by slow volatilization in mixed solutions of CH_2Cl_2/n-hexane (1/5). CCDC 2300783.

Table s1 Crystal data and structure refinement for 3c′.

Identification code	221119HUANGHY2_0m
Empirical formula	$C_{28}H_{25}OP$
Formula weight	408.45
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.961(2)
b/Å	9.9168(16)
c/Å	21.452(3)
α/°	90
β/°	106.577(3)
γ/°	90
Volume/Å^3	2846.6(8)
Z	4
ρ_{calc}g/cm^3	0.953
μ/mm^{-1}	0.110
F(000)	864.0
Crystal size/mm^3	0.03 × 0.02 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.112 to 55.226
Index ranges	$-18 \le h \le 18$, $-12 \le k \le 12$, $-28 \le l \le 22$

Reflections collected	16736
Independent reflections	6460 [R_{int} = 0.0952, R_{sigma} = 0.1130]
Data/restraints/parameters	6460/1/273
Goodness-of-fit on F^2	0.836
Final R indexes [I>=2σ (I)]	R_1 = 0.0555, wR_2 = 0.1352
Final R indexes [all data]	R_1 = 0.1132, wR_2 = 0.1540
Largest diff. peak/hole / e $Å^{-3}$	0.22/-0.35

Table s2 Bond Lengths for 23c′.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	O1	1.4832(17)	C17	C18	1.392(3)
P1	C16	1.815(2)	C12	C11	1.387(3)
P1	C17	1.801(2)	C11	C10	1.370(4)
P1	C23	1.791(3)	C11	C14	1.510(3)
C1	C16	1.490(3)	C3	C2	1.384(3)
C1	C6	1.388(3)	C23	C28	1.390(3)
C1	C2	1.390(3)	C23	C24	1.389(3)
C8	C13	1.394(3)	C22	C21	1.368(3)
C8	C15	1.464(3)	C9	C10	1.383(3)
C8	C9	1.395(3)	C28	C27	1.386(4)
C16	C15	1.341(3)	C18	C19	1.384(3)
C6	C5	1.390(3)	C19	C20	1.357(4)
C13	C12	1.374(3)	C20	C21	1.376(4)
C4	C3	1.394(3)	C27	C26	1.386(4)
C4	C5	1.374(3)	C24	C25	1.372(4)
C4	C7	1.515(3)	C26	C25	1.369(4)
C17	C22	1.390(3)			

Table s3 Bond Angles for 3c′.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	P1	C16	111.71(10)	C13	C12	C11	122.2(2)
O1	P1	C17	110.72(10)	C12	C11	C14	120.8(3)
O1	P1	C23	112.10(11)	C10	C11	C12	116.5(2)
C17	P1	C16	108.43(10)	C10	C11	C14	122.7(3)
C23	P1	C16	106.89(11)	C16	C15	C8	130.9(2)
C23	P1	C17	106.76(11)	C2	C3	C4	121.2(2)
C6	C1	C16	122.23(19)	C28	C23	P1	123.75(18)
C6	C1	C2	117.7(2)	C24	C23	P1	118.4(2)
C2	C1	C16	120.01(19)	C24	C23	C28	117.9(3)
C13	C8	C15	125.4(2)	C4	C5	C6	122.2(2)

C13	C8	C9	116.6(2)	C3	C2	C1	121.2(2)
C9	C8	C15	118.0(2)	C21	C22	C17	121.6(2)
C1	C16	P1	117.83(16)	C10	C9	C8	120.9(2)
C15	C16	P1	115.67(17)	C27	C28	C23	120.9(3)
C15	C16	C1	126.1(2)	C19	C18	C17	120.6(2)
C1	C6	C5	120.4(2)	C11	C10	C9	122.4(2)
C12	C13	C8	121.2(2)	C20	C19	C18	121.0(3)
C3	C4	C7	120.8(2)	C19	C20	C21	119.3(3)
C5	C4	C3	117.2(2)	C26	C27	C28	119.9(3)
C5	C4	C7	122.0(2)	C25	C24	C23	121.1(3)
C22	C17	P1	120.76(18)	C22	C21	C20	120.4(3)
C22	C17	C18	117.1(2)	C25	C26	C27	119.4(3)
C18	C17	P1	121.35(19)	C26	C25	C24	120.8(3)

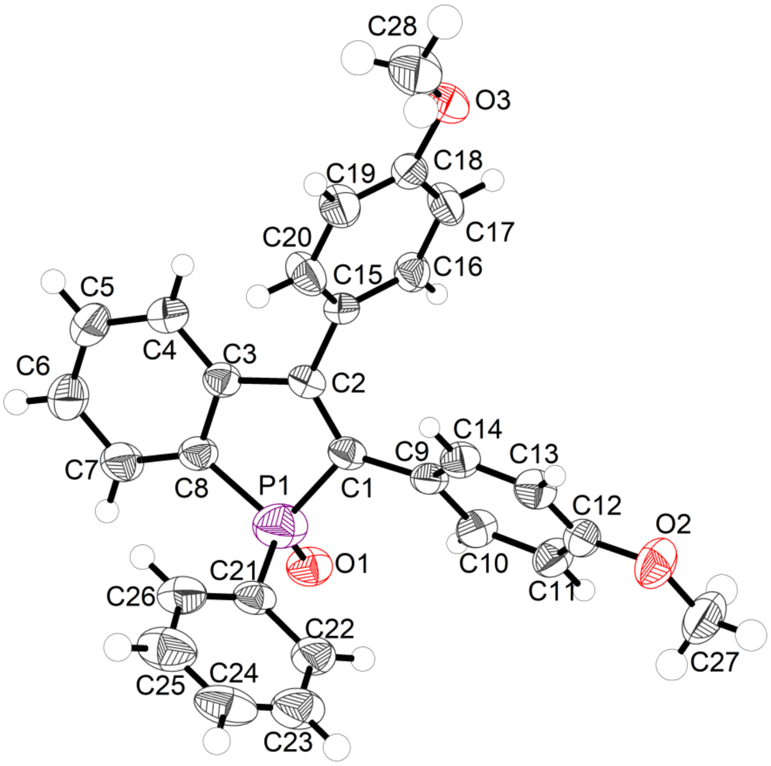


Figure s6. Crystal plot of compound **3j**. (The ellipsoid probability =50%). The single-crystal was obtained by slow volatilization in mixed solutions of CH_2Cl_2/n-hexane (1/5). CCDC 2300782.

Table s4 Crystal data and structure refinement for 3j.

Identification code	221109HUANHY1_0m
Empirical formula	$C_{28}H_{23}O_3P$
Formula weight	438.43

Temperature/K	296.15
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	22.937(4)
b/Å	8.7952(15)
c/Å	11.1318(19)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2245.7(7)
Z	4
ρ_{calc}g/cm^3	1.297
μ/mm^{-1}	0.150
F(000)	920.0
Crystal size/mm^3	0.03 × 0.02 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.632 to 55.39
Index ranges	$-29 \le h \le 21$, $-11 \le k \le 9$, $-14 \le l \le 13$
Reflections collected	13137
Independent reflections	5008 [R_{int} = 0.0400, R_{sigma} = 0.0452]
Data/restraints/parameters	5008/1/291
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0421, wR_2 = 0.0963
Final R indexes [all data]	R_1 = 0.0562, wR_2 = 0.1046
Largest diff. peak/hole / e Å^{-3}	0.27/-0.23
Flack parameter	0.09(5)

Table s5 Bond Lengths for 3j.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	O1	1.481(2)	C3	C4	1.380(5)
P1	C1	1.818(3)	C10	C11	1.388(4)
P1	C21	1.802(3)	C14	C13	1.377(4)
P1	C8	1.792(3)	C21	C26	1.376(5)
O2	C12	1.368(4)	C21	C22	1.399(5)
O2	C27	1.433(5)	C8	C7	1.377(4)
O3	C18	1.373(4)	C15	C2	1.484(4)
O3	C28	1.414(5)	C15	C20	1.388(4)
C9	C1	1.478(4)	C17	C18	1.387(5)
C9	C10	1.385(4)	C18	C19	1.375(5)

C9	C14	1.402(4)	C7	C6	1.382(5)
C16	C15	1.386(4)	C4	C5	1.393(5)
C16	C17	1.376(4)	C26	C25	1.390(5)
C12	C11	1.373(4)	C20	C19	1.386(4)
C12	C13	1.386(5)	C5	C6	1.373(5)
C1	C2	1.358(4)	C22	C23	1.383(5)
C3	C8	1.408(4)	C24	C23	1.360(7)
C3	C2	1.489(4)	C24	C25	1.374(7)

Table s6 Bond Angles for 3j.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	P1	C1	118.70(15)	C3	C8	P1	109.0(2)
O1	P1	C21	112.80(14)	C7	C8	P1	129.7(2)
O1	P1	C8	118.25(14)	C7	C8	C3	121.3(3)
C21	P1	C1	103.48(13)	C12	C11	C10	119.5(3)
C8	P1	C1	93.01(13)	C16	C15	C2	120.3(3)
C8	P1	C21	108.15(16)	C16	C15	C20	117.6(3)
C12	O2	C27	117.9(3)	C20	C15	C2	122.1(3)
C18	O3	C28	117.7(3)	C16	C17	C18	119.9(3)
C10	C9	C1	119.5(2)	C14	C13	C12	120.4(3)
C10	C9	C14	117.1(3)	O3	C18	C17	115.9(3)
C14	C9	C1	123.2(3)	O3	C18	C19	124.2(3)
C17	C16	C15	121.4(3)	C19	C18	C17	119.9(3)
O2	C12	C11	124.4(3)	C1	C2	C3	114.6(3)
O2	C12	C13	115.8(3)	C1	C2	C15	125.0(3)
C11	C12	C13	119.8(3)	C15	C2	C3	120.4(2)
C9	C1	P1	120.4(2)	C8	C7	C6	119.1(3)
C2	C1	P1	109.6(2)	C3	C4	C5	119.5(3)
C2	C1	C9	129.7(3)	C21	C26	C25	120.9(4)
C8	C3	C2	113.6(3)	C19	C20	C15	121.7(3)
C4	C3	C8	118.8(3)	C6	C5	C4	121.0(3)
C4	C3	C2	127.6(3)	C23	C22	C21	119.3(4)
C9	C10	C11	122.2(3)	C5	C6	C7	120.3(3)
C13	C14	C9	121.1(3)	C18	C19	C20	119.4(3)
C26	C21	P1	123.3(3)	C23	C24	C25	119.5(4)
C26	C21	C22	118.7(3)	C24	C23	C22	121.7(4)
C22	C21	P1	117.9(3)	C24	C25	C26	119.9(4)

9. Symbolic Z-matrix of the calculated structures.

1a with O_2:

Charge =0 Multiplicity = 3

O	0.11989000	-1.84801300	2.10533700
P	0.10857200	-0.59892600	1.27547700
C	1.61424000	-0.29737300	0.30089800
C	2.36508000	-1.40146900	-0.12319400
C	3.50782100	-1.20886600	-0.89865900
C	3.90579100	0.08342500	-1.25006400
C	3.16748200	1.18708800	-0.81745300
C	2.02578400	0.99888100	-0.03758400
C	-1.28892200	-0.53998700	0.10213800
C	-1.33975000	0.33826300	-0.98933700
C	-2.45365700	0.34432100	-1.82813900
C	-3.51684600	-0.52898100	-1.58550800
C	-3.46467000	-1.41273500	-0.50602200
C	-2.35321100	-1.42010100	0.33760100
H	2.05532900	-2.39929100	0.17299300
H	4.09115500	-2.06479100	-1.22476800
H	4.79670600	0.23113200	-1.85341700
H	3.48553400	2.19201400	-1.07887200
H	1.46403000	1.86127500	0.31268200
H	-0.50777900	1.00461300	-1.19560000
H	-2.48940900	1.02450100	-2.67400400
H	-4.38205500	-0.52412800	-2.24213200
H	-4.28716300	-2.09774600	-0.32261900
H	-2.28925000	-2.10959500	1.17383000
H	-0.00771800	0.62056900	1.99542200
O	-0.61978900	3.08217500	1.29857700
O	-1.57170300	3.06465600	0.54311900

resonant (λ^3) **1a** with O_2:

Charge =0 Multiplicity = 3

O	0.03903600	2.11017100	0.49971700
P	-0.11717300	1.01890900	-0.77583300
O	2.97639100	2.53028600	-0.30949300
O	3.52290100	1.54555900	0.14584100
C	0.97100200	-0.36036800	-0.20663200
C	1.21954100	-0.58981900	1.15496200
C	2.05661400	-1.63113300	1.54959000
C	2.64615100	-2.46048600	0.58988800
C	2.40534900	-2.23790300	-0.76585200
C	1.57938300	-1.18297400	-1.16281600
C	-1.75934700	0.32996500	-0.29508500

C	-2.12343100	-0.96539700	-0.69398600
C	-3.39505800	-1.46128800	-0.41122600
C	-4.32008100	-0.67084300	0.27498500
C	-3.96487500	0.61787100	0.67523200
C	-2.69457000	1.12027400	0.38727900
H	0.76069900	0.06051000	1.89355800
H	2.24834200	-1.80172300	2.60531200
H	3.29618200	-3.27353700	0.90023000
H	2.86914800	-2.87452800	-1.51390000
H	1.41422400	-0.99522700	-2.22130900
H	-1.40420800	-1.59717600	-1.20883600
H	-3.66134400	-2.46849900	-0.71911600
H	-5.30970000	-1.05885200	0.49816000
H	-4.67725500	1.23552300	1.21517300
H	-2.41617500	2.11800300	0.70969700
H	0.60698900	2.83633000	0.21197100

int-1:

Charge =0 Multiplicity = 2

O	-0.08794100	2.58757100	-0.09534200
P	-0.04031200	1.18658400	-0.67592300
C	1.48031700	0.28068900	-0.23916200
C	2.30495800	0.81119400	0.76529100
C	3.49072200	0.16194000	1.10538100
C	3.86691500	-1.00829800	0.44138900
C	3.06149900	-1.52535000	-0.57605900
C	1.87716500	-0.87770800	-0.92580900
C	-1.48202800	0.17936500	-0.18722400
C	-1.47140800	-1.22315500	-0.13379400
C	-2.63490200	-1.91619800	0.19764400
C	-3.81511800	-1.22098100	0.47071500
C	-3.82960600	0.17506500	0.41792500
C	-2.67165900	0.87504200	0.08600600
H	2.00656700	1.72672800	1.26594600
H	4.12252900	0.56932300	1.88921400
H	4.79169700	-1.51096100	0.70869200
H	3.36173300	-2.42505500	-1.10491000
H	1.27125100	-1.26788900	-1.73926500
H	-0.55626300	-1.77397700	-0.32206500
H	-2.61774500	-3.00094300	0.24931900
H	-4.71909600	-1.76529400	0.72741600
H	-4.74325200	0.71900200	0.63895600
H	-2.67034300	1.96011200	0.05447300

int-1 with HOO·:

Charge =0 Multiplicity = 3

O	-0.07577700	1.88394000	-0.95837500
P	0.02852800	0.80895500	0.13902700
O	-1.45594600	3.60429100	0.24064700
O	-1.54492100	2.85880200	1.32401900
C	-1.28666500	-0.43585700	-0.01386300
C	-2.04782100	-0.46570000	-1.19228900
C	-3.07634000	-1.39658000	-1.32869900
C	-3.35659900	-2.29068200	-0.29256000
C	-2.61502200	-2.24752000	0.89047700
C	-1.58925000	-1.31482900	1.03724300
C	1.64581800	-0.01968000	0.04090100
C	1.86769300	-1.31806200	0.52773500
C	3.14641300	-1.86964800	0.47754400
C	4.21090500	-1.13213200	-0.04674600
C	3.99396400	0.16148200	-0.52797800
C	2.71943200	0.72187100	-0.48044700
H	-1.82533900	0.24013800	-1.98601900
H	-3.66042000	-1.42401400	-2.24379200
H	-4.15971500	-3.01332600	-0.40207300
H	-2.84478800	-2.93001400	1.70311100
H	-1.03809100	-1.26226500	1.97225300
H	1.04437900	-1.90632600	0.91902100
H	3.31100400	-2.87904900	0.84267800
H	5.20585700	-1.56567500	-0.08242600
H	4.81826800	0.73331100	-0.94362800
H	2.53908100	1.72140600	-0.86262400
H	-0.88017500	3.01924600	-0.40013800

int-1 with **2a:**

Charge =0 Multiplicity = 2

O	0.22745000	2.38716600	1.31456400
P	-0.47618900	1.27473400	0.55721200
C	-2.28028700	1.48783900	0.43661700
C	-2.83953800	2.72727900	0.78489600
C	-4.22232600	2.90035500	0.74413700
C	-5.05294600	1.84011400	0.37148100
C	-4.49977200	0.59835600	0.04981700
C	-3.11857200	0.41496200	0.09233500
C	0.20548200	1.02012900	-1.11274700
C	-0.47522900	0.33081500	-2.12856500
C	0.15944400	0.07576200	-3.34333900
C	1.47534200	0.49586000	-3.55277300

C	2.15379800	1.18599200	-2.54570000
C	1.52532700	1.44796300	-1.33044600
H	-2.18452400	3.53924600	1.08468200
H	-4.65309200	3.86298200	1.00414200
H	-6.12983400	1.97874900	0.34303500
H	-5.14254200	-0.23442400	-0.22031400
H	-2.70154900	-0.56287500	-0.12285600
H	-1.49744100	0.00239900	-1.98099400
H	-0.37609400	-0.44988600	-4.12889700
H	1.96777500	0.28870800	-4.49841900
H	3.17560400	1.51789200	-2.70394100
H	2.04887200	1.97774600	-0.54259900
C	3.17620000	-0.69869200	0.89197200
C	3.25137400	0.53365200	1.57315700
C	4.46353900	1.21529000	1.64537400
C	5.61107800	0.68398200	1.05085600
C	5.54259900	-0.53681600	0.37479800
C	4.33550000	-1.22582900	0.29206400
H	2.35407300	0.96312600	2.00666800
H	4.50933600	2.16824200	2.16393700
H	6.55368800	1.21998300	1.11131500
H	6.43160100	-0.95185900	-0.09101700
H	4.27475600	-2.17129800	-0.23703500
C	1.92689700	-1.37566000	0.78136300
C	0.83014200	-1.88806000	0.67282000
C	-0.48710100	-2.40600400	0.50839400
C	-1.37201100	-2.47659300	1.60307800
C	-0.94070900	-2.81225500	-0.76291400
C	-2.67149800	-2.94578500	1.42846300
H	-1.02877500	-2.15332700	2.57998600
C	-2.24370700	-3.27688500	-0.92825200
H	-0.26707400	-2.73837600	-1.60956100
C	-3.11244100	-3.34773500	0.16475600
H	-3.34460900	-2.99018200	2.27916300
H	-2.58323000	-3.58290000	-1.91345200
H	-4.12721100	-3.71048500	0.03161800

int-2:

Charge =0 Multiplicity = 2

O	-1.05531700	0.91795000	2.42554900
P	-0.56681700	0.76304300	1.00978700
C	-1.61228600	1.63089700	-0.20720500
C	-2.40584600	2.68638600	0.26080900
C	-3.21309700	3.39791000	-0.62663900

C	-3.23499700	3.05614600	-1.98054300
C	-2.45555500	1.99554700	-2.44848900
C	-1.64891500	1.28009700	-1.56409300
C	1.13801300	1.37315800	0.80260200
C	1.66877300	1.78312800	-0.42677700
C	3.00925300	2.15351200	-0.51871900
C	3.82280300	2.12353100	0.61597200
C	3.29186800	1.73606200	1.84764200
C	1.95149100	1.36339800	1.94354400
H	-2.39189600	2.92691300	1.31938900
H	-3.82872200	4.21469700	-0.26157000
H	-3.86630700	3.60940800	-2.66980500
H	-2.48445300	1.71991500	-3.49856200
H	-1.06274600	0.43902300	-1.92319500
H	1.04057900	1.80829400	-1.31160100
H	3.42025700	2.46045400	-1.47572400
H	4.86852100	2.40698700	0.54018900
H	3.92138000	1.72331700	2.73250100
H	1.52072300	1.06820600	2.89524800
C	1.95137500	-1.58037700	-0.41244200
C	2.94384100	-1.93188300	0.55335100
C	4.27250900	-2.04886800	0.18059000
C	4.66645600	-1.83375100	-1.14787200
C	3.70461100	-1.49682800	-2.11126400
C	2.37023700	-1.37340300	-1.76322900
H	2.63901100	-2.08475100	1.58282200
H	5.01596100	-2.30457500	0.92998600
H	5.71045500	-1.92815000	-1.42936800
H	4.00648100	-1.32843000	-3.14106100
H	1.62593900	-1.10851700	-2.50733900
C	0.62355700	-1.45302300	-0.05580000
C	-0.52068200	-0.99107800	0.38696700
C	-1.79949100	-1.76120000	0.37480800
C	-2.80168100	-1.53562700	1.33220100
C	-2.01604200	-2.72803200	-0.62125300
C	-3.98912400	-2.26701400	1.28805900
H	-2.64209300	-0.79702000	2.11046300
C	-3.20105000	-3.45753500	-0.65732400
H	-1.24602500	-2.89587000	-1.36884600
C	-4.19475700	-3.22805100	0.29790700
H	-4.75485600	-2.08483200	2.03653600
H	-3.35303500	-4.20004700	-1.43558400
H	-5.12196900	-3.79287000	0.26749000

3a:

Charge =0 Multiplicity = 1

O	-2.00521900	0.05775200	2.40986100
P	-1.42831100	0.38925500	1.06133100
C	-2.55392400	-0.04498300	-0.30541600
C	-3.80414100	-0.58147400	0.02067500
C	-4.69425600	-0.93695700	-0.99466100
C	-4.33640000	-0.75863200	-2.33155800
C	-3.08601500	-0.22487500	-2.65909400
C	-2.19509300	0.13081400	-1.64929000
C	-0.83347800	2.08072200	0.76118800
C	-1.49413800	3.28813900	0.93707400
C	-0.81005800	4.48233800	0.67306200
C	0.51865200	4.44479600	0.24901300
C	1.18701500	3.22653100	0.07877200
C	0.50815200	2.03238000	0.32942800
H	-4.06024400	-0.71734900	1.06688800
H	-5.66428300	-1.35449100	-0.74132700
H	-5.02901200	-1.03704800	-3.12063500
H	-2.80758000	-0.08970300	-3.70011800
H	-1.22068200	0.54032300	-1.90162900
H	-2.52399300	3.30692600	1.28147500
H	-1.31197300	5.43584400	0.80552700
H	1.04766200	5.37315700	0.05416300
H	2.22450600	3.21255700	-0.23662600
C	2.46768400	0.43169400	-0.19132600
C	2.93497200	0.91407600	-1.42415800
C	4.25203200	0.68415100	-1.82256800
C	5.12221900	-0.02179900	-0.99026200
C	4.66777300	-0.49997300	0.24117000
C	3.35085200	-0.27774900	0.63709900
H	2.25678100	1.45808800	-2.07505800
H	4.59698600	1.05567900	-2.78306100
H	6.14838500	-0.19814000	-1.29870700
H	5.34014500	-1.04863800	0.89397100
H	2.99088700	-0.65686800	1.58786500
C	1.06199700	0.65181000	0.22915500
C	0.19318500	-0.33421700	0.58888200
C	0.37247700	-1.79478600	0.54529000
C	-0.21683400	-2.59695800	1.54121100
C	1.07955500	-2.42385300	-0.49638000
C	-0.07790900	-3.98349600	1.50587600
H	-0.78075000	-2.12260600	2.33850600
C	1.21086900	-3.80909800	-0.52813000

H	1.51797000	-1.82074100	-1.28354800
C	0.63742100	-4.59487400	0.47514900
H	-0.53296100	-4.58690600	2.28590100
H	1.75709000	-4.27764100	-1.34176800
H	0.74183200	-5.67563700	0.44813000

ts-1:

Charge =0 Multiplicity = 3

O	-0.01380400	1.83148100	1.02438000
P	-0.02594100	0.80301300	-0.14042500
O	0.62935000	3.80262500	-0.22738000
O	0.71139300	3.15102000	-1.35680400
C	1.40116800	-0.31728900	-0.00110100
C	2.14716100	-0.32105000	1.18756100
C	3.25328500	-1.16071600	1.30835200
C	3.62522700	-1.99035200	0.24758300
C	2.89733700	-1.97245500	-0.94447700
C	1.79454700	-1.12946300	-1.07582200
C	-1.55250400	-0.18357700	-0.02994000
C	-1.66679400	-1.46487300	-0.59278600
C	-2.88187300	-2.14436700	-0.53389700
C	-3.99105200	-1.55118800	0.07439000
C	-3.88165500	-0.27455500	0.63084400
C	-2.67069600	0.41262300	0.57602800
H	1.85168100	0.33354900	2.00105700
H	3.82585200	-1.16812500	2.23113000
H	4.48820600	-2.64222200	0.34546200
H	3.19667600	-2.60383400	-1.77561400
H	1.25248300	-1.09381400	-2.01704800
H	-0.80716100	-1.94185300	-1.05209700
H	-2.96176600	-3.14057700	-0.95879000
H	-4.93651400	-2.08363000	0.11641700
H	-4.73994100	0.18540500	1.11157300
H	-2.57346300	1.39922500	1.01714400
H	0.33265700	3.01324100	0.48514600

ts-1':

Charge =0 Multiplicity = 3

O	0.11989000	-1.84801300	2.10533700
P	0.10857200	-0.59892600	1.27547700
C	1.61424000	-0.29737300	0.30089800
C	2.36508000	-1.40146900	-0.12319400
C	3.50782100	-1.20886600	-0.89865900
C	3.90579100	0.08342500	-1.25006400

C	3.16748200	1.18708800	-0.81745300
C	2.02578400	0.99888100	-0.03758400
C	-1.28892200	-0.53998700	0.10213800
C	-1.33975000	0.33826300	-0.98933700
C	-2.45365700	0.34432100	-1.82813900
C	-3.51684600	-0.52898100	-1.58550800
C	-3.46467000	-1.41273500	-0.50602200
C	-2.35321100	-1.42010100	0.33760100
H	2.05532900	-2.39929100	0.17299300
H	4.09115500	-2.06479100	-1.22476800
H	4.79670600	0.23113200	-1.85341700
H	3.48553400	2.19201400	-1.07887200
H	1.46403000	1.86127500	0.31268200
H	-0.50777900	1.00461300	-1.19560000
H	-2.48940900	1.02450100	-2.67400400
H	-4.38205500	-0.52412800	-2.24213200
H	-4.28716300	-2.09774600	-0.32261900
H	-2.28925000	-2.10959500	1.17383000
H	-0.00771800	0.62056900	1.99542200
O	-0.61978900	3.08217500	1.29857700
O	-1.57170300	3.06465600	0.54311900

ts-2:

Charge =0 Multiplicity = 2

O	0.41998400	-0.75052100	-2.18651400
P	-0.20300300	-0.67529700	-0.81056600
C	-1.95434800	-1.16987900	-0.77781700
C	-2.48632600	-1.75358400	-1.93914000
C	-3.83814800	-2.08939500	-1.99416000
C	-4.67090600	-1.83233900	-0.90208000
C	-4.15151400	-1.22741700	0.24501700
C	-2.80163900	-0.88670000	0.30658900
C	0.71630900	-1.62229900	0.43991100
C	0.14677800	-2.10963800	1.62684700
C	0.94832500	-2.73643200	2.57941600
C	2.32209300	-2.87431400	2.36342500
C	2.89212300	-2.39460100	1.18245200
C	2.09630500	-1.77223600	0.22257800
H	-1.83043600	-1.93374500	-2.78502100
H	-4.24311400	-2.55070500	-2.89033800
H	-5.72473900	-2.09106600	-0.94956600
H	-4.80082300	-1.00303700	1.08603700
H	-2.42091600	-0.36985200	1.18161500
H	-0.92035900	-2.02218100	1.79984200

H	0.49924200	-3.12184900	3.49035300
H	2.94346000	-3.35827700	3.11141800
H	3.95838100	-2.50180400	1.00643100
H	2.53310700	-1.40276000	-0.69855900
C	2.73420500	1.50855800	-0.35524700
C	3.10168100	1.19528800	-1.68484700
C	4.42291300	0.87961700	-1.98265200
C	5.39592600	0.87602600	-0.97761600
C	5.03994000	1.18850000	0.33855000
C	3.72309500	1.50415800	0.65287800
H	2.33035900	1.15060700	-2.44523600
H	4.69451500	0.62474900	-3.00270900
H	6.42544300	0.62791700	-1.21792100
H	5.79272700	1.18228400	1.12133800
H	3.43858300	1.73623000	1.67385700
C	1.37955800	1.77005700	-0.04628400
C	0.14874500	1.65946000	0.06342200
C	-1.17629000	2.10382400	0.42258600
C	-2.16331700	2.30017900	-0.55925800
C	-1.50965300	2.29062000	1.77666900
C	-3.45113500	2.68130000	-0.19311300
H	-1.91228600	2.13544600	-1.60192300
C	-2.80252400	2.66761600	2.13510000
H	-0.74891500	2.13173700	2.53409900
C	-3.77704000	2.86250600	1.15313700
H	-4.20565700	2.82603200	-0.96025100
H	-3.04957000	2.80884300	3.18328800
H	-4.78477400	3.15180600	1.43568800