Photocatalytic Dehydrogenative C(sp^2)–P Coupling Reaction Between Dibenzo[*b,f*][*1,4*]oxazepanes and Phosphine Oxides

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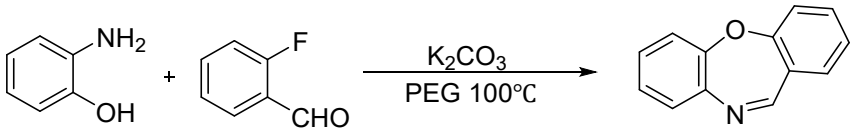
Supporting Information

1. General Information

^{1}H-NMR, ^{13}C-NMR and ^{31}P-NMR spectra were recorded with solvent $CDCl_3$ on JNM-ECZ400S/L1 400 spectrometer (400 MHz for ^{1}H, 101 MHz for ^{13}C and 162 MHz for ^{31}P). Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.16). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), td (doublet of triplet). Exact ESI mass spectra were recorded on a Bruker Daltonics MicroTOF-Q. ESI-MS were obtained on a Thermo-ITQ. Mass spectral data (MS) was recorded using an Agilent-6110 mass spectrometer. For thin layer chromatography (TLC), pre-coated Qingdao Haiyang TLC plates (GF254) were used, and compounds were visualized with a UV light at 254 nm. Flash chromatographic separations were performed on 200-300 mesh silica gel (from Qingdao Haiyang Chem. Company, Ltd.). Unless otherwise noted, all reagents were purchased from commercial sources (Adamas, Energy, Aldrich) and used as received without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Dibenzo[*b,f*][1,4]oxazepine derivatives **1** were prepared according to the reported literature (Y. R. Jorapur, G. Rajagopal, P. J. Saikia and R. R. Pal, *Tetrahedron Letters,* 2008, **49**, 1495-1497).

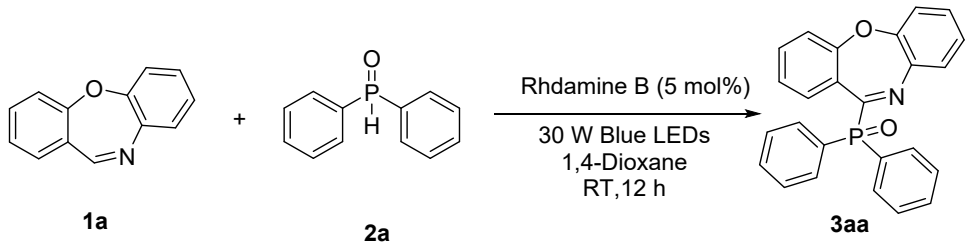
2.Substrate Preparation



Polyethylene glycol (8.0 g) was added into a 100 ml round-bottomed flask and heated in an oil bath at 70 ℃ until the polyethylene glycol melted, then potassium carbonate (0.6 g, 4.0 mmol), 2-aminophenol (0.6 g, 4.4 mmol) and 2-fluorobenzaldehyde (0.417 g, 4.0 mmol) were added successively. The reaction mixture was heated at 100 ℃ for 5 h. TLC monitoring confirmed that the raw material reaction was complete. Post-treatment: Transfer the reaction system to 500 ml glass beaker, and after the mixture is cooled to room temperature, add 150 ml distilled water to remove the PEG. Then, ethyl acetate (3×50 ml) and saturated salt water (3×50 ml) were extracted successively,

anhydrous sodium sulfate was dried, and the resulting organic phase was removed under vacuum conditions. A light-yellow solid was obtained by silica gel chromatography (ethyl acetate: petroleum ether =1:10, v/v). Various **1a** derivatives can be obtained by using the corresponding reaction materials.

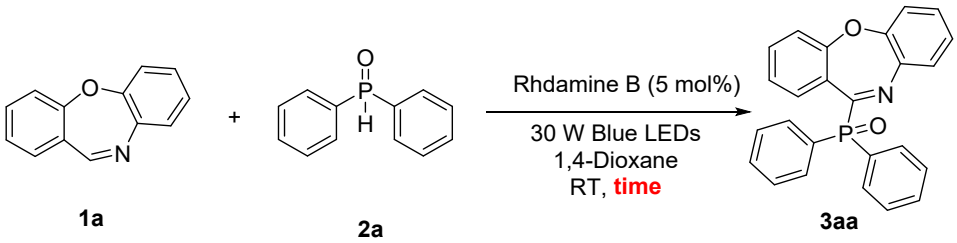
3. General Procedure



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

All reactions were performed in 10 ml reaction tubes. The reaction of dibenzo[*b,f*][*1,4*]oxazepine derivative **1a** (19.5 mg, 0.1 mmol) and diphenyl phosphine **2a** (40.4 mg, 0.2 mmol) and 5 mol% rhodamine B (5.4 mg) in 1,4-dioxane (1.0 mL) solvent was carried out under aerobic (air) conditions at room temperature by irradiation with 30 W blue LEDs and the reaction mixture was stirred for 12 h at room temperature. The electrodes were then cleaned with 1,4-dioxane, and then the combined solvents were dried with anhydrous sodium sulfate, and the solvents were removed by distillation under reduced pressure, followed by column chromatographic separation and purification (petroleum ether: ethyl acetate = 10:1) to obtain the desired product (35.6 mg, 90%).

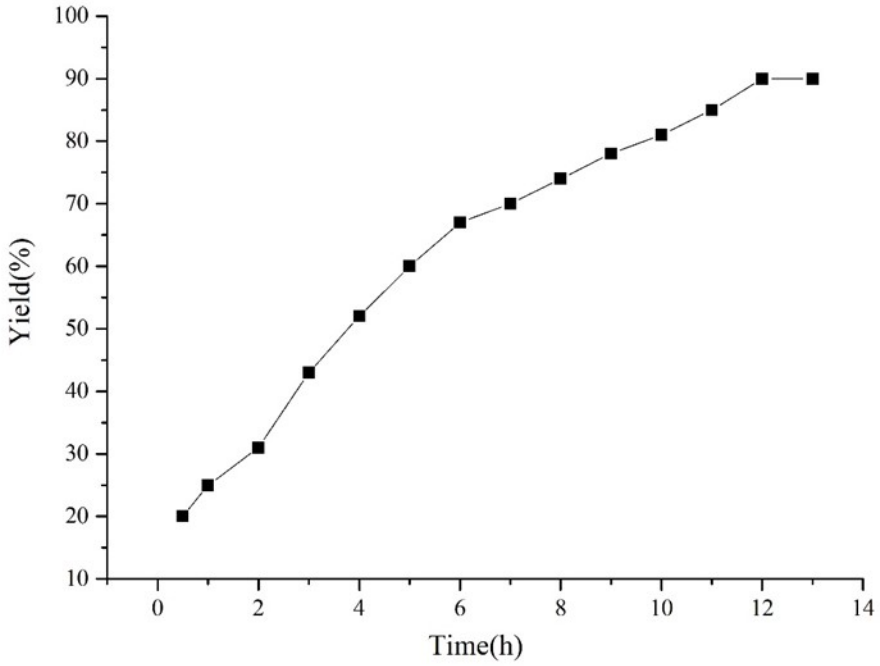
4. Time-Yield Correlation Experiments



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

Time（h）	0.5	1	2	3	4	5	6	7	8	9	10	11	12
Yield（%	23	25	31	43	52	59	67	70	74	78	81	85	90

)



Time-Yield plot

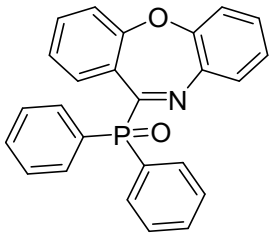
5. **Comparative Tabular Data**

entry	oxidizing agent	catalyst	temperature	yield	Ref.
1	/	$Pd(OAc)_2$ (10 mol%)	80 ℃	76%	1
2	$Mn(acac)_3$ (3.0 eq)	/	80 ℃	94%	2
3	**O_2**	**rhodamine B (5 mol%)**	**RT**	**90%**	**This work**

1. W. Hu, F. Teng, H. Hu, S. Luo and Q. Zhu, *J. Org. Chem.*, 2019, **84**, 6524-6535.
2. X. Liu, S. Yuan, Y. Liu, M. Ni, J. Xu, S. Gui, Y.-Y. Peng and Q. Ding, *J. Org. Chem.*, 2023, **88**, 198-210.

6. Characterization

Dibenzo[*b, f*][*1,4*]oxazepin-11-yldiphenylphosphine oxide 3aa

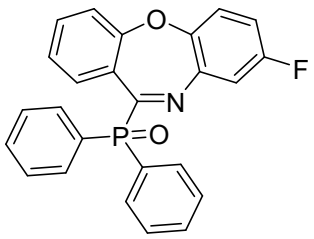


3aa

Synthesize according to general procedure. Isolated yield: 35.6 mg, 90% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.97 (ddt, *J* = 11.8, 6.8, 1.6 Hz, 4H), 7.54–7.50 (m, 1H), 7.50–7.45 (m, 4H), 7.44 (dt, *J* = 5.0, 1.7 Hz, 1H), 7.42–7.39 (m, 1H), 7.26–7.20 (m, 2H), 7.17 (d, *J* = 6.3 Hz, 1H), 7.15 (d, *J* = 6.9 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.77 (d, *J* = 125.0 Hz), 161.47 (d, *J* = 7.1 Hz), 152.20, 140.51 (d, *J* = 27.4 Hz), 133.70, 132.26 (d, *J* = 9.1 Hz), 132.07 (d, *J* = 2.7 Hz), 131.99 (d, *J* = 104.0 Hz), 130.56, 129.87, 128.65, 128.48 (d, *J* = 12.1 Hz), 126.68 (d, *J* = 27.1 Hz), 125.81, 125.30, 121.14, 120.90. **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 26.95. **MS** (HRMS) *m/z* calcd for $C_{25}H_{19}NO_2P$ $(M+H)^+$ = 396.1148, found = 396.1153.

(8-fluorodibenzo[*b, f*] [*1,4*]oxazepin-11-yl)diphenylphosphine oxide 3ba



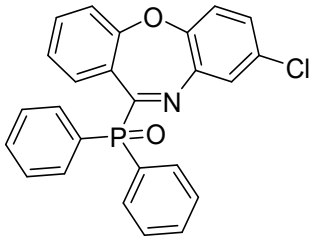
3ba

Synthesize according to general procedure. Isolated yield: 28.9 mg, 70% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.97–7.89 (m, 4H), 7.54–7.49 (m, 2H), 7.48–7.43 (m, 4H), 7.42–7.39 (m, 1H), 7.16 (td, *J* = 7.6, 1.2 Hz, 1H), 7.12 (dt, *J* = 8.2, 1.3 Hz, 1H), 7.08 (ddd, *J* = 8.6, 5.1, 0.7 Hz, 1H), 6.94–6.91 (m, 1H), 6.90 (dd, *J* = 3.2, 2.3 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.37 (d, *J* = 123.0 Hz), 161.50 (d, *J* = 7.0 Hz), 159.92 (d, *J* = 244.2 Hz), 148.38 (d, *J* = 2.9 Hz),

141.26 (d, *J* = 38.6 Hz), 133.99, 132.26, 132.17, 131.14, 130.71, 128.55 (d, *J* = 12.2 Hz), 126.53 (d, *J* = 26.5 Hz), 125.47, 121.90 (d, *J* = 9.2 Hz), 120.75, 116.12 (d, *J* = 23.4 Hz), 114.69 (d, *J* = 24.3 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 27.26. **MS** (HRMS) *m/z* calcd for $C_{25}H_{18}FNO_2P$ $(M+H)^+$ = 414.1054, found = 414.1058.

(8-chlorodibenzo[*b, f*][*1,4*]oxazepin-11-yl)diphenylphosphine oxide 3ca

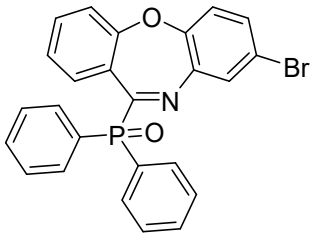


3ca

Synthesize according to general procedure. Isolated yield: 30.8 mg, 72% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.96–7.88 (m, 4H), 7.56–7.51 (m, 2H), 7.50–7.45 (m, 4H), 7.45–7.41 (m, 1H), 7.21–7.16 (m, 3H), 7.13 (dt, *J* = 8.2, 1.2 Hz, 1H), 7.07 (d, *J* = 8.5 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.46 (d, *J* = 123.1 Hz), 161.29 (d, *J* = 6.9 Hz), 150.86, 141.24 (d, *J* = 27.6 Hz), 134.01, 132.25, 132.16, 130.97 (d, *J* = 20.5 Hz), 130.73, 129.40, 128.62, 128.50, 128.11, 126.48 (d, *J* = 26.5 Hz), 125.56, 122.19, 120.82. **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 27.21. **MS** (HRMS) *m/z* calcd for $C_{25}H_{18}ClNO_2P$ $(M+H)^+$ = 430.0758, found = 430.0763.

(8-bromodibenzo[*b, f*][*1,4*]oxazepin-11-yl)diphenylphosphine oxide 3da

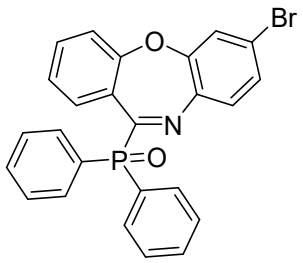


3da

Synthesize according to general procedure. Isolated yield: 31.2 mg, 66% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.98–7.90 (m, 4H), 7.57–52 (m, 2H), 7.51–7.46 (m, 4H), 7.45–7.41 (m, 1H), 7.37 (d, *J* = 2.5 Hz, 1H), 7.33 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.19 (td, *J* = 7.6, 1.2 Hz, 1H), 7.13 (dt, *J* = 8.2, 1.2 Hz, 1H), 7.02 (d, *J* = 8.5 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.36 (d, *J* = 122.8 Hz), 161.08 (d, *J* = 6.9 Hz), 151.24, 141.43 (d, *J* = 27.5 Hz), 133.83, 132.17, 132.09, 131.99, 130.94, 130.87, 130.58, 128.39 (d, *J* = 12.2 Hz), 126.32 (d, *J* = 26.6 Hz), 125.40, 122.42, 120.65, 118.10. **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 27.13. **MS** (HRMS) *m/z* calcd for $C_{25}H_{18}BrNO_2P$ $(M+H)^+$ = 474.0253, found = 474.0257.

(7-bromodibenzo[*b, f*][*1,4*]oxazepin-11-yl)diphenylphosphine oxide 3ea

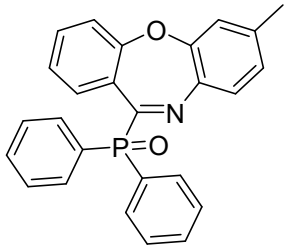


3ea

Synthesize according to general procedure. Isolated yield: 27.0 mg, 57% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.93 (ddt, *J* = 11.8, 6.9, 1.5 Hz, 4H), 7.56–7.51 (m, 2H), 7.47 (ddt, *J* = 7.0, 5.5, 2.4 Hz, 4H), 7.44 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.33 (d, *J* = 2.1 Hz, 1H), 7.28 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.19 (td, *J* = 7.6, 1.2 Hz, 1H), 7.14 (dt, *J* = 8.1, 1.2 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 169.37 (d, *J* = 124.1 Hz), 161.05 (d, *J* = 6.9 Hz), 152.37, 139.57 (d, *J* = 27.7 Hz), 133.91, 132.26, 132.17, 131.19, 130.70, 129.62, 129.13–128.90 (m), 128.50 (d, *J* = 12.3 Hz), 126.55 (d, *J* = 26.8 Hz), 125.66, 124.50, 122.70, 120.89. **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 27.28. **MS** (HRMS) *m/z* calcd for $C_{25}H_{18}BrNO_2P$ $(M+H)^+$ = 474.0253, found = 474.0260.

(7-methyldibenzo[*b, f*][*1,4*]oxazepin-11-yl)diphenylphosphine oxide 3fa

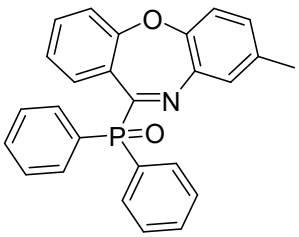


3fa

Synthesize according to general procedure. Isolated yield: 24.5 mg, 60% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.98–7.89 (m, 4H), 7.54–7.49 (m, 2H), 7.48–7.42 (m, 4H), 7.40 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.19–7.09 (m, 3H), 6.95 (d, *J* = 7.0 Hz, 2H), 2.31 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.40 (d, *J* = 126.3 Hz), 161.04 (d, *J* = 7.2 Hz), 151.62, 140.56, 137.85 (d, *J* = 27.7 Hz), 133.28, 132.05, 131.96, 131.93 (d, *J* = 103.9 Hz), 131.74 (d, *J* = 2.8 Hz), 130.26, 128.25, 128.13, 126.29, 124.97, 121.30, 120.63, 20.90. **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 26.80. **MS** (HRMS) *m/z* calcd for $C_{26}H_{21}NO_2P$ $(M+H)^+$ = 410.1304, found = 410.1310.

(8-methyldibenzo[*b, f*][*1,4*]oxazepin-11-yl)diphenylphosphine oxide 3ga



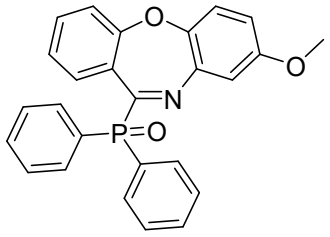
3ga

Synthesize according to general procedure. Isolated yield: 23.3 mg, 57% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14–8.09 (m, 1H), 8.00–7.90 (m, 4H), 7.56–7.51 (m, 2H), 7.50–7.45 (m, 4H), 7.42 (td, *J* = 7.8, 1.6 Hz, 1H), 7.19–7.12 (m, 2H), 7.04 (d, *J* = 1.9 Hz, 3H), 2.28 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.72, 159.70, 149.82, 148.73, 134.19, 133.37, 132.50 (d, *J* = 2.6 Hz), 132.01 (d, *J* = 9.2 Hz), 130.61 (d, *J* = 11.4 Hz), 128.97–128.71 (m), 128.55, 128.23 (d, *J* = 12.2 Hz), 126.09, 124.93,

121.70, 121.04, 120.57, 20.60. **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 26.93. **MS** (HRMS) *m/z* calcd for $C_{26}H_{21}NO_2P$ $(M+H)^+$ = 410.1304, found = 410.1308.

(8-methoxydibenzo[*b, f*][1,4]oxazepin-11-yl)diphenylphosphine oxide 3ha

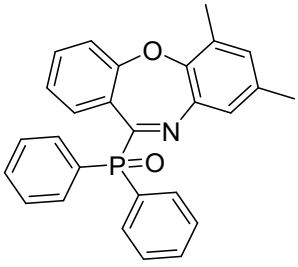


3ha

Synthesize according to general procedure. Isolated yield: 19.5 mg, 46% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14–8.09 (m, 1H), 7.95 (ddd, *J* = 11.8, 8.2, 1.4 Hz, 4H), 7.53 (td, *J* = 7.4, 1.4 Hz, 2H), 7.50–7.45 (m, 4H), 7.42 (td, *J* = 7.8, 1.4 Hz, 1H), 7.19–7.12 (m, 2H), 7.07 (d, *J* = 8.8 Hz, 1H), 6.78 (dd, *J* = 8.8, 3.1 Hz, 1H), 6.73 (d, *J* = 3.1 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 169.89, 161.73, 157.20, 146.08, 140.80, 133.70, 132.43, 132.28, 132.19, 131.39, 130.55, 128.50, 126.63 (d, *J* = 26.4 Hz), 125.15, 121.11 (d, *J* = 77.4 Hz), 115.43, 112.55, 29.80. **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 27.19. **MS** (HRMS) *m/z* calcd for $C_{26}H_{21}NO_3P$ $(M+H)^+$ = 426.1254, found = 426.1256.

(6,8-dimethyldibenzo[*b, f*][*1,4*]oxazepin-11-yl)diphenylphosphine oxide 3ia



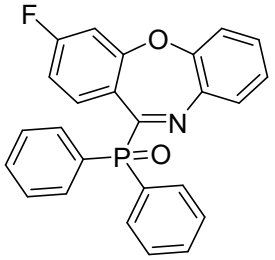
3ia

Synthesize according to general procedure. Isolated yield: 25.0 mg, 59% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.03–7.92 (m, 4H), 7.54–7.50 (m, 1H), 7.50–7.46 (m, 4H), 7.45 (dt, *J* = 3.2, 1.7 Hz, 1H), 7.40 (ddd, *J* = 8.1,

7.3, 1.6 Hz, 1H), 7.18 (dt, *J* = 8.2, 1.3 Hz, 1H), 7.14 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.90 (dd, *J* = 18.7, 2.2 Hz, 2H), 2.42 (s, 3H), 2.23 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.91 (d, *J* = 125.8 Hz), 161.30 (d, *J* = 7.1 Hz), 147.92, 139.99 (d, *J* = 27.3 Hz), 134.52, 133.06, 132.43, 131.99 (d, *J* = 9.1 Hz), 131.73 (d, *J* = 2.9 Hz), 131.59, 131.40, 130.28, 129.75, 128.19 (d, *J* = 12.1 Hz), 126.02, 124.81, 120.72, 20.39, 16.03. **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 26.86. **MS** (HRMS) *m/z* calcd for $C_{27}H_{23}NO_2P$ $(M+H)^+$ = 424.1461, found = 424.1465.

(3-fluorodibenzo[*b, f*][1,4]oxazepin-11-yl)diphenylphosphine oxide 3ja

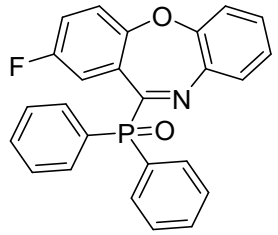


3ja

Synthesize according to general procedure. Isolated yield: 27.7 mg, 67% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27–8.20 (m, 1H), 8.00–7.92 (m, 4H), 7.54–7.50 (m, 1H), 7.50–7.45 (m, 4H), 7.44 (dt, *J* = 3.2, 1.7 Hz, 1H), 7.25–7.19 (m, 2H), 7.15 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.11 (dd, *J* = 8.3, 1.5 Hz, 1H), 6.89 (dd, *J* = 6.0, 2.0 Hz, 1H), 6.88–6.85 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.09, 166.84, 164.28, 162.56 (dd, *J* = 11.4, 7.2 Hz), 151.42, 140.00 (d, *J* = 27.2 Hz), 131.98, 131.89, 130.94, 129.69, 128.40, 128.23 (d, *J* = 12.3 Hz), 125.88, 122.91 (dd, *J* = 27.6, 3.5 Hz), 120.82, 112.39 (d, *J* = 21.5 Hz), 108.57 (d, *J* = 23.4 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 27.06. **MS** (HEMS) *m/z* calcd for $C_{25}H_{18}FNO_2P$ $(M+H)^+$ = 414.1054, found = 414.1060.

(2-fluorodibenzo[*b, f*][*1, 4*]oxazepin-11-yl)diphenylphosphine oxide 3ka

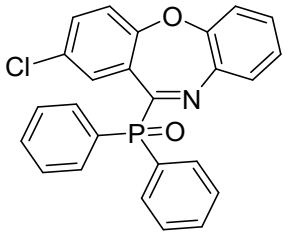


3ka

Synthesize according to general procedure. Isolated yield: 30.1 mg, 73% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (ddt, *J* = 11.8, 6.9, 1.5 Hz, 5H), 7.56–7.52 (m, 1H), 7.52 –7.47 (m, 4H), 7.46 (dt, *J* = 3.2, 1.7 Hz, 1H), 7.28–7.22 (m, 2H), 7.19–7.13 (m, 2H), 7.11 (dd, *J* = 6.5, 2.0 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.16 (d, *J* = 125.1 Hz), 160.10, 157.66, 157.09 (d, *J* = 6.9 Hz), 151.76, 139.93 (d, *J* = 26.6 Hz), 131.93, 131.78, 130.74, 130.67–129.64 (m), 128.27, 127.25 (dd, *J* = 27.1, 8.1 Hz), 126.17–125.10 (m), 122.38–121.34 (m), 121.13–120.46 (m), 120.45–119.77 (m), 117.28–116.12 (m). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 27.09. **MS** (HRMS) *m/z* calcd for $C_{25}H_{18}FNO_2P$ $(M+H)^+$ = 414.1054, found = 414.1057.

(2-chlorodibenzo[*b, f*][*1, 4*]oxazepin-11-yl)diphenylphosphine oxide 3la



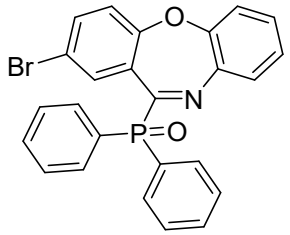
3la

Synthesize according to general procedure. Isolated yield: 22.7 mg, 53% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (dd, *J* = 2.5, 0.6 Hz, 1H), 7.98–7.92 (m, 4H), 7.57–7.52 (m, 2H), 7.51–7.45 (m, 4H), 7.38 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.27 (d, *J* = 6.6 Hz, 1H), 7.24 (d, *J* = 1.9 Hz, 1H), 7.22 (d, *J* = 1.9 Hz, 1H), 7.20–7.16 (m, 1H), 7.15–7.12 (m, 1H), 7.09 (dd, *J* = 8.7, 1.2 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.52 (d, *J* = 124.7 Hz), 159.90 (d, *J* = 7.0 Hz), 151.87, 140.21 (d, *J* = 26.5 Hz), 133.52, 132.30, 132.21, 131.11, 130.81, 130.17 (d, *J* = 8.6 Hz), 128.71, 128.59, 128.47, 127.74 (d, *J* =

27.1 Hz), 126.06, 122.13, 120.98. **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 26.73. **MS** (HRMS) *m/z* calcd for $C_{25}H_{18}ClNO_2P$ $(M+H)^+$ = 430.0758, found = 430.0767.

(2-bromodibenzo[*b, f*][*1, 4*]oxazepin-11-yl)diphenylphosphine oxide 3ma

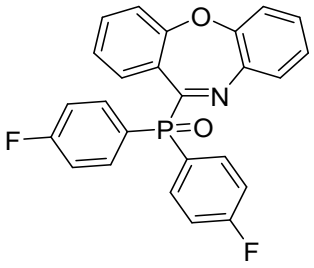


3ma

Synthesize according to general procedure. Isolated yield: 30.0 mg, 63% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35 (dd, *J* = 2.4, 0.6 Hz, 1H), 8.00–7.92 (m, 4H), 7.53–7.50 (m, 2H), 7.50–7.46 (m, 4H), 7.45 (dt, *J* = 3.2, 1.7 Hz, 1H), 7.24–7.22 (m, 1H), 7.21 (d, *J* = 1.0 Hz, 1H), 7.17–7.14 (m, 1H), 7.14–7.10 (m, 1H), 7.01 (dd, *J* = 8.7, 1.3 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.15 (d, *J* = 124.8 Hz), 160.16 (d, *J* = 6.8 Hz), 151.53, 139.91 (d, *J* = 26.5 Hz), 136.25 (d, *J* = 5.2 Hz), 132.83 (d, *J* = 6.5 Hz), 132.03, 131.95, 131.87, 130.83, 129.92, 128.30 (d, *J* = 12.0 Hz), 127.90 (d, *J* = 27.2 Hz), 125.85, 122.29 (d, *J* = 6.7 Hz), 120.75, 118.02. **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 27.06. **MS** (HRMS) *m/z* calcd for $C_{25}H_{18}BrNO_2P$ $(M+H)^+$ = 474.0253, found = 474.0261.

Dibenzo[*b, f*][*1,4*]oxazepin-11-ylbis(4-fluorophenyl)phosphine oxide 3ab



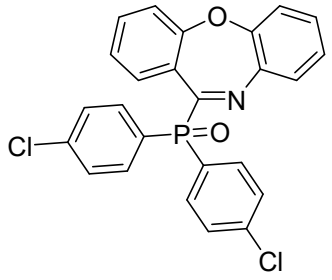
3ab

Synthesize according to general procedure. Isolated yield: 22.4 mg, 52% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.95 (tdd, *J* = 8.7, 5.5, 2.0 Hz, 4H), 7.46 (td, *J* = 7.7, 1.6 Hz, 1H), 7.29–7.26 (m, 1H), 7.25 (dd, *J* = 3.2, 2.1

Hz, 1H), 7.23–7.21 (m, 1H), 7.19 (d, *J* = 0.7 Hz, 1H), 7.19–7.17 (m, 3H), 7.16 (dd, *J* = 2.6, 1.9 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.24 (d, *J* = 127.3 Hz), 165.15 (dd, *J* = 253.8, 3.4 Hz), 161.31 (d, *J* = 7.3 Hz), 152.02, 142.69, 140.17 (d, *J* = 27.9 Hz), 134.57 (dd, *J* = 10.6, 8.9 Hz), 133.77, 130.12 (d, *J* = 32.8 Hz), 129.47, 128.42, 127.55 (dd, *J* = 107.7, 3.4 Hz), 126.49 (d, *J* = 7.8 Hz), 125.76, 125.23, 120.94 (d, *J* = 24.1 Hz), 115.82 (dd, *J* = 21.4, 13.3 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 25.37. **MS** (HRMS) *m/z* calcd for $C_{25}H_{17}F_2NO_2P$ $(M+H)^+$ = 432.0959, found = 432.0963.

bis(4-chlorophenyl)(dibenzo[*b, f*][*1,4*]oxazepin-11-yl)phosphine oxide 3ac

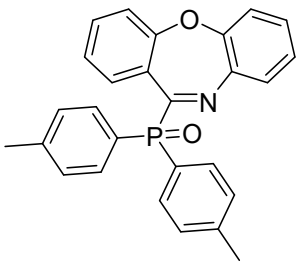


3ac

Synthesize according to general procedure. Isolated yield: 25.0 mg, 54% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.91–7.84 (m, 4H), 7.48–7.43 (m, 5H), 7.28 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.24 (t, *J* = 2.0 Hz, 1H), 7.23–7.20 (m, 1H), 7.19 (dd, *J* = 1.5, 0.7 Hz, 1H), 7.18–7.17 (m, 1H), 7.16 (dd, *J* = 2.4, 1.3 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.67, 167.40, 161.47 (d, *J* = 7.3 Hz), 152.17, 140.27 (d, *J* = 27.9 Hz), 138.96 (d, *J* = 3.6 Hz), 134.01, 133.64, 133.54, 130.69, 130.34 (d, *J* = 6.8 Hz), 129.64, 128.98 (d, *J* = 7.2 Hz), 126.40 (d, *J* = 27.9 Hz), Unknown NMR (162 MHz, Chloroform-*d*) δ 25.26. 125.90, 125.43 (d, *J* = 14.3 Hz), 121.14 (t, *J* = 18.7 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 25.26. **MS** (HRMS) *m/z* calcd for $C_{25}H_{17}Cl_2NO_2P$ $(M+H)^+$ = 464.0368, found = 464.0371.

Dibenzo[*b, f*][*1,4*]oxazepin-11-yldi-p-tolylphosphine oxide 3ad

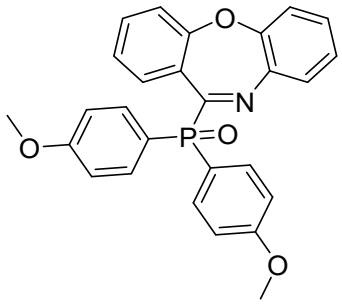


3ad

Synthesize according to general procedure. Isolated yield: 34.7 mg, 82% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.89–7.82 (m, 4H), 7.38 (td, *J* = 7.7, 1.7 Hz, 1H), 7.26 (dd, *J* = 5.1, 3.0 Hz, 4H), 7.24 (d, *J* = 1.8 Hz, 1H), 7.20 (ddd, *J* = 8.5, 7.0, 1.8 Hz, 1H), 7.16–7.13 (m, 2H), 7.12 (q, *J* = 2.0, 1.6 Hz, 2H), 2.34 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 169.21 (d, *J* = 124.6 Hz), 161.46 (d, *J* = 7.1 Hz), 152.21, 142.50 (d, *J* = 2.8 Hz), 140.58 (d, *J* = 27.1 Hz), 133.62 (d, *J* = 18.0 Hz), 132.30, 132.21, 130.59 (d, *J* = 23.1 Hz), 129.46, 129.39, 129.34, 129.18, 129.05, 126.76 (d, *J* = 27.0 Hz), 126.06–124.86 (m), 121.42–120.50 (m), 21.74 (d, *J* = 11.4 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 27.64. **MS** (HRMS) *m/z* calcd for $C_{27}H_{23}NO_2P$ $(M+H)^+$ = 424.1461, found = 424.1467.

Dibenzo[*b, f*][*1, 4*]oxazepin-11-ylbis(4-methoxyphenyl)phosphine oxide 3ae



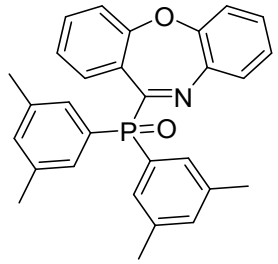
3ae

Synthesize according to general procedure. Isolated yield: 21.4 mg, 47% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.85 (tt, *J* = 9.7, 2.4 Hz, 4H), 7.42 (td, *J* = 7.7, 1.6 Hz, 1H), 7.26–7.23 (m, 1H), 7.22–7.18 (m, 1H), 7.17–7.13 (m, 4H), 6.99–6.95 (m, 4H), 3.82 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 162.38,

161.28, 152.04, 133.96, 133.92, 130.46 (d, J = 20.5 Hz), 129.52, 128.48, 125.36, 123.77, 122.67, 120.81, 114.02, 113.83, 113.71, 55.27. **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 27.39. **MS** (HRMS) *m/z* calcd for $C_{27}H_{23}NO_4P$ $(M+H)^+$ = 456.1359, found = 456.1365.

dibenzo[*b, f*][*1, 4*]oxazepin-11-ylbis(3,5-dimethylphenyl)phosphine oxide 3af

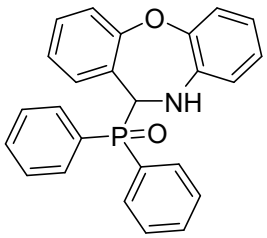


3af

Synthesize according to general procedure. Isolated yield: 24.4 mg, 54% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (dd, J = 8.2, 1.6 Hz, 1H), 7.56 (dd, J = 12.1, 1.7 Hz, 4H), 7.45–7.38 (m, 1H), 7.28–7.21 (m, 2H), 7.18 (t, J = 1.5 Hz, 1H), 7.17 (t, J = 1.8 Hz, 2H), 7.14 (q, J = 1.5 Hz, 3H), 2.34 (s, 12H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 169.60, 168.37, 161.32 (d, J = 7.0 Hz), 152.08, 140.49 (d, J = 27.3 Hz), 137.91, 137.79, 134.14–133.56 (m), 133.45 (d, J = 2.8 Hz), 132.05, 131.02, 130.89–130.03 (m), 129.64, 129.55, 128.06 (d, J = 29.6 Hz), 126.57 (d, J = 26.8 Hz), 120.73 (dt, J = 63.0, 31.0 Hz), 21.30. **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 27.93. **MS** (HRMS) *m/z* calcd for $C_{29}H_{27}NO_4P$ $(M+H)^+$ = 452.1774, found = 452.1783.

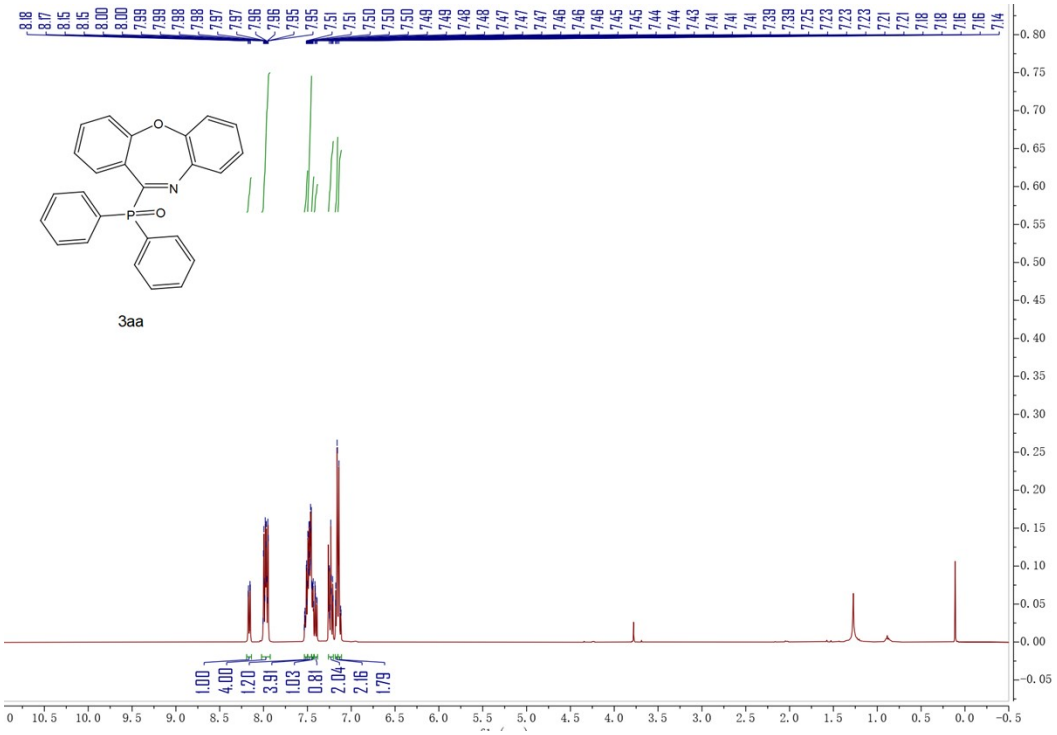
(10,11-dihydrodibenzo[b,f][1,4]oxazepin-11-yl)diphenylphosphine oxide B



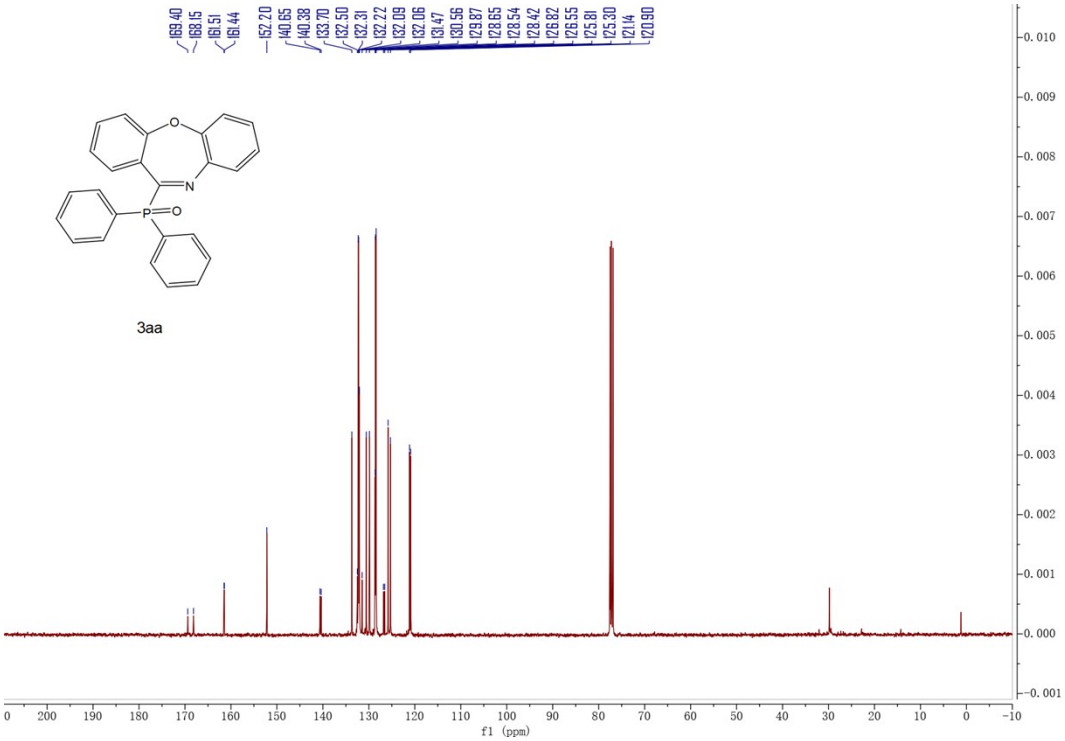
B

Light yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.77 (m, 2H), 7.51 (dddd, *J* = 11.1, 8.5, 6.4, 1.4 Hz, 3H), 7.46 – 7.39 (m, 3H), 7.30 (tdd, *J* = 8.2, 3.1, 1.3 Hz, 2H), 7.21 (ddt, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.09 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.04 (dt, *J* = 7.7, 1.7 Hz, 1H), 6.89 (dd, *J* = 7.6, 1.3 Hz, 1H), 6.84 (ddd, *J* = 7.9, 7.1, 1.5 Hz, 1H), 6.77 (ddd, *J* = 21.2, 8.0, 1.5 Hz, 2H), 6.66 (ddd, *J* = 8.0, 7.1, 1.6 Hz, 1H), 5.40 (d, *J* = 11.7 Hz, 1H), 4.59 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.03 (d, *J* = 6.3 Hz), 146.50, 136.73 (d, *J* = 5.9 Hz), 132.20 (d, *J* = 2.8 Hz), 131.94, 131.85, 130.21 (d, *J* = 5.0 Hz), 129.69, 128.55 (d, *J* = 11.5 Hz), 128.34 (d, *J* = 11.5 Hz), 124.81, 124.42, 123.47, 120.93, 60.28 (d, *J* = 73.0 Hz).**^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.97. **HRMS** (ESI) m/z calcd for $C_{25}H_{21}NO_2P$ $(M+H)^+$ = 398.1310, found 398.1308.

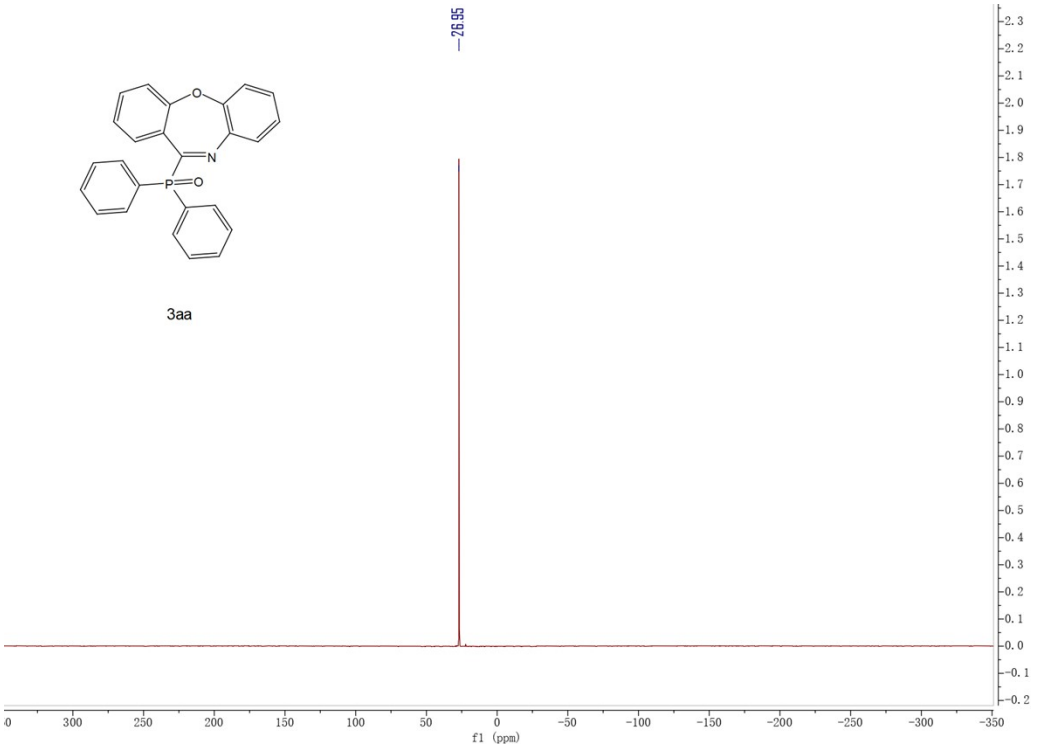
7. ^{1}H NMR、^{13}C NMR and ^{31}P NMR Spectra



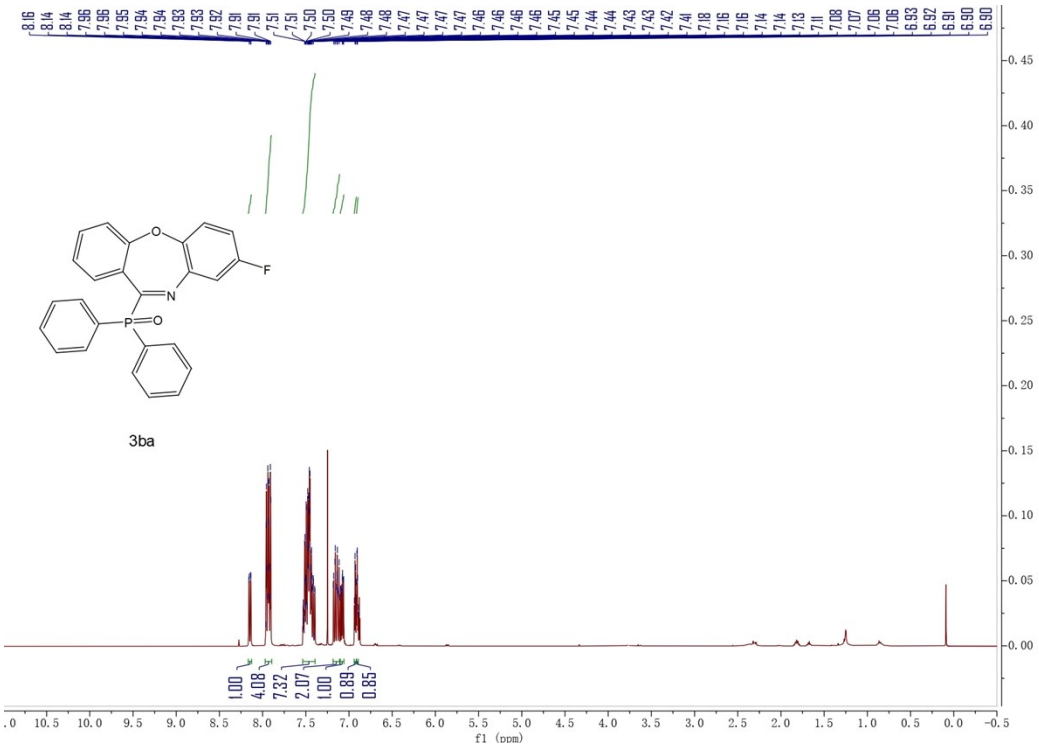
^{1}H NMR spectrum of 3aa ($CDCl_3$, 400 MHz)



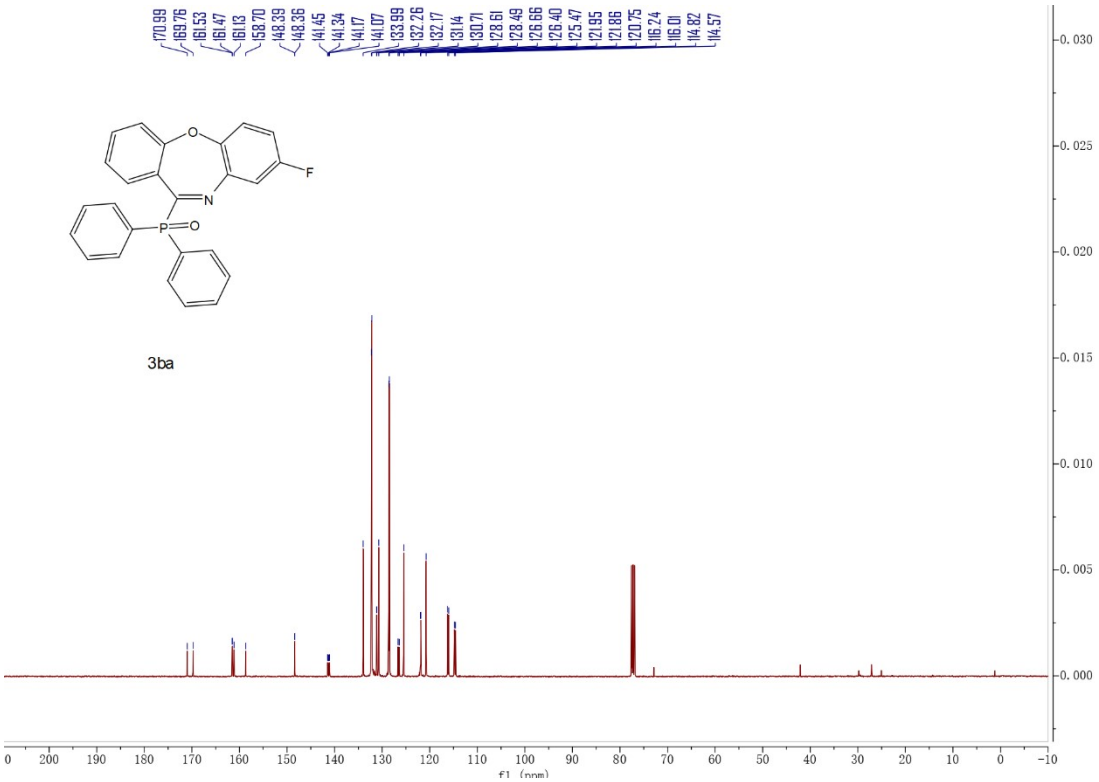
^{13}C NMR spectrum of 3aa ($CDCl_3$, 101 MHz)



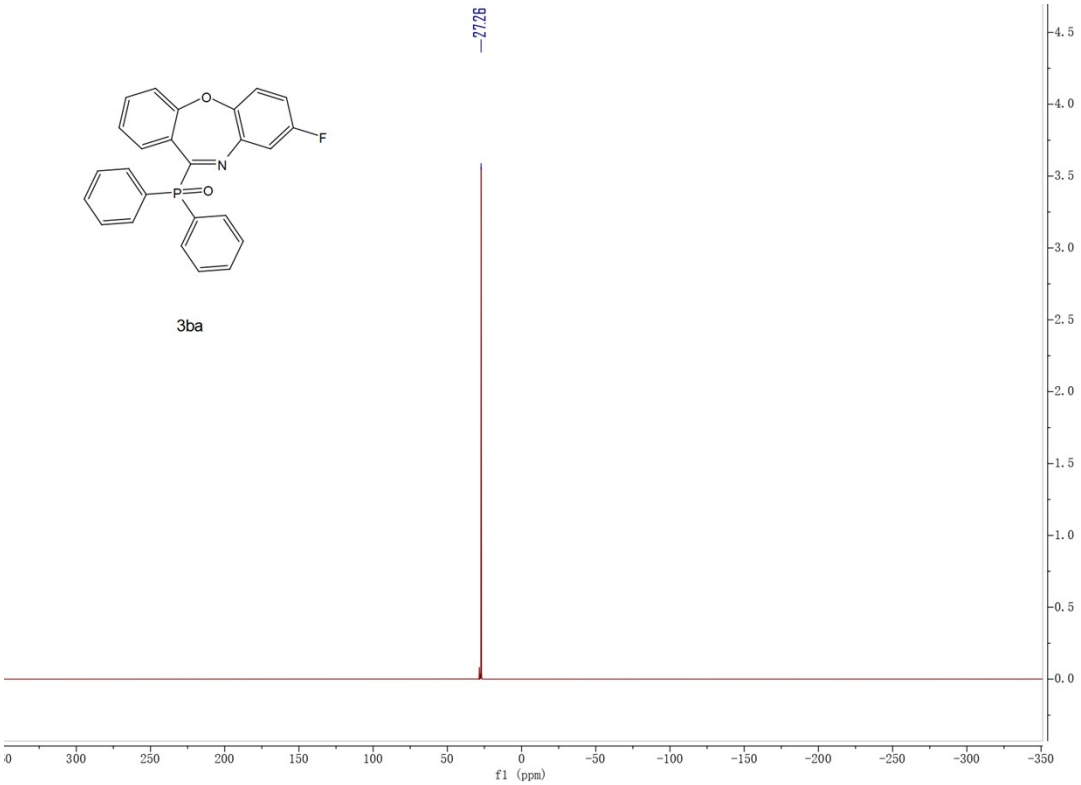
^{31}P NMR spectrum of 3aa ($CDCl_3$, 162 MHz)



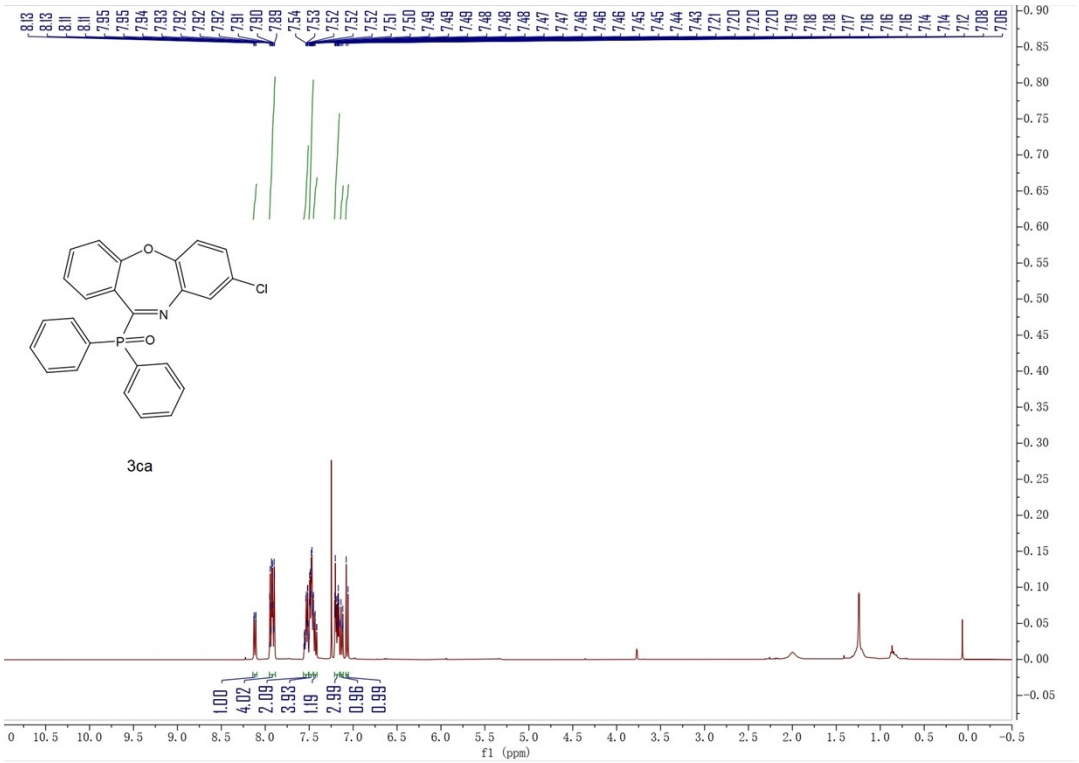
^{1}H NMR spectrum of 3ba ($CDCl_3$, 400 MHz)



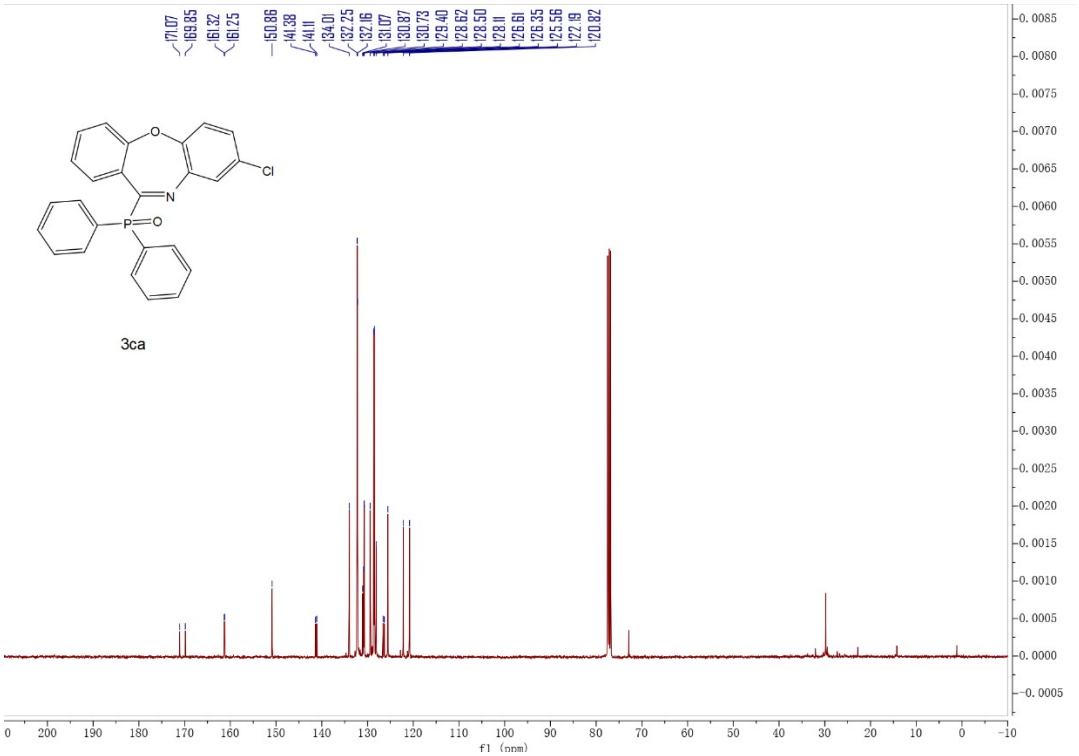
^{13}C NMR spectrum of 3ba ($CDCl_3$, 101 MHz)



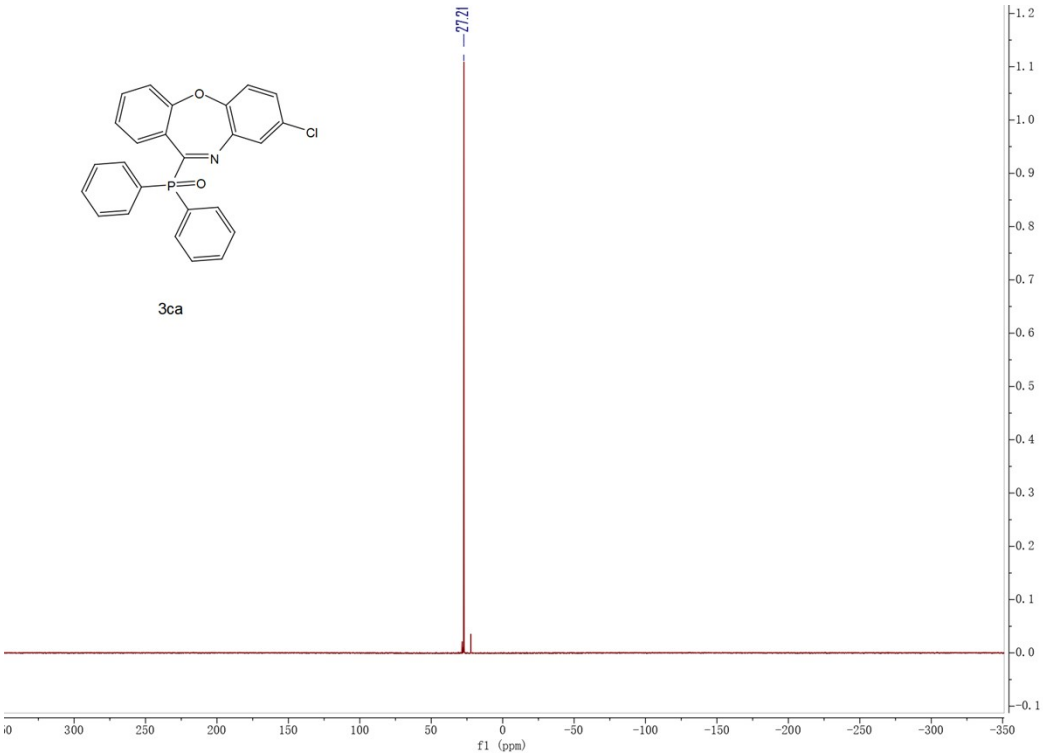
^{31}P NMR spectrum of 3ba ($CDCl_3$, 162 MHz)



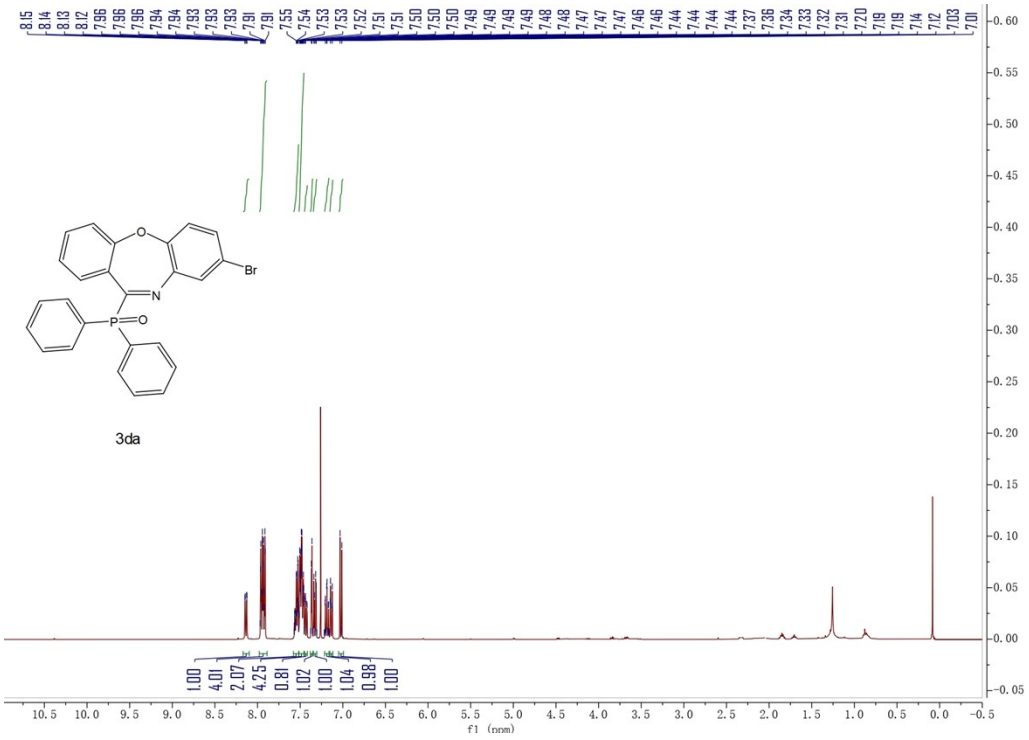
^{1}H NMR spectrum of 3ca ($CDCl_3$, 400 MHz)



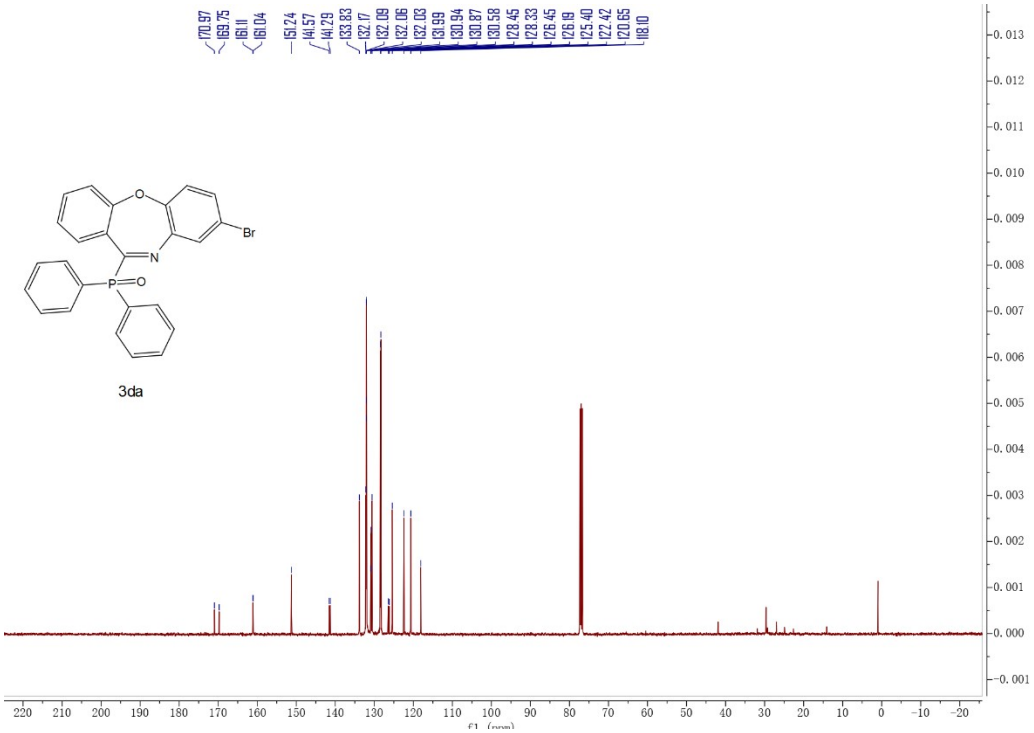
^{13}C NMR spectrum of 3ca ($CDCl_3$, 101 MHz)



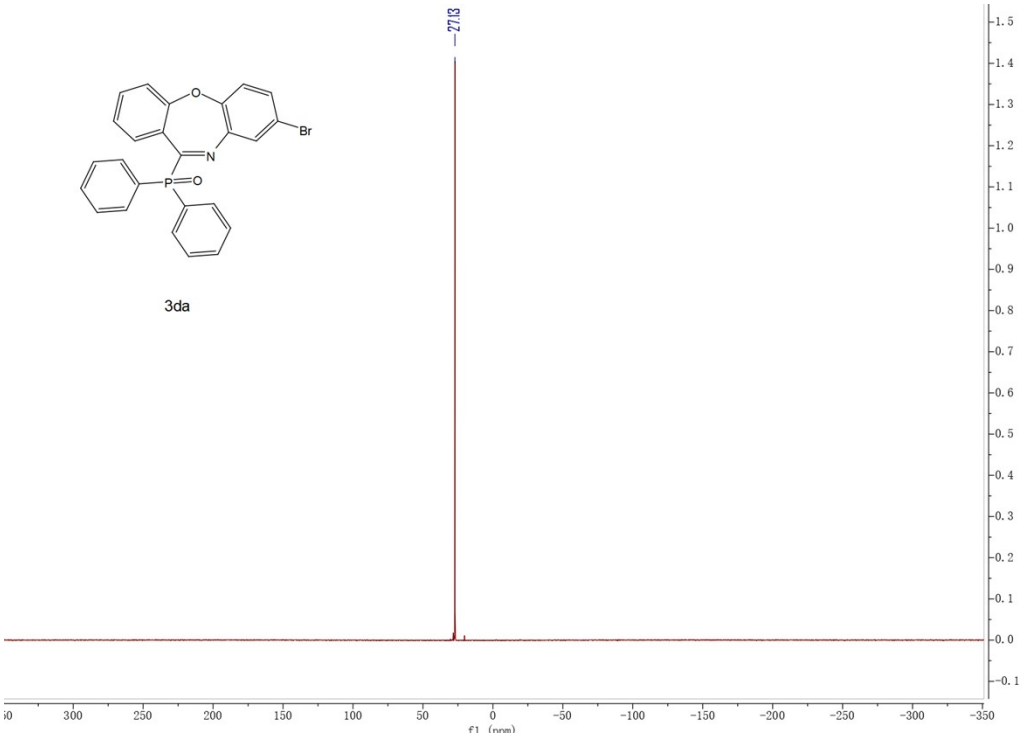
^{31}P NMR spectrum of 3ca ($CDCl_3$, 162 MHz)



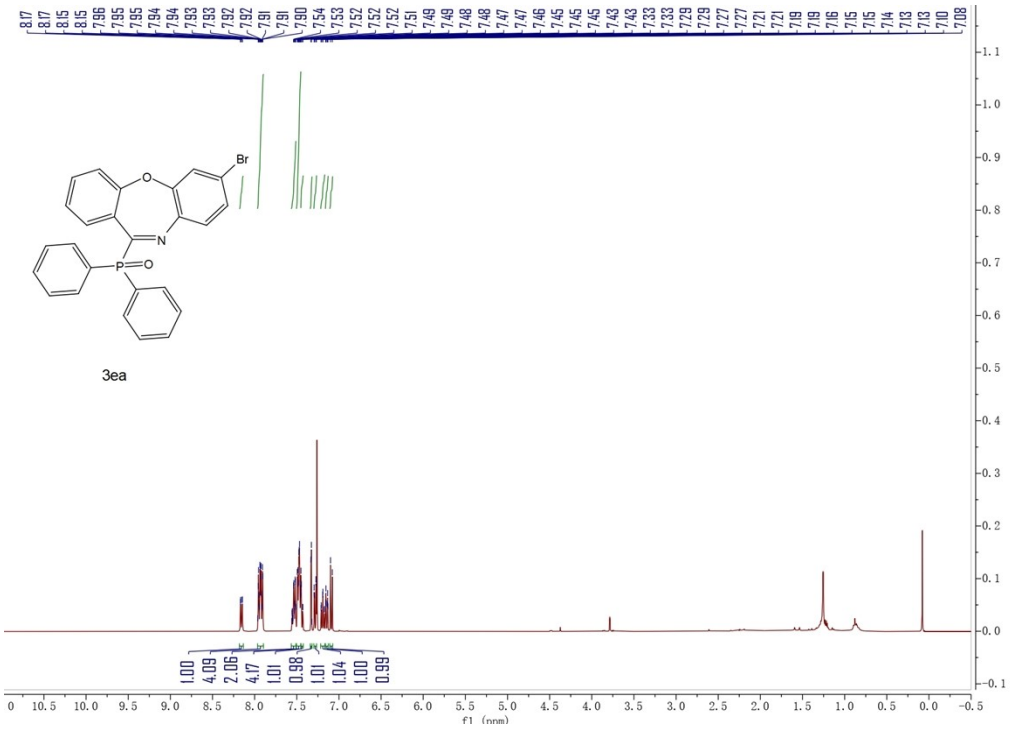
^{1}H NMR spectrum of 3da ($CDCl_3$, 400 MHz)



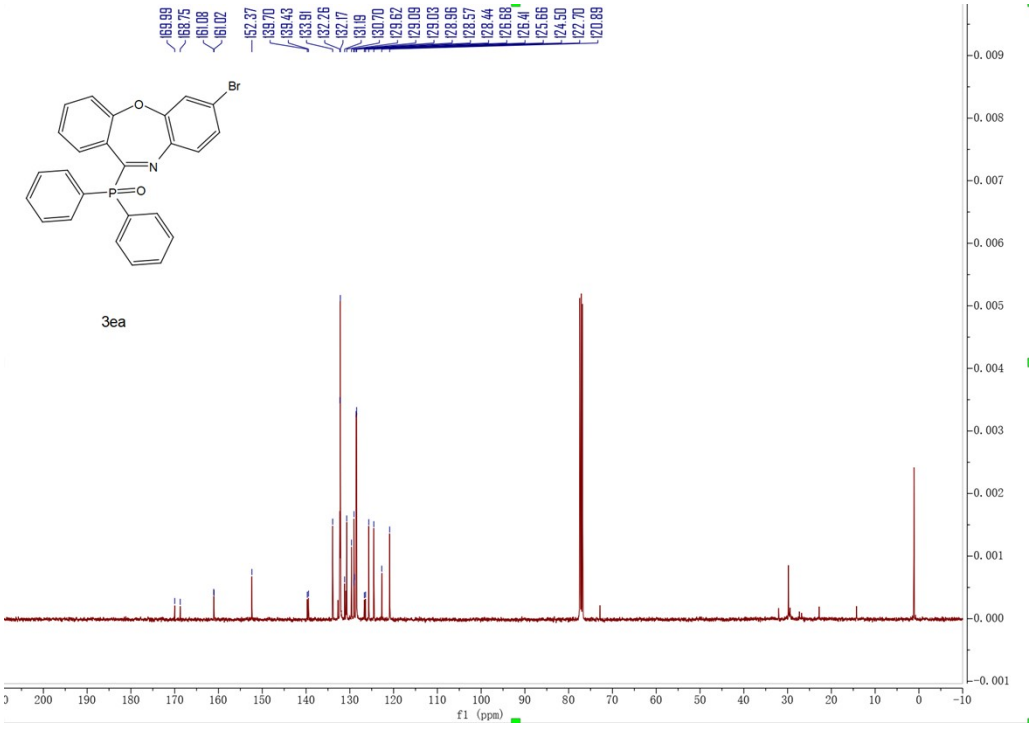
^{13}C NMR spectrum of 3da ($CDCl_3$, 101 MHz)



^{31}P NMR spectrum of 3da ($CDCl_3$, 162 MHz)

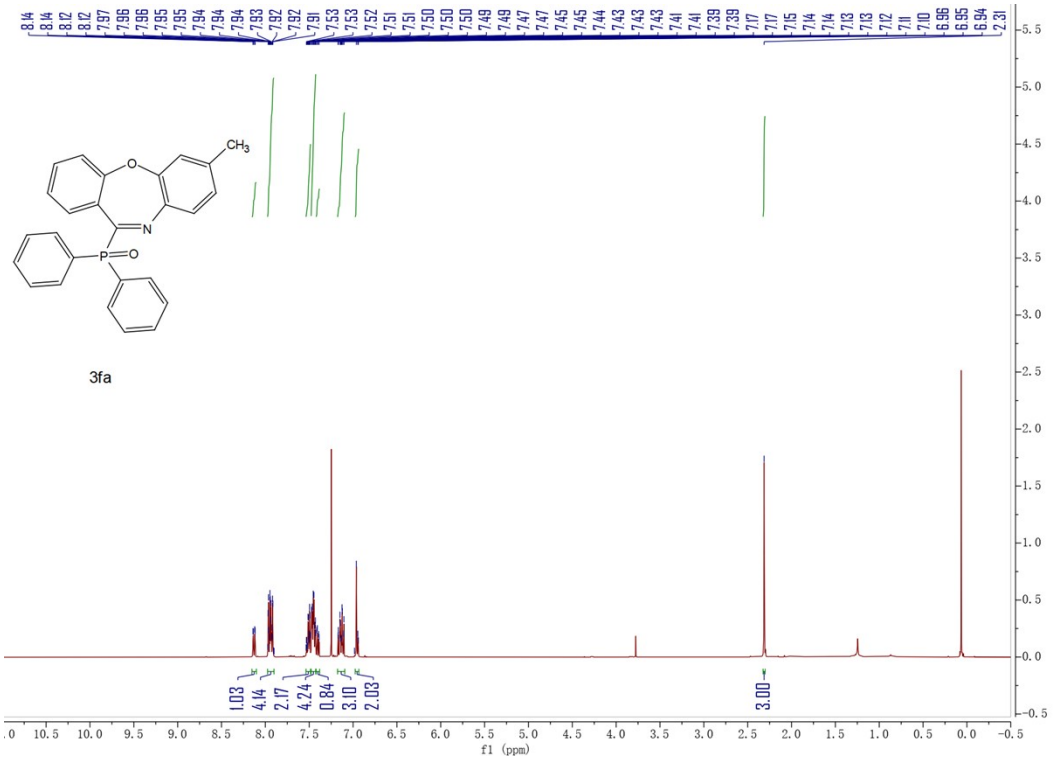


^{1}H NMR spectrum of 3ea ($CDCl_3$, 400 MHz)

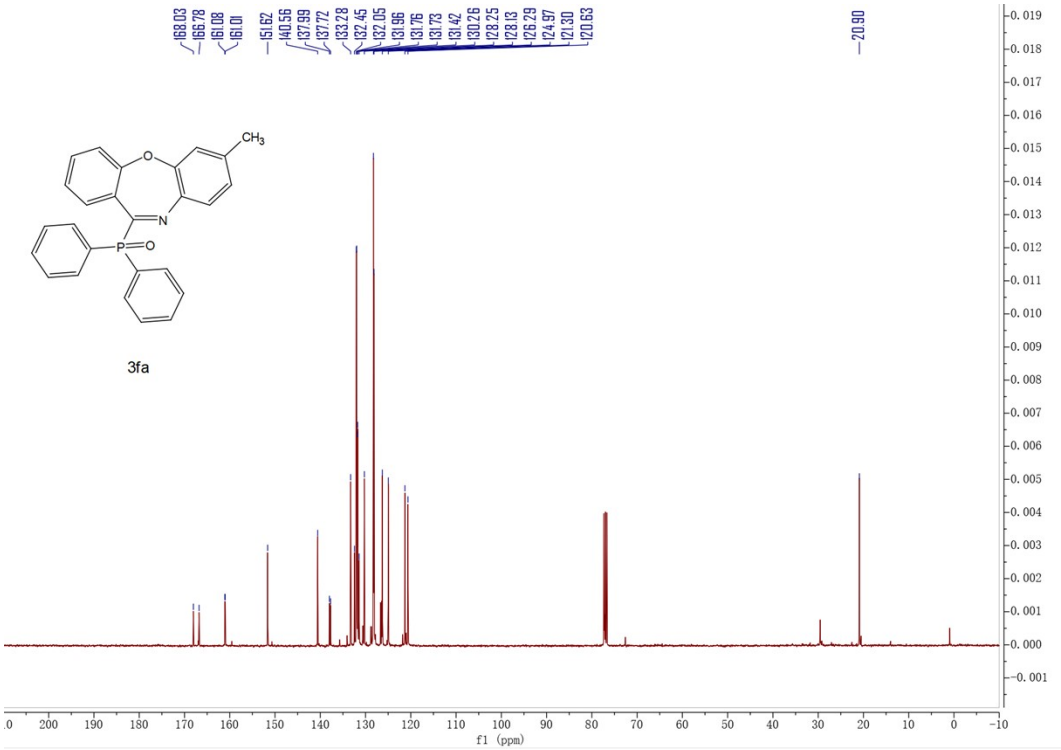


^{13}C NMR spectrum of 3ea ($CDCl_3$, 101 MHz)

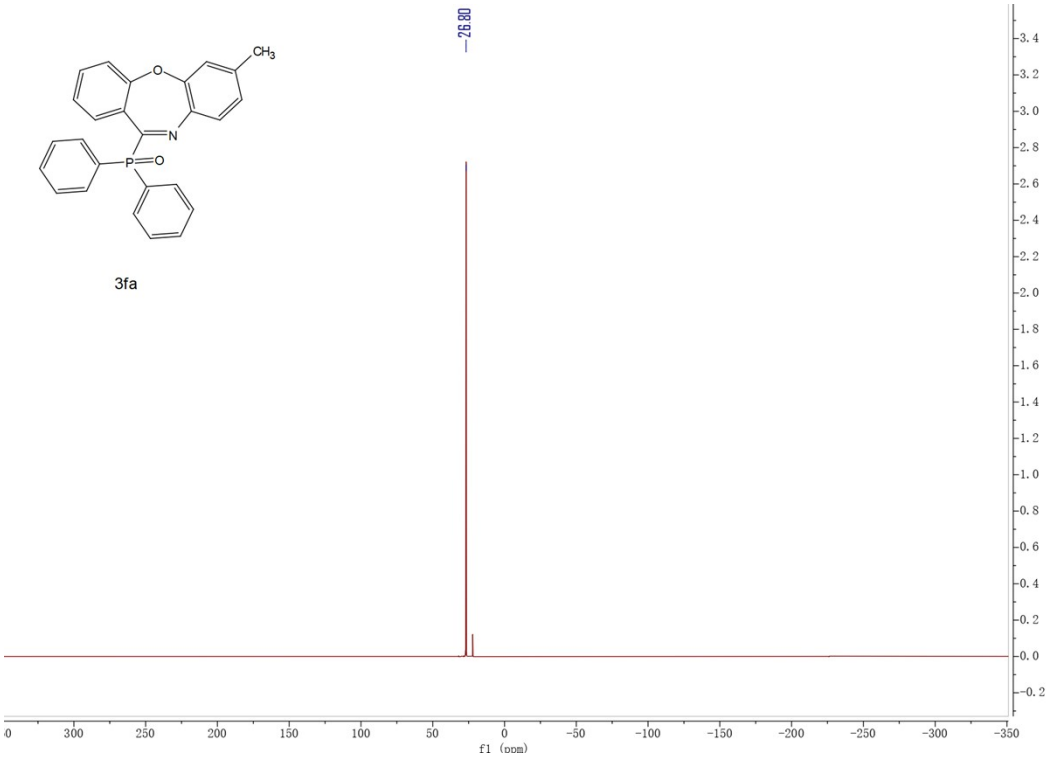
^{31}P NMR spectrum of 3ea ($CDCl_3$, 162 MHz)



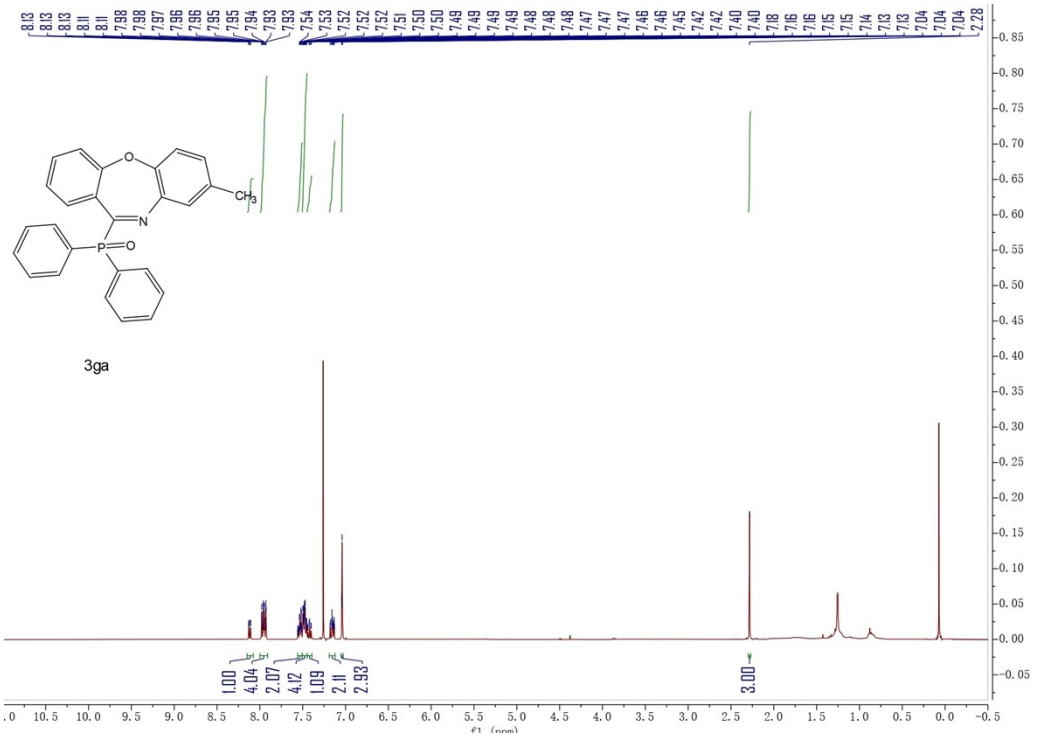
^{1}H NMR spectrum of 3fa ($CDCl_3$, 400 MHz)



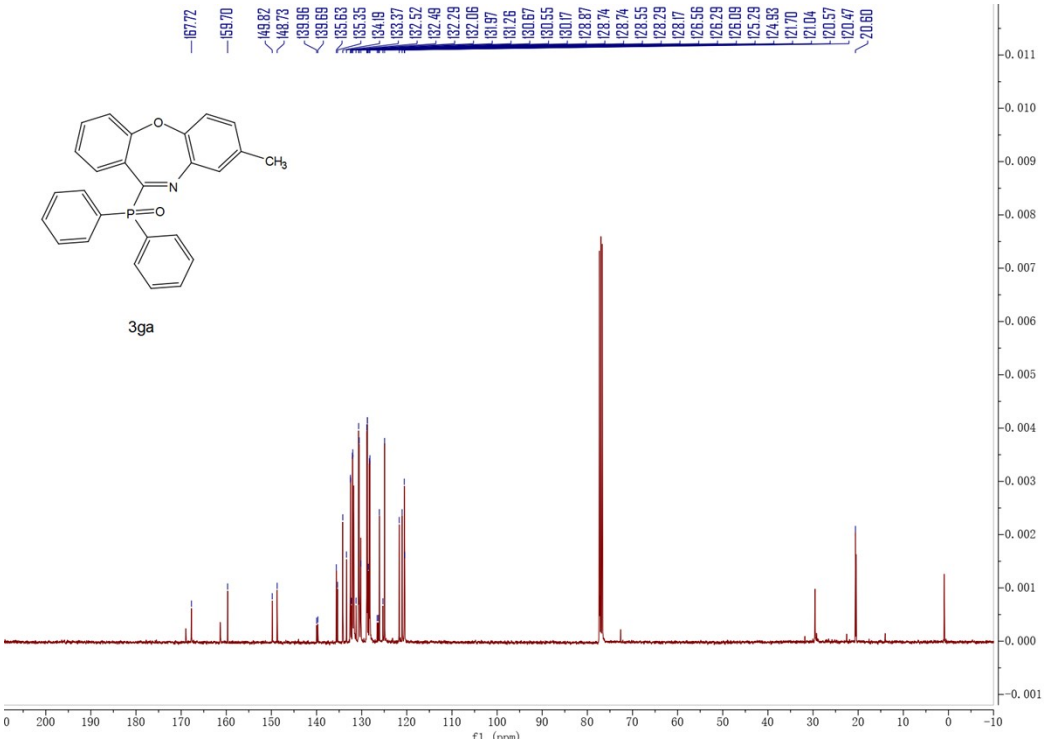
^{13}C NMR spectrum of 3fa ($CDCl_3$, 101 MHz)



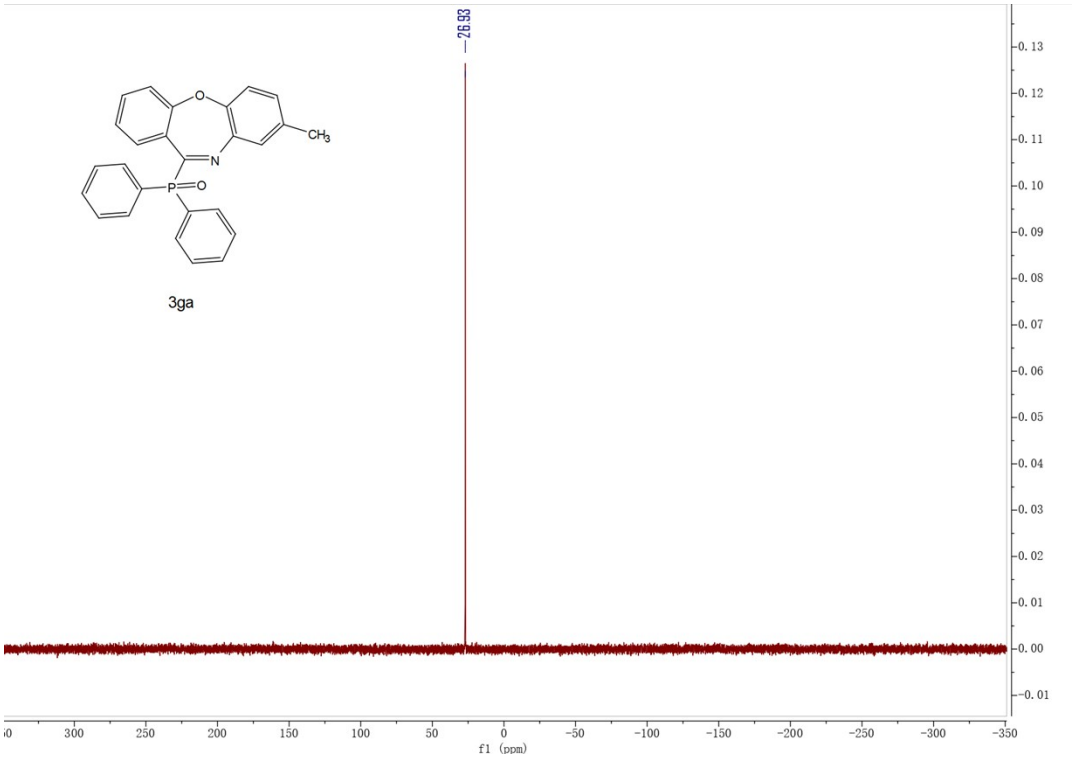
^{31}P NMR spectrum of 3fa ($CDCl_3$, 162 MHz)



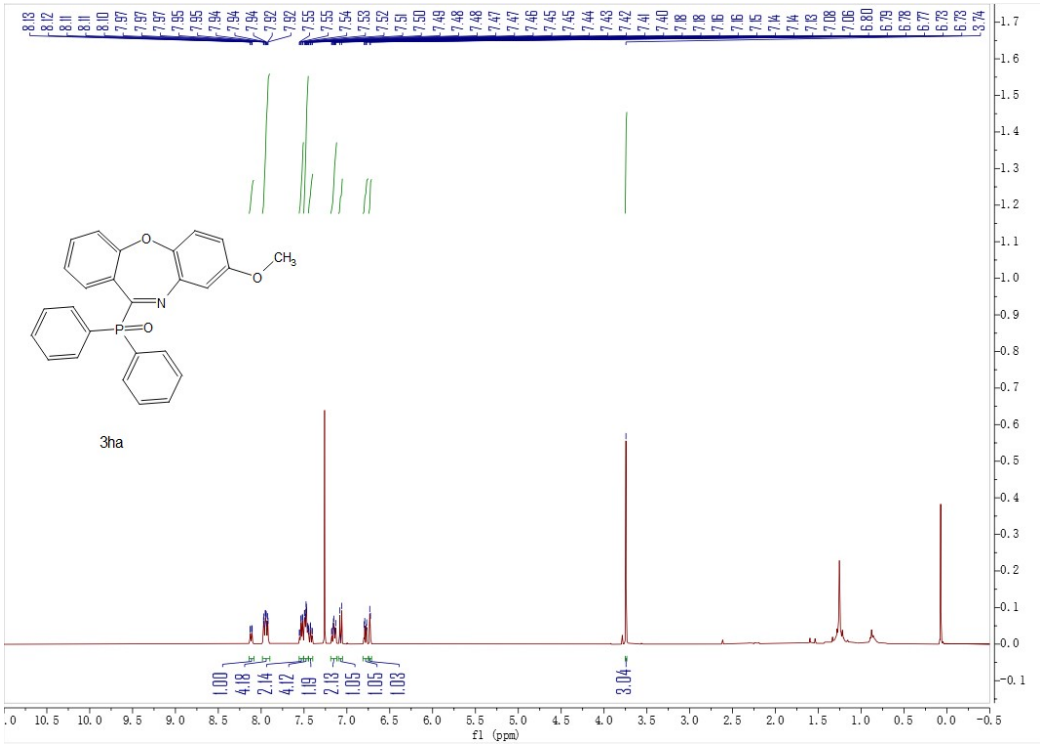
^{1}H NMR spectrum of 3ga ($CDCl_3$, 400 MHz)



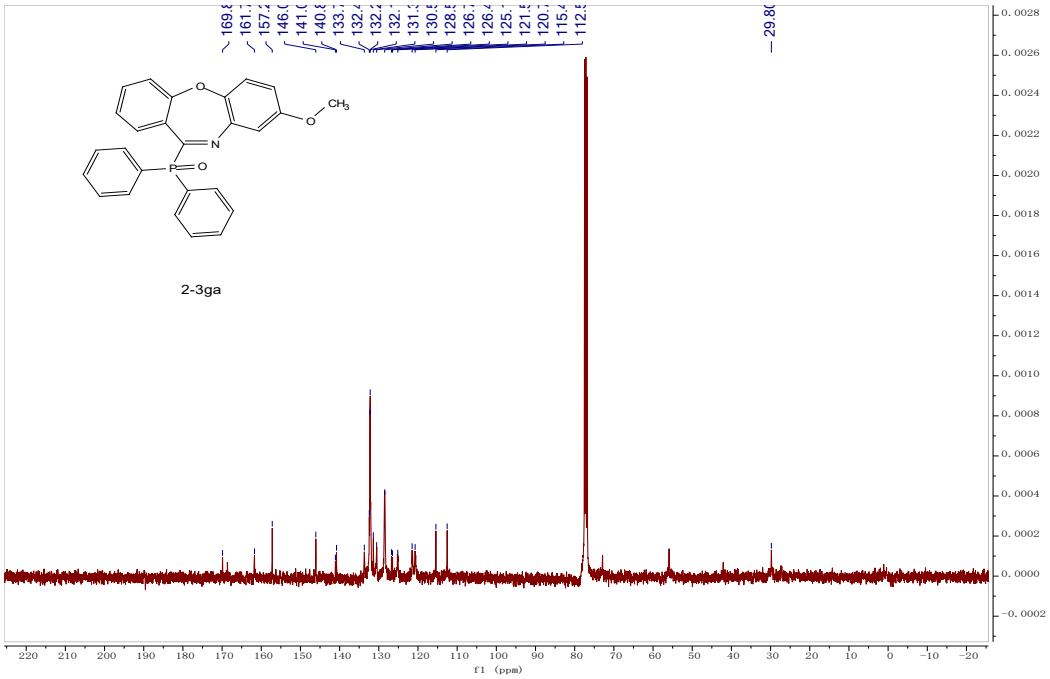
^{13}C NMR spectrum of 3ga ($CDCl_3$, 101 MHz)



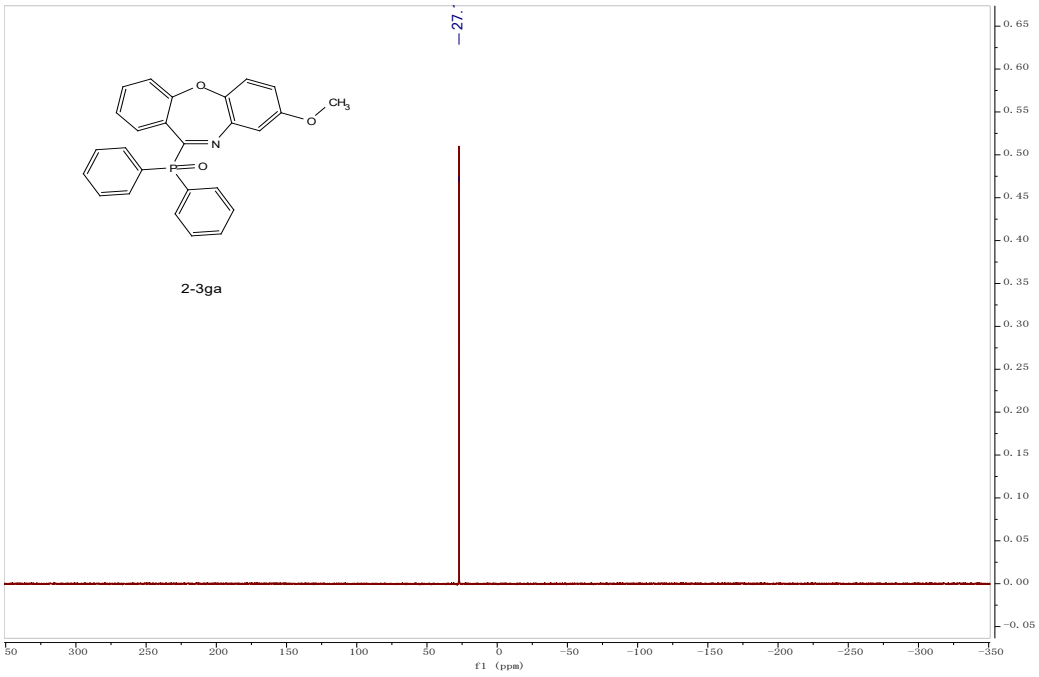
^{31}P NMR spectrum of 3ga ($CDCl_3$, 162 MHz)



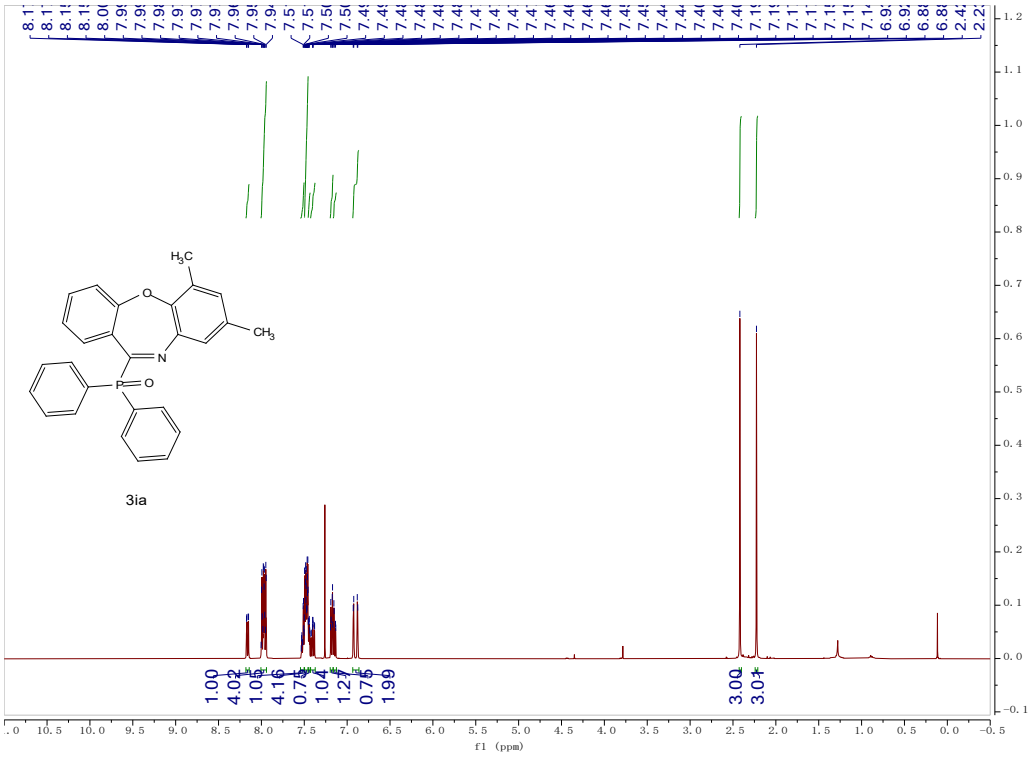
^{1}H NMR spectrum of 3ha ($CDCl_3$, 400 MHz)



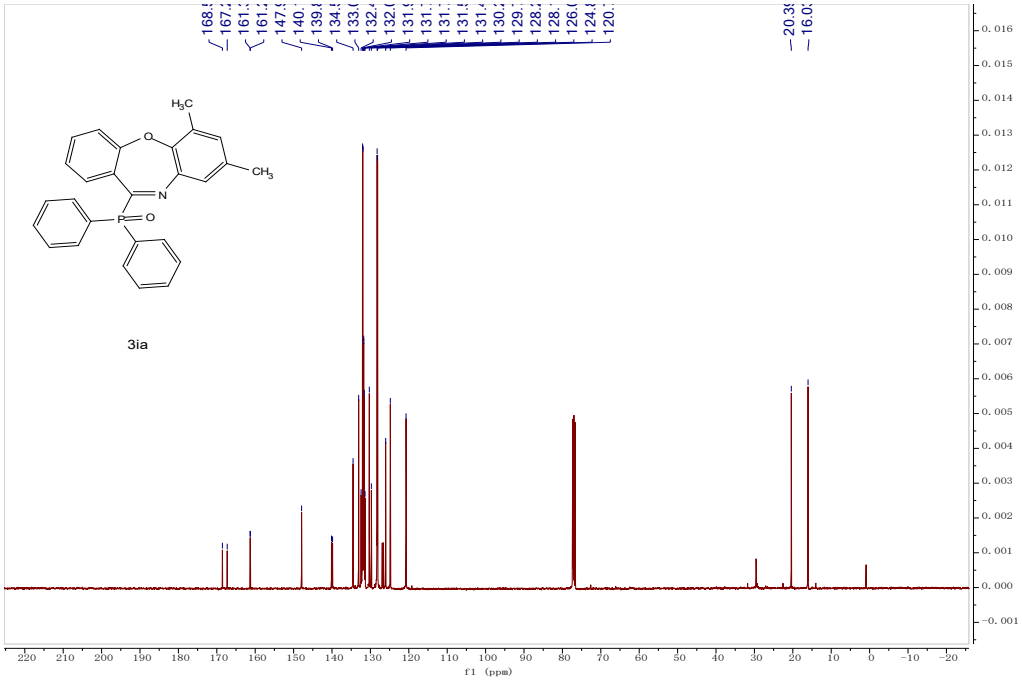
^{13}C NMR spectrum of 3ha ($CDCl_3$, 101 MHz)



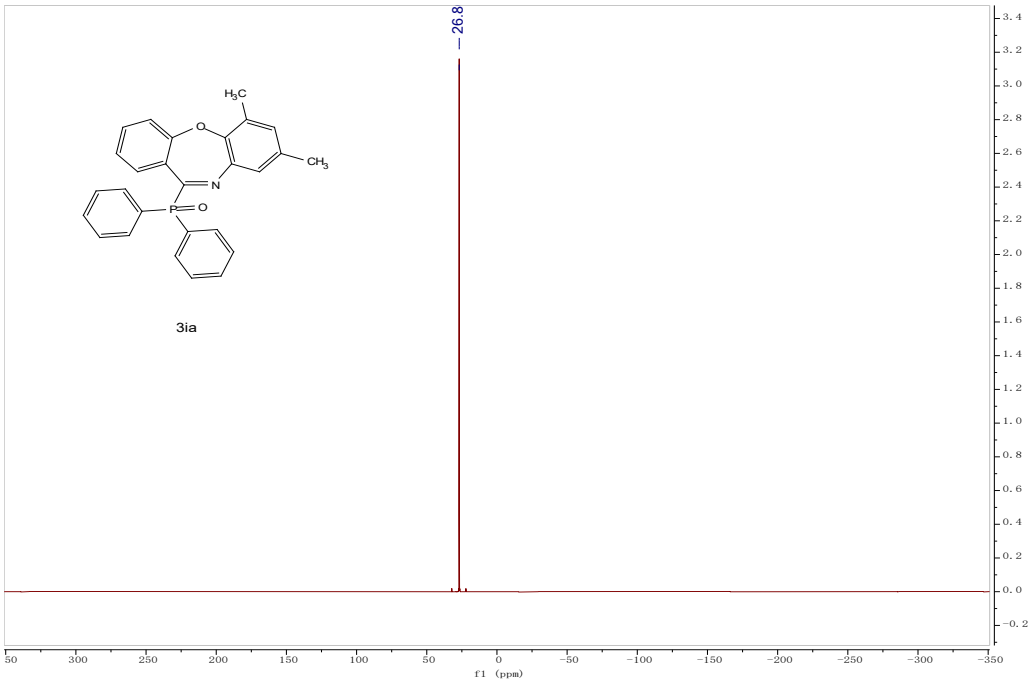
^{31}P NMR spectrum of 3ha ($CDCl_3$, 162 MHz)



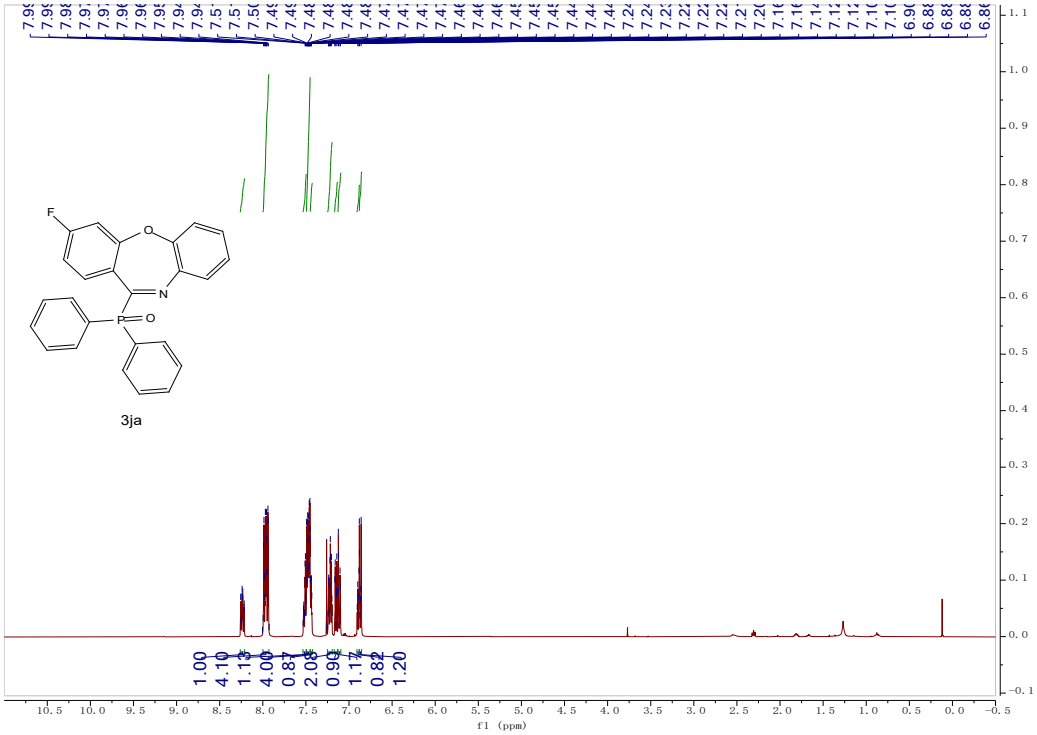
^{1}H NMR spectrum of 3ia ($CDCl_3$, 400 MHz)



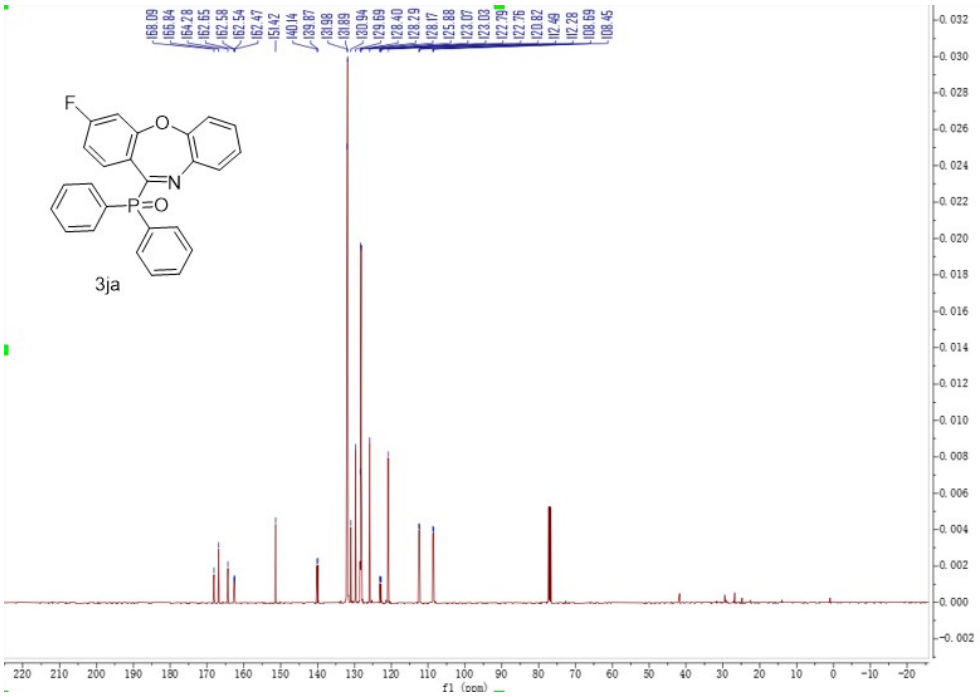
^{13}C NMR spectrum of 3ia ($CDCl_3$, 101 MHz)



^{31}P NMR spectrum of 3ia ($CDCl_3$, 162 MHz)

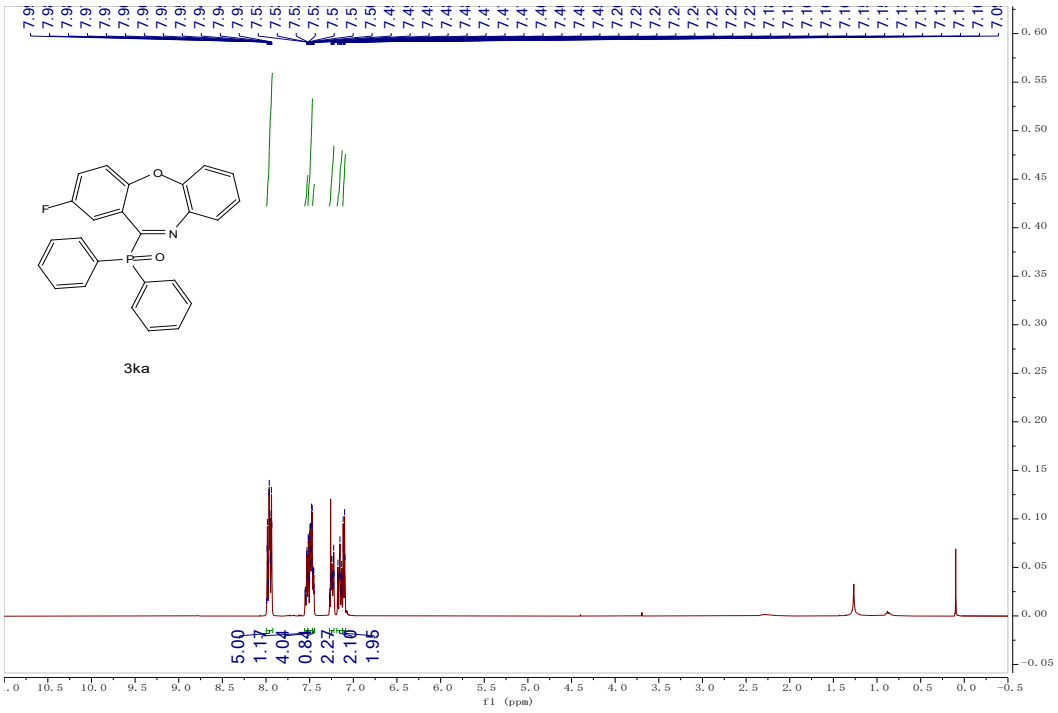


^{1}H NMR spectrum of 3ja ($CDCl_3$, 400 MHz)

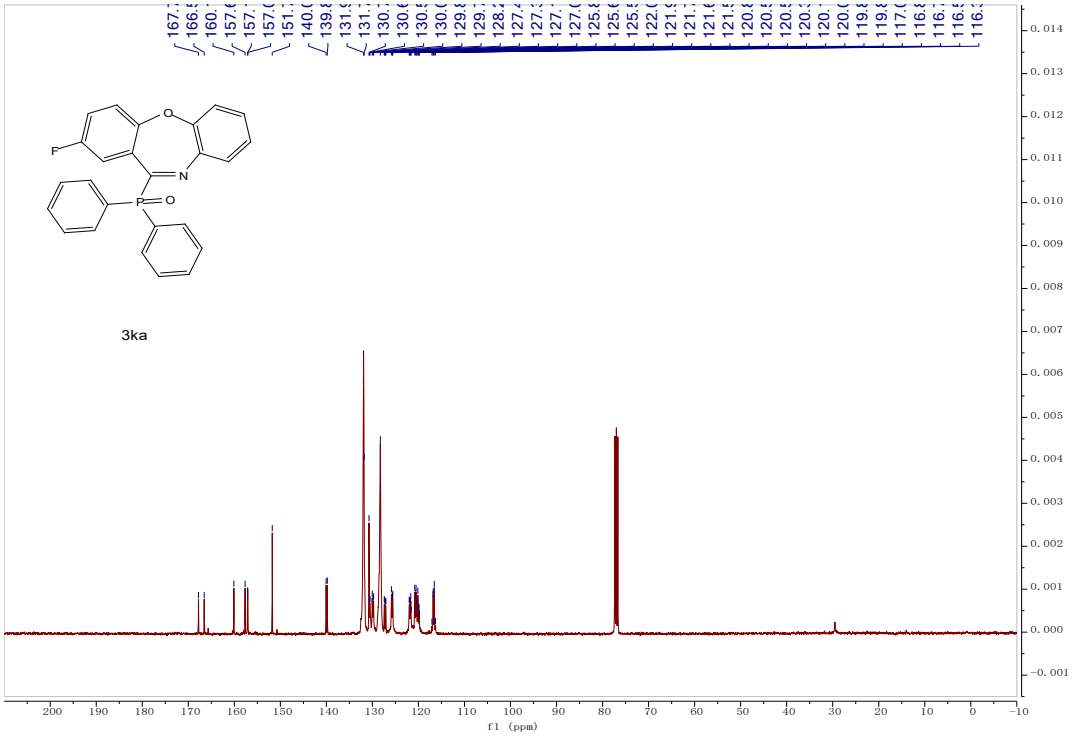


^{13}C NMR spectrum of 3ja ($CDCl_3$, 101 MHz)

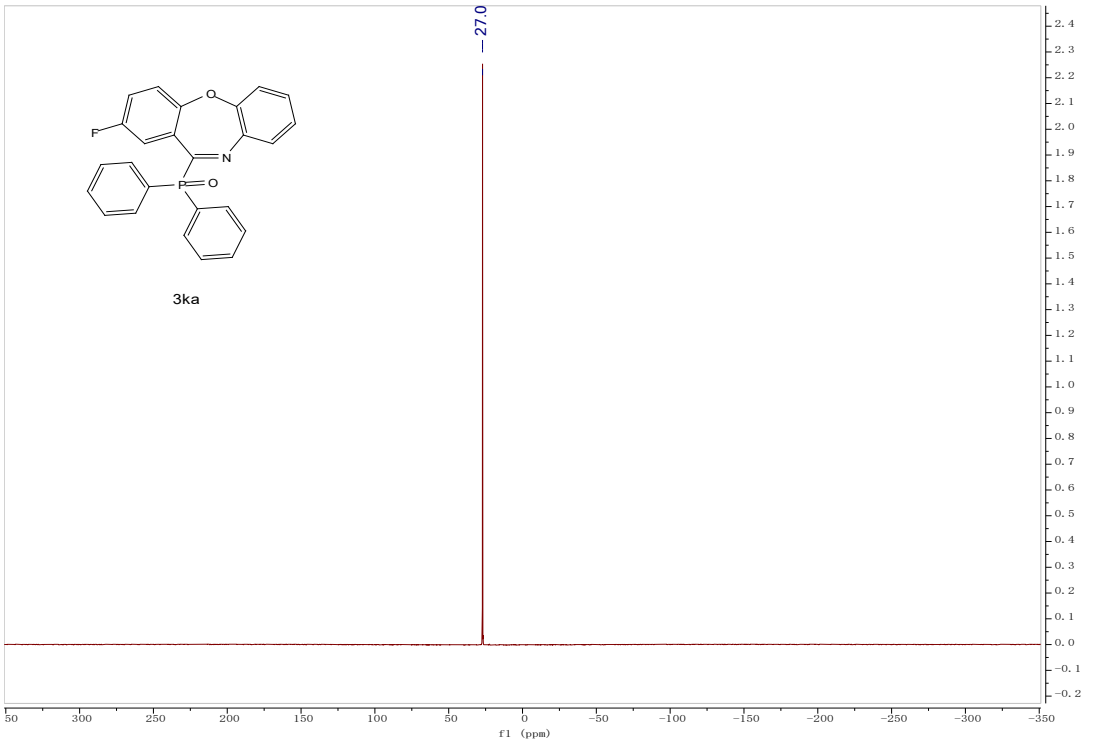
^{31}P NMR spectrum of 3ja ($CDCl_3$, 162 MHz)



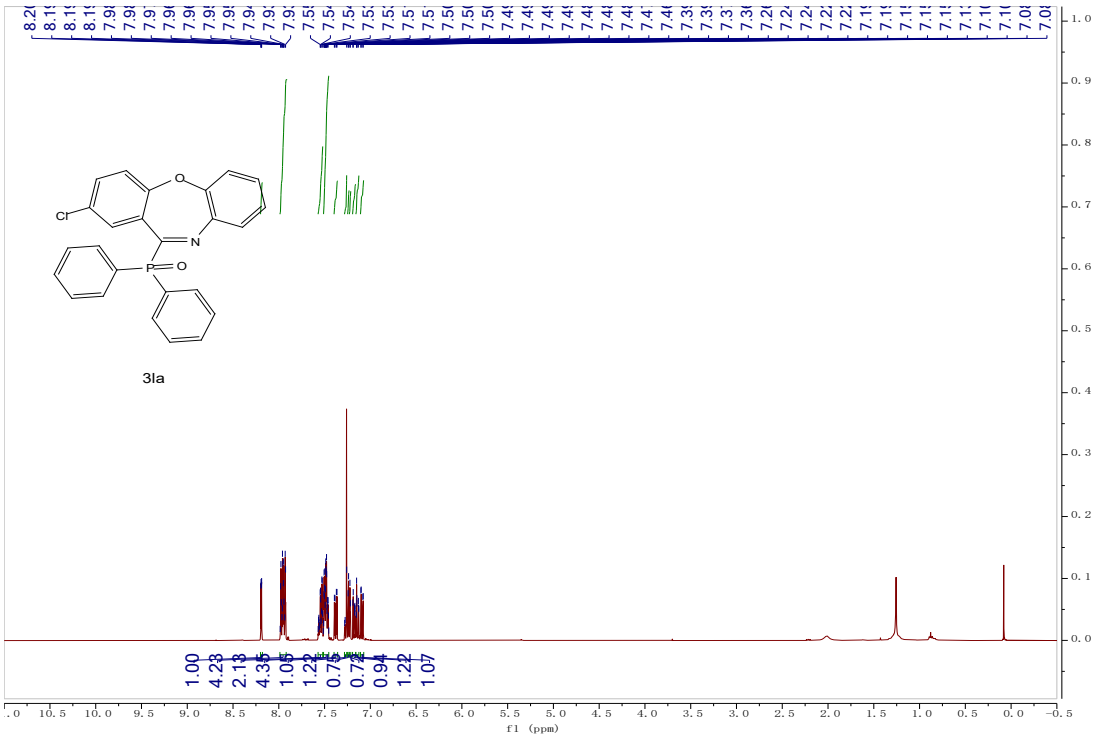
^{1}H NMR spectrum of 3ka ($CDCl_3$, 400 MHz)



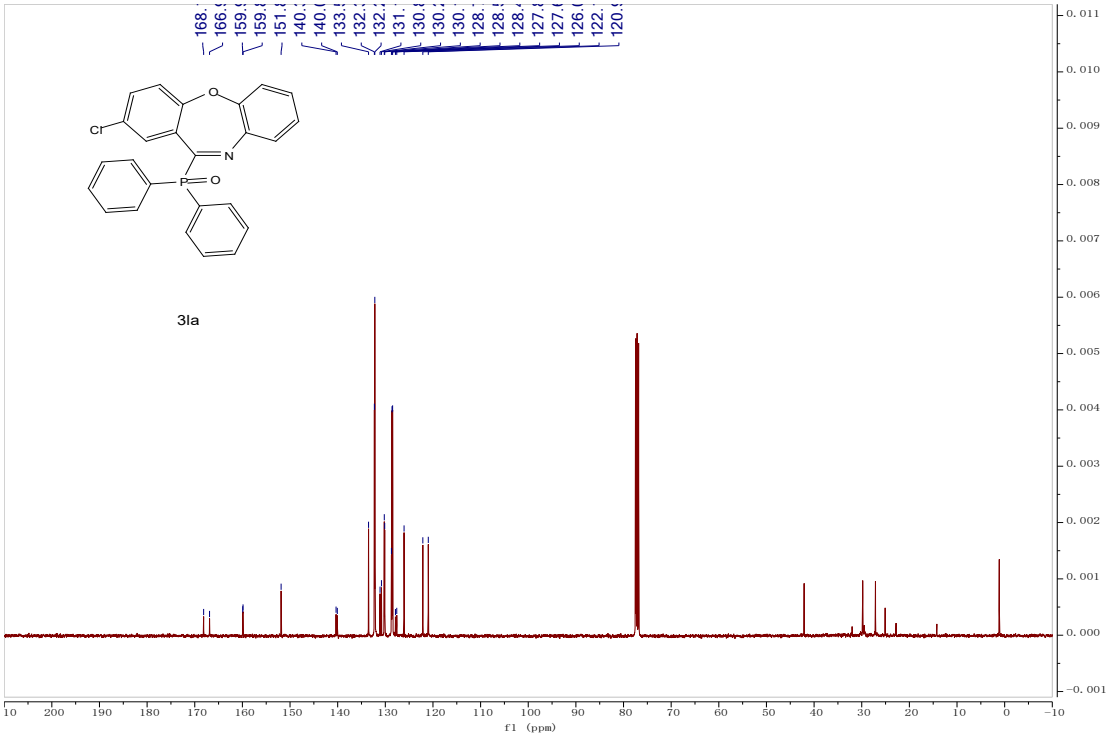
^{13}C NMR spectrum of 3ka ($CDCl_3$, 101 MHz)



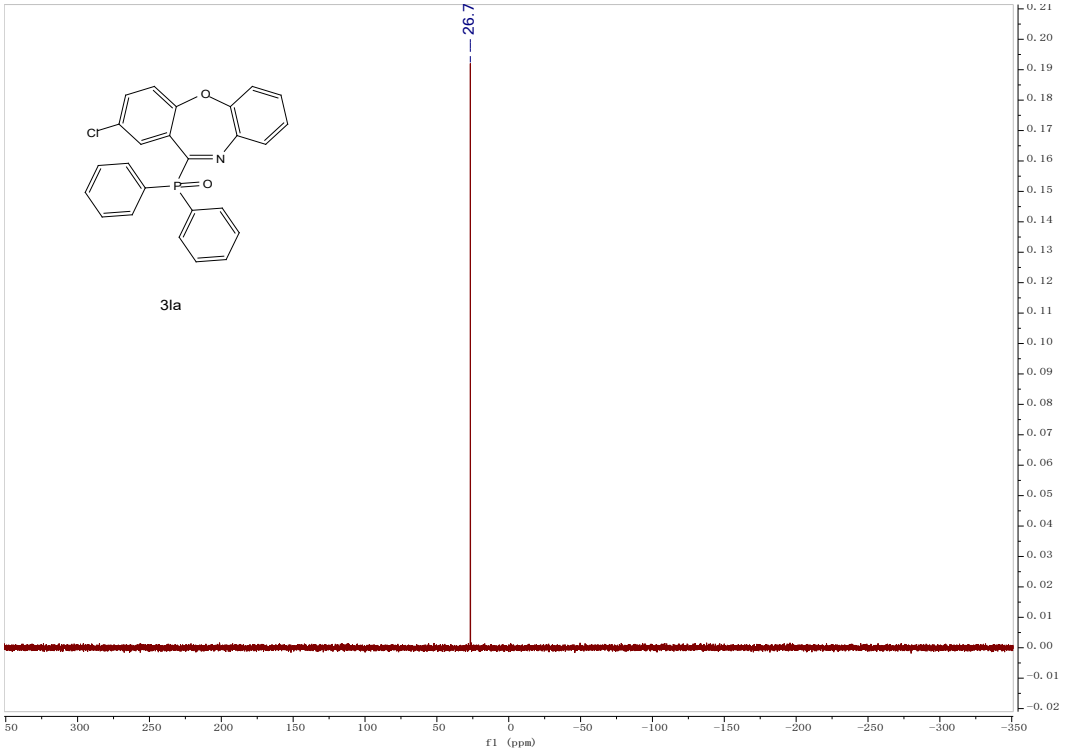
^{31}P NMR spectrum of 3ka ($CDCl_3$, 162 MHz)



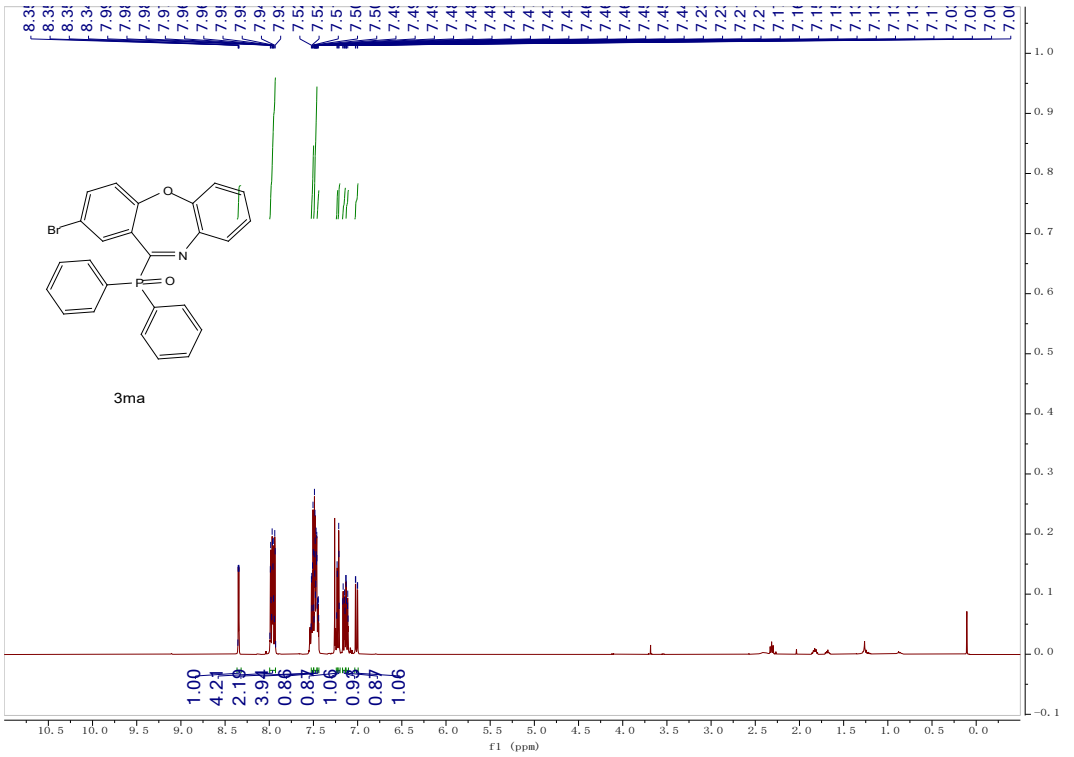
^{1}H NMR spectrum of 3la ($CDCl_3$, 400 MHz)



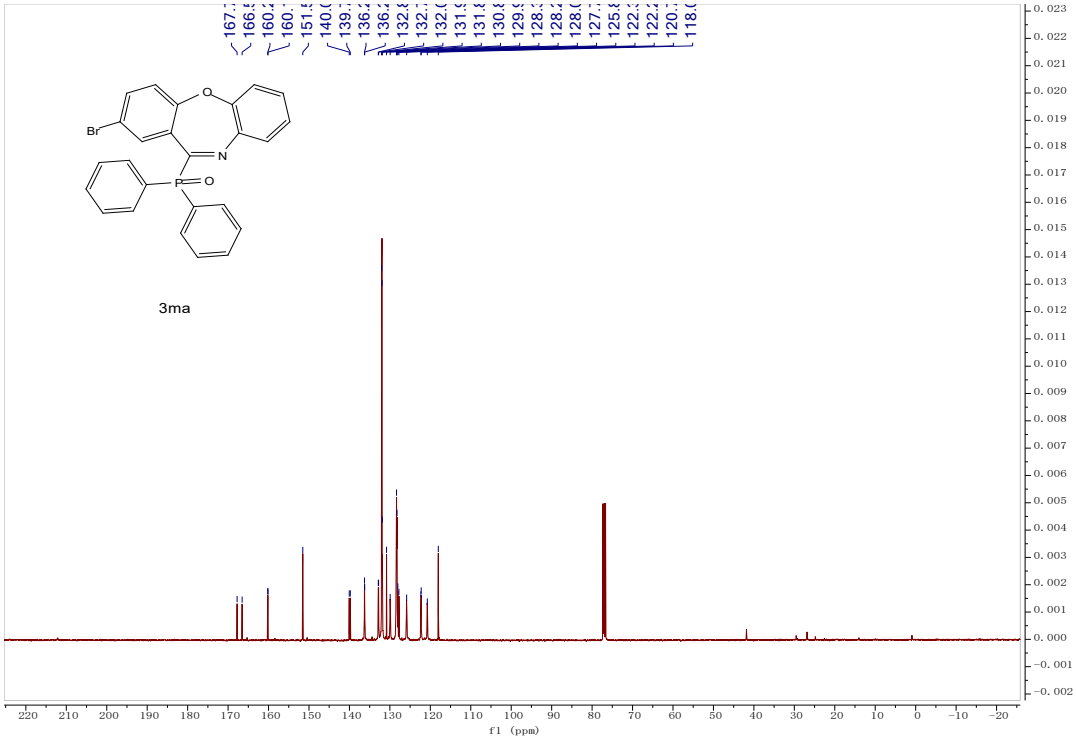
^{13}C NMR spectrum of 3la ($CDCl_3$, 101 MHz)



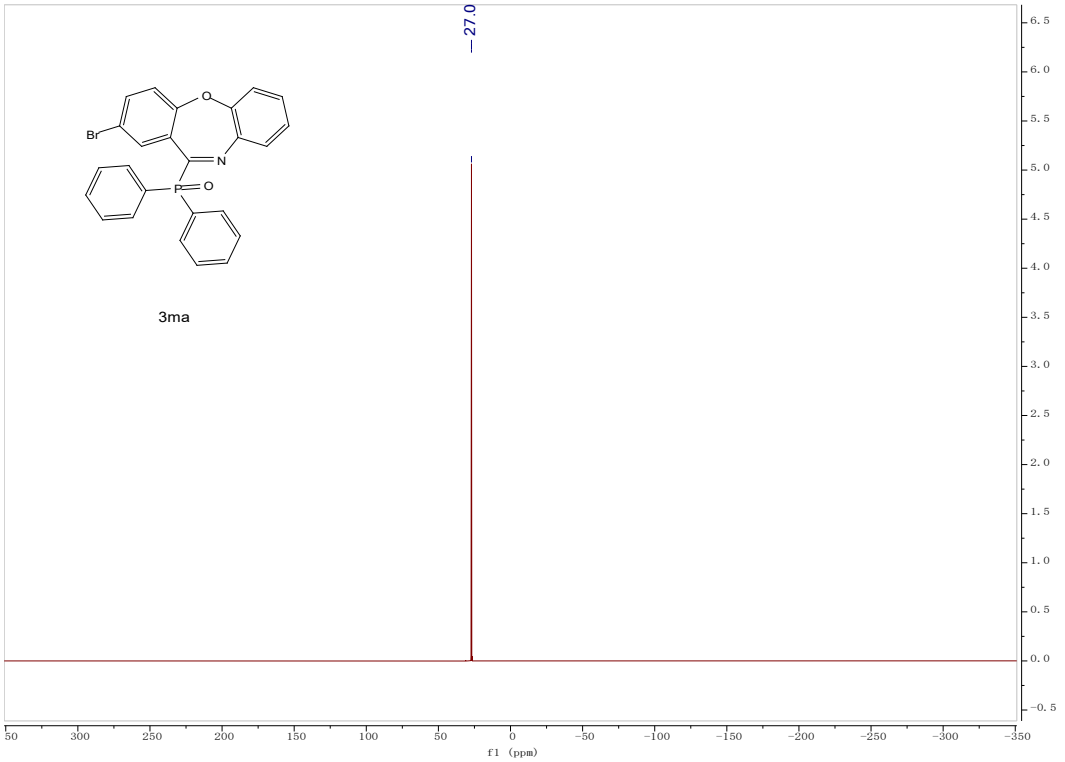
^{31}P NMR spectrum of 3la ($CDCl_3$, 162 MHz)



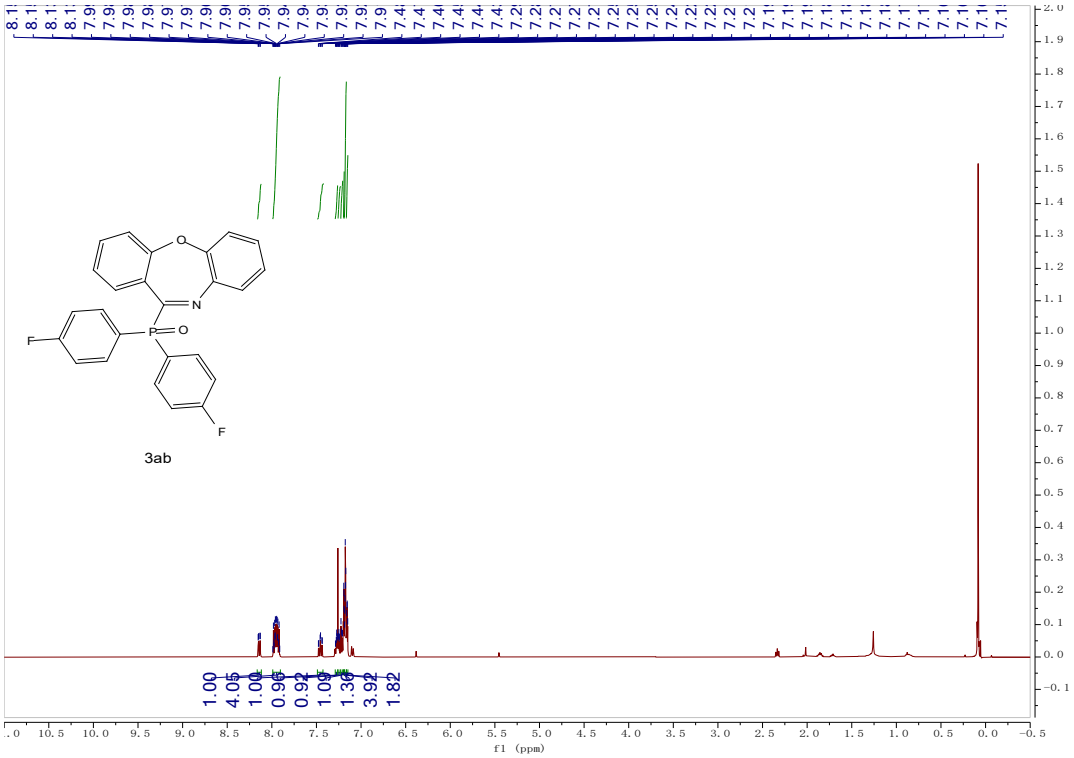
^{1}H NMR spectrum of 3ma ($CDCl_3$, 400 MHz)



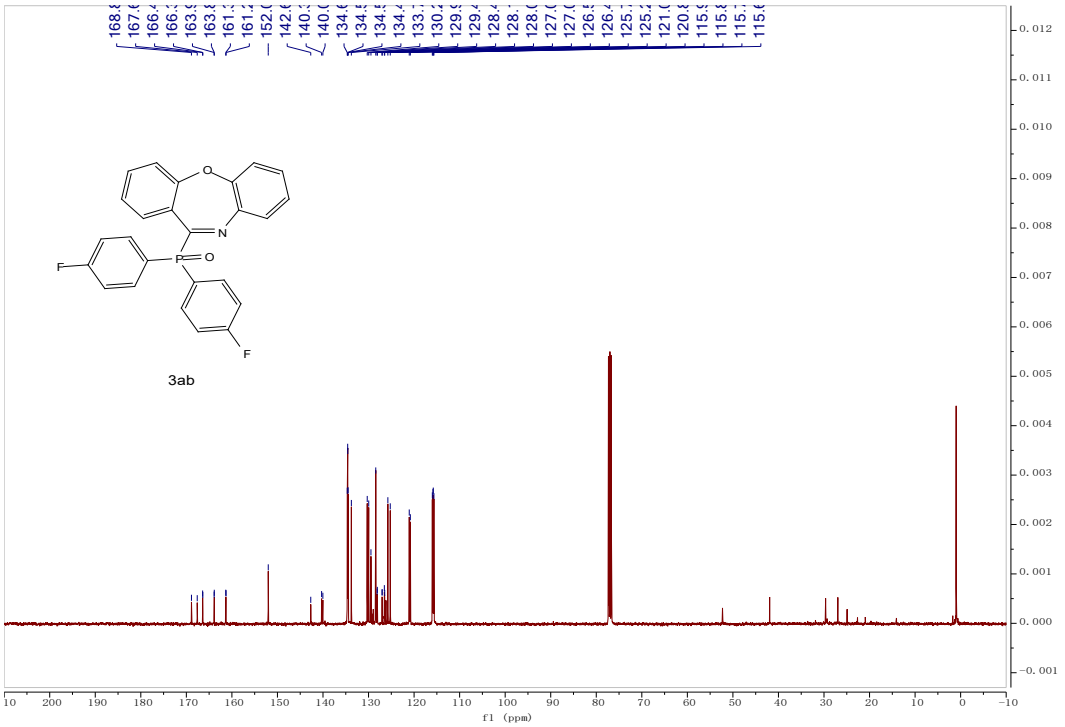
^{13}C NMR spectrum of 3ma ($CDCl_3$, 101 MHz)



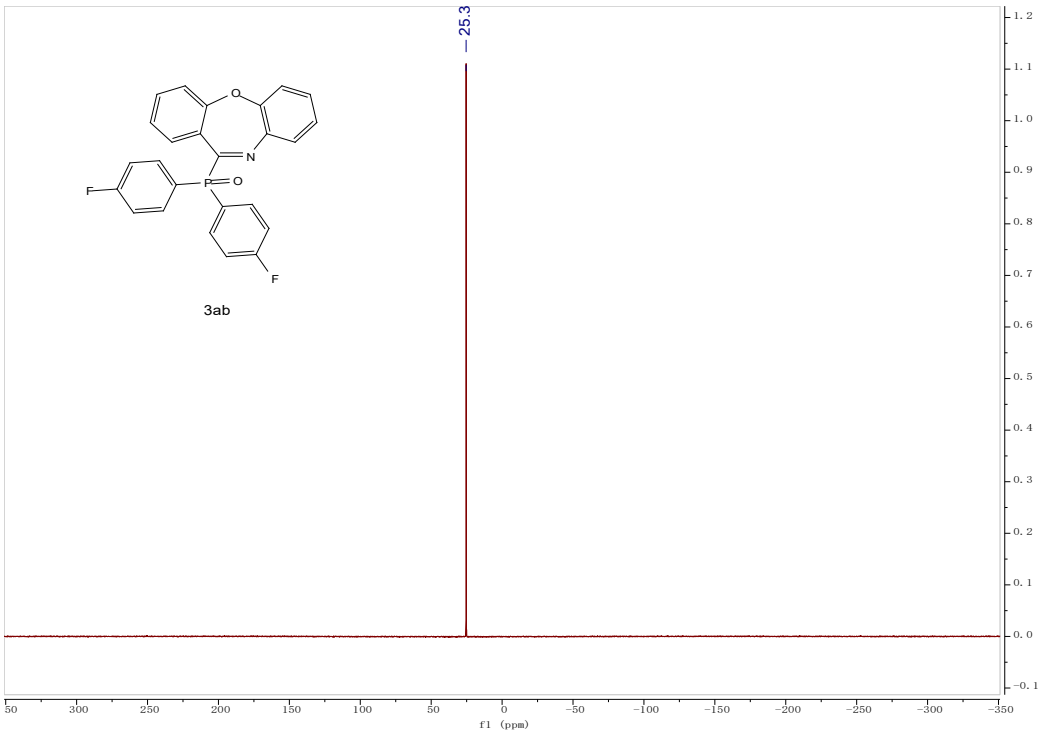
^{31}P NMR spectrum of 3ma ($CDCl_3$, 162 MHz)



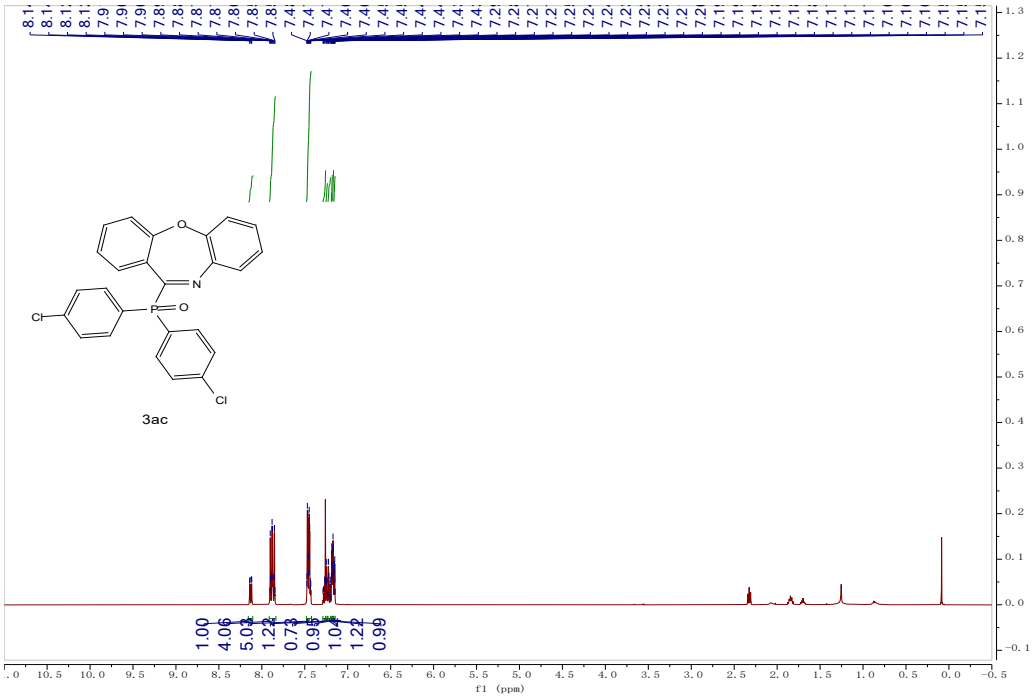
^{1}H NMR spectrum of 3ab ($CDCl_3$, 400 MHz)



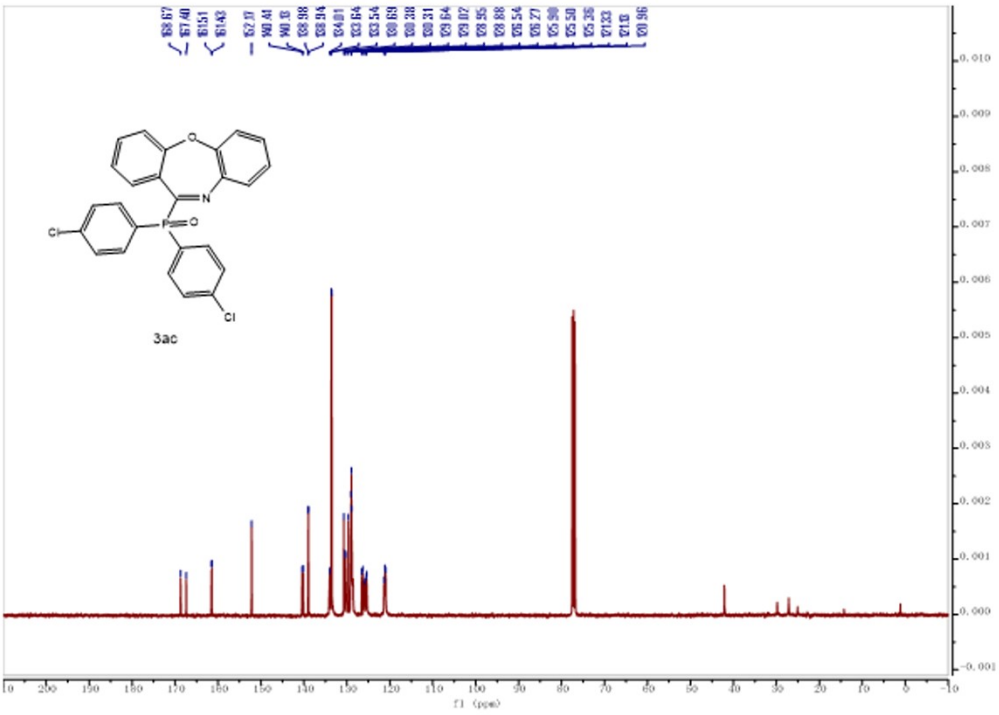
^{13}C NMR spectrum of 3ab ($CDCl_3$, 101 MHz)



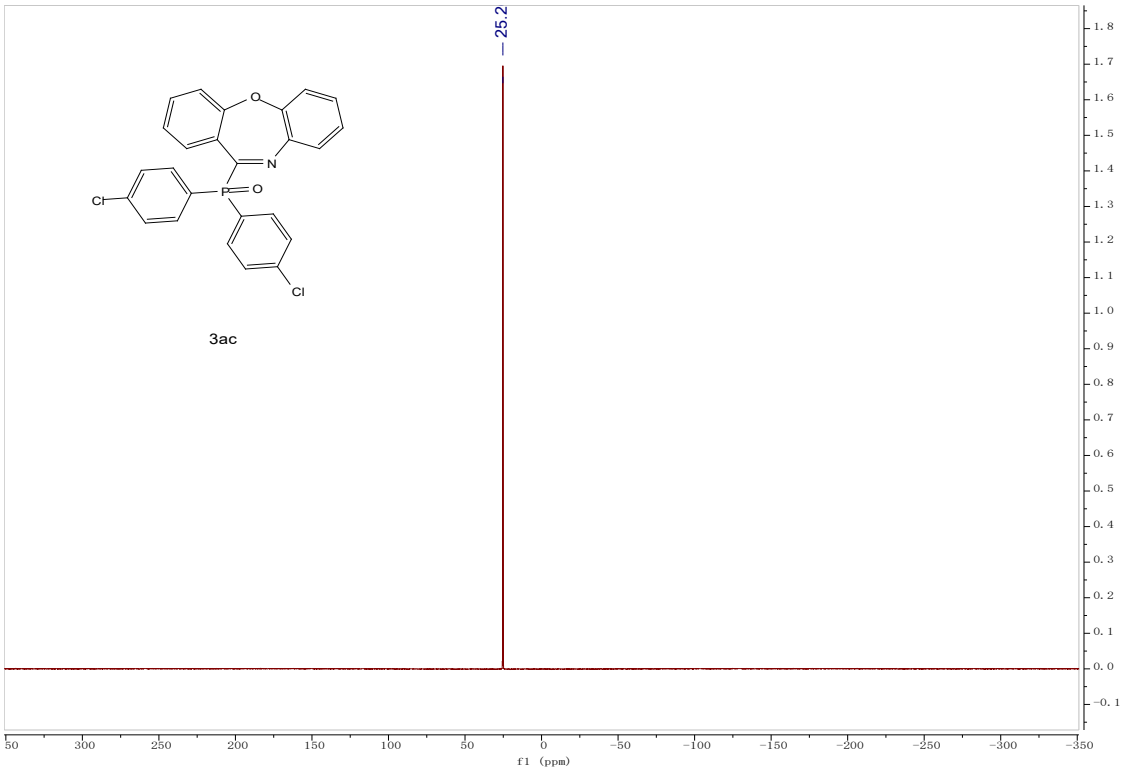
^{31}P NMR spectrum of 3ab ($CDCl_3$, 162 MHz)



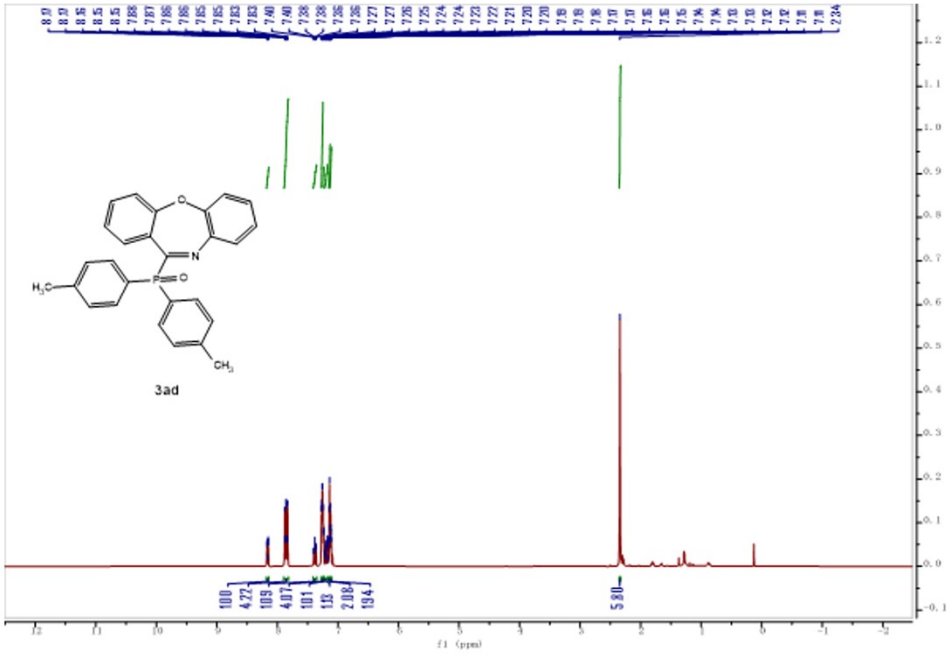
^{1}H NMR spectrum of 3ac ($CDCl_3$, 400 MHz)



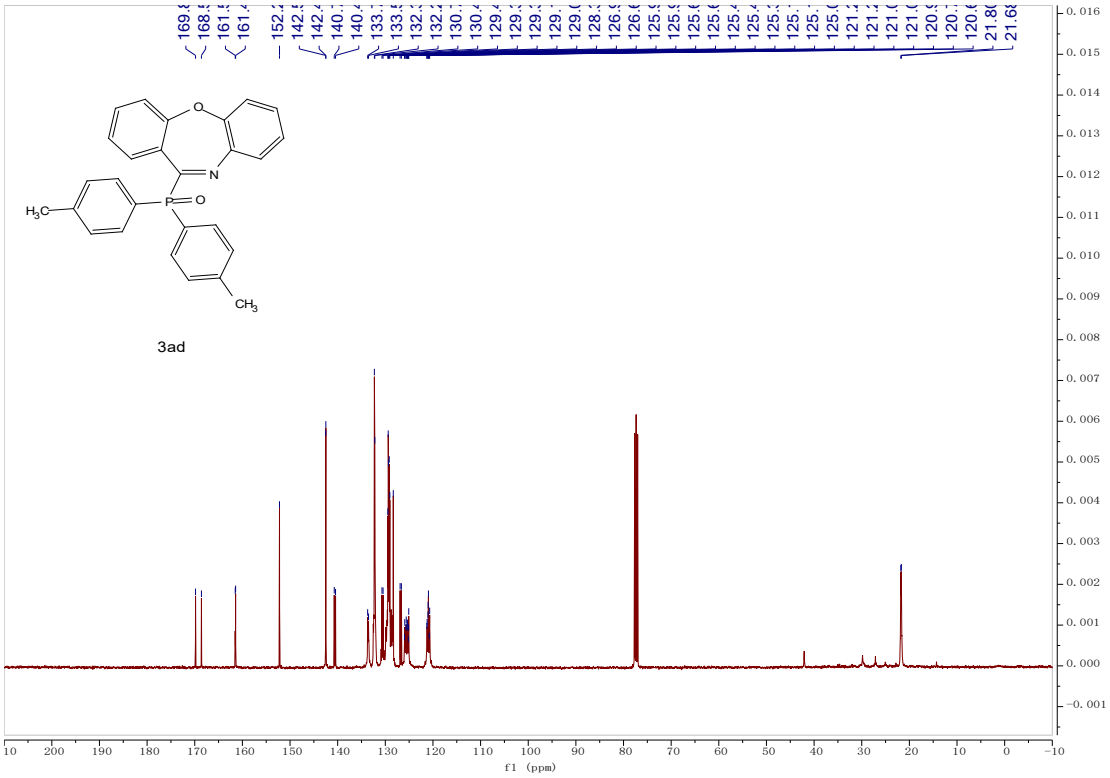
^{13}C NMR spectrum of 3ac ($CDCl_3$, 101 MHz)



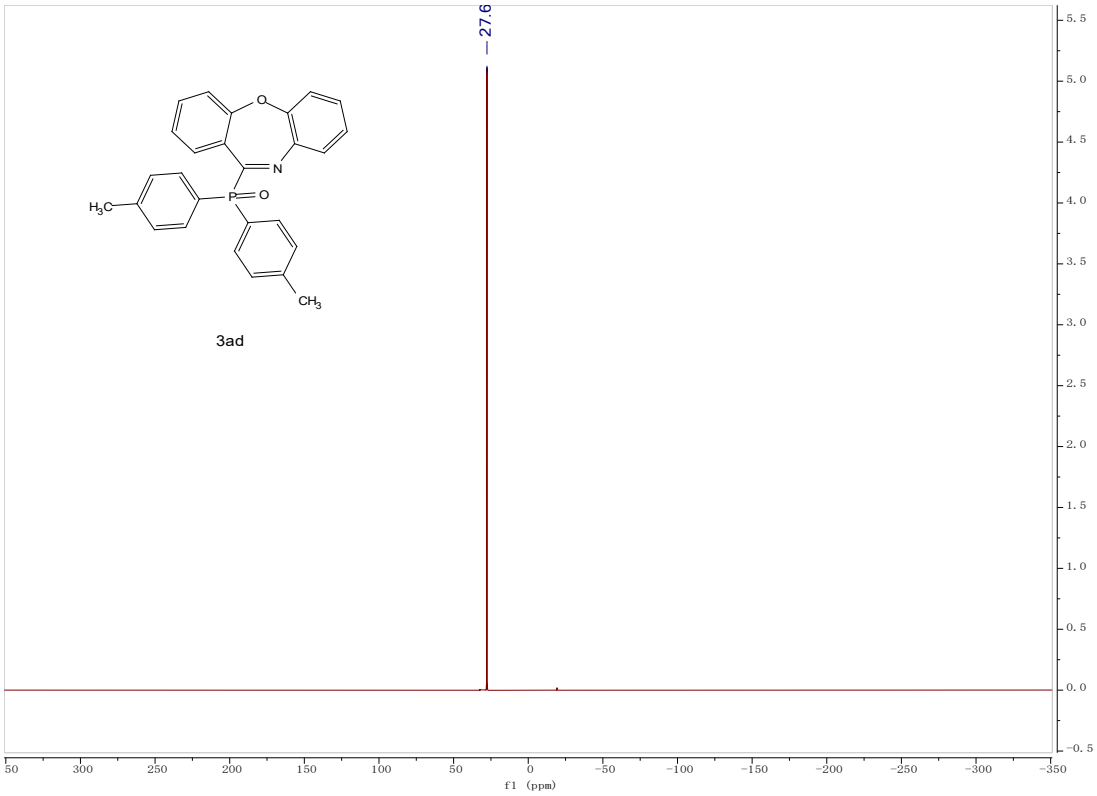
^{31}P NMR spectrum of 3ac ($CDCl_3$, 162 MHz)



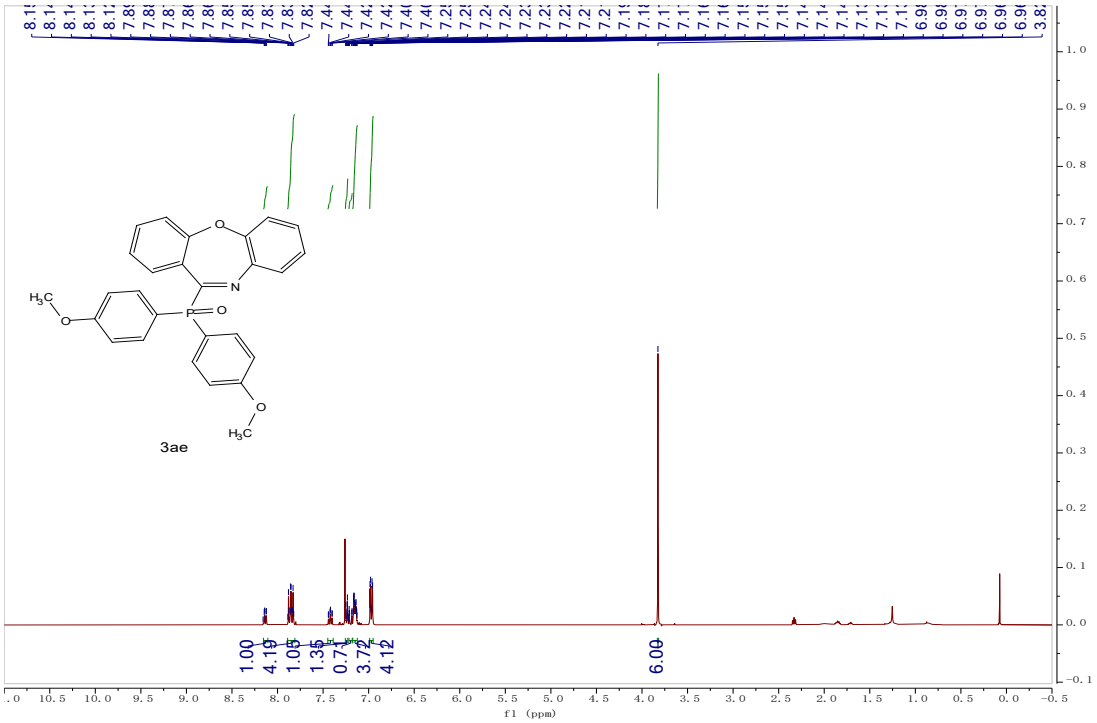
^{1}H NMR spectrum of 3ad ($CDCl_3$, 400 MHz)



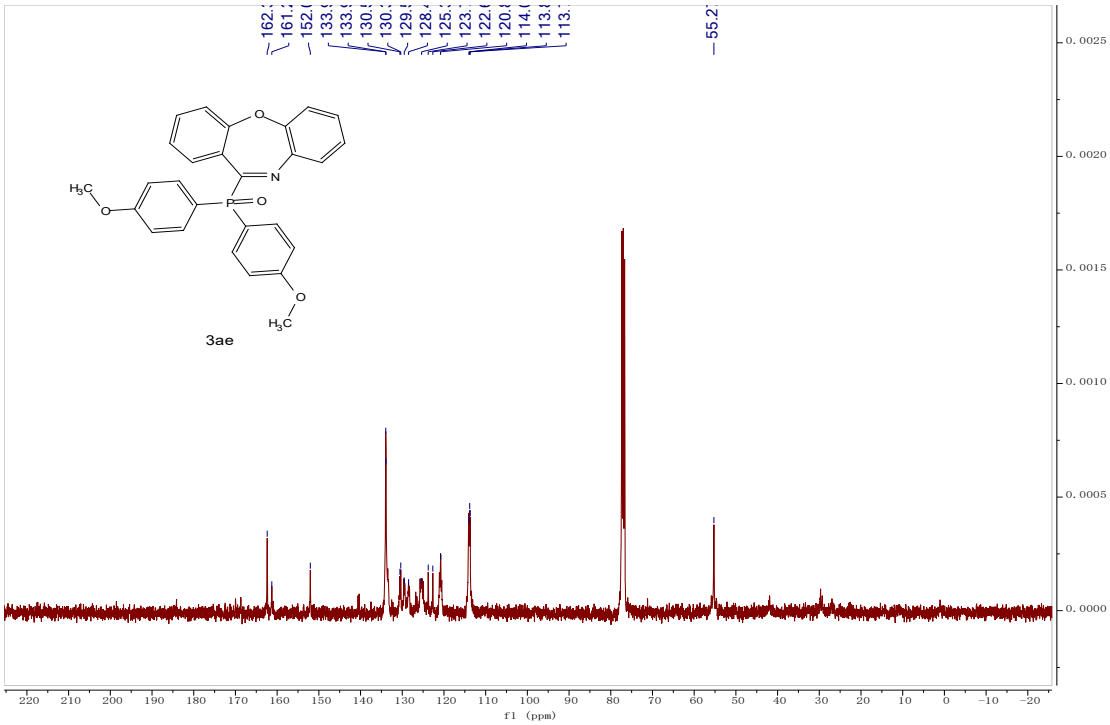
^{13}C NMR spectrum of 3ad ($CDCl_3$, 101 MHz)



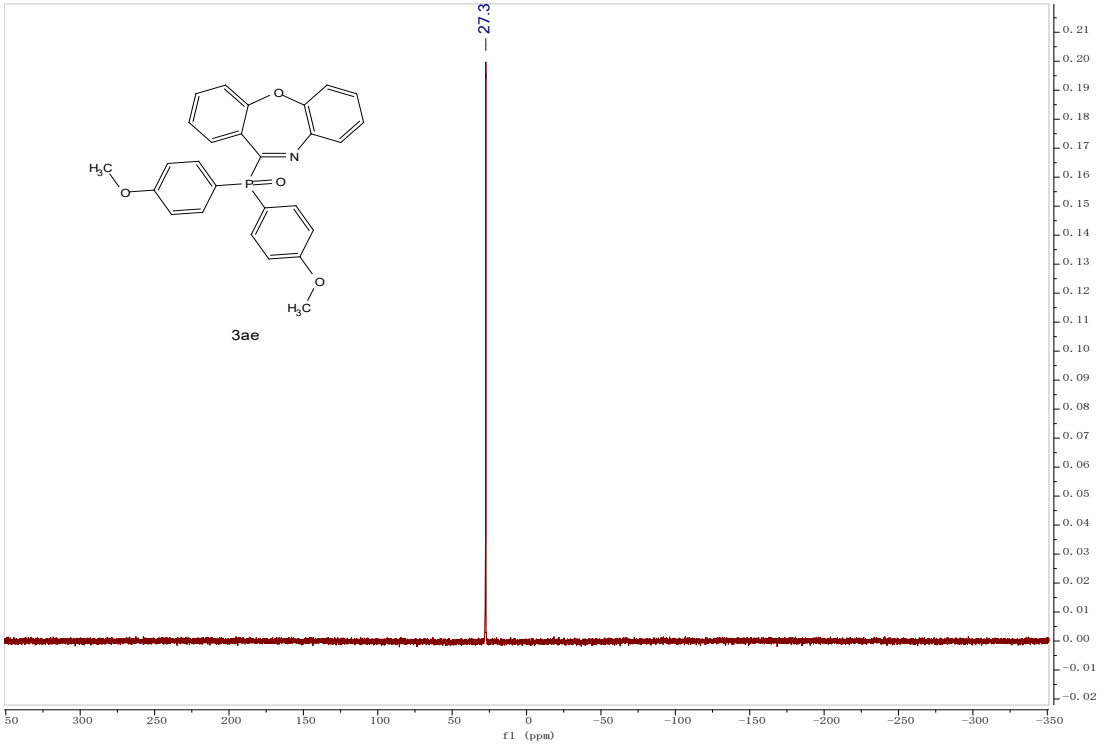
^{31}P NMR spectrum of 3ad ($CDCl_3$, 162 MHz)



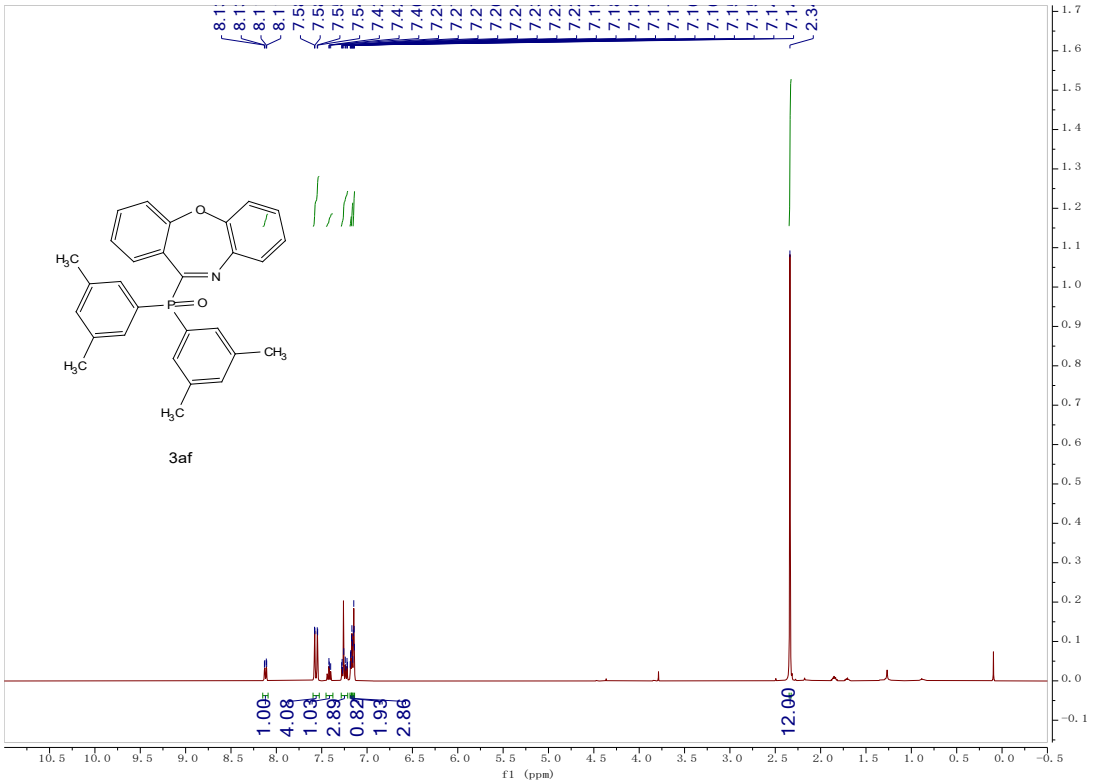
^{1}H NMR spectrum of 3ae ($CDCl_3$, 400 MHz)



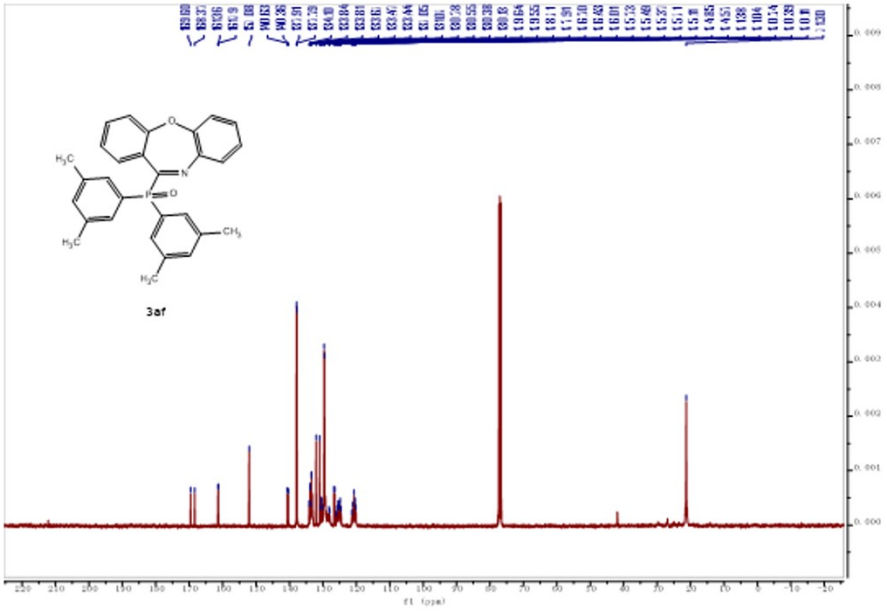
^{13}C NMR spectrum of 3ae ($CDCl_3$, 101 MHz)



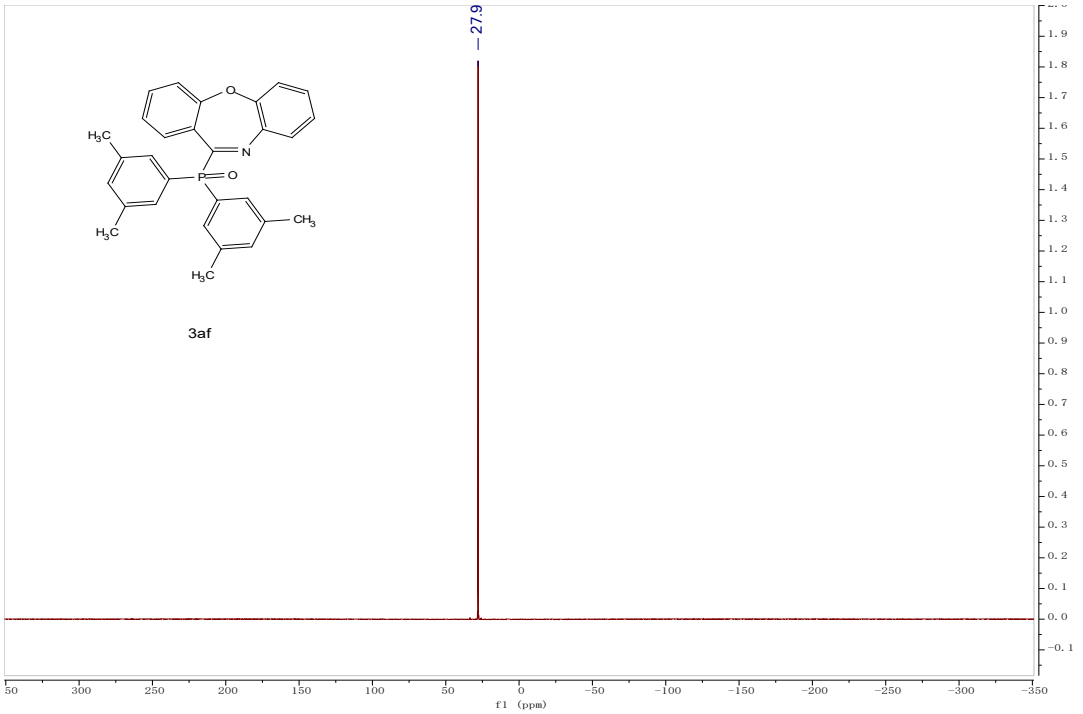
^{31}P NMR spectrum of 3ae ($CDCl_3$, 162 MHz)



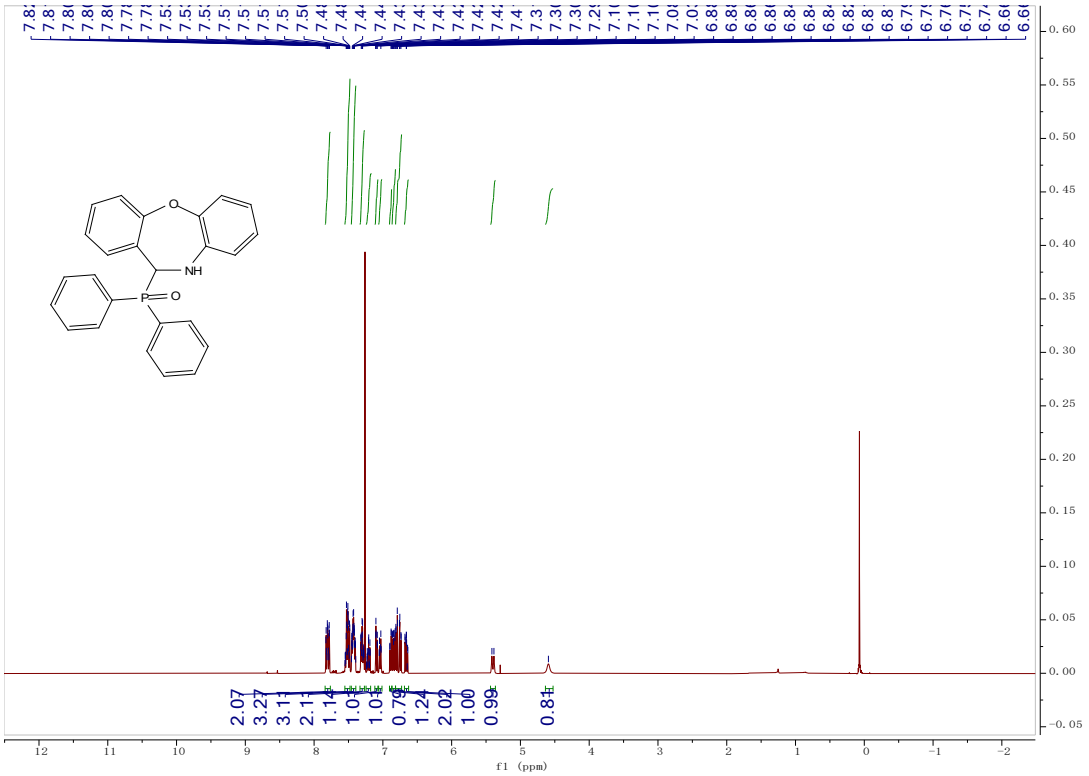
^{1}H NMR spectrum of 3af ($CDCl_3$, 400 MHz)



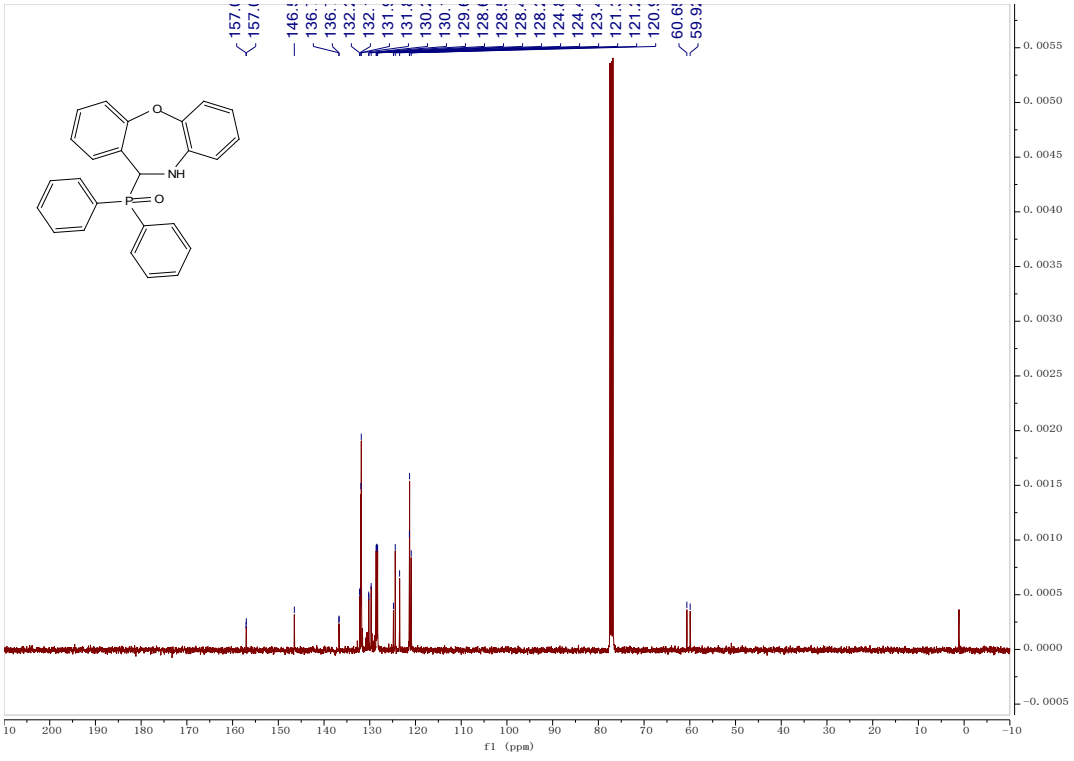
^{13}C NMR spectrum of 3af ($CDCl_3$, 101 MHz)



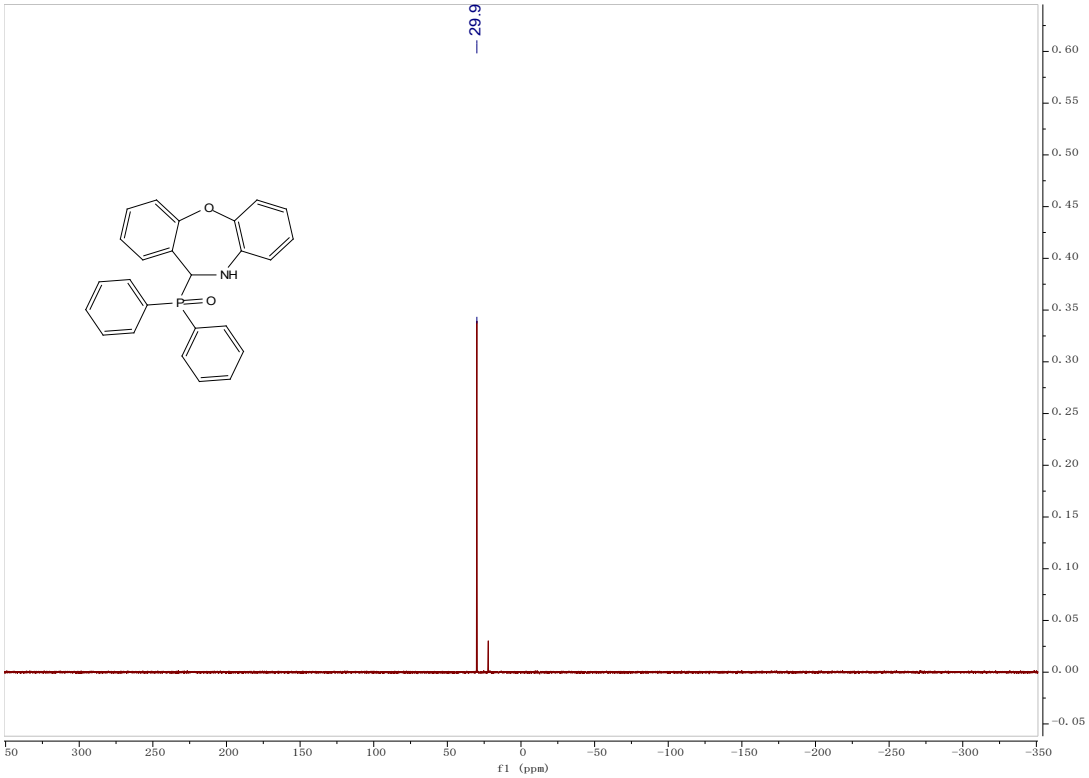
^{31}P NMR spectrum of 3af ($CDCl_3$, 162 MHz)



^{1}H NMR spectrum of B ($CDCl_3$, 400 MHz)



^{13}C NMR spectrum of B ($CDCl_3$, 101 MHz)



^{31}P NMR spectrum of B ($CDCl_3$, 162 MHz)