Supporting Information

A metal-free radical cascade reaction of phosphine oxides with 2-aryloxy phenylacetylenes to assemble diphosphonyl xanthene derivatives

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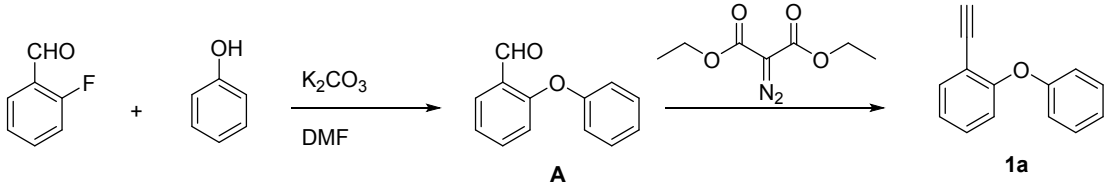
Table of Contents

General information.

Column chromatography was performed on silica gel (100-200，300−400 mesh). NMR spectra were obtained using a Bruker Avance 400/600 spectrometer (1H at 400/600 MHz and ^{13}C at 100/150 MHz). Chemical shifts were reported in ppm. ^{1}H NMR spectra were referenced to $CDCl_3$ (7.26 ppm) and CD_3OD (3.31 ppm), and 13C-NMR spectra were referenced to $CDCl_3$ (77.0 ppm) and CD_3OD (49.9 ppm). Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and J, coupling constant in Hz. High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer (Thermo Scientific, USA) equipped with ESI or APCI ionization source. Unless stated otherwise, commercial reagents were used without further purification.

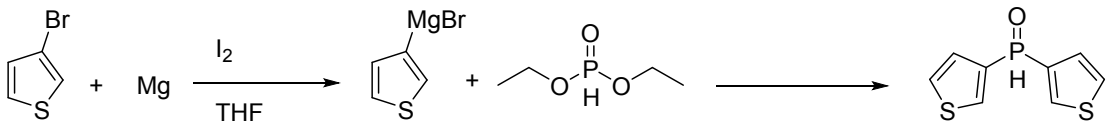
General Procedure for the Synthesis of Substrate 1.[1]



A solution of 2-fluorobenzaldehyde (1.24 g, 10 mmol), phenol (1.13 g, 12 mmol) and K_2CO_3 (1.66 g, 12 mmol) in 10 mL DMF was stirred at nitrogen atmosphere at reflux for 4 h. Then the reaction solution was cooled to rt and water (40 mL) was added, and extracted with EtOAc (20 mL x 3). The organic layer was dried with Na_2SO_4, and concentrated by rotary evaporator under reduced pressure. The residue was purified by flash column chromatography to give **A** as colorless oil in 85% yield (1.68 g).

To a solution of **A** (1.58 g, 8 mmol) and K_2CO_3 (1.66 g, 12 mmol) in 10 mL dry methanol was added diethyl 2-diazomalonate (2.66 g, 14 mmol), and the mixture was stirred at rt for 3 h. The solution was filtrated, and the filtrate was concentrated by rotary evaporator under reduced pressure. The residue was purified by flash column chromatography to give **1a** as white solid in 73% yield (1.13 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, J = 7.6, 1.3 Hz, 1H), 7.23 – 7.12 (m, 3H), 7.04 – 6.85 (m, 4H), 6.75 (d, J = 8.3 Hz, 1H), 3.10 (s, 1H).

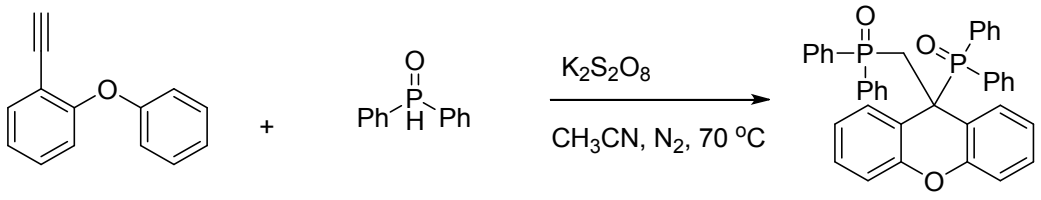
General Procedure for the Synthesis of Substrate 2.[2]



To a solution of I_2 (13 mg, 0.05 mmol), Mg (132 mg, 5.5 mol) in dry 5 mL THF at nitrogen atmosphere was slowly added 3-bromothiophene (815 mg, 5 mmol in 10 mL dry THF). Then the reaction was stirred at rt for 2 h, and diethyl phosphonate (345 mg, 2.5 mmol) was added. The mixture was stirred at rt for overnight, and the reaction was quenched with water (10 mL), extracted with EtOAc (20 mL x 3). The combined organic layer was dried with Na_2SO_4 and concentrated by rotary evaporator under reduced pressure. The residue was purified by flash

column chromatography to give di(thiophen-3-yl)phosphine oxide as white solid in 50% yield (265 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 524.0, 1H), 7.70 (dd, *J* = 8.4, 3.8 Hz, 2H), 7.55 (dd, *J* = 9.0, 3.5 Hz, 2H), 7.16 – 7.11 (m, 2H).

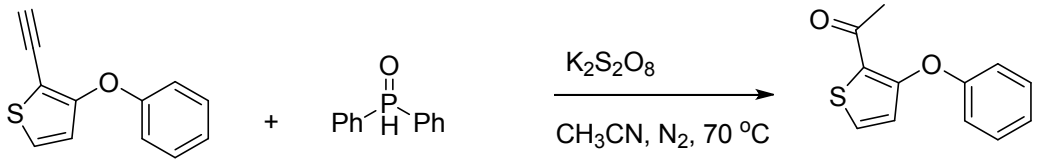
General Procedure for the Synthesis of 3.



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

A solution of **1a** (38.8 mg, 0.2 mmol), **2a** (200 mg, 1 mmol) and $K_2S_2O_8$ (135 mg, 0.5 mmol) in CH_3CN (2 mL) was stirred at 70 °C at nitrogen atmosphere for 7 h. Then the mixture was concentrated by rotary evaporator under reduced pressure. The residue was purified by flash column chromatography to give **3a** as white solid.

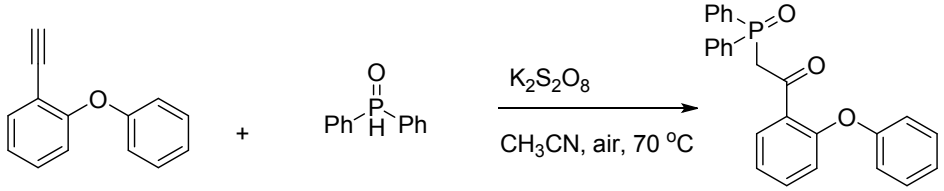
The Reaction of 1q with 2a



1q **2a** **3q'**

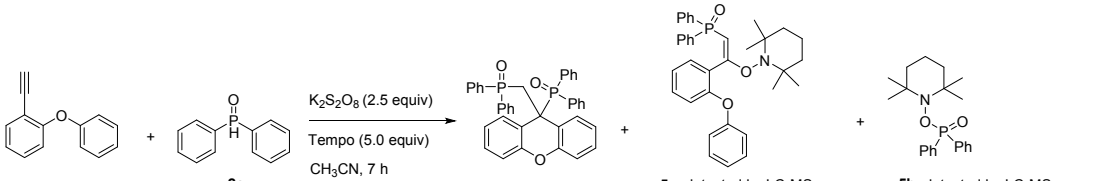
A solution of **1q** (40 mg, 0.2 mmol), **2a** (200 mg, 1 mmol) and $K_2S_2O_8$ (135 mg, 0.5 mmol) in CH_3CN (2 mL) was stirred at 70 °C at nitrogen atmosphere for 7 h. Then the mixture was concentrated by rotary evaporator under reduced pressure. The residue was purified by flash column chromatography to give **3q'** as light yellow oil in 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 5.5 Hz, 1H), 7.31 (dd, *J* = 8.3, 7.7 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 2H), 6.54 (d, *J* = 5.5 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.7, 156.7, 156.5, 132.2, 130.1, 127.6, 124.5, 120.8, 118.6, 29.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{12}H_{10}O_2S+H]^+$, 219.0480; found, 219.0484.

Control Experiments

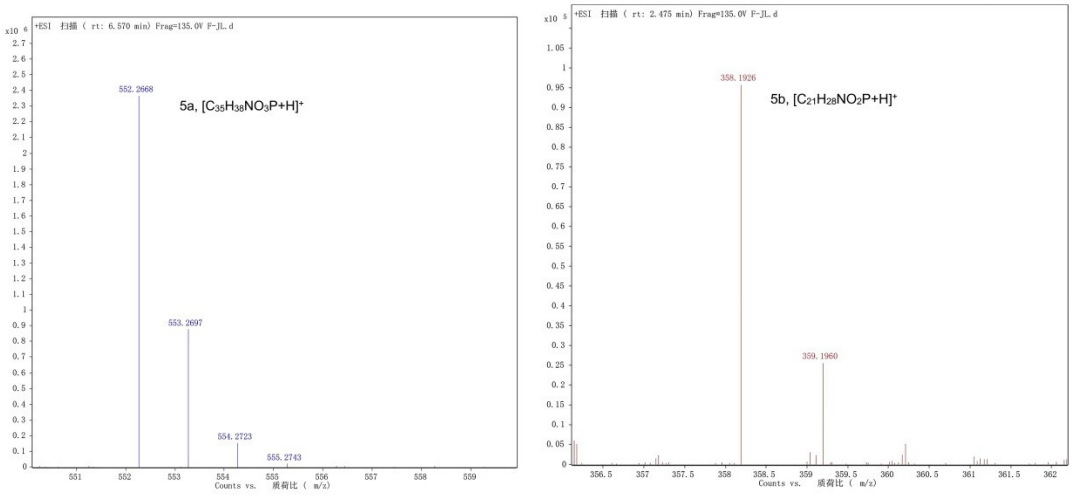


1a **2a** **3a'**

A solution of **1a** (38.8 mg, 0.2 mmol), **2a** (200 mg, 1 mmol) and $K_2S_2O_8$ (135 mg, 0.5 mmol) in CH_3CN (2 mL) was stirred at 70 °C at air atmosphere for 7 h. Then the mixture was concentrated by rotary evaporator under reduced pressure. The residue was purified by flash column chromatography to give **3a′** as colorless oil in 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 4H), 7.49 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.41 – 7.38 (m, 2H), 7.35 – 7.30 (m, 4H), 7.28 – 7.24 (m, 3H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.98 – 6.93 (m, 3H), 6.68 (d, *J* = 8.3 Hz, 1H), 4.30 (d, *J* = 14.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9 (d, *J* = 5.9 Hz), 156.4, 155.7, 134.0, 132.4 (d, *J* =102.0 Hz), 131.9 (d, *J* = 2.8 Hz), 131.1 (d, *J* = 9.8 Hz), 130.8, 130.3, 130.1, 128.5 (d, *J* = 12.2 Hz), 124.4, 123.2, 119.7, 118.3, 46.7 (d, *J* = 60.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{26}H_{21}O_3P+H]^+$, 413.1301; found, 413.1322.



A solution of **1a** (38.8 mg, 0.2 mmol), **2a** (200 mg, 1 mmol), $K_2S_2O_8$ (135 mg, 0.5 mmol) and Tempo (156 mg, 1 mmol) in CH_3CN (2 mL) was stirred at 70 °C at nitrogen atmosphere for 7 h. Then the mixture was analyzed with LC-MS.



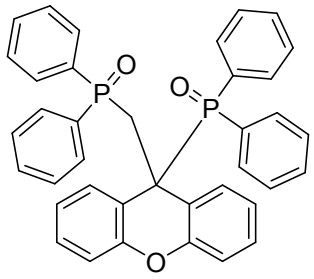
Reference

1 B. Schmidt, R. Berger, A. Kelling and U. Schilde, *Chem. Eur. J.* 2011, **17**, 7032 – 7040.

2 R. Lhermet, E. Moser, E. Jeanneau, H. Olivier-Bourbigou and P. –A. R. Breuil, *Chem. Eur. J.* 2017, **23**, 7433 –7437.

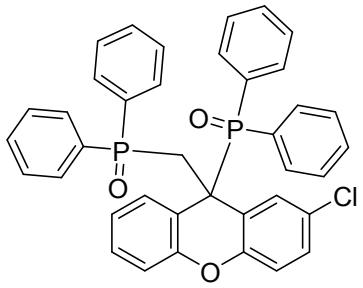
Analytical Data of Products

((9-(diphenylphosphoryl)-9*H*-xanthen-9-yl)methyl)diphenylphosphine oxide (**3a**)



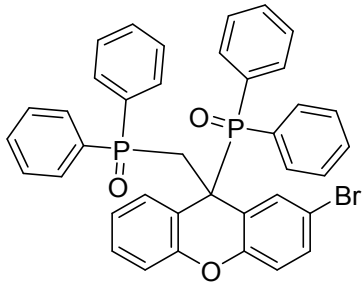
White solid (101.3 mg, 85%); mp: 241.1-243.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 4H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.27– 7.07 (m, 10H), 7.14 – 7.04 (m, 6H), 6.97 (t, *J* = 7.7 Hz, 2H), 6.65 (t, *J* = 7.5 Hz, 2H), 6.47 (d, *J* = 8.1 Hz, 2H), 3.71 (dd, *J* = 10.9, 6.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7 (d, *J* = 4.6 Hz), 133.3 (d, *J* = 99.3 Hz), 132.7 (d, *J* = 7.7 Hz), 132.0 (d, *J* = 2.6 Hz), 131.1 (d, *J* = 2.7 Hz), 130.7 (d, *J* = 9.4 Hz), 130.5 (d, *J* = 3.5 Hz), 129.4 (d, *J* = 92.0 Hz), 129.3 (d, *J* = 2.7 Hz), 128.1 (d, *J* = 11.5 Hz), 128.0 (d, *J* = 10.0 Hz), 121.9 (d, *J* = 2.5 Hz), 117.0 (dd, *J* = 2.8, 2.3 Hz), 115.7 (d, *J* = 2.3 Hz), 45.6 (dd, *J* = 61.8, 4.2 Hz), 35.3 (d, *J* = 67.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.80 (d, *J* = 46.0 Hz), 27.87 (d, *J* = 46.1 Hz). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $[C_{38}H_{30}NaO_3P_2 + Na]^+$, 619.1562; found, 619.1564.

(2-chloro-9-((diphenylphosphoryl)methyl)-9H-xanthen-9-yl)diphenylphosphine oxide (**3b**)



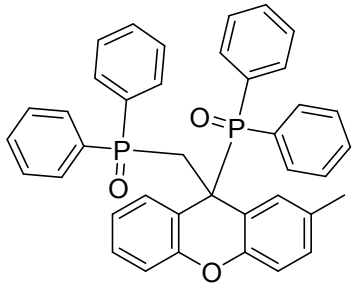
White solid (95.8 mg, 76%); mp: 256.6-258.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 6.89 (m, 24H), 6.75 (d, *J* = 6.8 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 6.54 (d, *J* = 8.7 Hz, 1H), 3.88 – 3.55 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.4, 149.4 (d, *J* = 4.1 Hz), 132.60 (t, *J* = 7.3 Hz), 133.3 (d, *J* = 97.1 Hz), 133.2 (d, *J* =100.7 Hz), 132.6 – 132.5 (m), 132.2, 132.1, 131.4, 130.7 – 130.4 (m), 130.3, 129.4 (d, *J* = 43.4 Hz), 128.7 (d, *J* = 20.9 Hz), 128.50 – 127.88 (m), 126.8, 122.2, 118.9, 117.0, 116.5, 115. 8, 45.7 (d, *J* = 61.7 Hz), 35.1 (d, *J* = 66.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.9 (d, *J* = 44.9 Hz), 27.1 (d, *J* = 42.6 Hz). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $[C_{38}H_{29}NaClO_3P_2 + Na]^+$, 653.1173; found, 653.1174.

(2-bromo-9-((diphenylphosphoryl)methyl)-9H-xanthen-9-yl)diphenylphosphine oxide (**3c**)



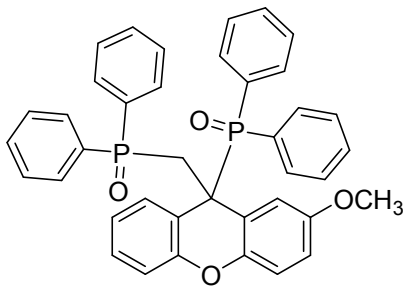
White solid (107.8 mg, 80%); mp: 265.3-267.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 6.84 (m, 24H), 6.75 (s, 1H), 6.62 (d, *J* = 6.2 Hz, 1H), 6.49 (d, *J* = 7.3 Hz, 1H), 3.72 (d, *J* = 54.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.3 (d, *J* = 3.9 Hz), 149.9 (d, *J* = 3.3 Hz), 133.8, 133.3 (d, *J* = 97.5 Hz), 132.9, 132.7 – 132.4 (m), 132.2, 132.1, 131.3, 130.8 – 130.3 (m), 129.5, 129.3 (d, *J* = 24.7 Hz), 128.6 (d, *J* = 23.5 Hz), 128.52 – 127.76 (m), 122.2, 119.4, 117.4, 116.6, 115.8, 114.2, 45.6 (d, *J* = 60.2 Hz), 35.1 (d, *J* = 67.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.8 (d, *J* = 43.9 Hz), 27.1 (d, *J* = 41.1 Hz). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $[C_{38}H_{29}NaBrO_3P_2 + Na]^+$, 697.0668; found, 697.0665.

((9-(diphenylphosphoryl)-2-methyl-9H-xanthen-9-yl)methyl)diphenylphosphine oxide (**3d**)



White solid (100.1 mg, 82%); mp: 233.5-235.3 °C; ^{1}H NMR (400 MHz, MeOD) δ 7.92 (s, 1H), 7.64 – 7.56 (m, 3H), 7.51 – 7.31 (m, 16H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.67 – 6.55 (m, 2H), 6.44 (s, 1H), 3.94 – 3.79 (m, 2H), 1.87 (s, 3H). ^{13}C NMR (151 MHz, MeOD) δ 150.9 (d, *J* = 4.5 Hz), 148.9 (d, *J* = 4.8 Hz), 133.1 (d, *J* = 99.5 Hz), 133.0 (d, *J* = 99.6 Hz), 132.7 – 132.0 (m), 131.6, 131.0, 130.8 (d, *J* = 3.1 Hz), 130.2, 130.2, 130.0, 129.4 (d, *J* = 3.0 Hz), 129.2, 128.7 (d, *J* = 34.7 Hz), 128. 3– 127.9 (m), 121.7, 116.9, 115.8, 115.6, 45. 7 (dd, *J* = 63.1, 4.2 Hz), 34.3 (d, *J* = 68.5 Hz), 19.4. ^{31}P NMR (162 MHz, MeOD) δ 33.1 (d, *J* = 46.9 Hz), 30.3 (d, *J* = 46.9 Hz). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{39}H_{33}O_3P_2 + H]^+$, 611.1894; found, 611.1901.

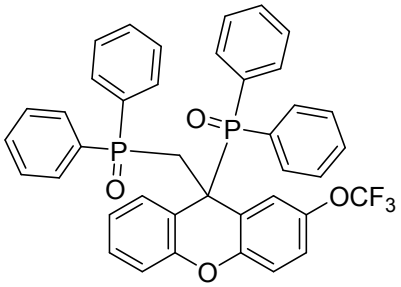
((9-(diphenylphosphoryl)-2-methoxy-9H-xanthen-9-yl)methyl)diphenylphosphine oxide (**3e**)



White solid (100.2 mg, 80%); mp: 216.3-218.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.57 (m, 2H), 7.50 – 7.41 (m, 6H), 7.35– 7.20 (m, 11H), 7.18– 7.10 (m, 2H), 7.04 (s, 1H), 6.79 (d, *J* = 6.5 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.61 – 6.38 (m, 3H), 3.95 – 3.69 (m, 2H), 3.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9 (d, *J* = 2.8 Hz), 150.9 (d, *J* = 4.5 Hz), 145.0 (d, *J* = 4.9 Hz), 133.7 (d, *J* = 93.0 Hz), 133.0 (d, *J* = 95.4 Hz), 132.8 (d, *J* = 7.8 Hz), 132.5 (d, *J* = 7.7 Hz), 132.0 (d, *J* = 2.5 Hz), 131.9 (d, *J* = 2.5 Hz), 131.2 (d, *J* = 2.6 Hz), 131.1 (d, *J* = 2.6 Hz), 130.7 (d, *J* = 9.4 Hz), 130.0 (d, *J* = 3.3 Hz), 129.9 (d, *J* = 34.5 Hz), 129.2 (d, *J* = 2.7 Hz), 129.0 (d, *J* = 36.0 Hz), 128.2 (d, *J* = 7.9 Hz), 128.1 (d, *J* = 7.2 Hz), 127.9 (d, *J* = 11.7 Hz), 121.8 (d, *J* = 2.3 Hz), 117.2 (t, *J* = 3.0 Hz), 116.9 (d, *J* = 2.9 Hz), 116.8 (d, *J* = 3.3 Hz), 116.6 (d, *J* = 2.5 Hz), 115.7 (d, *J* = 2.2 Hz), 114.0 (d, *J* = 3.0 Hz), 55.4, 46.1 (dd, *J* = 61.8,

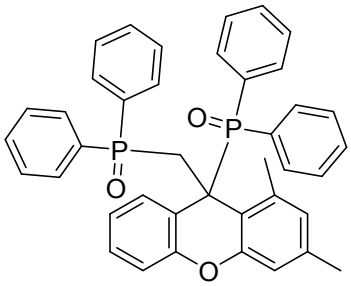
4.2 Hz), 35.5 (d, J = 66.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.2 (d, J = 45.4 Hz), 28.0 (d, J = 45.5 Hz). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $[C_{39}H_{32}NaO_4P_2 + Na]^+$, 649.1668; found, 649.1665.

((9-(diphenylphosphoryl)-2-(trifluoromethoxy)-9H-xanthen-9-yl)methyl)diphenylphosphine oxide (**3f**)



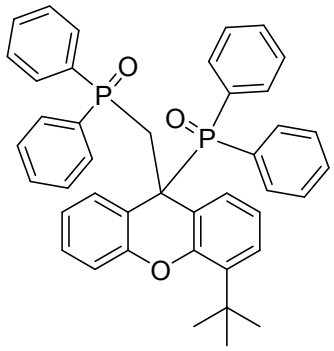
White solid (88.4 mg, 65%); mp: 241.6-243.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.62 (m, 2H), 7.62 – 7.49 (m, 3H), 7.48 – 7.32 (m, 9H), 7.28 – 7.07 (m, 8H), 6.93 (d, J = 6.6 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 6.76 (dd, J = 20.0, 7.4 Hz, 2H), 6.42 (d, J = 8.8 Hz, 1H), 3.84 –3.64 (m, 2H). ^{13}C NMR (151 MHz, MeOD) δ 150.7 (d, J = 4.5 Hz), 149.2 (d, J = 4.4 Hz), 143.29, 133.1–132.3 (m), 132.0 (d, J = 7.7 Hz), 131.8, 130.2–130.1 (m), 129.78 (d, J = 2.2 Hz), 128.4–28.0 (m), 127.5 (d, J = 27.6 Hz), 122.5 (d, J = 2.4 Hz), 122.2, 122.0, 120.5 (q, J = 255.9 Hz), 118.9, 117.01, 115.9 (d, J = 1.5 Hz), 115.51 (t, J = 2.2 Hz), 45.9 (dd, J = 62.4, 4.8 Hz), 34.6 (d, J = 68.0 Hz). ^{31}P NMR (162 MHz, MeOD) δ 33.3 (d, J = 44.9 Hz), 30.1 (d, J = 44.8 Hz). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $[C_{39}H_{29}NaF_3O_4P_2 + Na]^+$, 703.1385; found, 703.1384.

((9-(diphenylphosphoryl)-1,3-dimethyl-9H-xanthen-9-yl)methyl)diphenylphosphine oxide (**3g**)



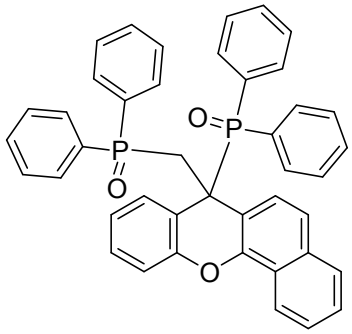
White solid (93.6 mg, 75%); mp: 171.2-173.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 21H), 6.90 – 6.80 (m, 2H), 6.57 –6.48 (m, 2H), 6.31 – 6.27 (m, 1H), 4.17 – 4.02 (m, 2H), 2.27 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.2 (d, J = 4.5 Hz), 149.7 (d, J = 4.4 Hz), 140.1 (d, J = 3.8 Hz), 139.0 (d, J = 2.7 Hz), 134.3 (d, J = 92.0 Hz), 133.7 (d, J = 92.9 Hz), 132.3 (d, J = 7.8 Hz), 132.1(d, J = 93.6 Hz), 131.6 (d, J = 2.1 Hz), 131.4 (d, J = 7.6 Hz), 131.3 (d, J = 2.1 Hz), 131.2 (d, J = 87.0 Hz), 131.0 (d, J = 2.1 Hz), 130.7– 130.5(m), 129.9 (d, J = 3.6 Hz), 129.3 (d, J = 1.9 Hz), 128.7 (d, J = 2.5 Hz), 128.3 (d, J = 11.6 Hz), 127.8 (d, J = 11.6 Hz), 127.7 (d, J = 12.9 Hz), 127.6 (d, J = 11.0 Hz), 121.2 (d, J = 2.0 Hz), 118.8 (t, J = 2.7 Hz), 115.5 (d, J = 1.9 Hz), 115.2 (d, J = 2.0 Hz), 113.9 (d, J = 1.8 Hz), 47.7 (dd, J = 60.5, 4.1 Hz), 34.8 (d, J = 67.3 Hz), 24.55, 20.70. ^{31}P NMR (162 MHz, MeOD) δ 34.1 (d, J = 48.4 Hz), 29.3 (d, J = 48.3 Hz). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $[C_{40}H_{34}NaO_3P_2 + Na]^+$, 647.1875; found, 647.1876.

(4-(tert-butyl)-9-((diphenylphosphoryl)methyl)-9H-xanthen-9-yl)diphenylphosphine oxide (**3h**)



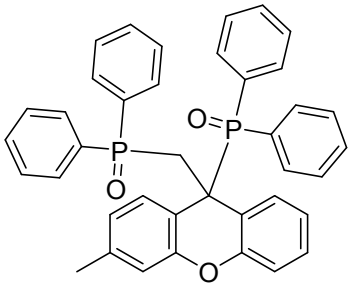
White solid (103.0 mg, 79%); mp: 282.9 – 284.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.46 (m, 4H), 7.46 – 7.31 (m, 5H), 7.31 (d, *J* = 4.4 Hz, 1H), 7.28 – 7.21 (m, 7H), 7.18 – 7.04 (m, 7H), 6.87 (t, *J* = 7.5 Hz, 1H), 6.76 (t, *J* = 7.8 Hz, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 3.00 – 3.75 (m, 2H), 1.22 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.2 (d, *J* = 4.5 Hz), 149.4 (d, *J* = 4.4 Hz), 135.8 (d, *J* = 2.1 Hz), 133.3, 132.9 (d, *J* = 97.5 Hz), 132.8 (d, *J* = 7.8 Hz), 132.7 (d, *J* = 7.7 Hz), 131.9 (d, *J* = 2.0 Hz), 131.8 (d, *J* = 2.5 Hz), 131.3 (d, *J* = 2.0 Hz), 131.0 (d, *J* = 2.1 Hz), 130.9 (d, *J* = 3.1 Hz), 130.8 (d, *J* = 3.2 Hz), 130.4 (d, *J* = 3.2 Hz), 129.5 (d, *J* = 16.4 Hz), 129.2 (d, *J* = 2.2 Hz), 129.0 (d, *J* = 3.6 Hz), 128.9 (d, *J* = 17.2 Hz), 128.14 – 127.69 (m), 126.8 (d, *J* = 2.7 Hz), 122.0 (d, *J* = 1.9 Hz), 121.2 (d, *J* = 1.9 Hz), 117.0 (t, *J* = 2.6 Hz), 116.5 (t, *J* = 2.2 Hz), 115.4 (d, *J* = 1.8 Hz), 46.1 (dd, *J* = 61.2, 3.6 Hz), 35.1 (d, *J* = 66.3 Hz), 34.7, 30.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.1 (d, *J* = 46.6 Hz), 28.8 (d, *J* = 46.5 Hz). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $[C_{42}H_{38}O_3P_2] + Na]^+$, 675.2188; found, 675.2185.

((7-(diphenylphosphoryl)-7H-benzo[c]xanthen-7-yl)methyl)diphenylphosphine oxide (**3i**)



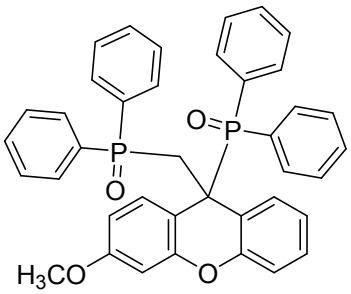
Colorless oil (98.2 mg, 76%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.46 (dd, *J* = 15.1, 5.8 Hz, 3H), 7.42 – 7.35 (m, 3H), 7.33 – 7.28 (m, 2H), 7.22 – 7.17 (m, 6H), 7.17 – 7.10 (m, 6H), 7.02 (t, *J* = 6.8 Hz, 4H), 6.92 (t, *J* = 6.2 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 3.86 – 3.71 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.5 (d, *J* = 4.1 Hz), 146.2 (d, *J* = 5.7 Hz), 133.8, 133.2 (d, *J* = 14.6 Hz), 132.6 – 132.5 (m), 132.1 (d, *J* = 1.4 Hz), 131.9 (d, *J* = 1.5 Hz), 131.2 (d, *J* = 1.5 Hz), 131.1, 132.8 – 132.6 (m), 129.8 (d, *J* = 12.0 Hz), 129.4 (d, *J* = 1.3 Hz), 129.2, 128.2 – 127.7 (m), 127.2, 126.9, 126.8, 125.7, 123.2 (d, *J* = 1.6 Hz), 122.4, 121.8, 121.2, 117.3, 115.9, 111.2, 46.0 (d, *J* = 59.6 Hz), 35.2 (d, *J* = 66.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.3 (d, *J* = 45.8 Hz), 28.3 (d, *J* = 45.8 Hz). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{42}H_{32}O_3P_2 + H]^+$, 647.1899; found, 647.1924.

((9-(diphenylphosphoryl)-3-methyl-9H-xanthen-9-yl)methyl)diphenylphosphine oxide (**3j**)



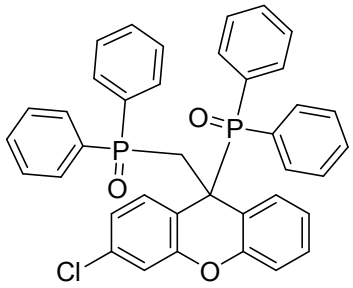
White solid (95.1 mg, 78%); mp: 202.8-204.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.52 – 7.48 (m, 2H), 7.45 – 7.39 (m, 2H), 7.34 – 7.33 (m, 3H), 7.31 – 7.25 (m, 7H), 7.22 – 7.15 (m, 5H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.52 (t, *J* = 8.8 Hz, 2H), 6.40 (s, 1H), 3.83 – 3.69 (m, 2H), 2.23 (s, 3H). ^{13}C NMR (150 MHz, MeOD) δ 150.9 (d, *J* = 4.4 Hz), 150.7 (d, *J* = 4.5 Hz), 140.0 (d, *J* = 2.3 Hz), 133.3 – 132.1 (m), 131.6 (d, *J* = 2.0 Hz), 131.4 (d, *J* = 2.0 Hz), 130.3, 130.2, 129.9 (d, *J* = 3.1 Hz), 129.7 (d, *J* = 3.0 Hz), 129.3 (d, *J* = 2.0 Hz), 128.2– 128.0 (m), 122.7 (d, *J* = 1.6 Hz), 121.6 (d, *J* = 1.6 Hz), 116.6, 116.1, 115.8, 113.4, 45.3 (dd, *J* = 63.5, 4.3 Hz), 34.7 (d, *J* = 68.3 Hz), 19.6. ^{31}P NMR (162 MHz, MeOD) δ 33.11 (d, *J* = 46.8 Hz), 30.78 (d, *J* = 46.7 Hz). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $[C_{39}H_{32}NaO_3P_2 + Na]^+$, 633.1713; found, 633.1715.

((9-(diphenylphosphoryl)-3-methoxy-9H-xanthen-9-yl)methyl)diphenylphosphine oxide (**3k**)



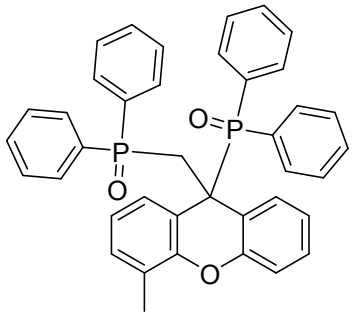
Colorless oil (82.6 mg, 66%); ^{1}H NMR (400 MHz, MeOD) δ 7.79 (s, 2H), 7.55 – 7.33 (m, 18H), 7.16 – 7.06 (m, 2H), 6.85 – 6.61 (m, 3H), 6.23 (s, 2H), 3.92 – 3.80 (m, 2H), 3.75 (s, 3H). ^{13}C NMR (150 MHz, MeOD) δ 160.9, 151.76 (d, *J* = 4.3 Hz), 150.87 (d, *J* = 4.7 Hz), 133.1, 132.4 – 132.2 (m), 131.6 (d, *J* = 1.7 Hz), 131.5 (d, *J* = 1.7 Hz), 131.0, 130.9, 130.8 (d, *J* = 2.6 Hz), 130.5, 130.4, 130.3, 130.3, 130.2, 129.8 (d, *J* = 2.9 Hz), 129.3 (d, *J* = 1.6 Hz), 128.7, 128.3 – 128.0 (m), 127.8, 127.7, 54.5, 45.1 (dd, *J* = 64.1, 4.1 Hz), 34.7 (d, *J* = 68.6 Hz). ^{31}P NMR (160 MHz, MeOD) δ 33.1 (d, *J* = 46.8 Hz), 30.8 (d, *J* = 46.8 Hz). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $[C_{39}H_{32}NaO_4P_2 + Na]^+$, 649.1670; found, 649.1663.

(3-chloro-9-((diphenylphosphoryl)methyl)-9H-xanthen-9-yl)diphenylphosphine oxide (**3l**)



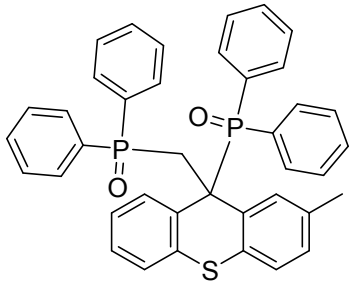
White solid (89.5 mg, 71%); mp: 226.7-228.5 °C; ^{1}H NMR (400 MHz, MeOD) δ 7.76 – 7.34 (m, 20H), 7.15 (s, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 7.0 Hz, 1H), 6.79 – 6.51 (m, 4H), 3.98 – 3.75 (m, 2H). ^{13}C NMR (151 MHz, MeOD) δ 151.3 (d, *J* = 4.2 Hz), 150.5 (d, *J* = 4.5 Hz), 134.6 (d, *J* = 2.7 Hz), 133.1 (d, *J* = 5.0 Hz), 132.7 – 132.2 (m), 131.7, 131.6, 131.2 (d, *J* = 2.7 Hz), 130.3 – 130.2 (m), 129.9 (d, *J* = 2.0 Hz), 129.6, 128. 6 – 128.0 (m), 127.6 (d, *J* = 28.0 Hz), 127.5, 122.2, 121.8, 116.3, 115.9, 115.7, 45.4 (dd, *J* = 62.9, 3.9 Hz), 34.6 (d, *J* = 67.9 Hz). ^{31}P NMR (162 MHz, MeOD) δ 33.1 (d, *J* = 45.2 Hz), 30.2 (d, *J* = 45.3 Hz). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $[C_{38}H_{29}NaClO_3P_2 + Na]^+$, 653.1167; found, 653.1173.

((9-(diphenylphosphoryl)-4-methyl-9H-xanthen-9-yl)methyl)diphenylphosphine oxide (**3m**)



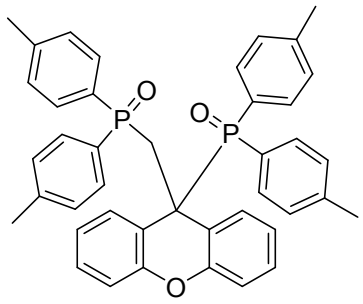
White solid (97.6 mg, 80%); mp: 221.3-223.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 4H), 7.42 (s, 2H), 7.37 – 7.11 (m, 15H), 7.07 (dd, *J* = 13.2, 7.3 Hz, 2H), 6.91 (d, *J* = 6.9 Hz, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.69 (t, *J* = 7.5 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 3.79 (dd, *J* = 10.3, 6.6 Hz, 2H), 1.99 (s, 3H). ^{13}C NMR (151 MHz, MeOD) δ 150.9 (d, *J* = 4.3 Hz), 149.0 (d, *J* = 4.3 Hz), 132.99 – 131.96 (m), 131.6, 131.5, 130.6 (d, *J* = 1.4 Hz), 130.4, 130.3, 130.1 (d, *J* = 2.6 Hz), 129.4 (d, *J* = 1.4 Hz), 128.72 – 127.64 (m), 127.3 (d, *J* = 2.6 Hz), 125.0, 121.7, 121.3, 116.3, 116.0, 115.8, 45.9 (dd, *J* = 62.8, 3.7 Hz), 34.5 (d, *J* = 67.9 Hz), 14.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.8 (d, *J* = 46.1 Hz), 28.4 (d, *J* = 46.1 Hz). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $[C_{39}H_{32}NaO_3P_2 + Na]^+$, 633.1713; found, 633.1722.

((9-(diphenylphosphoryl)-2-methyl-9H-thioxanthen-9-yl)methyl)diphenylphosphine oxide (**3n**)



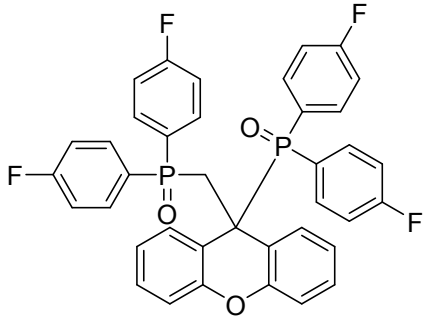
Yield: 60%, 75.1 mg; Yellow solid, mp: 190.2-192.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.16 (m, 21H), 7.00 – 6.83 (m, 4H), 6.67 (dd, *J* = 12.7, 7.6 Hz, 2H), 4.05 – 3.72 (m, 2H), 1.97 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 134.1, 133.8 (d, *J* = 3.3 Hz), 133. 7 (d, *J* =97.5 Hz), 133.3 (d, *J* =99.0 Hz), 133.1 (d, *J* = 7.7 Hz), 132.7 (d, *J* = 8.0 Hz), 131.9, 131.8 (d, *J* = 18.8 Hz), 131.3 (d, *J* = 4.8 Hz), 131.1 (d, *J* = 16.9 Hz), 130. 7 (d, *J* = 3.1 Hz), 130.6 (d, *J* = 3.1 Hz), 130.0 (d, *J* = 16.3 Hz), 129.4 (d, *J* = 17.9 Hz), 128.8, 128.3 – 127.5 (m), 126.6, 124.8, 124.7, 124.6, 51.5 (d, *J* = 59.9 Hz), 36.8 (d, *J* = 66.5 Hz), 21.0. ^{31}P NMR (162 MHz, MeOD) δ 32.6 (d, *J* = 47.3 Hz), 29.7 (d, *J* = 47.3 Hz). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $[C_{39}H_{32}NaO_2P_2S + Na]^+$, 649.1490; found, 649.1490.

(1,1-diphenylethane-1,2-diyl)bis(di-p-tolylphosphine oxide) (**4a**)



White solid (110.8 mg, 85%); mp: 294.5-296.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, *J* = 8.8 Hz, 4H), 7.18 (t, *J* = 9.3 Hz, 6H), 7.07 (d, *J* = 6.2 Hz, 6H), 6.97 (d, *J* = 6.2 Hz, 4H), 6.76 (t, *J* = 7.4 Hz, 2H), 6.54 (d, *J* = 8.0 Hz, 2H), 3.72 (dd, *J* = 10.7, 6.6 Hz, 2H), 2.32 (s, 6H), 2.28 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8 (d, *J* = 4.6 Hz), 142.3 (d, *J* = 2.7 Hz), 141.4 (d, *J* = 2.8 Hz), 132.7 (d, *J* = 8.1 Hz), 130.8 (d, *J* = 4.2 Hz), 130.7 (d, *J* = 9.5 Hz), 130.1 (d, *J* = 101.2 Hz), 129.0 (d, *J* = 2.6 Hz), 128.8 (d, *J* = 6.8 Hz), 128.7 (d, *J* = 6.0 Hz), 126.1 (d, *J* = 94.8 Hz), 121.8 (d, *J* = 2.4 Hz), 117.2 (t, *J* = 2.9 Hz), 115.5 (d, *J* = 2.2 Hz), 45.5 (dd, *J* = 61.9, 4.3 Hz), 35.3 (d, *J* = 66.9 Hz), 21.5, 21.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.32 (d, *J* = 45.3 Hz), 28.63 (d, *J* = 45.4 Hz). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $[C_{42}H_{38}NaO_3P_2 + Na]^+$, 675.2188; found, 675.2184.

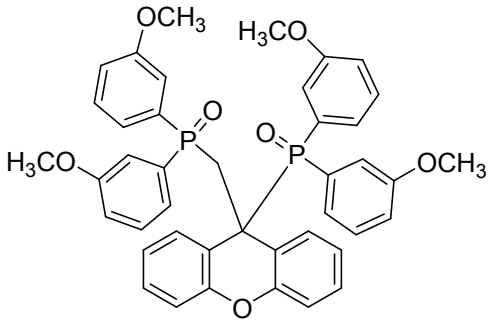
((9-(bis(4-fluorophenyl)phosphoryl)-9H-xanthen-9-yl)methyl)bis(4-fluorophenyl)phosphine oxide (**4b**)



White solid (86.8 mg, 63%); mp: 255.6 – 257.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.39 (m, 4H), 7.35 – 7.07 (m, 8H), 7.06 – 6.73 (m, 10H), 6.68 – 6.51 (m, 2H), 3.70 (br, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.2 (d, *J* = 252.0 Hz), 164.6 (d, *J* = 252.0 Hz), 150.7, 135.0 – 134.8 (m), 133.5 – 133.0 (m), 130.4, 129.8, 128.7 (d, *J* = 102.9 Hz), 124.9 (d, *J* = 96.1 Hz), 122.2, 116.6, 116.0, 115.7 – 115.5 (m), 45.7 (d, *J* = 61.0 Hz), 35.4 (d, *J* = 68.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.28 (d, *J* = 38.1 Hz),

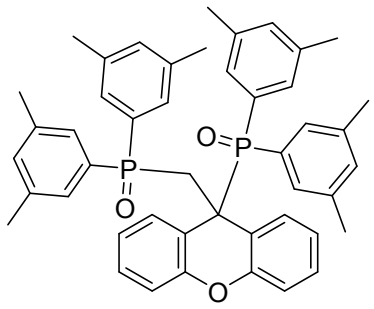
27.17 (d, J = 43.5 Hz). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $[C_{38}H_{26}F_4O_3P_2+Na]^+$, 691.1186; found, 691.1180.

((9-(bis(3-methoxyphenyl)phosphoryl)-9H-xanthen-9-yl)methyl)bis(3-methoxyphenyl)phosphine oxide (**4d**)



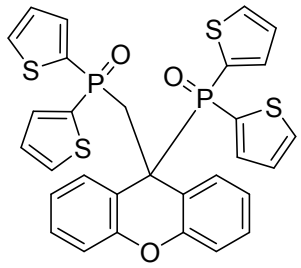
Light yellow oil (100.2 mg, 70%); ^{1}H NMR (400 MHz, MeOD) δ 7.21 – 7.11 (m, 4H), 7.03 – 6.95 (m, 6H), 6.93 (s, 1H), 6.90 – 6.84 (m, 7H), 6.78 (d, J = 12.9 Hz, 2H), 6.60 – 6.54 (m, 4H), 3.75 (dd, J = 10.7, 6.4 Hz, 2H), 3.59 (d, J = 2.9 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.1 (d, J = 14.4 Hz), 158.9 (d, J = 14.0 Hz), 150.7 (d, J = 4.3 Hz), 134.6 (d, J = 97.9 Hz), 130.6 (d, J = 91.4 Hz), 130.6 (d, J = 2.9 Hz), 129.4 – 129.0 (m), 124.96 (d, J = 7.6 Hz), 122. 7 (d, J = 9.6 Hz), 121.8 (d, J = 1.3 Hz), 118.7 (d, J = 1.4 Hz), 117.9 (d, J = 1.7 Hz), 117.1, 117.0 (d, J = 8.7 Hz), 115.7, 115.2 (d, J = 10.0 Hz), 55.2 (d, J = 18.6 Hz), 45.6 (dd, J = 61.9, 3.9 Hz), 35.7 (d, J = 67.0 Hz). ^{31}P NMR (162 MHz, MeOD) δ 33.5 (d, J = 46.8 Hz), 30.8 (d, J = 46.7 Hz). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{42}H_{39}O_7P_2 + H]^+$, 717.2166; found, 717.2161.

((9-(bis(3,5-dimethylphenyl)phosphoryl)-9H-xanthen-9-yl)methyl)bis(3,5-dimethylphenyl)phosphine oxide (**4e**)



White solid (69.4 mg, 49%); mp: 245.5-247.0 °C; ^{1}H NMR (400 MHz, MeOD) δ 7.39 (d, J = 11.4 Hz, 1H), 7.21 (s, 2H), 7.16 (t, J = 7.6 Hz, 2H), 7.05 (dd, J = 15.0, 8.7 Hz, 7H), 6.89 (d, J = 11.6 Hz, 4H), 6.79 (t, J = 7.5 Hz, 2H), 6.62 (d, J = 8.1 Hz, 2H), 3.78 (dd, J = 10.6, 5.9 Hz, 2H), 2.29 (s, 3H), 2.25 (s, 9H), 2.21 (s, 12H). ^{13}C NMR (151 MHz, MeOD) δ 151.0 (d, J = 4.0 Hz), 138.0, 138.0, 137.9, 133.7, 133.3, 131.9 (d, J = 98.0 Hz), 130.1, 130.0, 130.0, 129.2, 128.2, 128.1, 127.3, 121.4, 116.6, 115.4, 45.8 (d, J = 60.4 Hz), 34.2 (d, J = 66.1 Hz), 19.9, 19.8. ^{31}P NMR (162 MHz, MeOD) δ 33.6 (d, J = 46.4 Hz), 32.8 (d, J = 46.4 Hz). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $[C_{46}H_{46}NaO_3P_2 + Na]^+$, 731.2814; found, 731.2813.

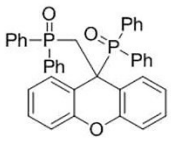
((9-(di(thiophen-2-yl)phosphoryl)-9H-xanthen-9-yl)methyl)di(thiophen-2-yl)phosphine oxide (**4f**)



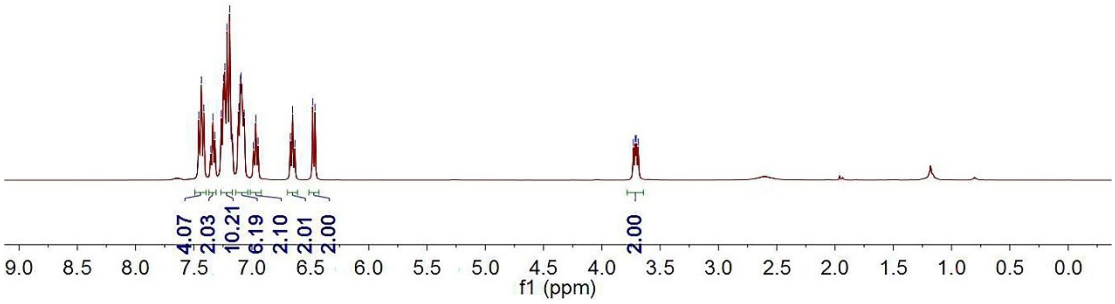
Yellow solid (79.4 mg, 64%); mp: 272.3-274.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (t, *J* = 4.2 Hz, 2H), 7.53 (t, *J* = 4.2 Hz, 2H), 7.31 – 7.24 (m, 3H), 7.19 (dd, *J* = 10.0, 4.6 Hz, 2H), 7.14 (d, *J* = 7.3 Hz, 3H), 7.09 (s, 2H), 6.95 (s, 2H), 6.88 (t, *J* = 7.4 Hz, 2H), 6.66 (d, *J* = 8.0 Hz, 2H), 3.91 (dd, *J* = 11.8, 7.3 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.1 (d, *J* = 4.7 Hz), 137.3 (d, *J* = 8.5 Hz), 135.3 (d, *J* = 10.2 Hz), 135.1 (d, *J* = 113.4 Hz), 134.6 (d, *J* = 4.1 Hz), 133.5 (d, *J* = 4.8 Hz), 130.2 (d, *J* = 3.8 Hz), 129.5 (d, *J* = 2.9 Hz), 128.7 (d, *J* = 107.3 Hz), 128.1 (d, *J* = 4.0 Hz), 128.0 (d, *J* = 4.6 Hz), 122.2 (d, *J* = 2.7 Hz), 115.8 (d, *J* = 3.0 Hz), 115.8 (d, *J* = 2.2 Hz), 46.9 (dd, *J* = 71.9, 4.4 Hz), 37.6 (d, *J* = 77.1 Hz). ^{31}P NMR (162 MHz, MeOD) δ 28.67 (d, *J* = 56.9 Hz), 20.60 (d, *J* = 57.0 Hz). ^{31}P NMR (162 MHz, MeOD) δ 28.7 (d, *J* = 56.9 Hz), 20.6 (d, *J* = 57.0 Hz). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $[C_{30}H_{22}NaO_3P_2S_4 + Na]^+$, 642.9819; found, 642.9816.

Copies of ^{1}H NMR and ^{13}C NMR spectra of products

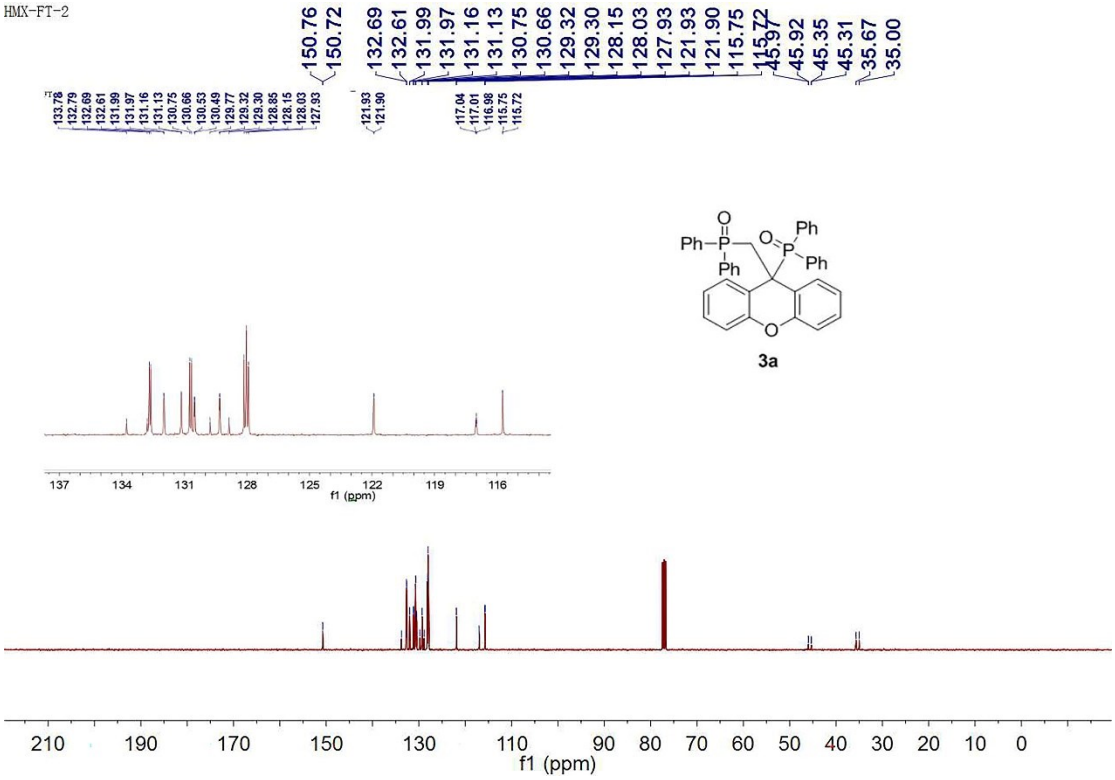
^{1}H NMR of **3a** in $CDCl_3$ (400 MHz)



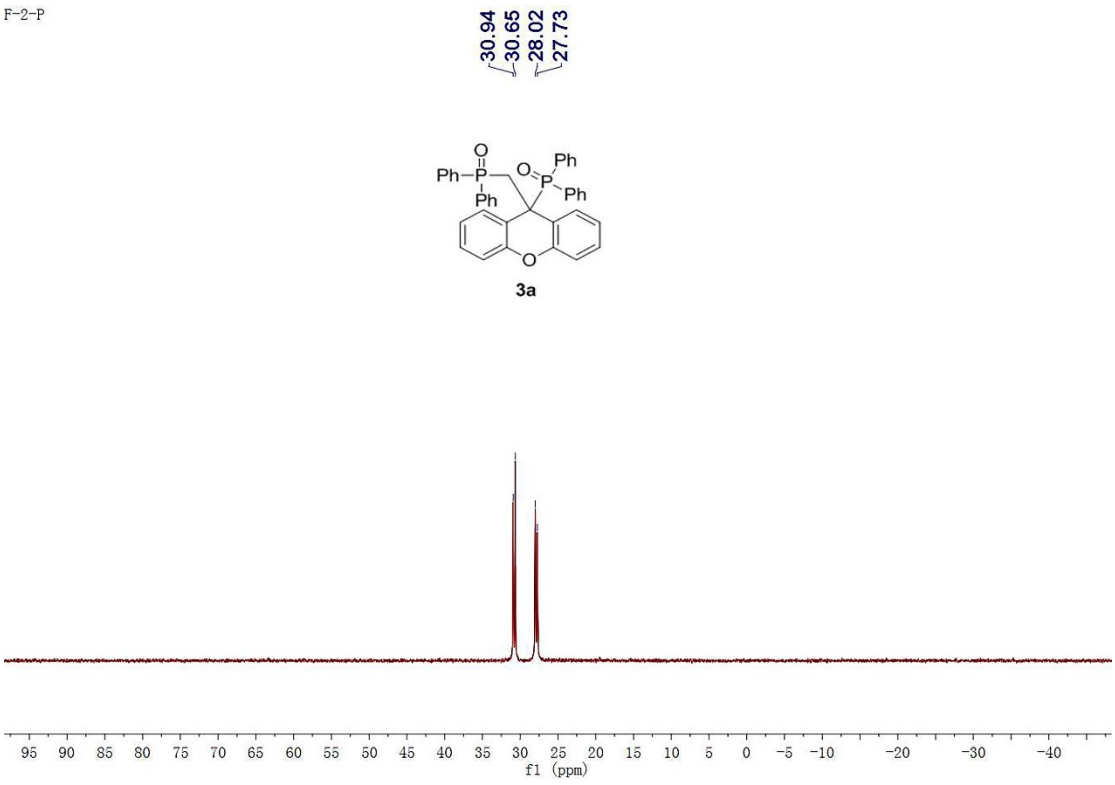
3a



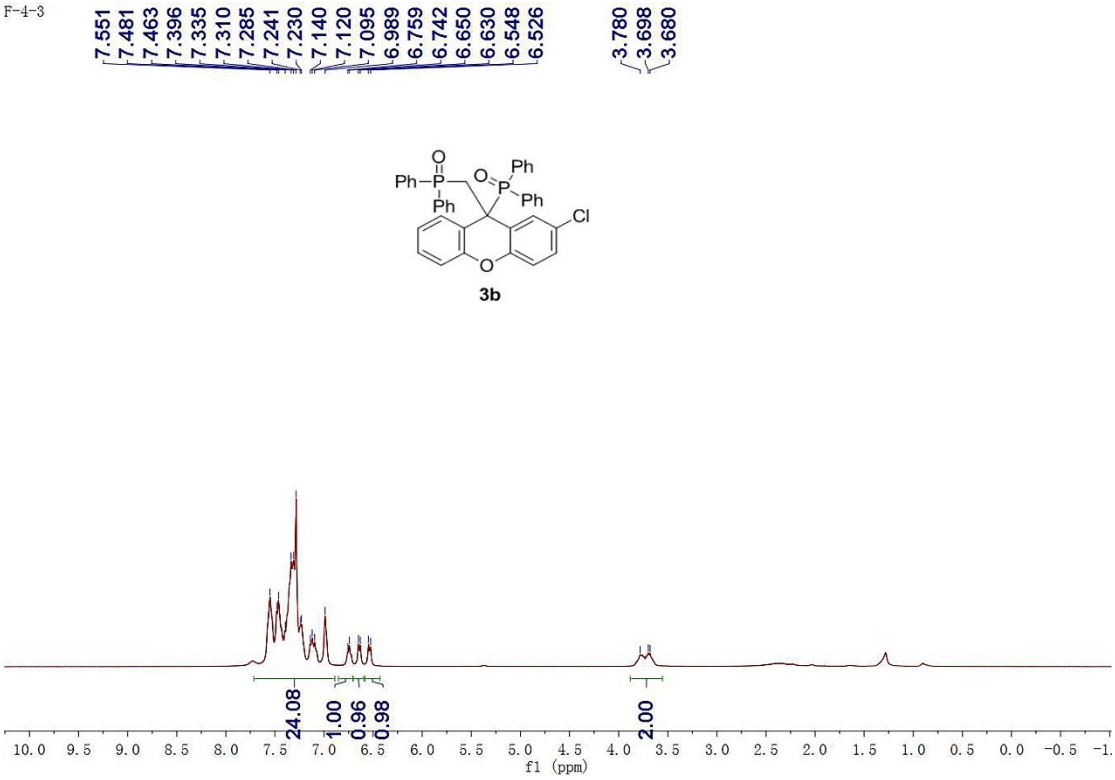
^{13}C NMR of **3a** in $CDCl_3$ (101 MHz)



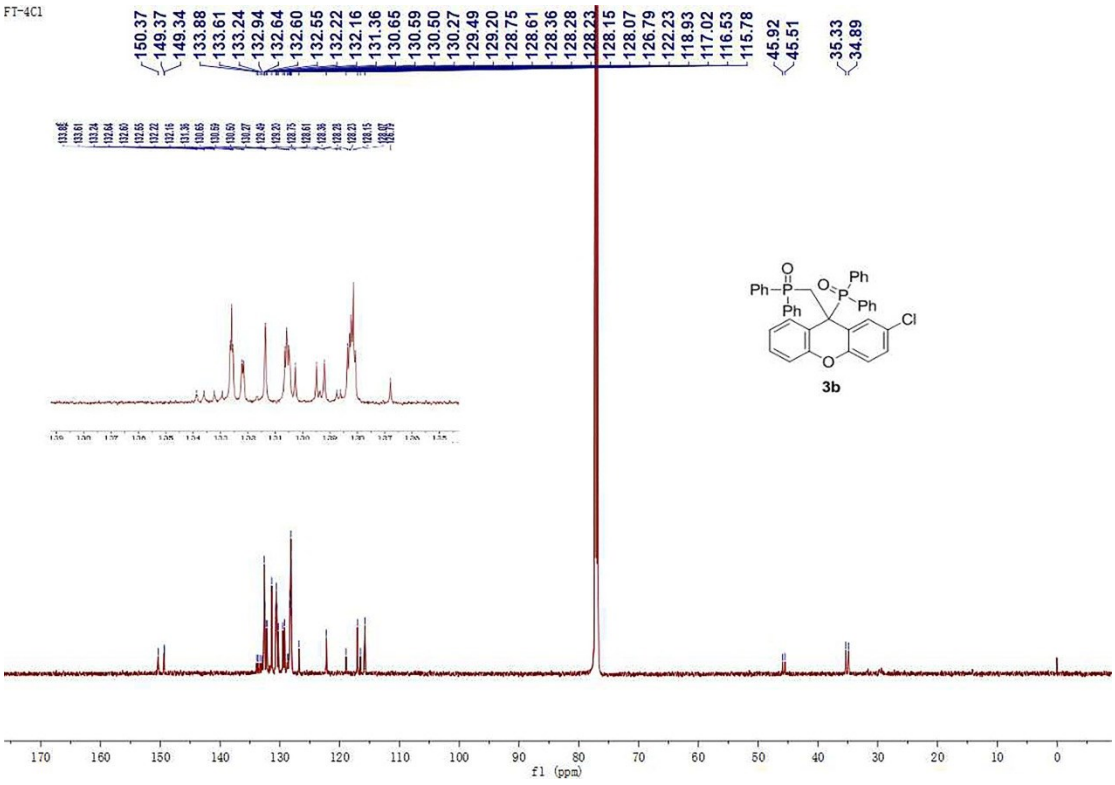
^{31}P NMR of **3a** in $CDCl_3$ (162 MHz)



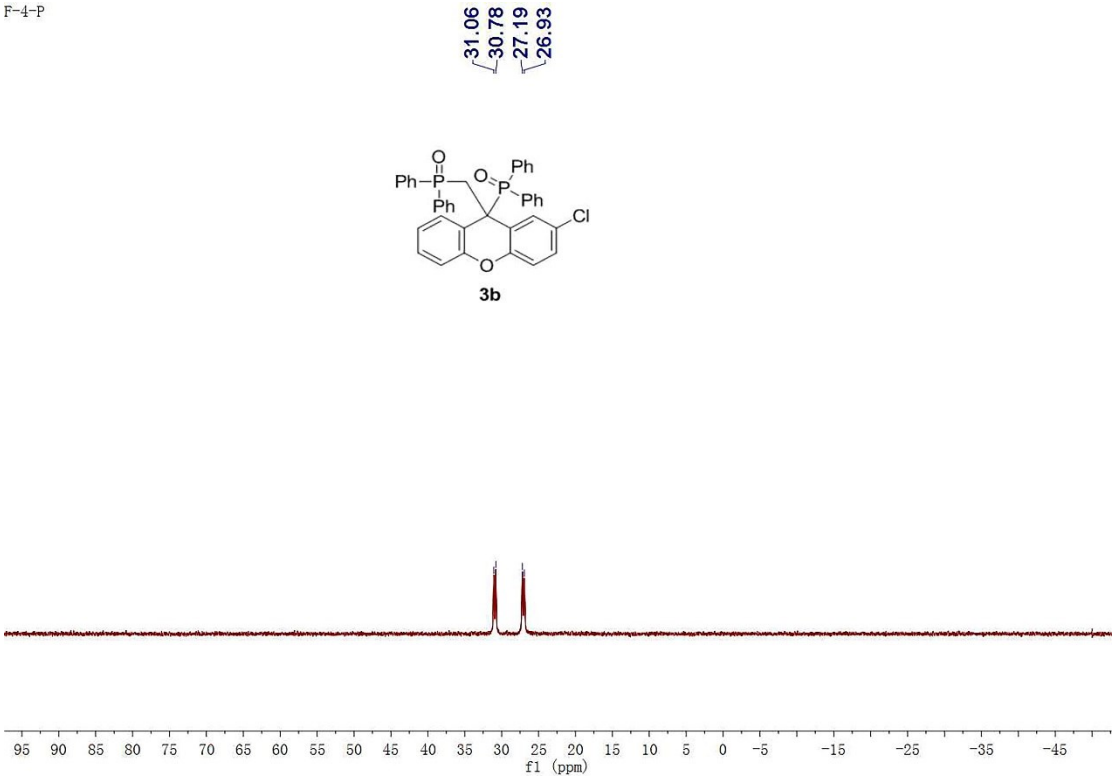
^{1}H NMR of **3b** in $CDCl_3$ (400 MHz)



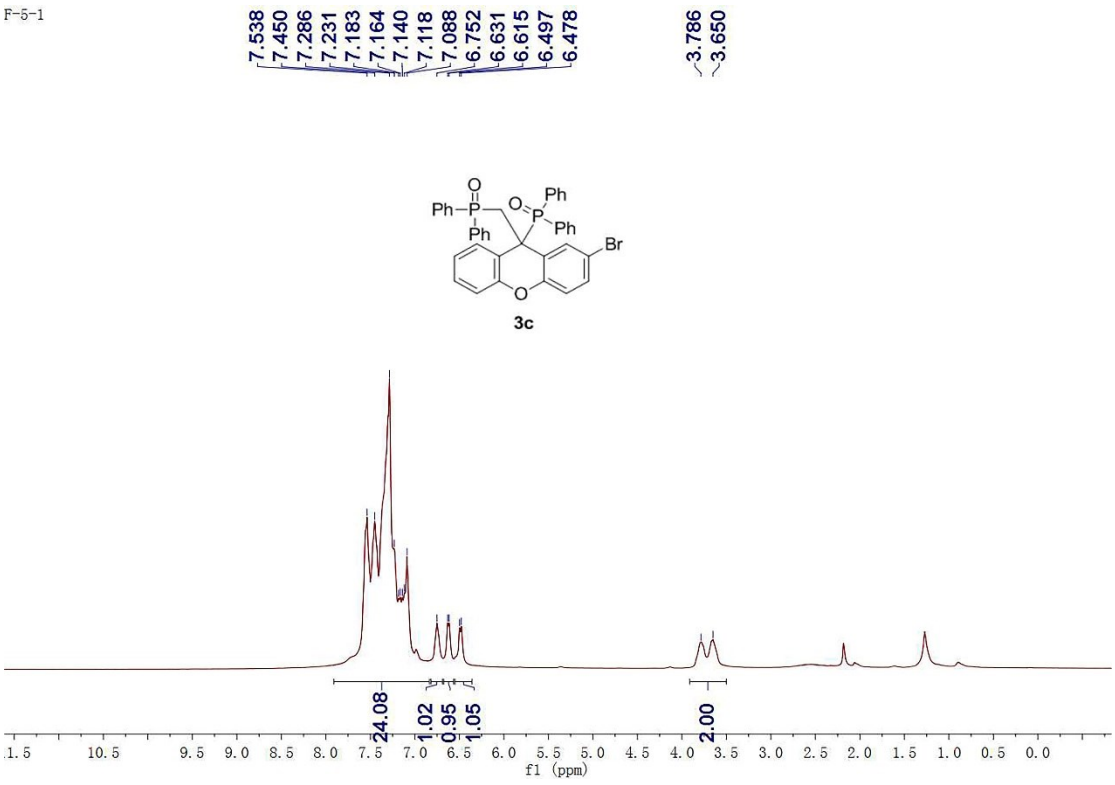
^{13}C NMR of **3b** in $CDCl_3$ (150 MHz)



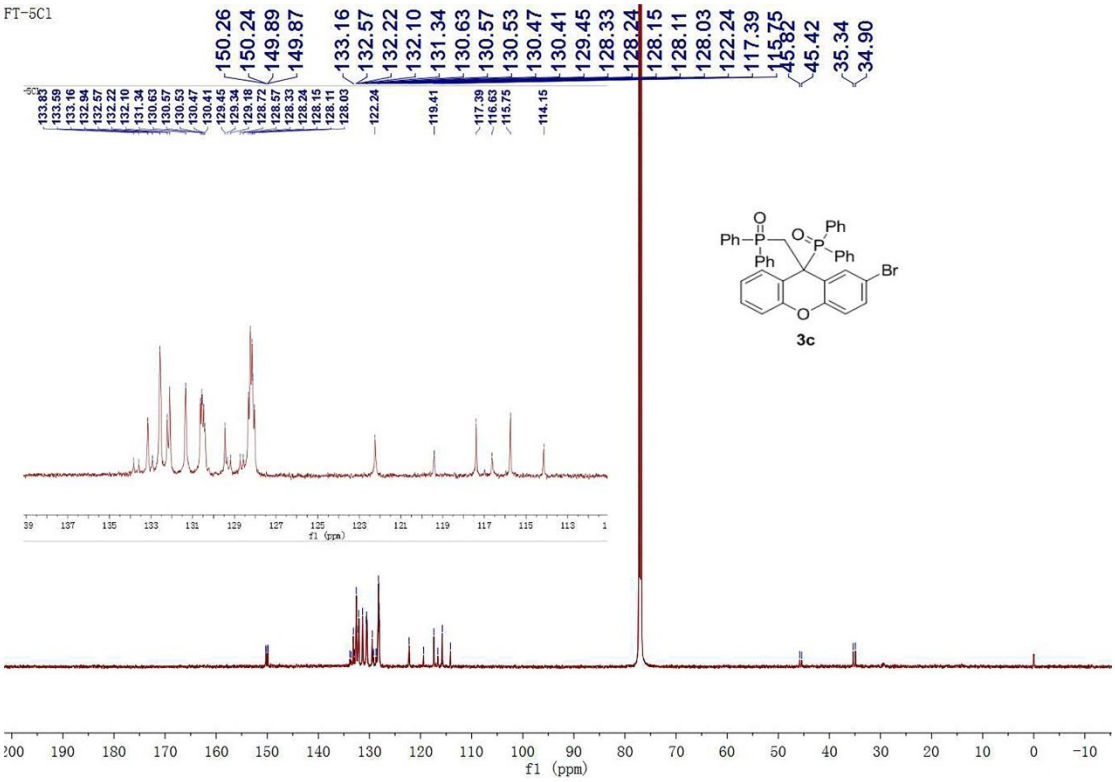
^{31}P NMR of **3b** in $CDCl_3$ (162 MHz)



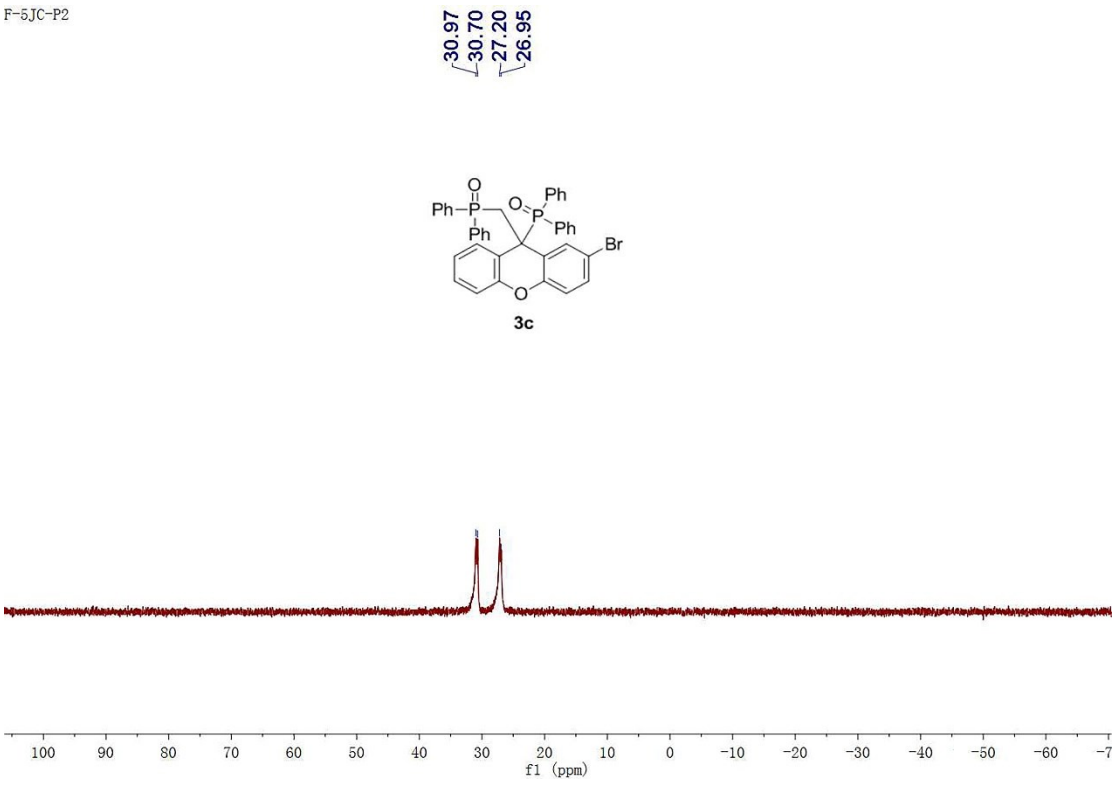
^{1}H NMR of **3c** in $CDCl_3$ (400 MHz)



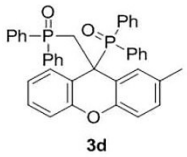
^{13}C NMR of **3c** in $CDCl_3$ (150 MHz)



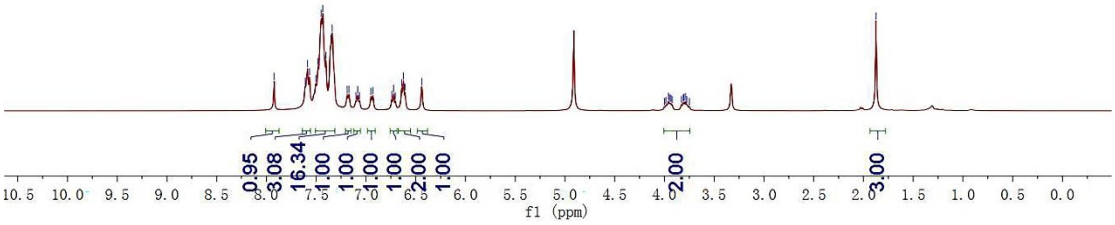
^{31}P NMR of **3c** in $CDCl_3$ (162 MHz)



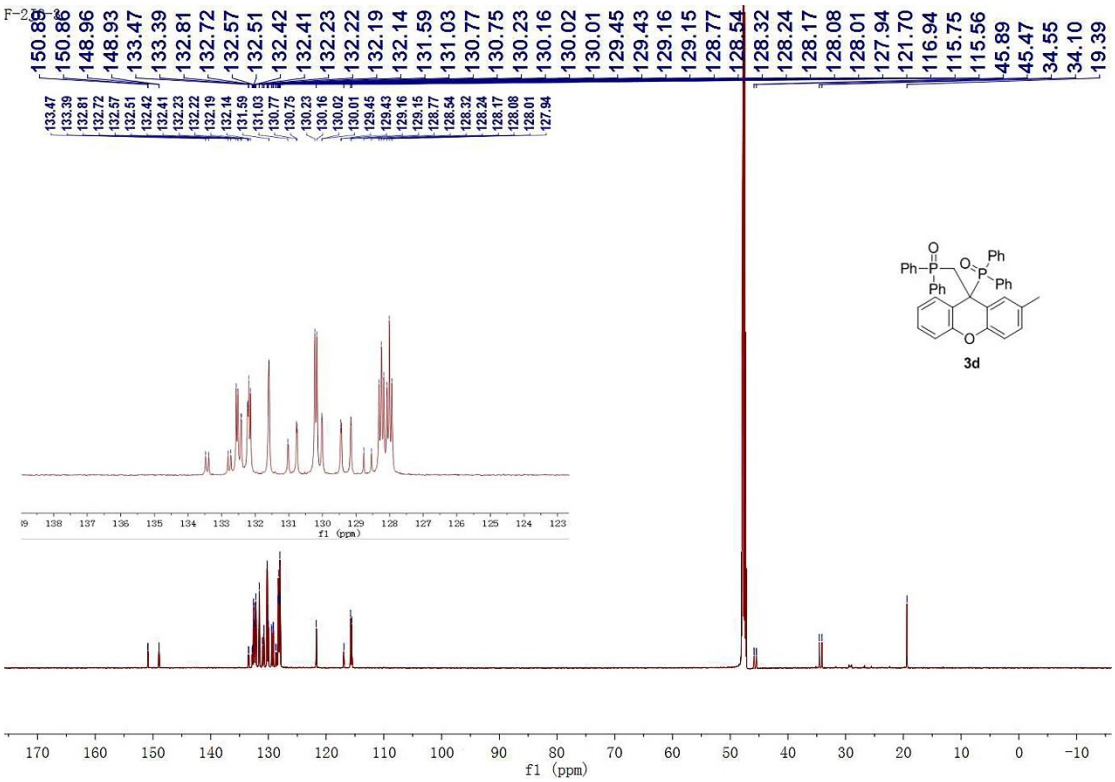
^{1}H NMR of **3d** in MeOD (400 MHz)



3d

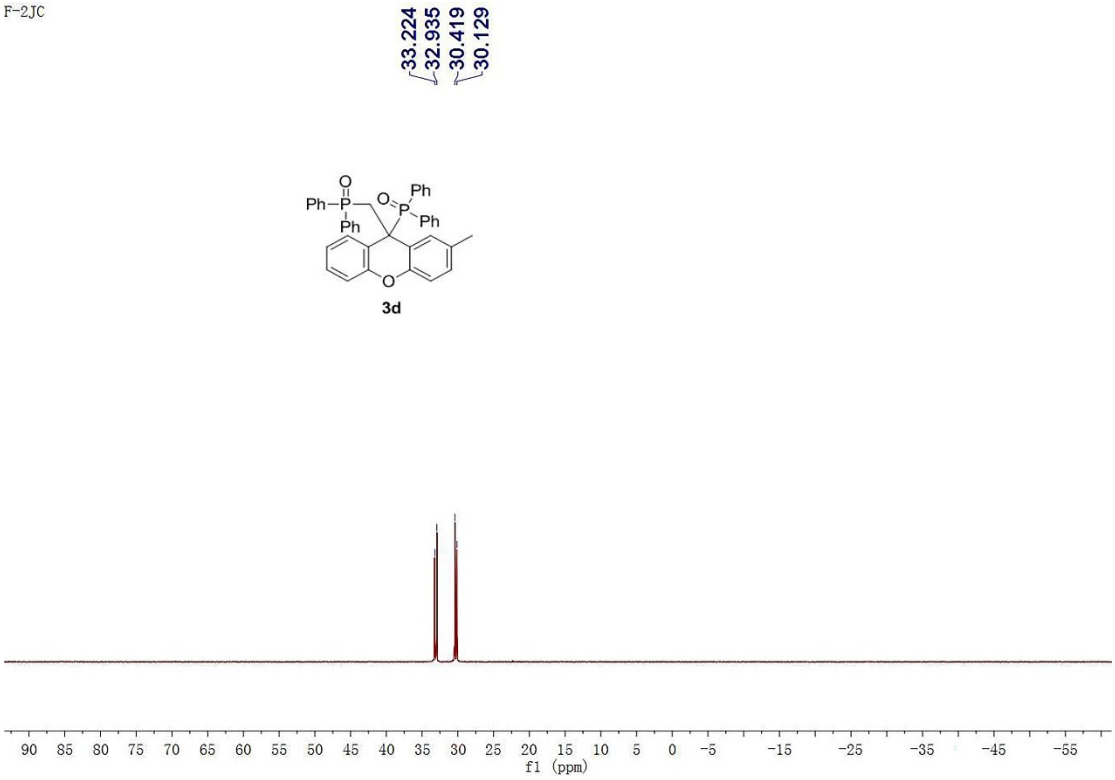


^{13}C NMR of **3d** in MeOD (150 MHz)

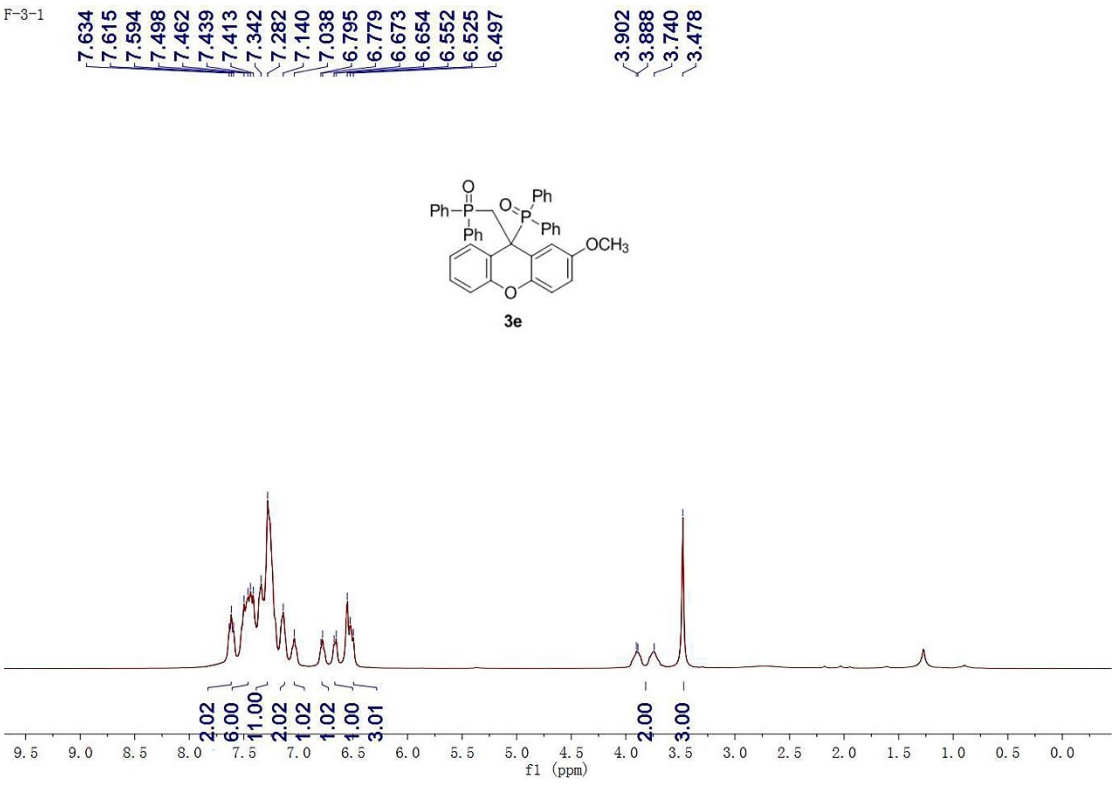


3d

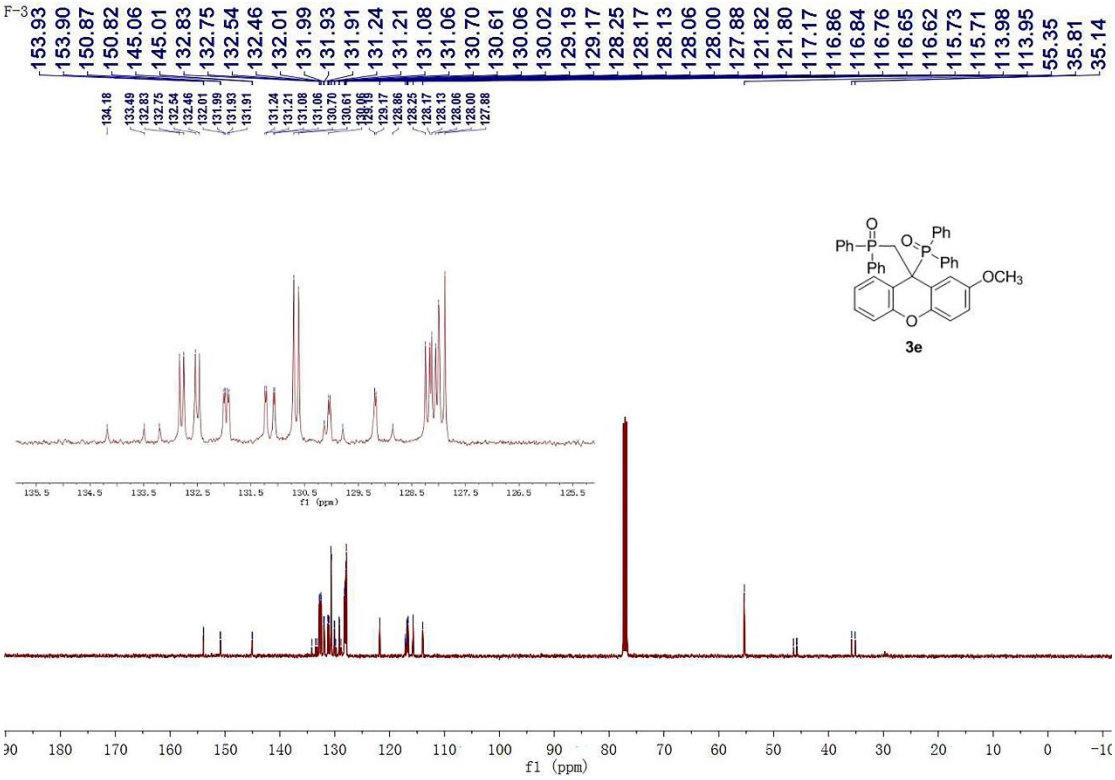
^{31}P NMR of **3d** in MeOD (162 MHz)



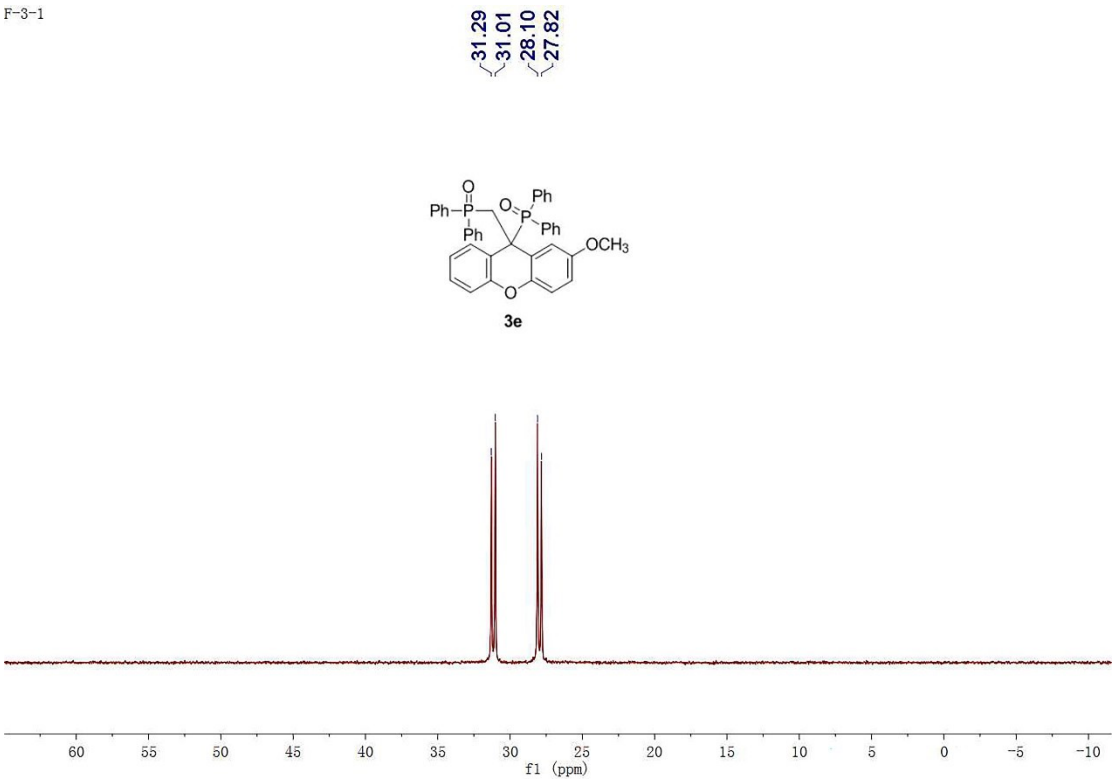
^{1}H NMR of **3e** in $CDCl_3$ (400 MHz)



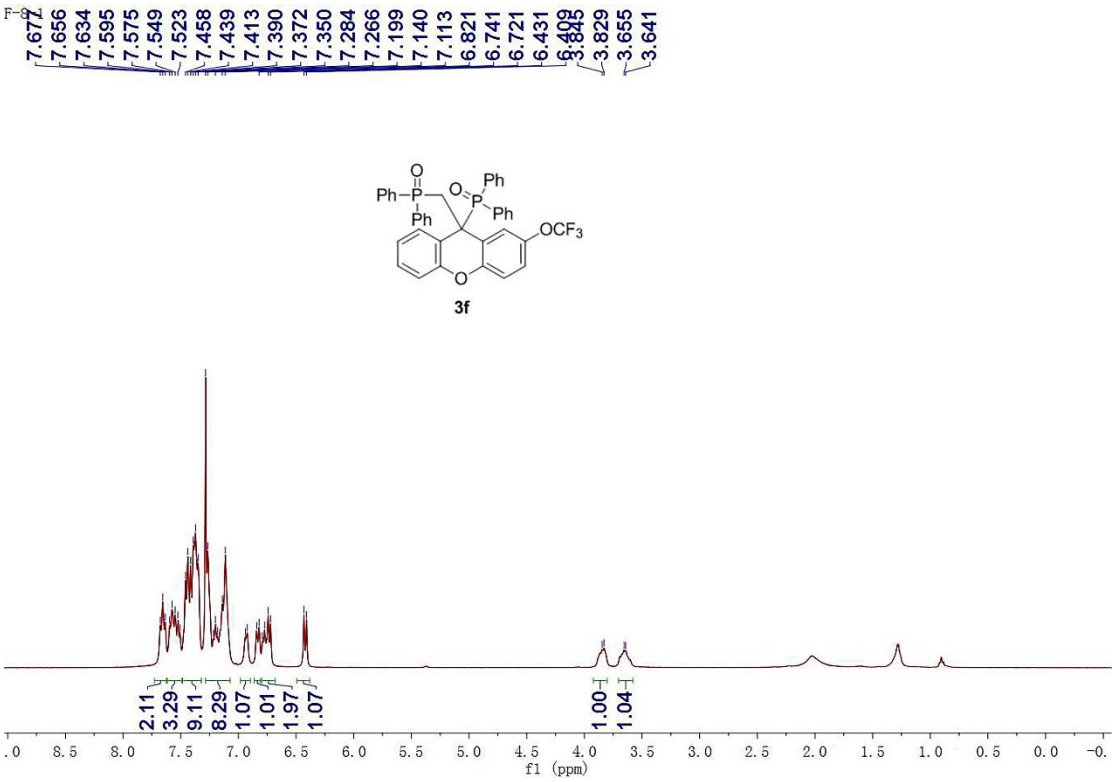
^{13}C NMR of **3e** in $CDCl_3$ (101 MHz)



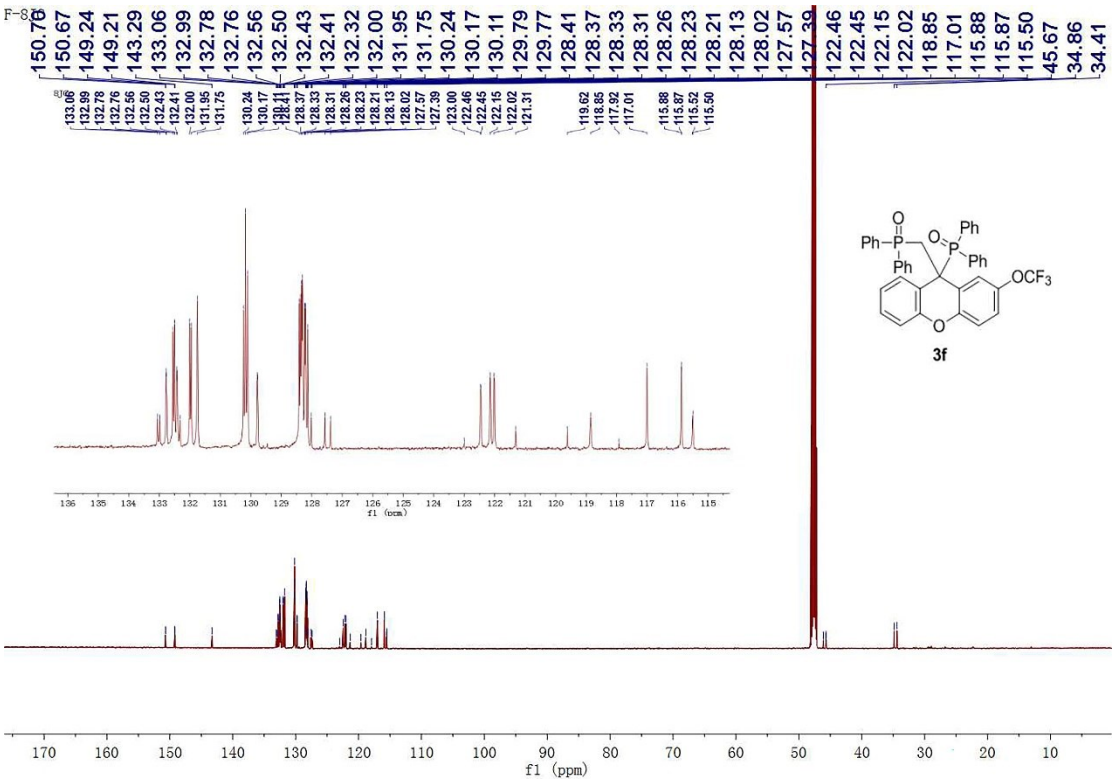
^{31}P NMR of **3e** in $CDCl_3$ (162 MHz)



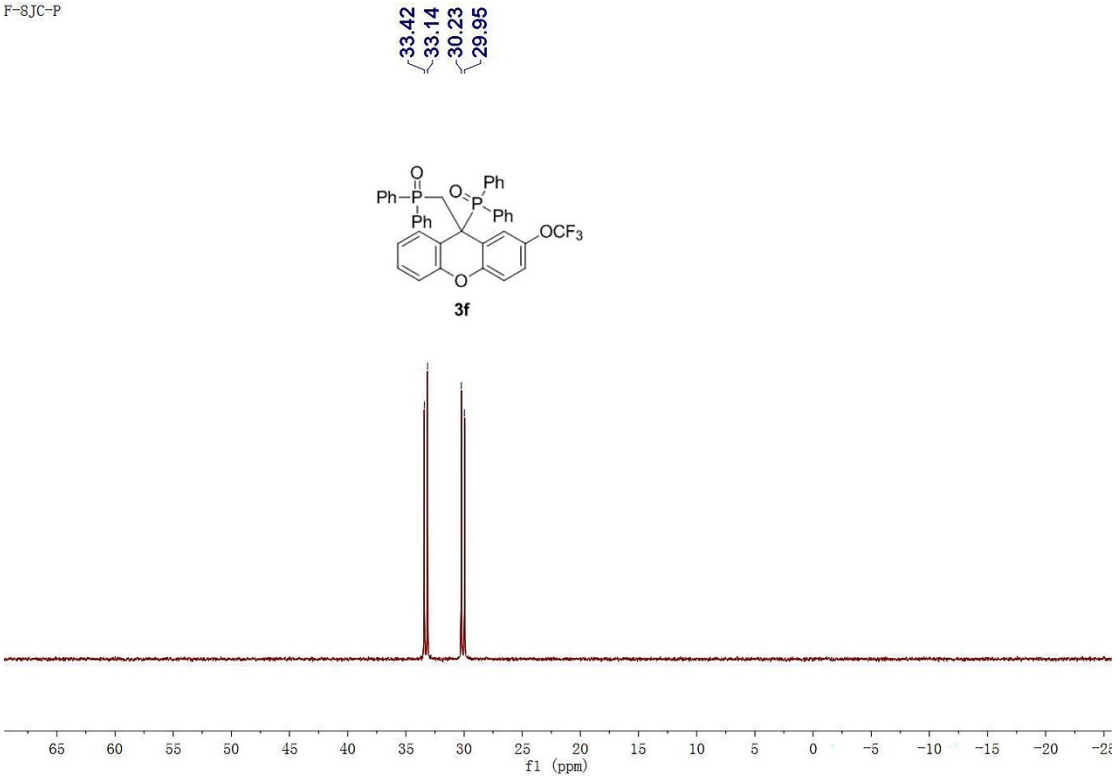
^{1}H NMR of **3f** in $CDCl_3$ (400 MHz)



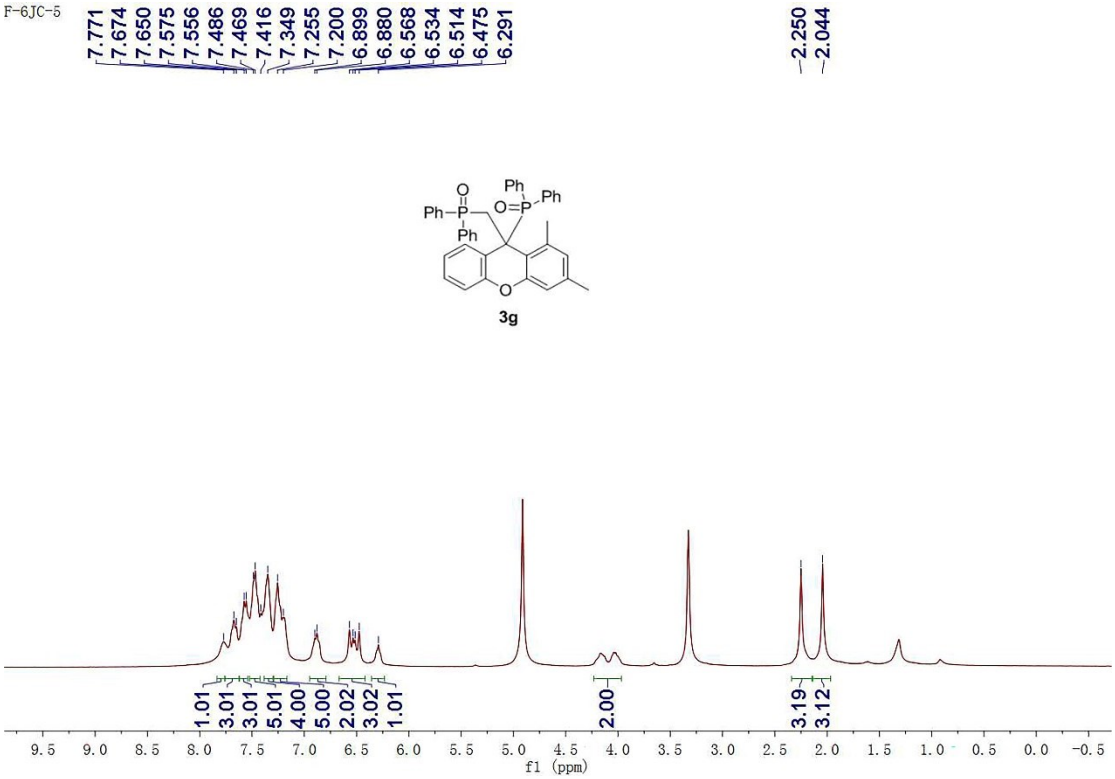
^{13}C NMR of **3f** in MeOD (150 MHz)



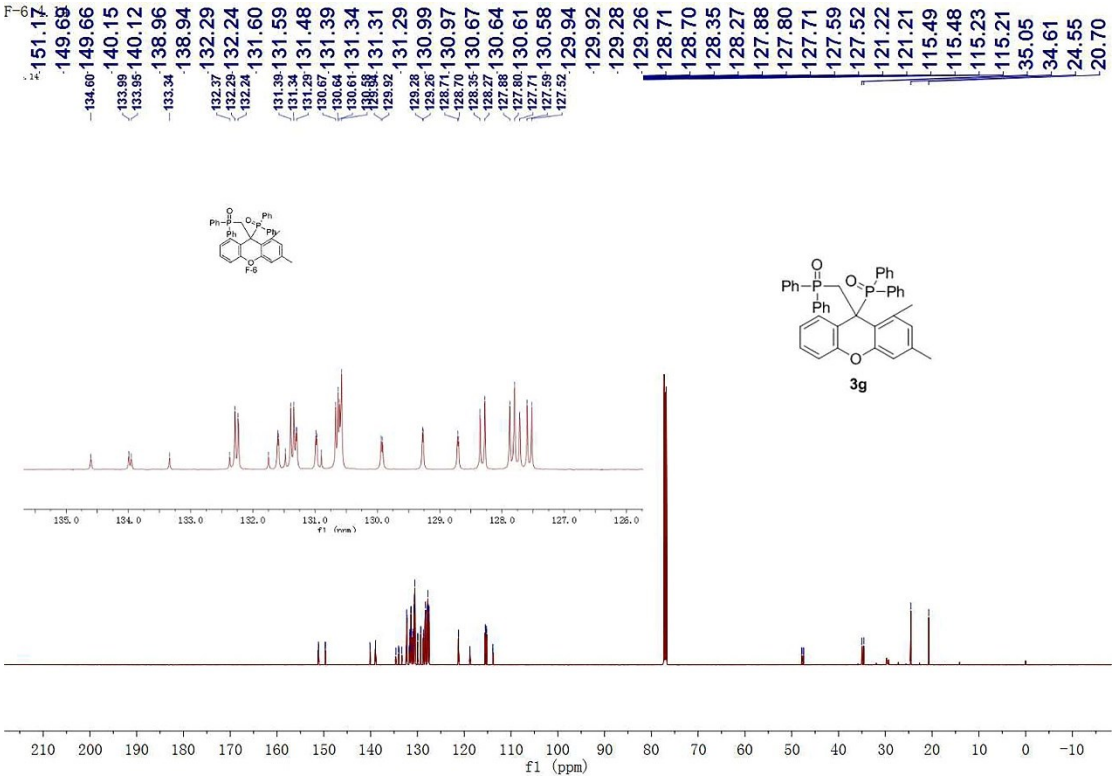
^{31}P NMR of **3f** in MeOD (162 MHz)



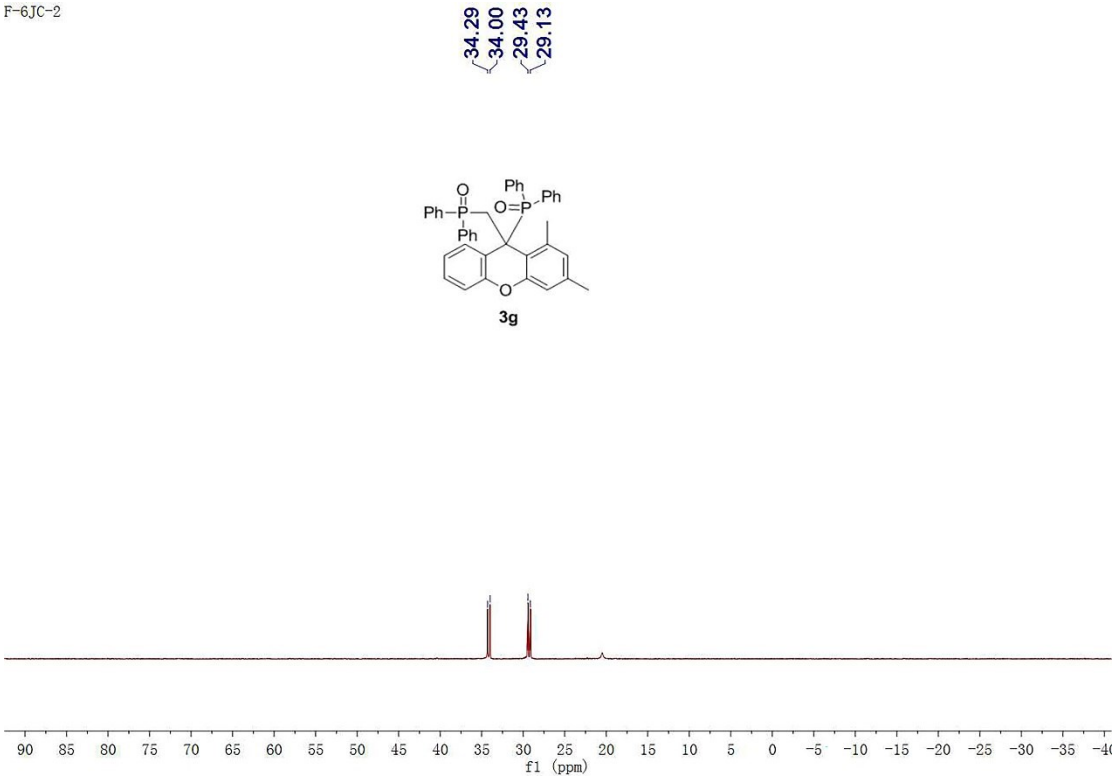
^{1}H NMR of **3g** in $CDCl_3$ (400 MHz)



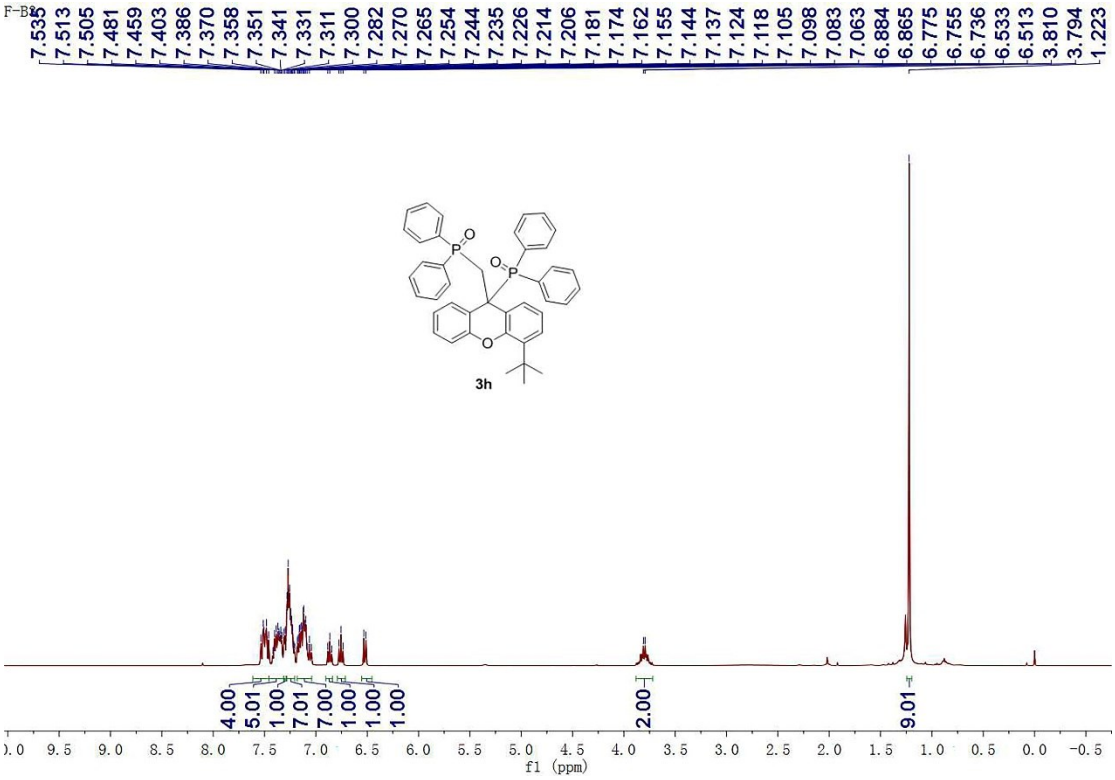
^{13}C NMR of **3g** in $CDCl_3$ (150 MHz)



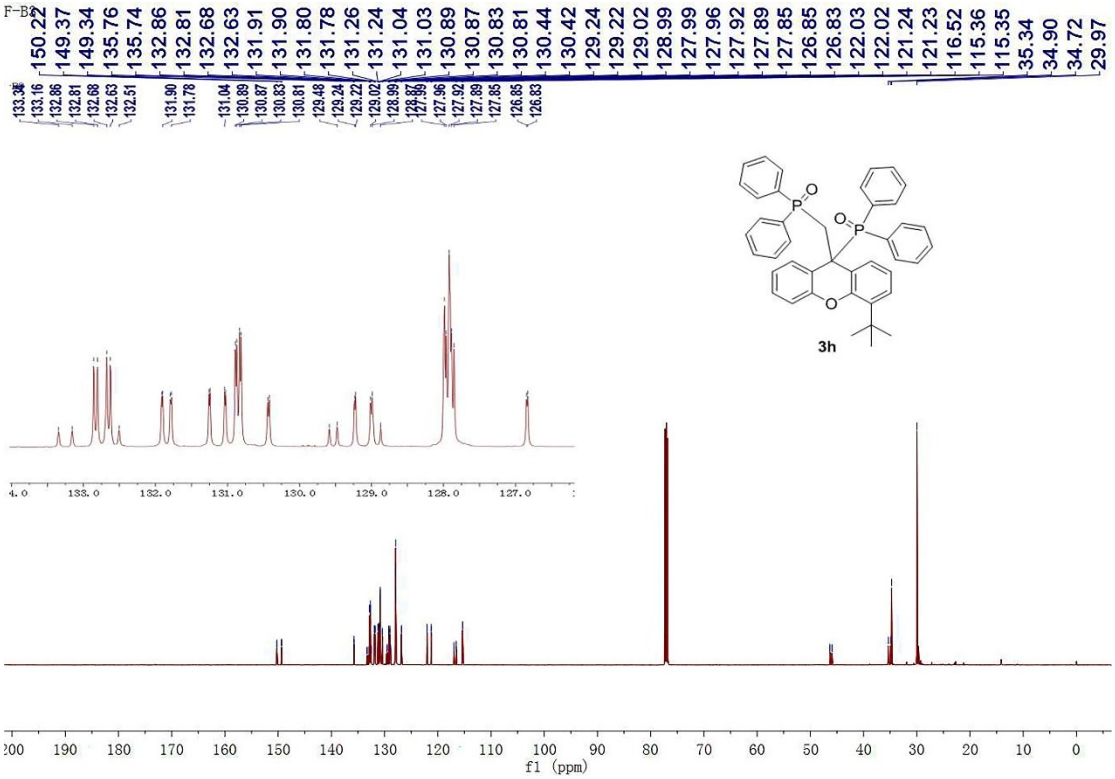
^{31}P NMR of **3g** in MeOD (162 MHz)



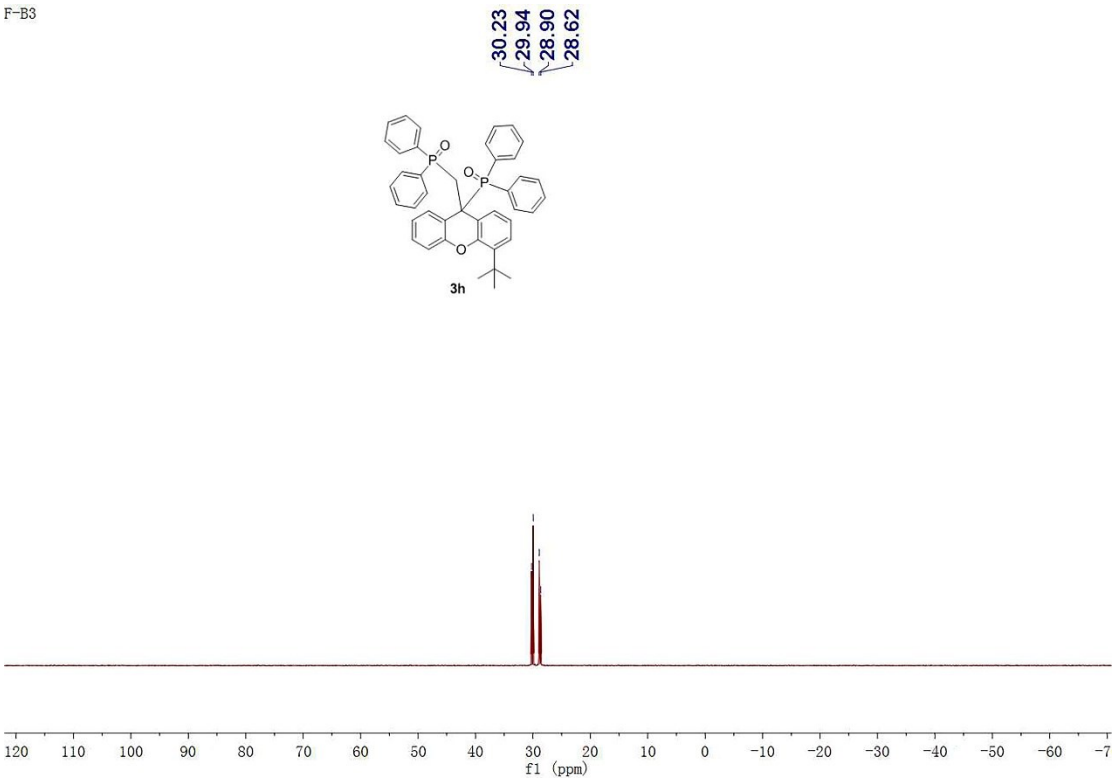
^{1}H NMR of **3h** in $CDCl_3$ (400 MHz)



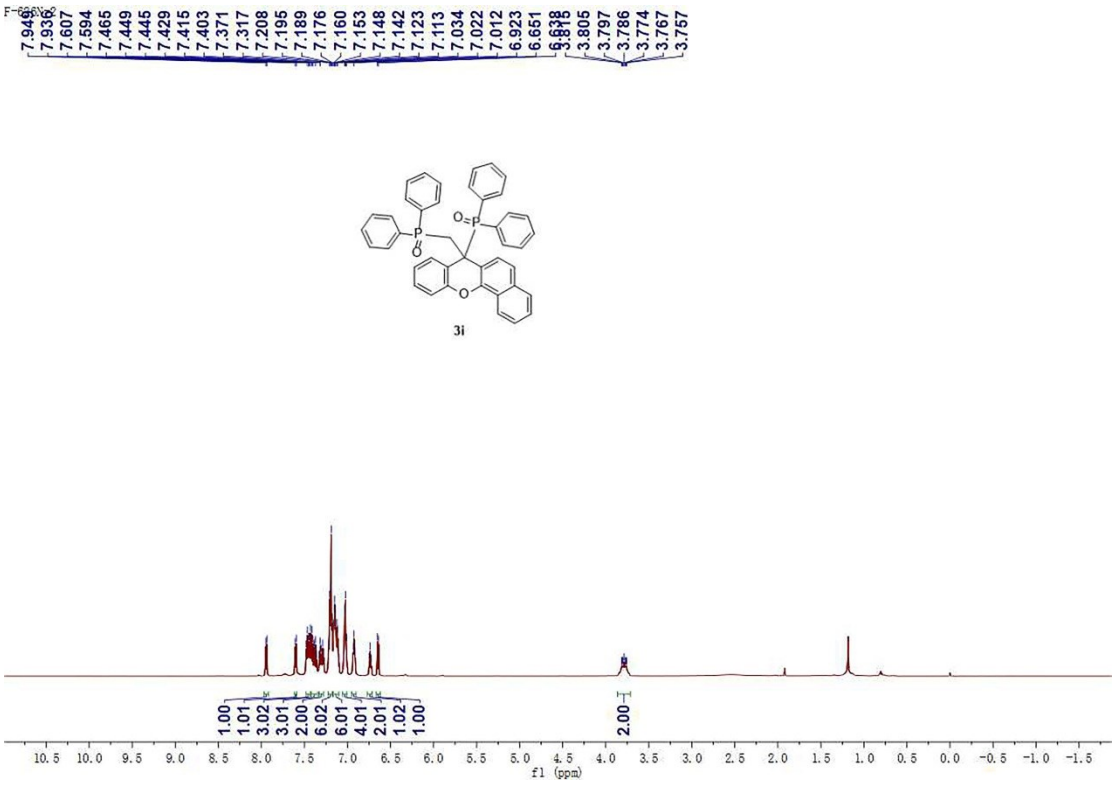
^{13}C NMR of **3h** in $CDCl_3$ (150 MHz)



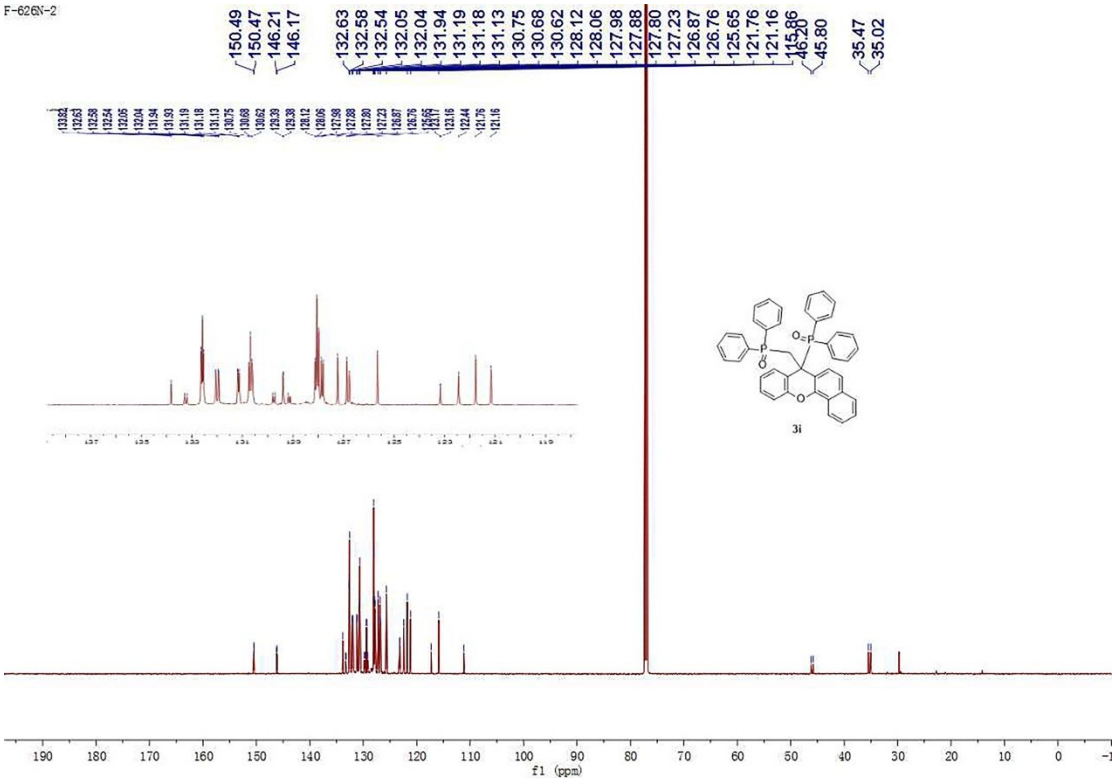
^{31}P NMR of **3h** in $CDCl_3$ (162 MHz)



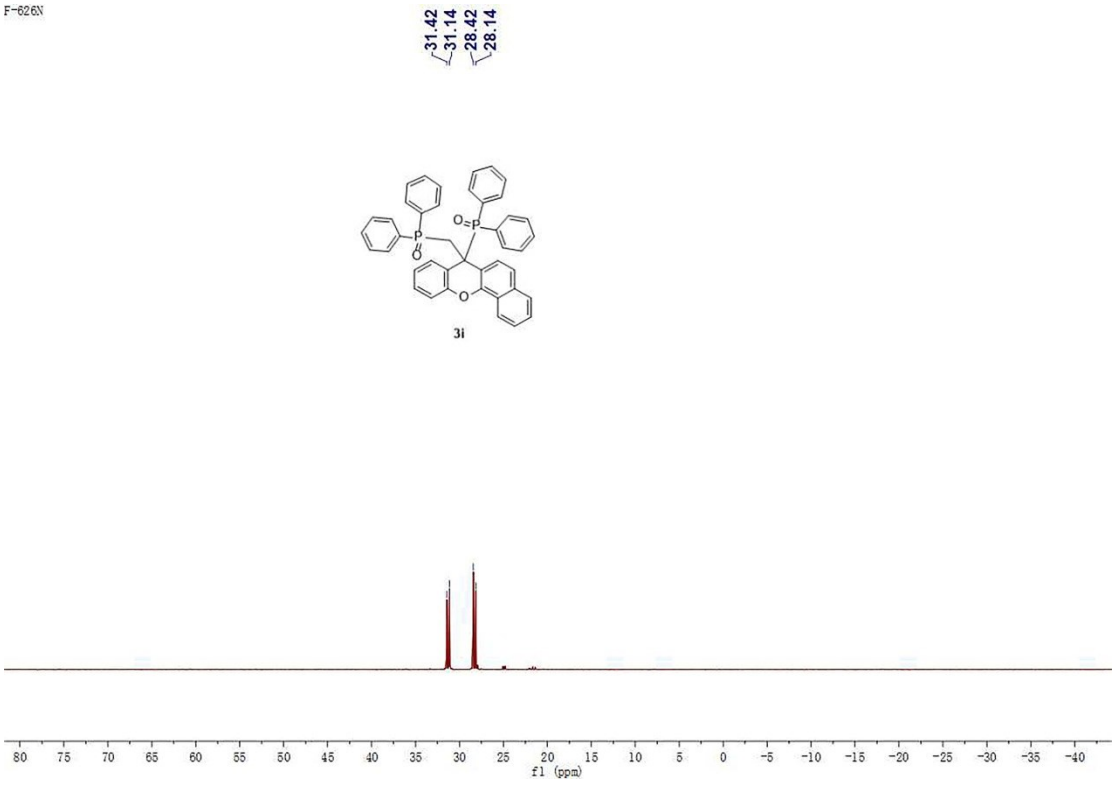
^{1}H NMR of **3i** in $CDCl_3$ (600 MHz)



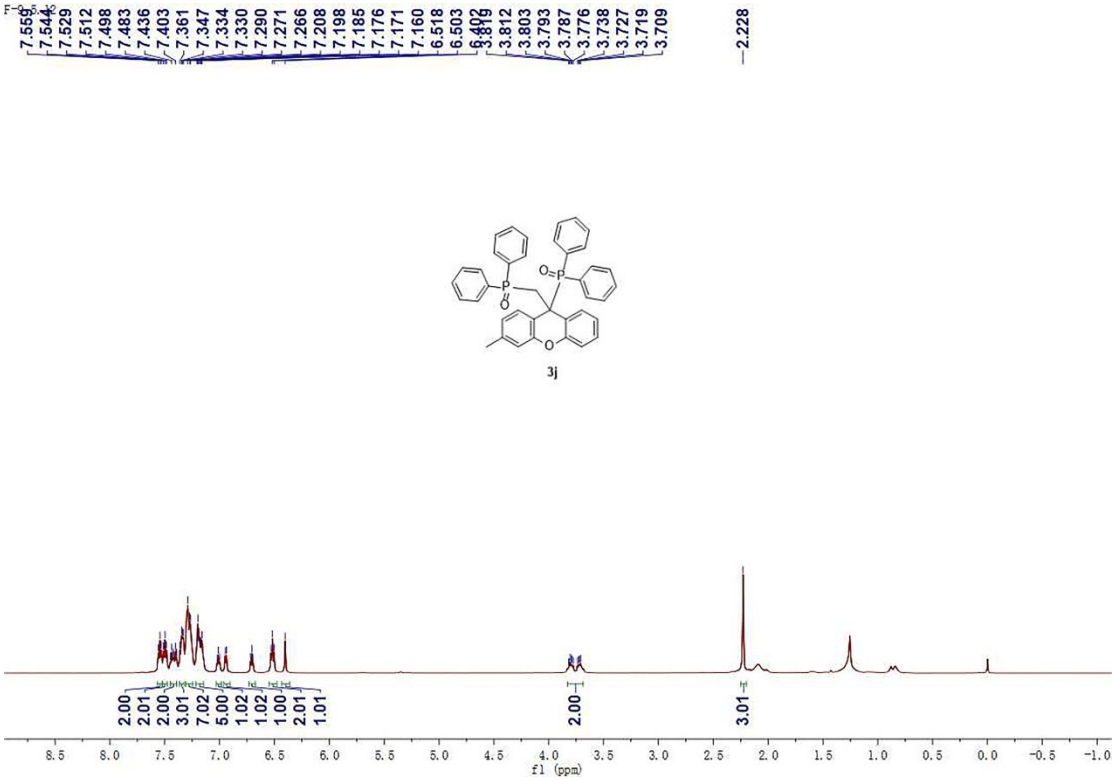
^{13}C NMR of **3i** in $CDCl_3$ (150 MHz)



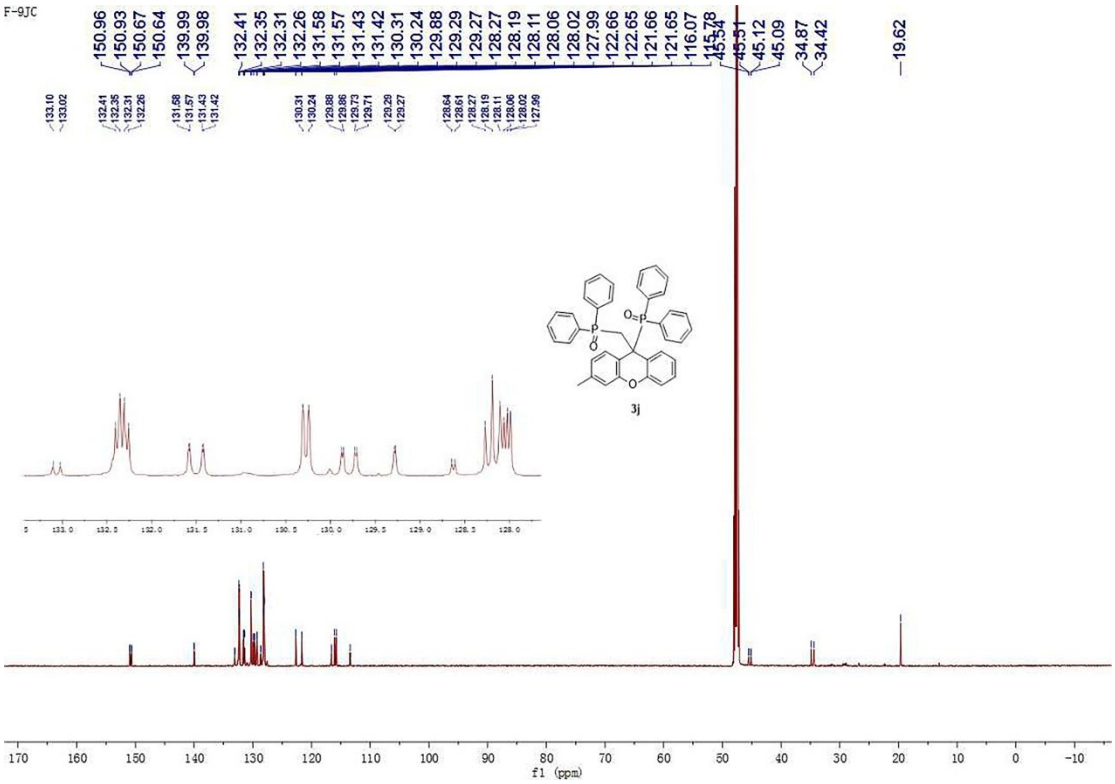
^{31}P NMR of **3i** in $CDCl_3$ (162 MHz)



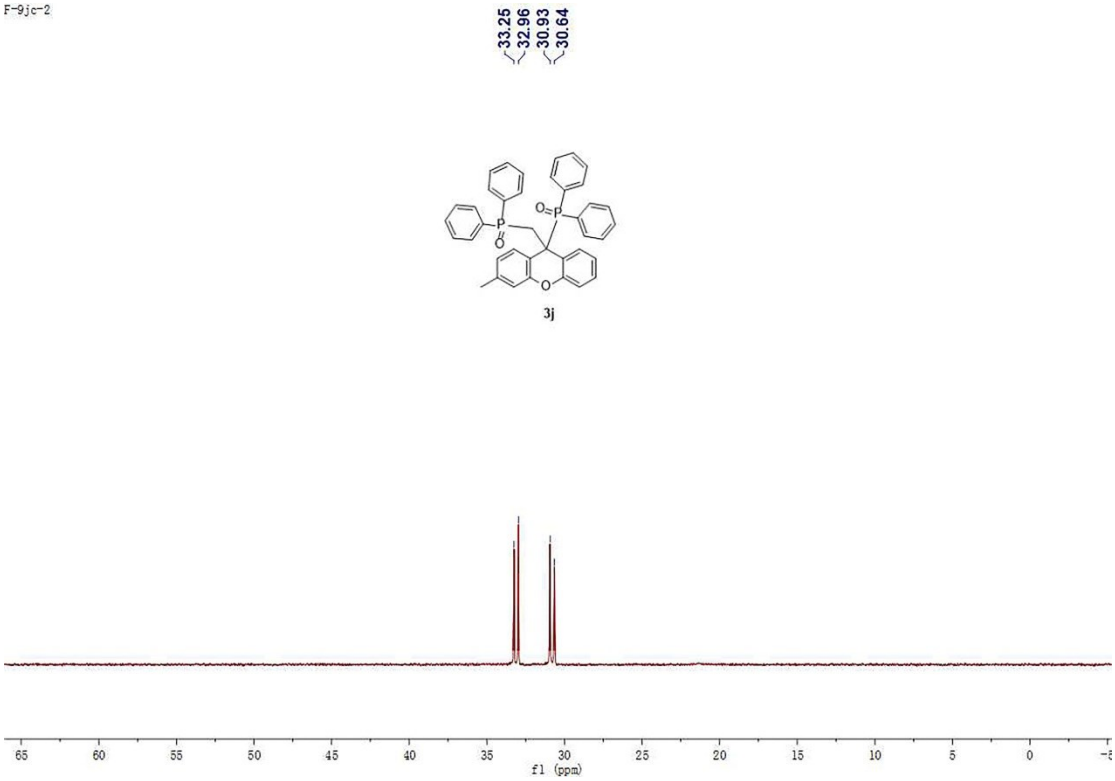
^{1}H NMR of **3j** in $CDCl_3$ (400 MHz)



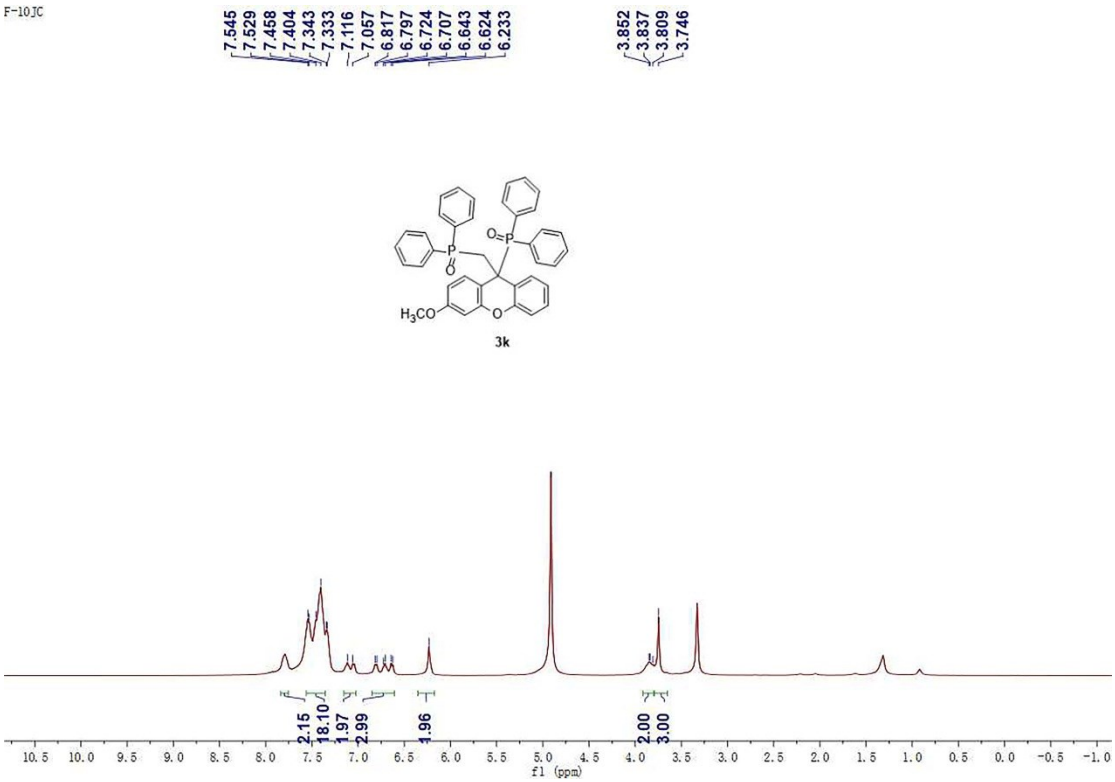
^{13}C NMR of **3j** in MeOD (150 MHz)



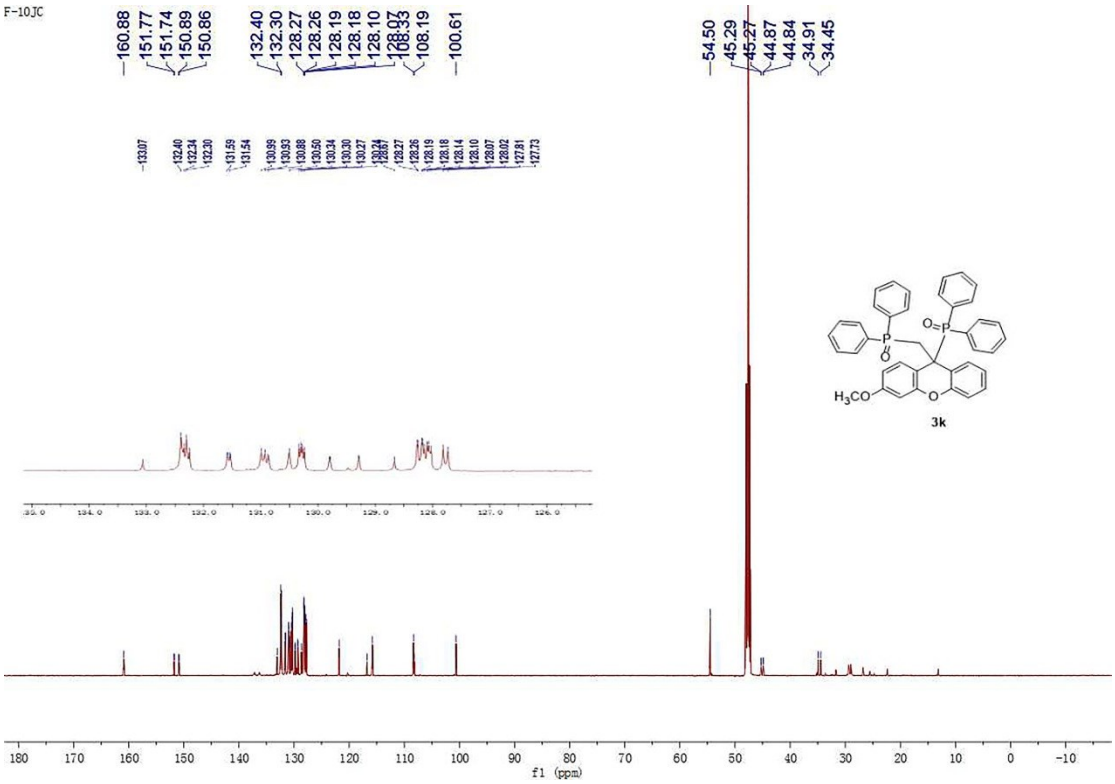
^{31}P NMR of **3j** in MeOD (162 MHz)



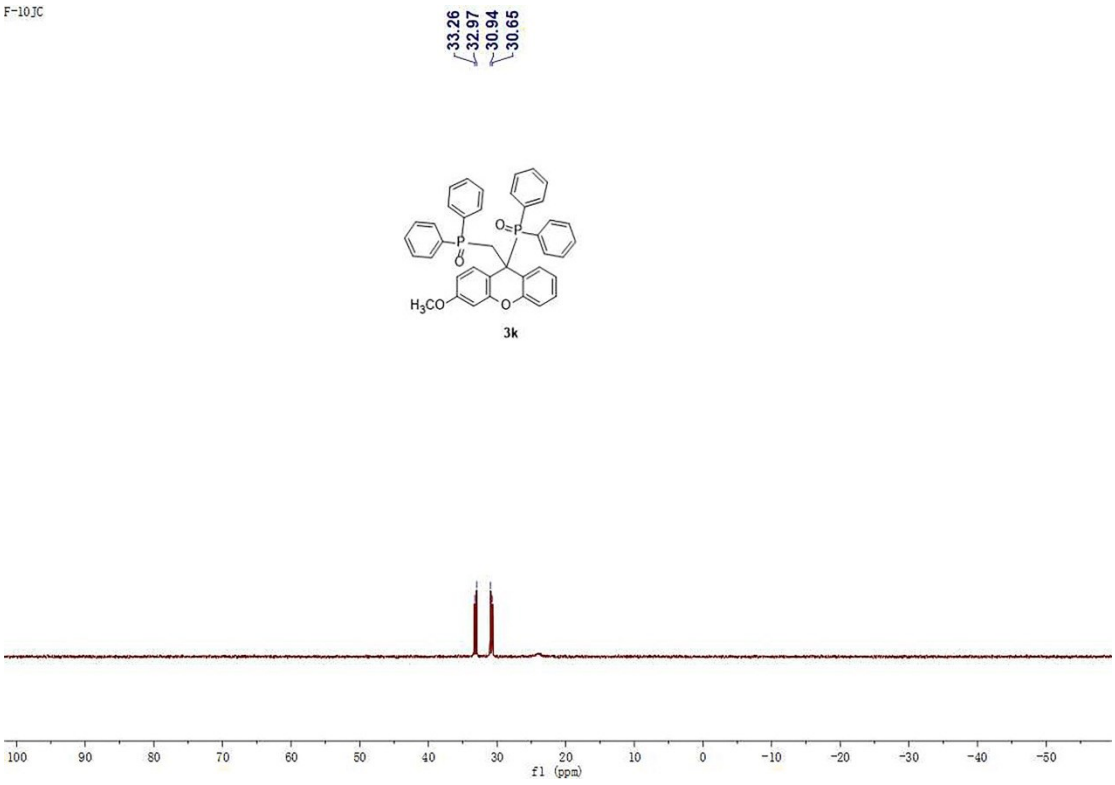
^{1}H NMR of **3k** in MeOD (400 MHz)



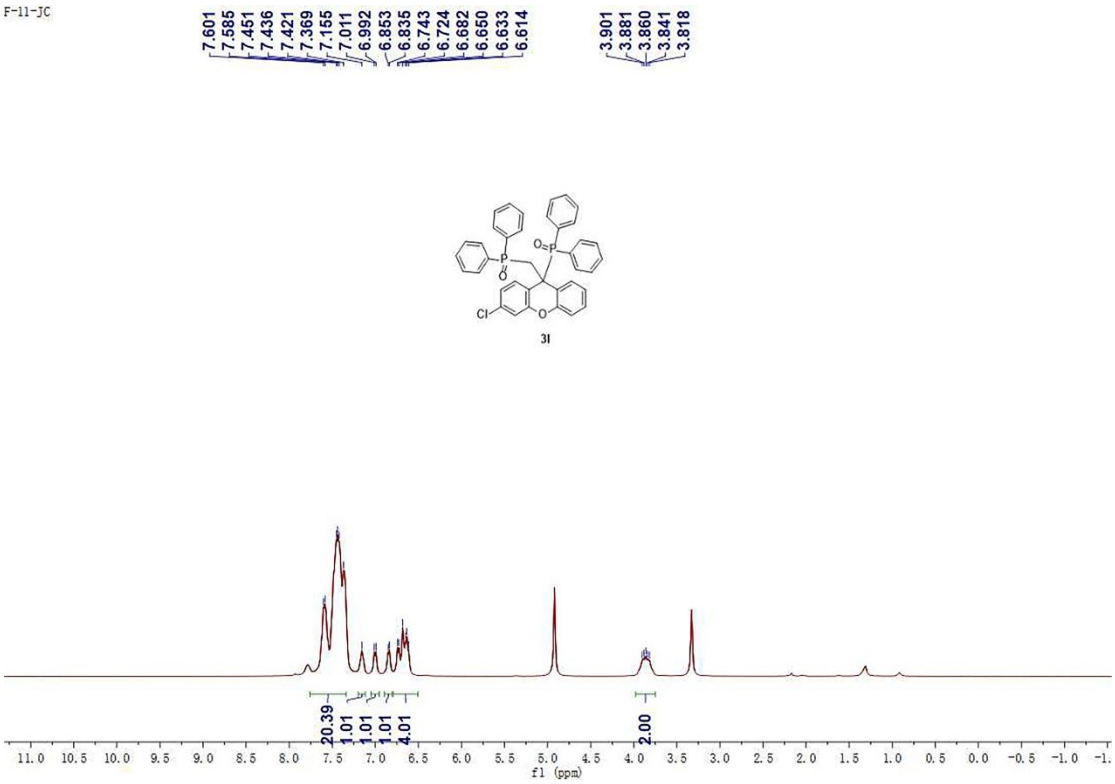
^{13}C NMR of **3k** in MeOD (150 MHz)



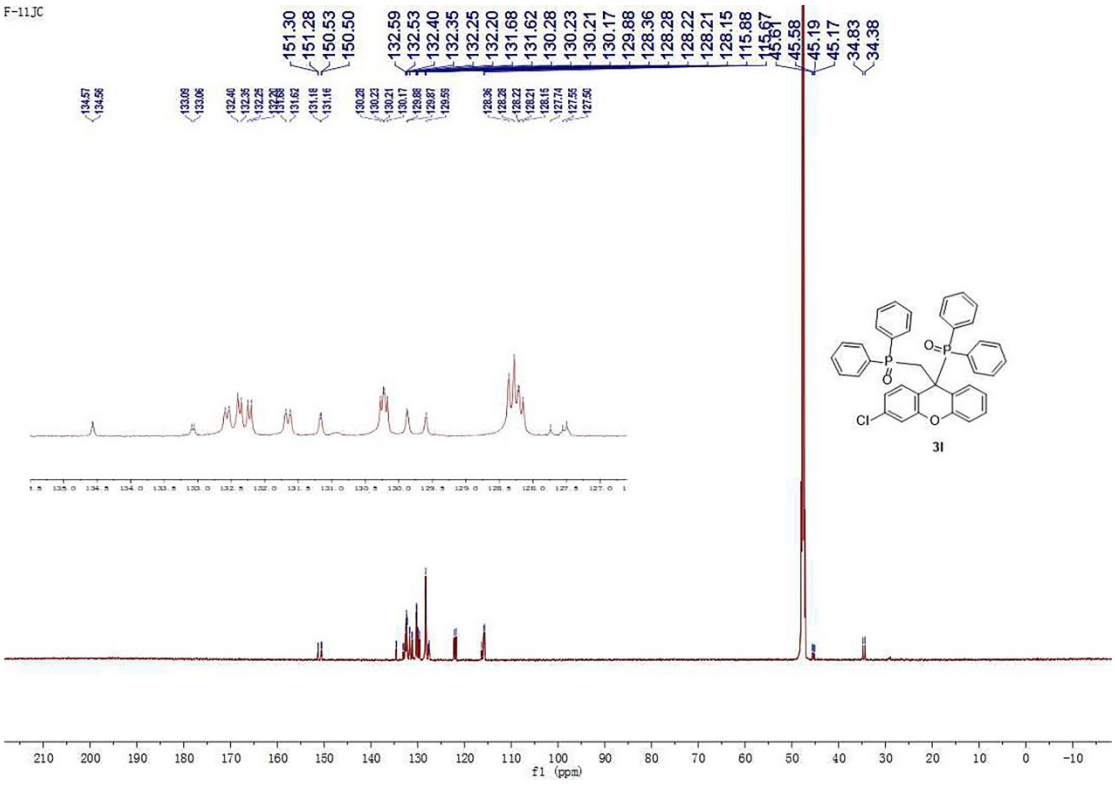
^{31}P NMR of **3k** in MeOD (162 MHz)



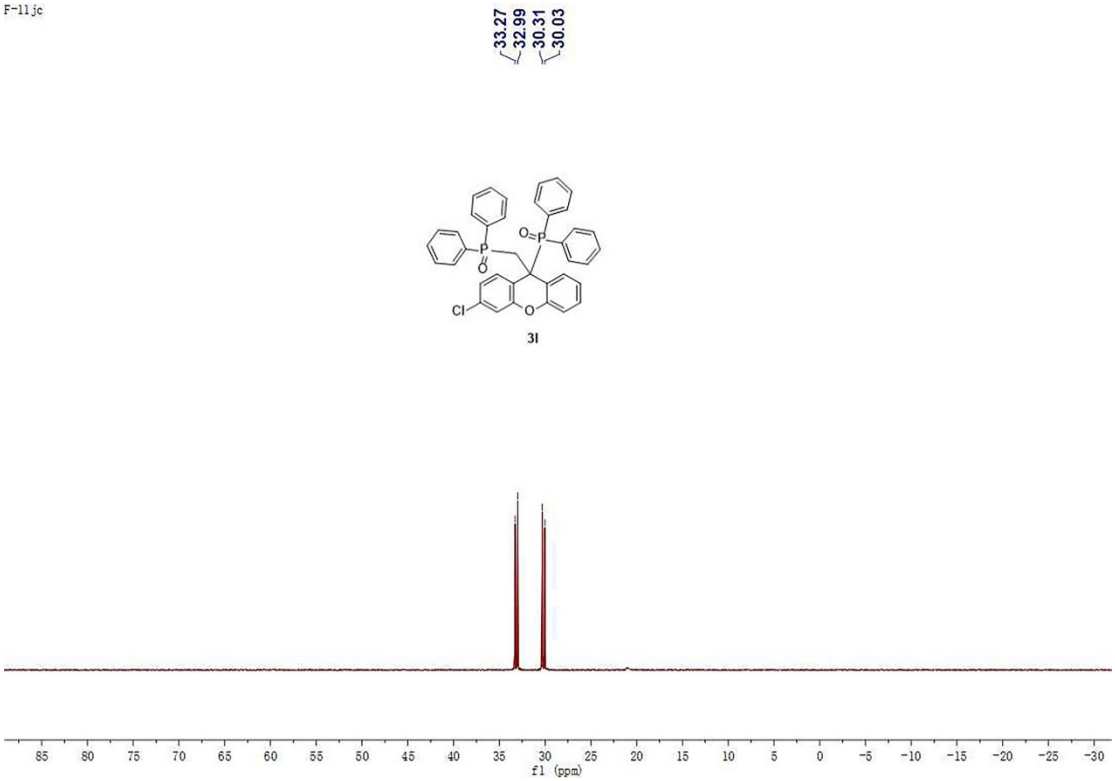
^{1}H NMR of **3l** in MeOD (400 MHz)



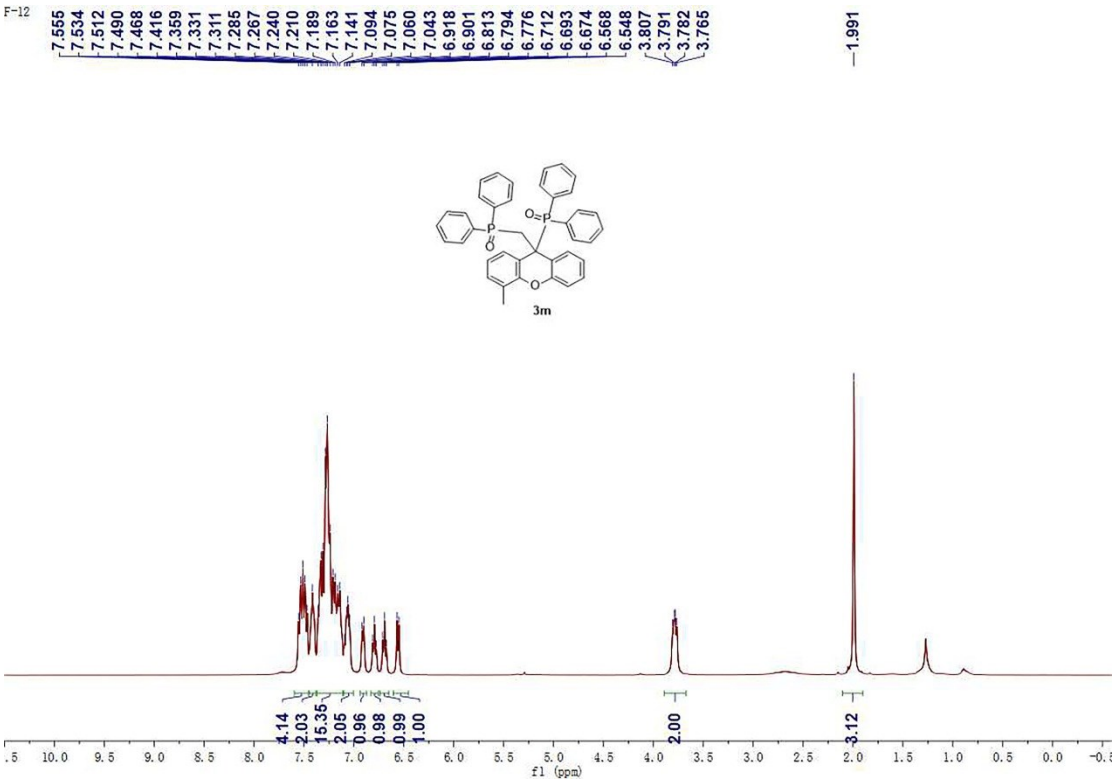
^{13}C NMR of **3l** in MeOD (150 MHz)



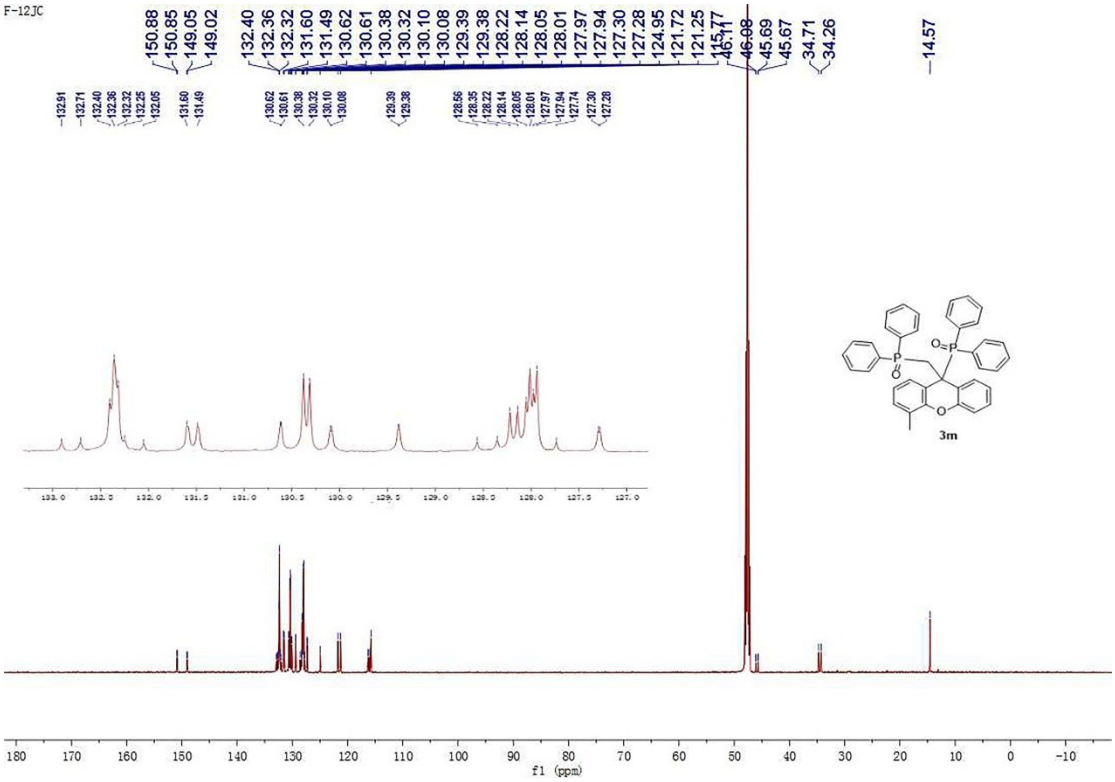
^{31}P NMR of **3l** in MeOD (162 MHz)



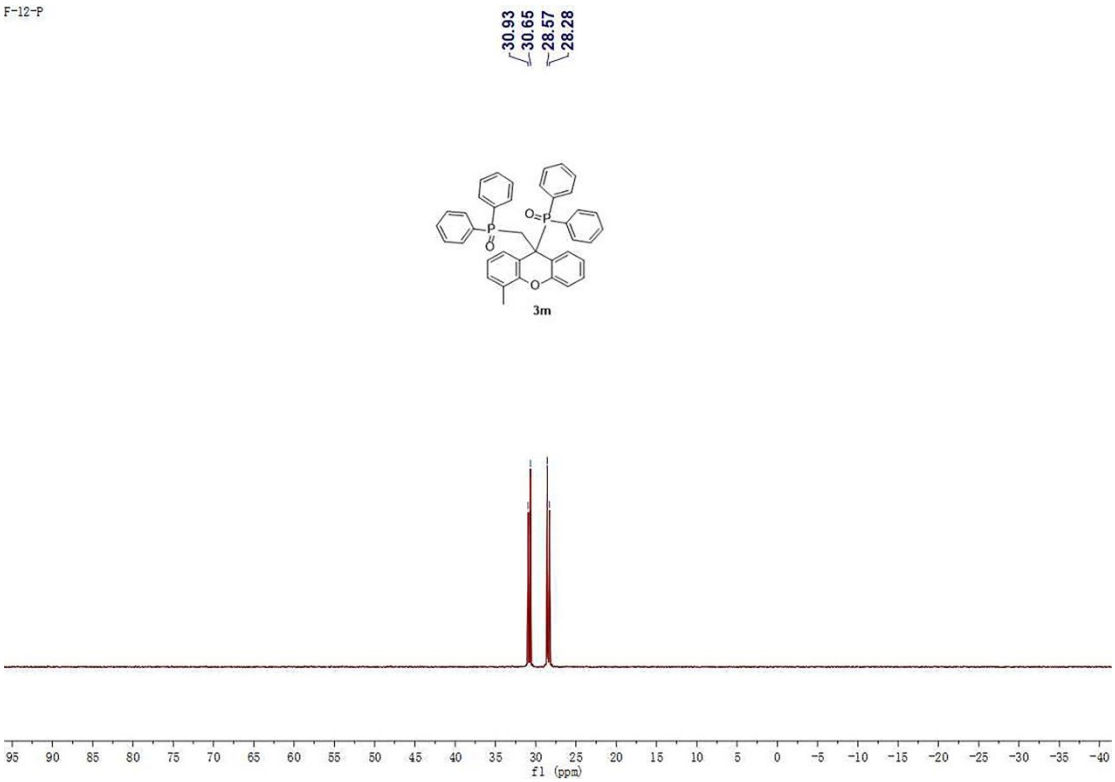
^{1}H NMR of **3m** in $CDCl_3$ (400 MHz)



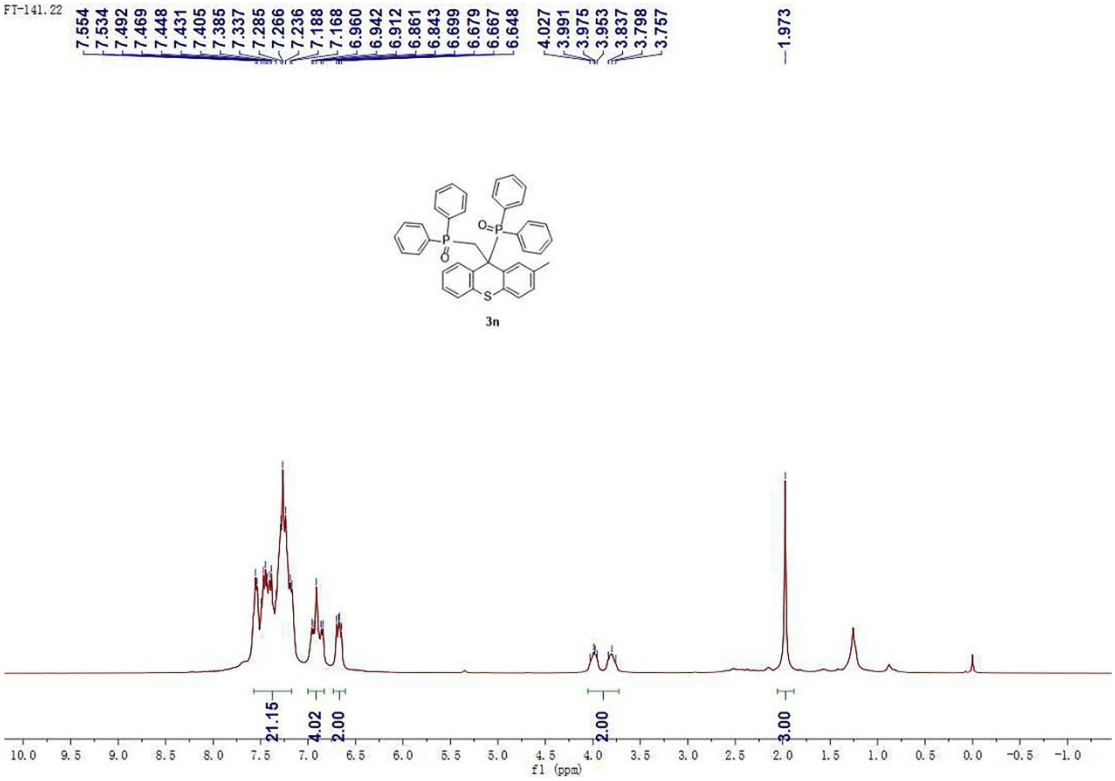
^{13}C NMR of **3m** in MeOD (150 MHz)



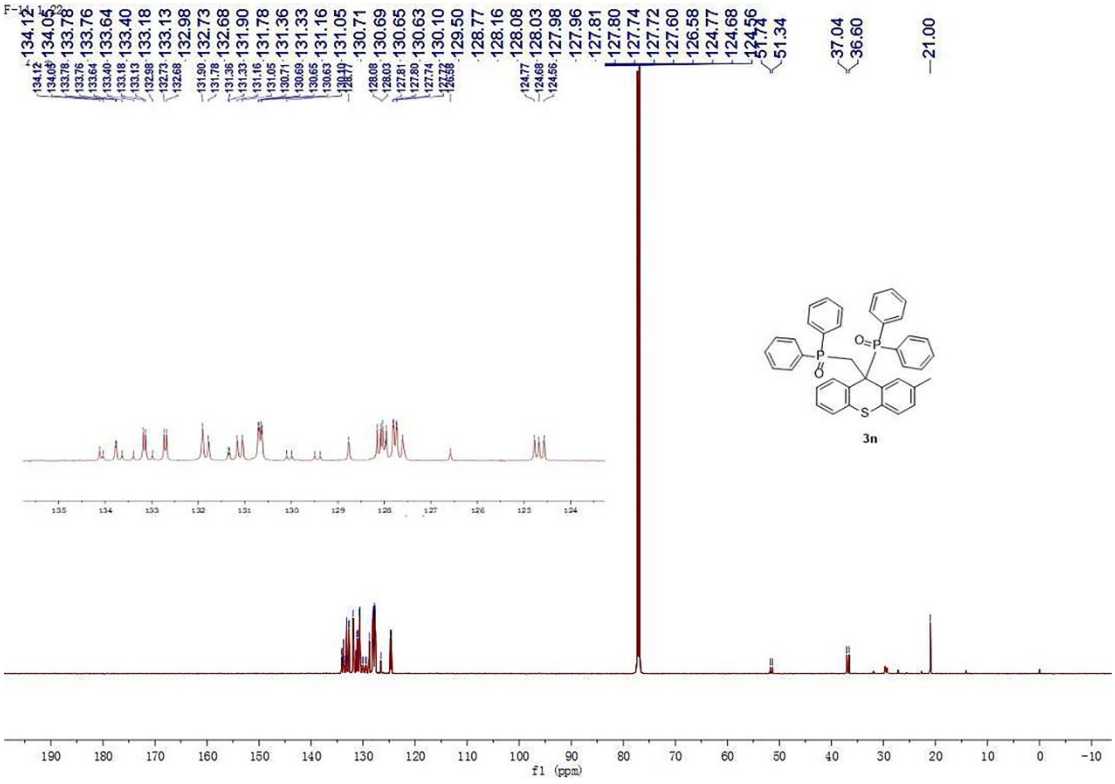
^{31}P NMR of **3m** in MeOD (162 MHz)



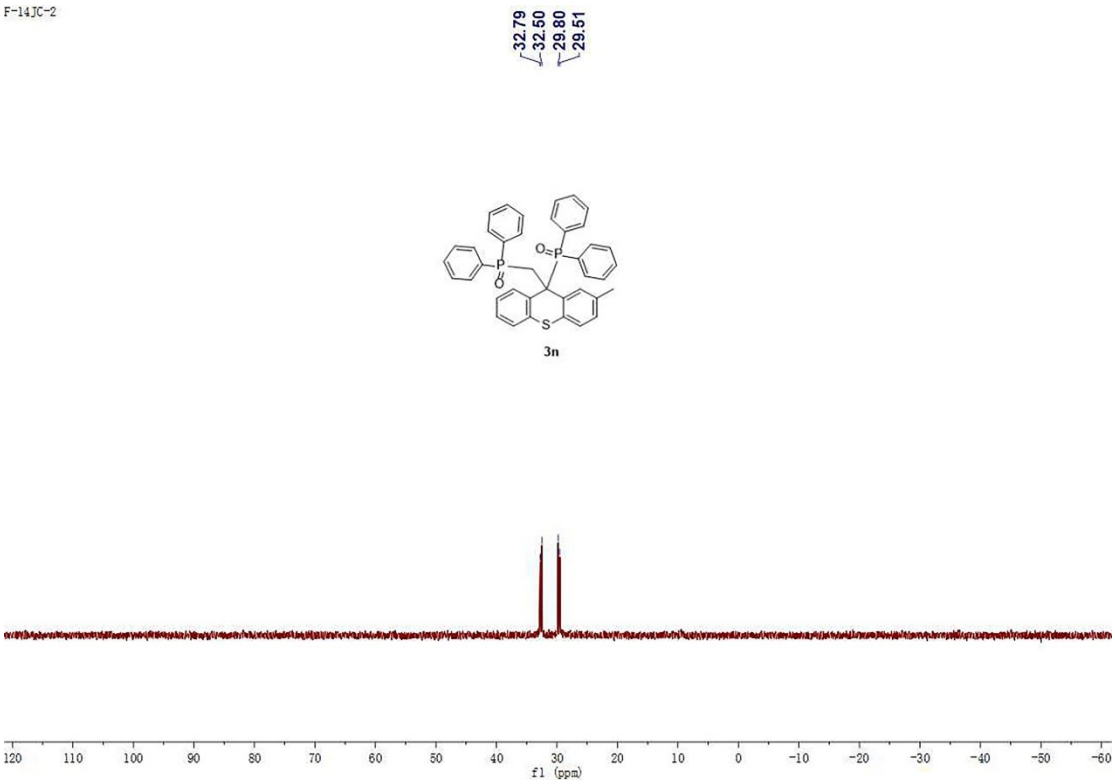
^{1}H NMR of **3n** in $CDCl_3$ (400 MHz)



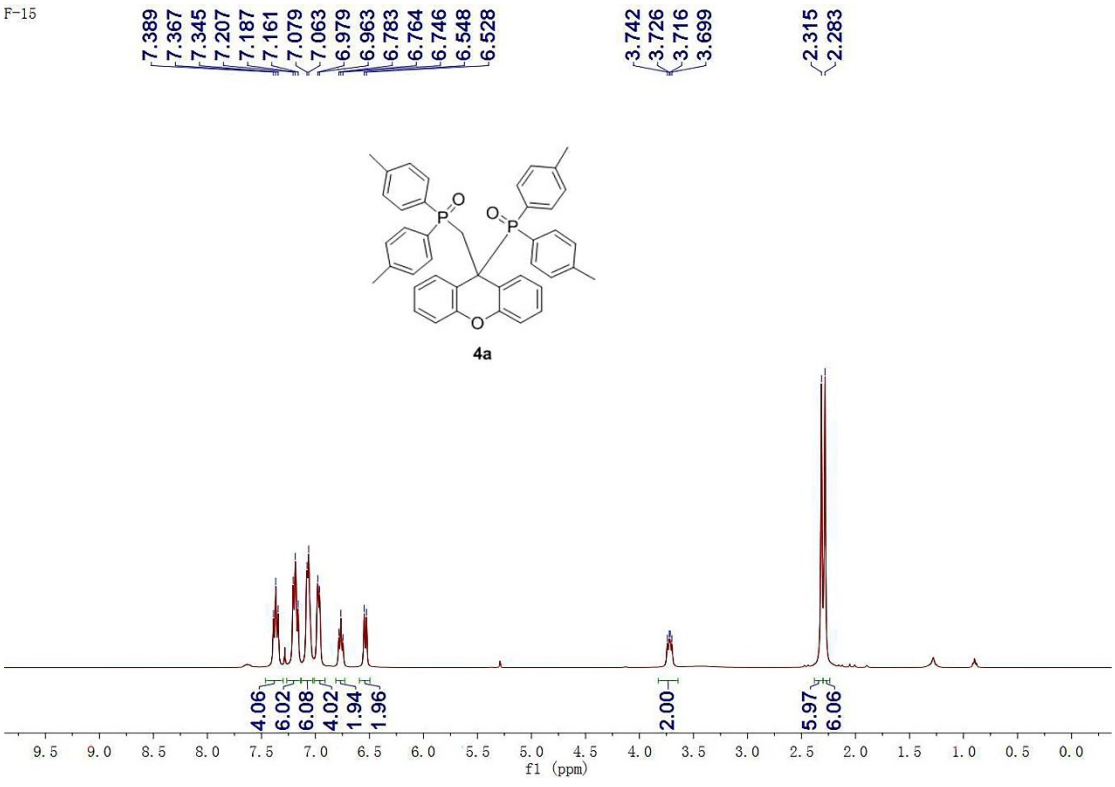
^{13}C NMR of **3n** in $CDCl_3$ (150 MHz)



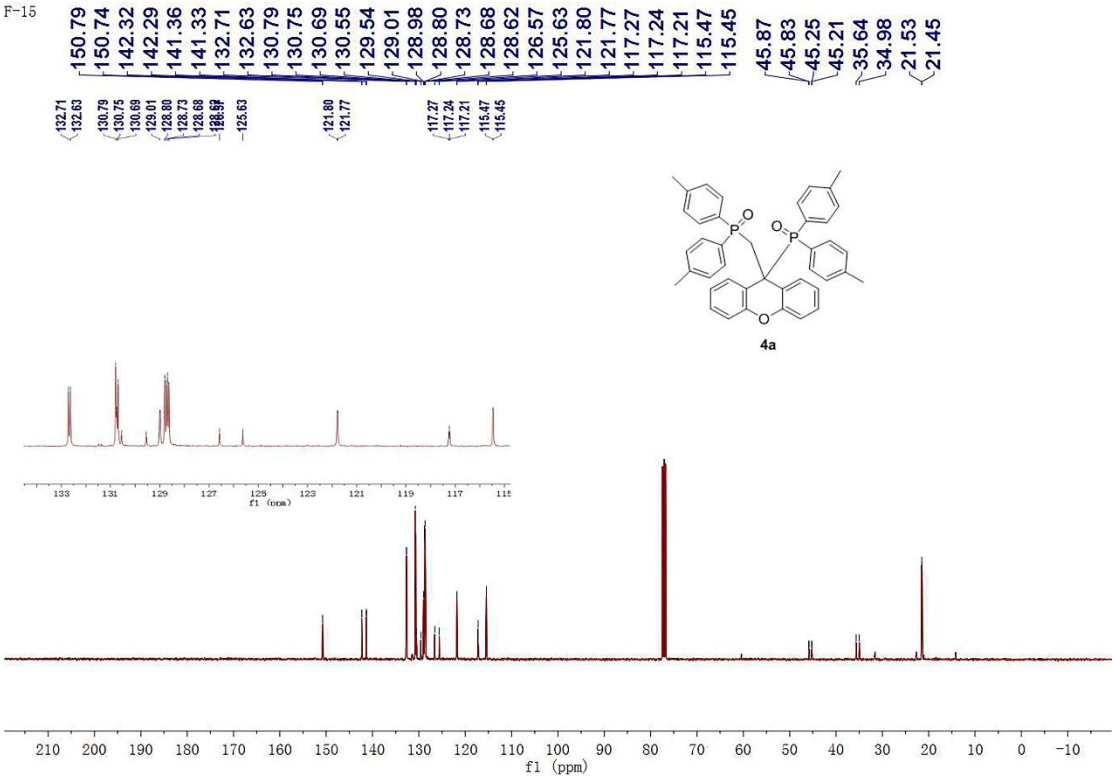
^{31}P NMR of **3n** in MeOD (162 MHz)



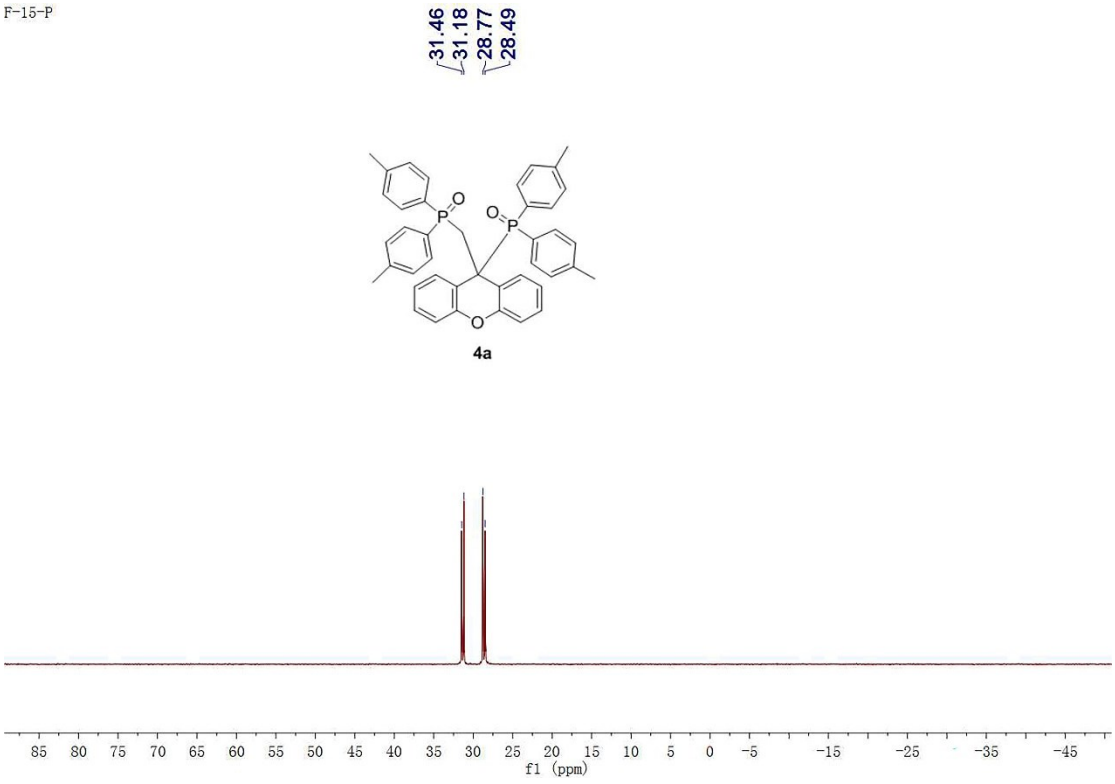
^{1}H NMR of **4a** in $CDCl_3$ (400 MHz)



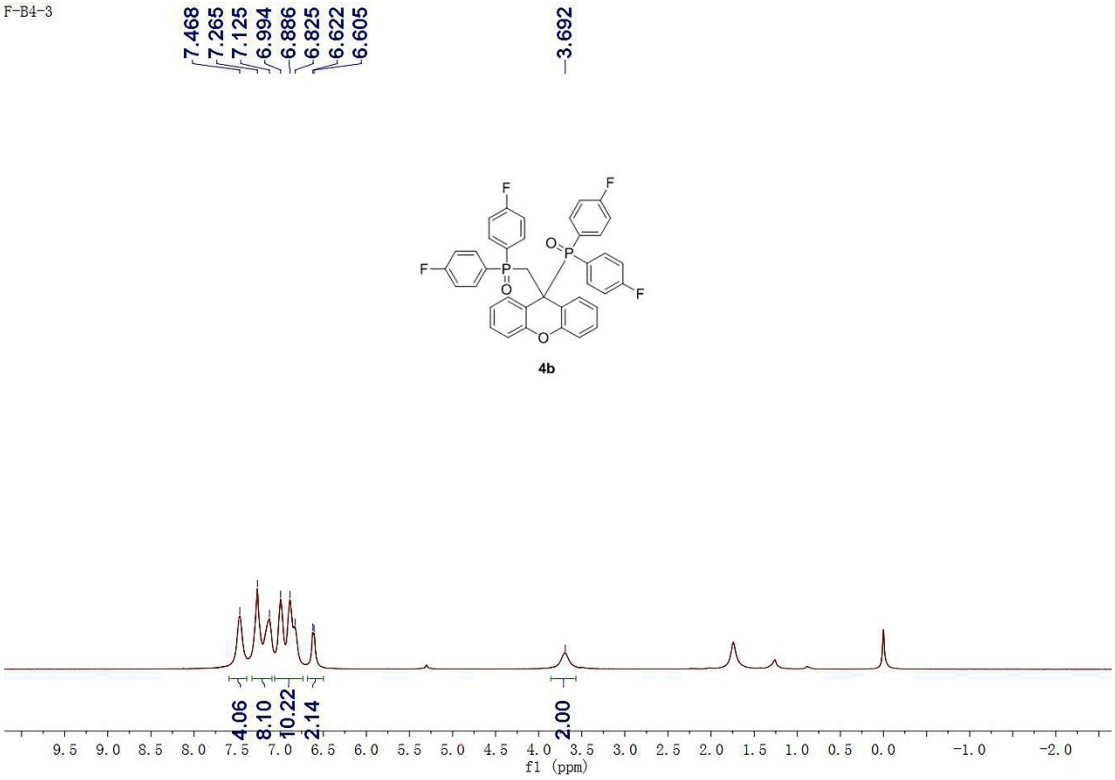
^{13}C NMR of **4a** in $CDCl_3$ (100 MHz)



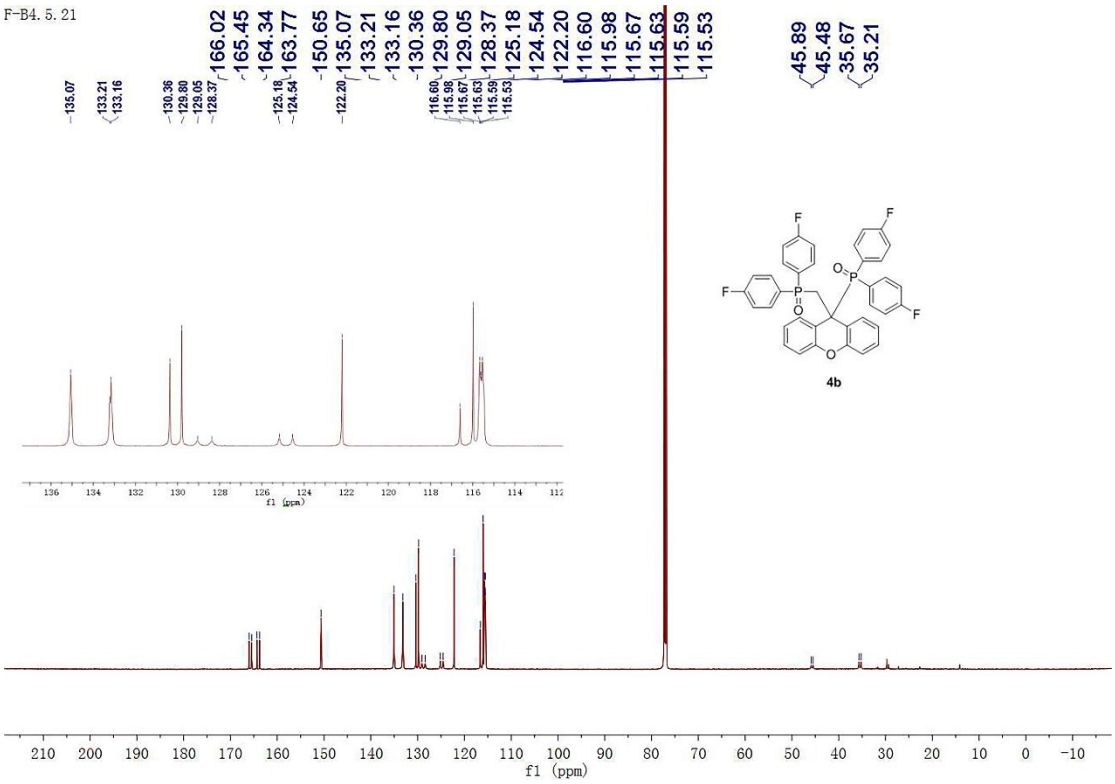
^{31}P NMR of **4a** in $CDCl_3$ (162 MHz)



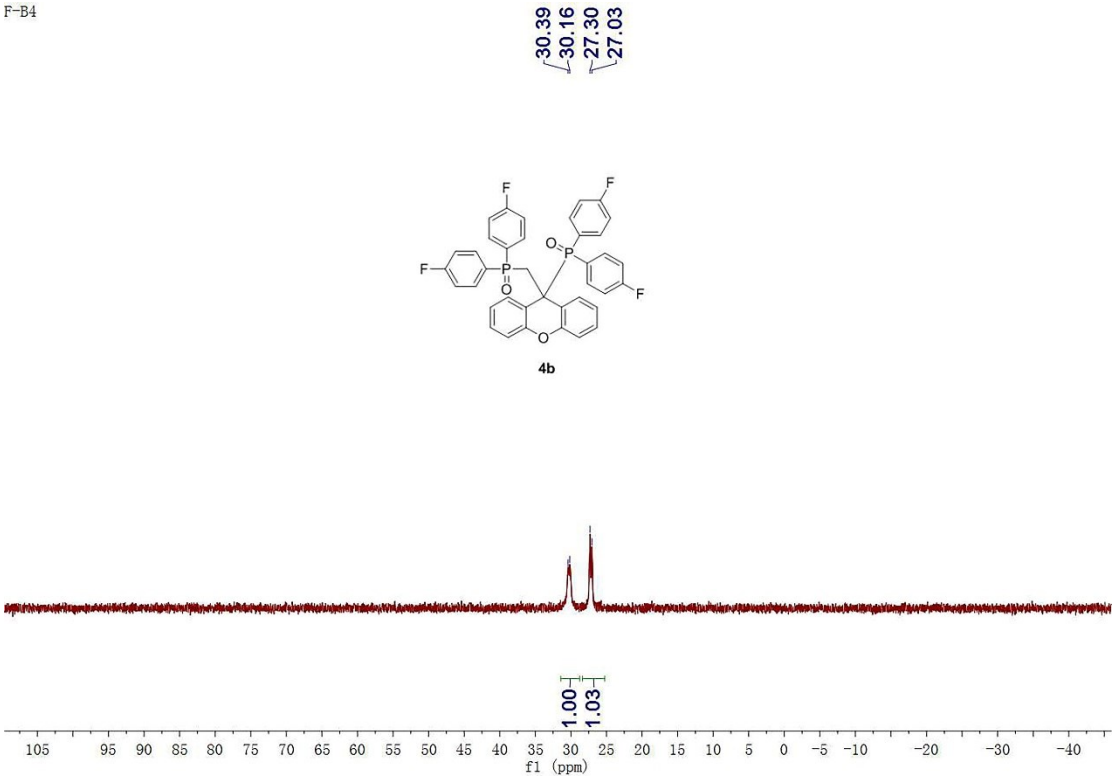
^{1}H NMR of **4b** in $CDCl_3$ (400 MHz)



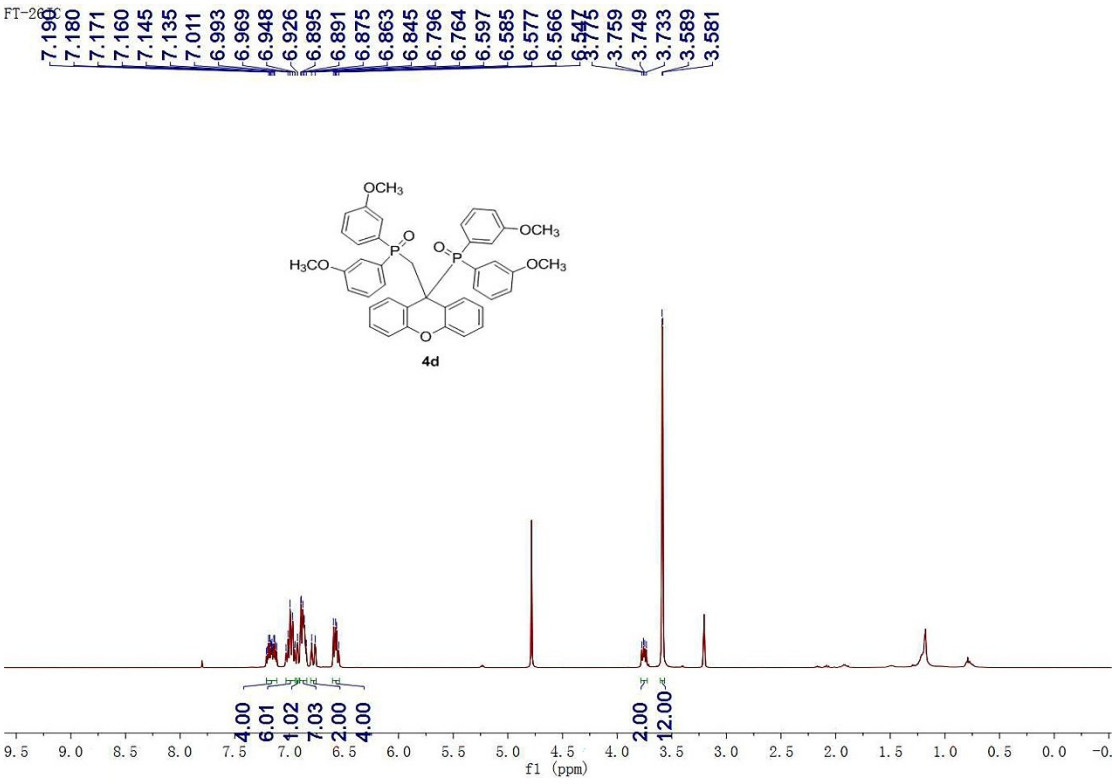
^{13}C NMR of **4b** in $CDCl_3$ (150 MHz)



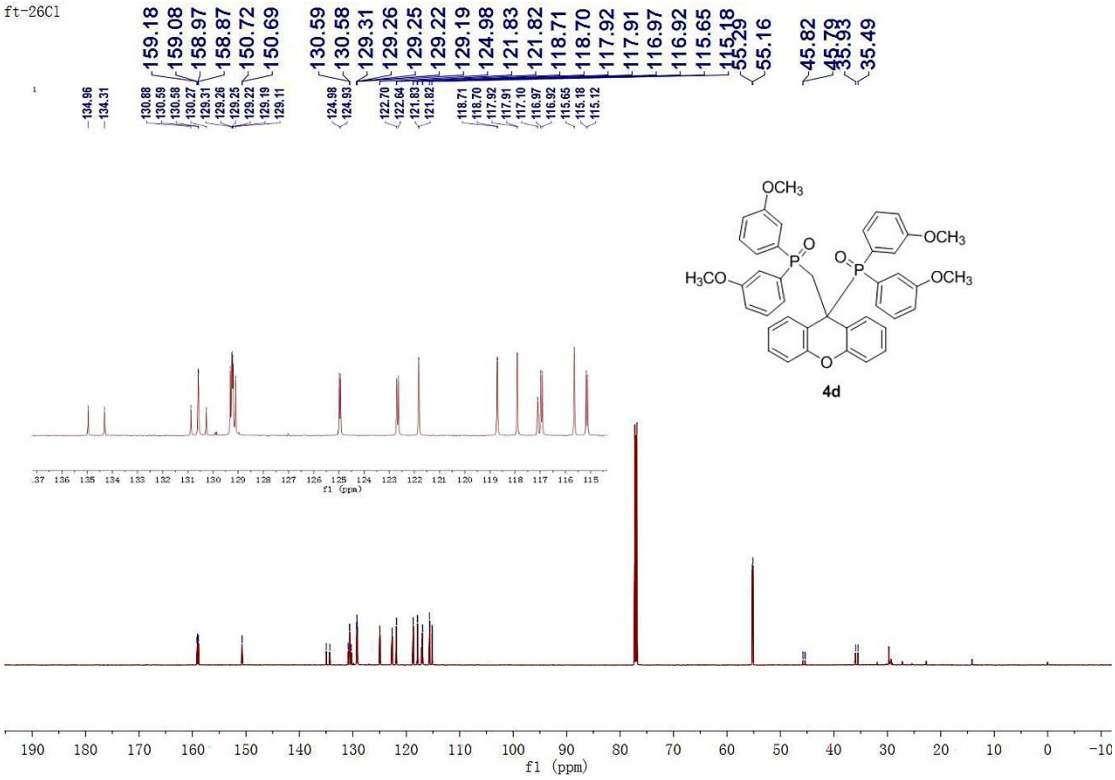
^{31}P NMR of **4b** in $CDCl_3$ (162 MHz)



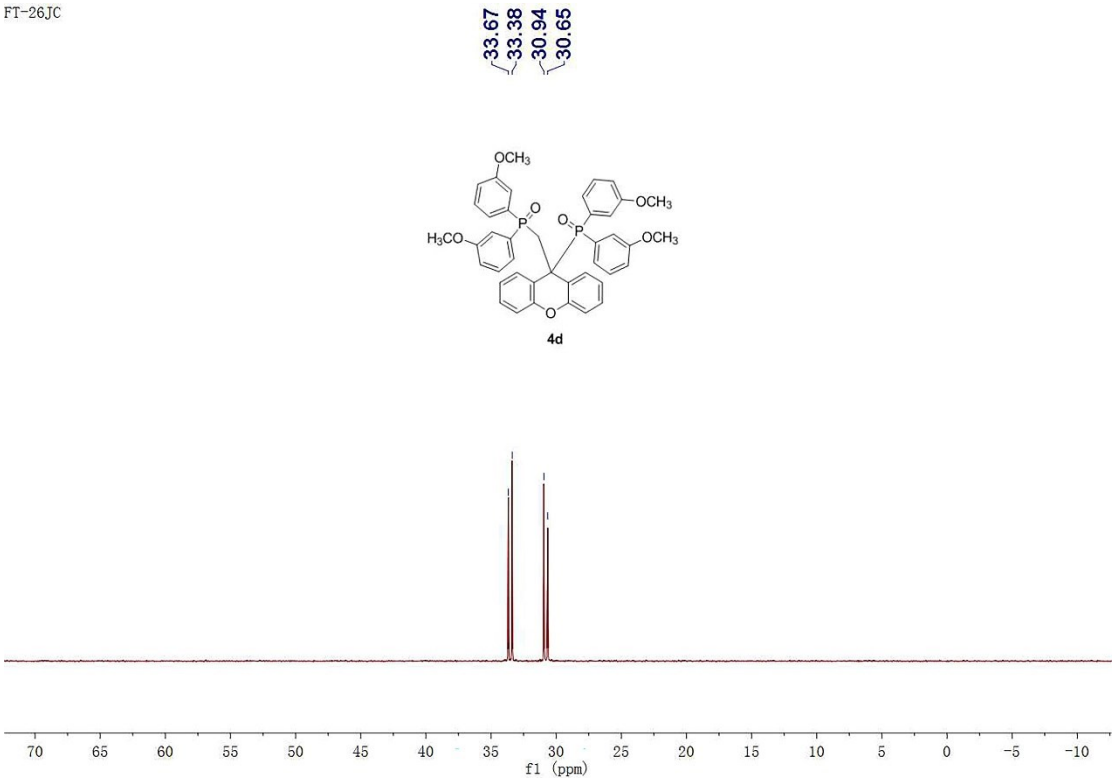
^{1}H NMR of **4d** in MeOD (400 MHz)



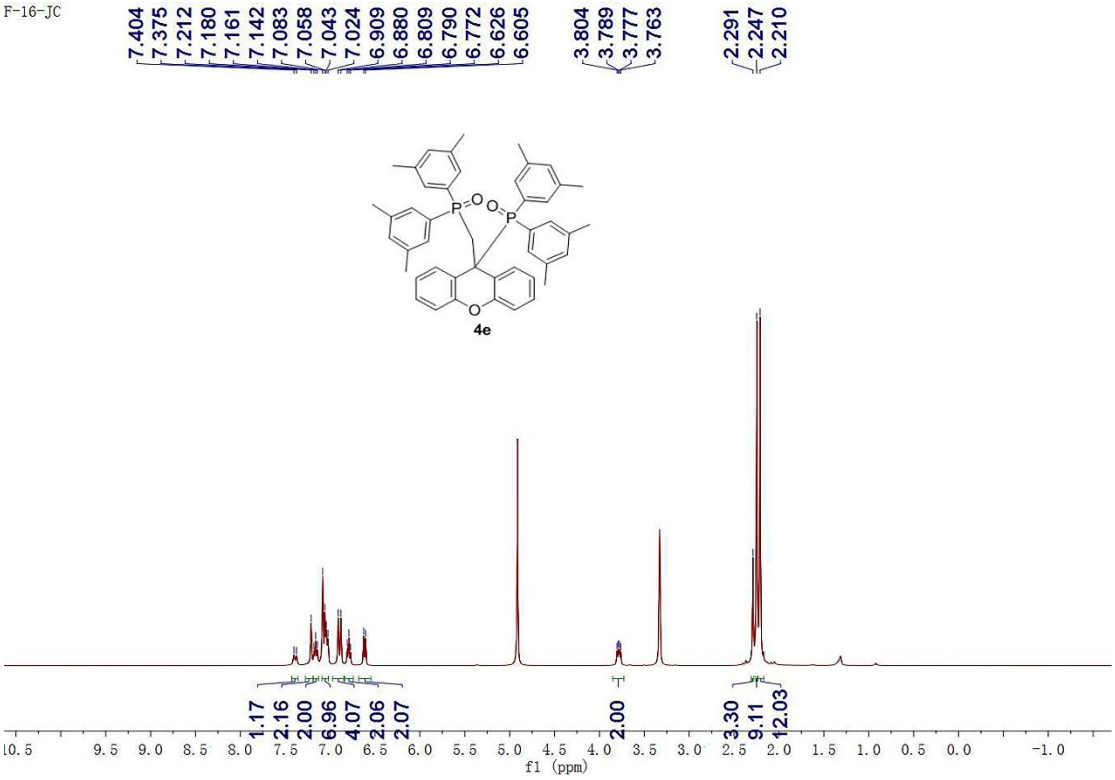
^{13}C NMR of **4d** in $CDCl_3$ (150 MHz)



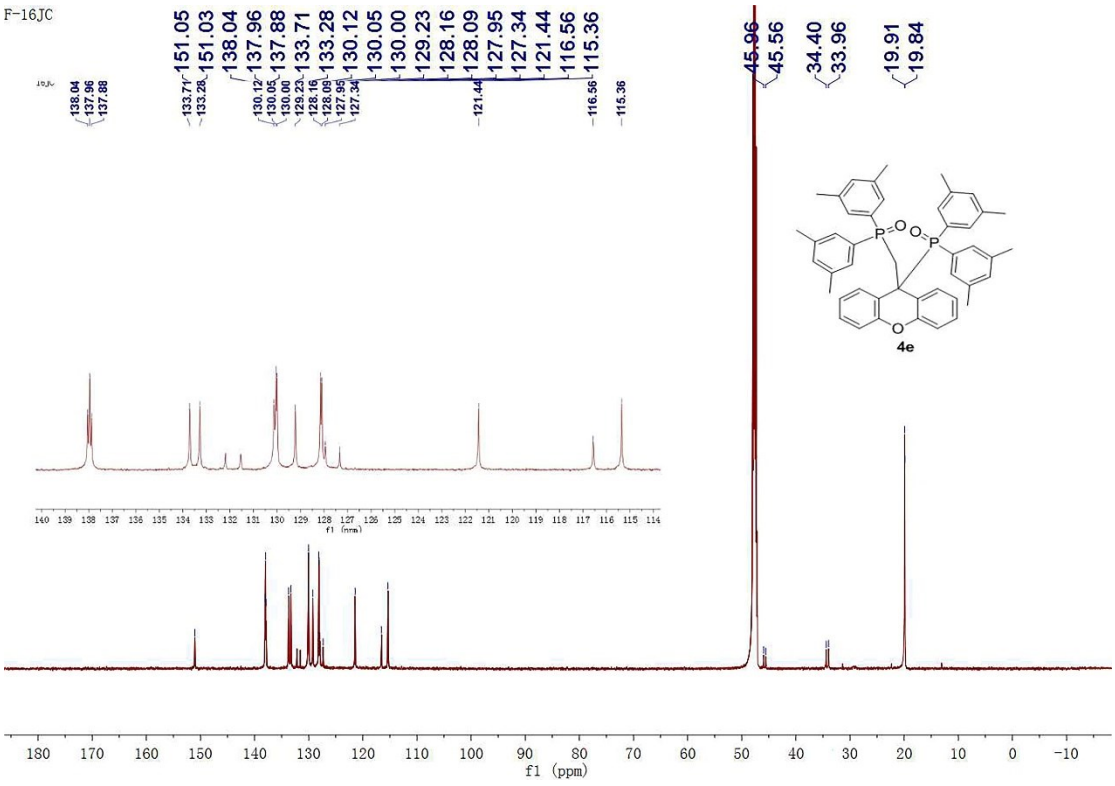
^{31}P NMR of **4d** in MeOD (162 MHz)



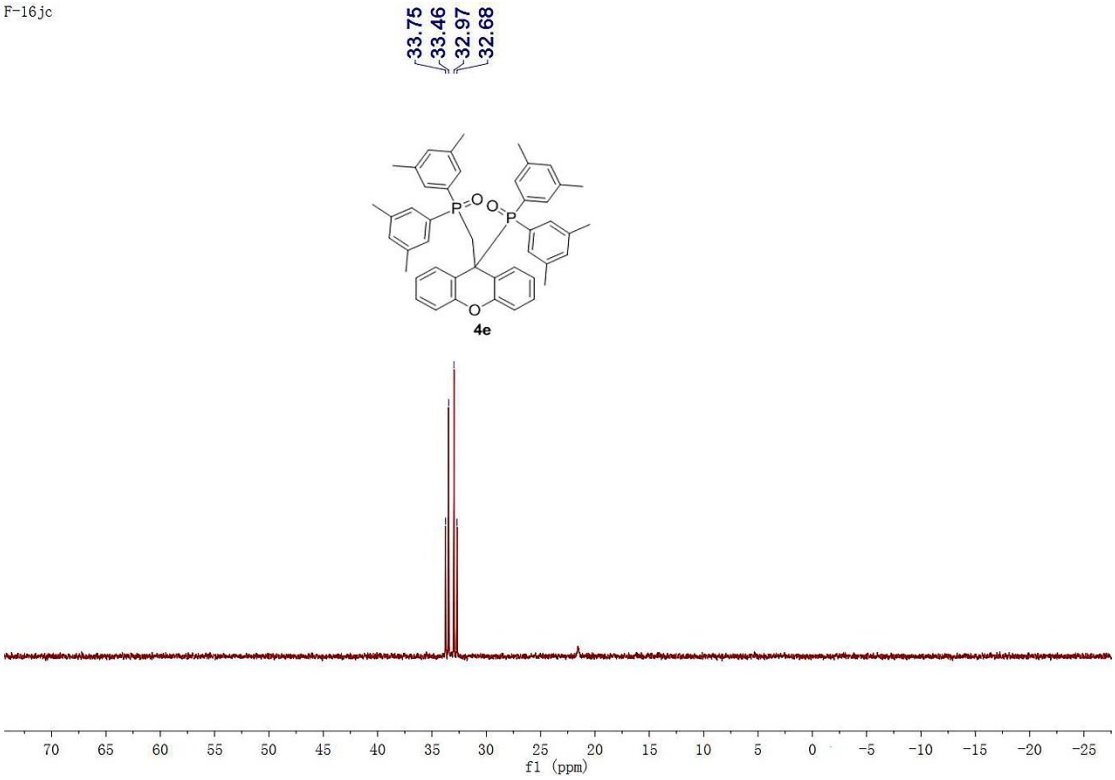
^{1}H NMR of **4e** in MeOD (400 MHz)



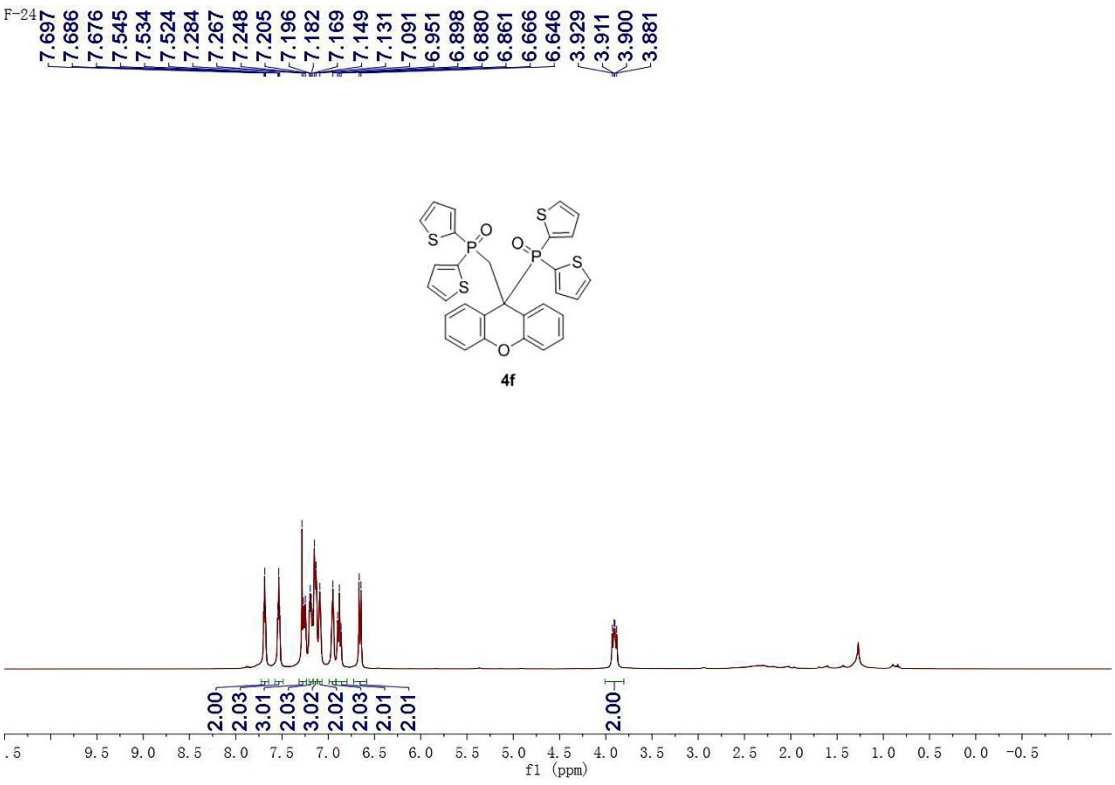
^{13}C NMR of **4e** in MeOD (150 MHz)



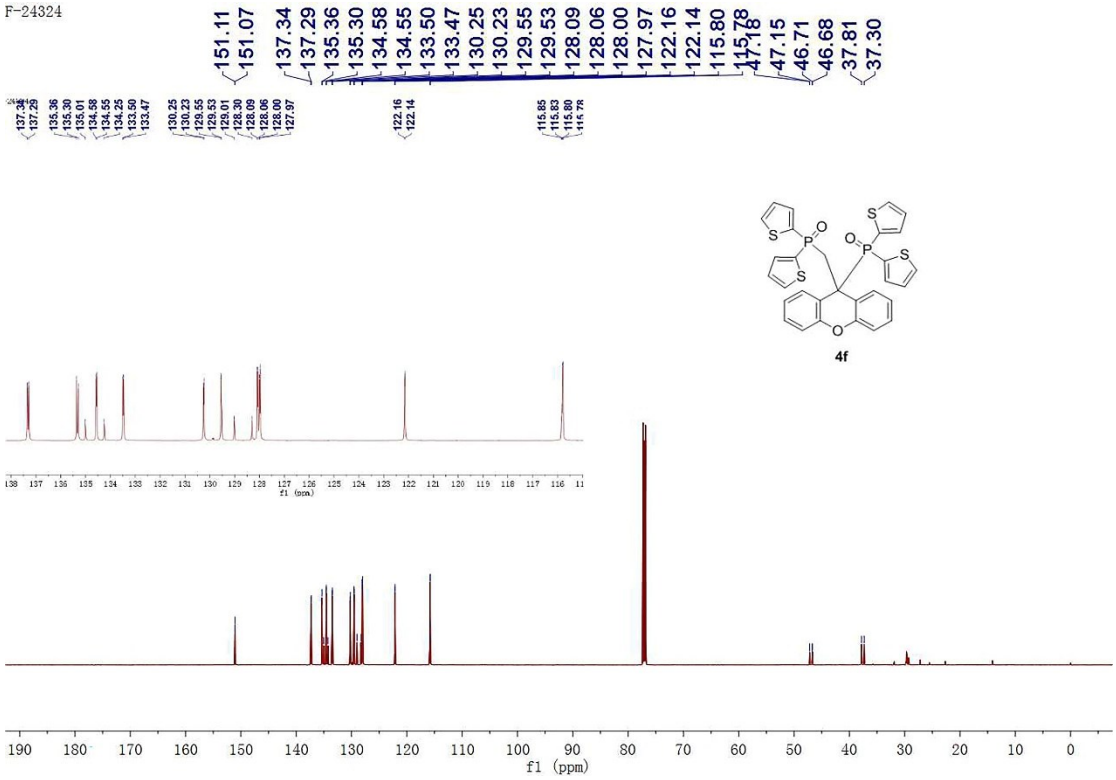
^{31}P NMR of **4e** in MeOD (162 MHz)



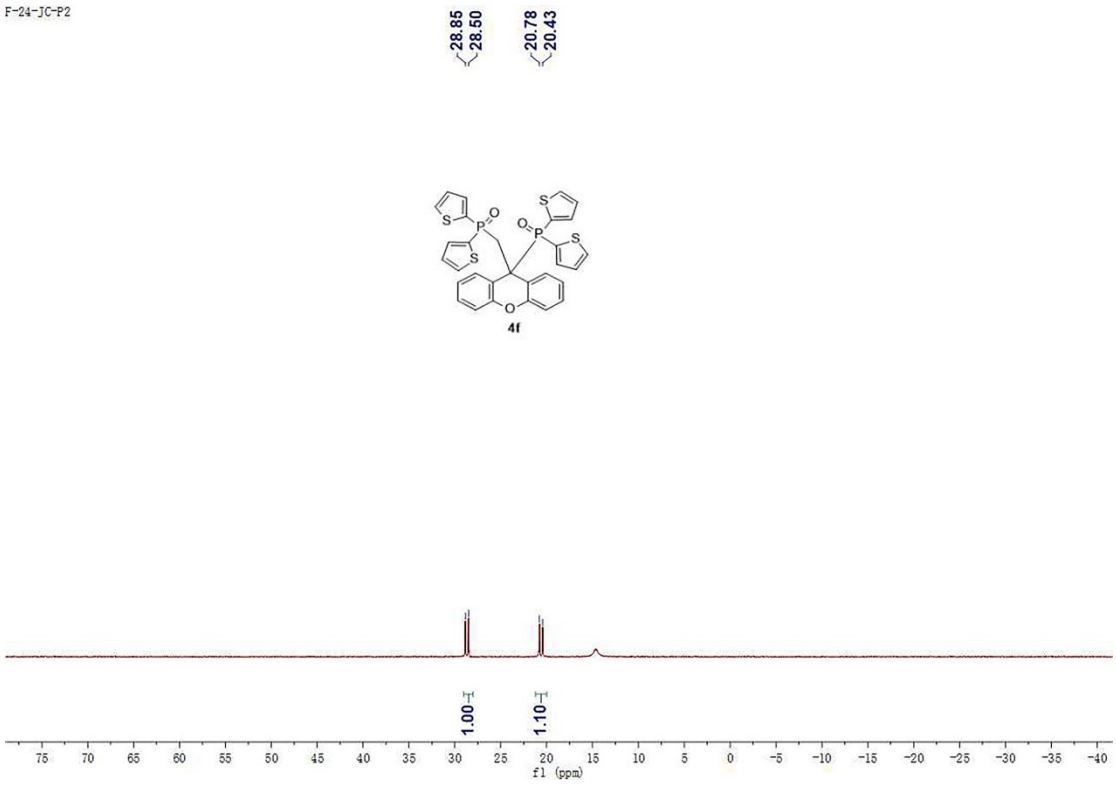
^{1}H NMR of **4f** in $CDCl_3$ (400 MHz)



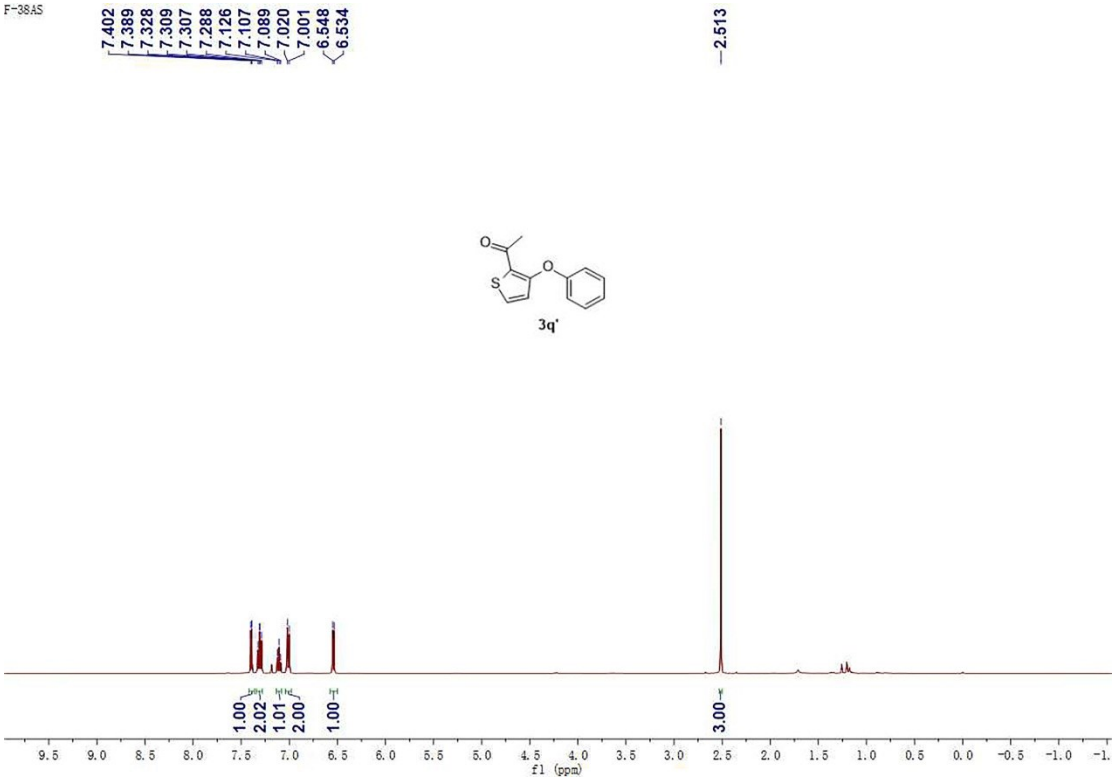
^{13}C NMR of **4f** in $CDCl_3$ (150 MHz)



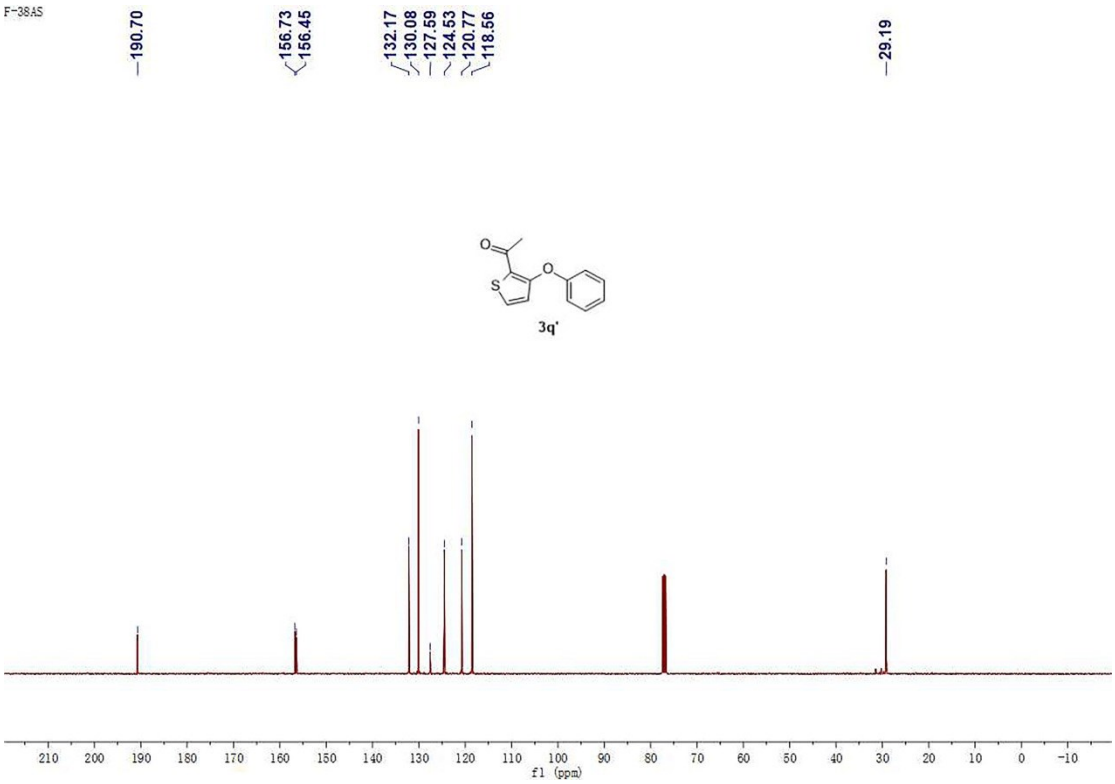
^{31}P NMR of **4f** in MeOD (162 MHz)



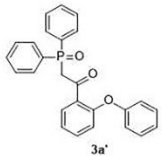
^{1}H NMR of **3q'** in $CDCl_3$ (400 MHz)

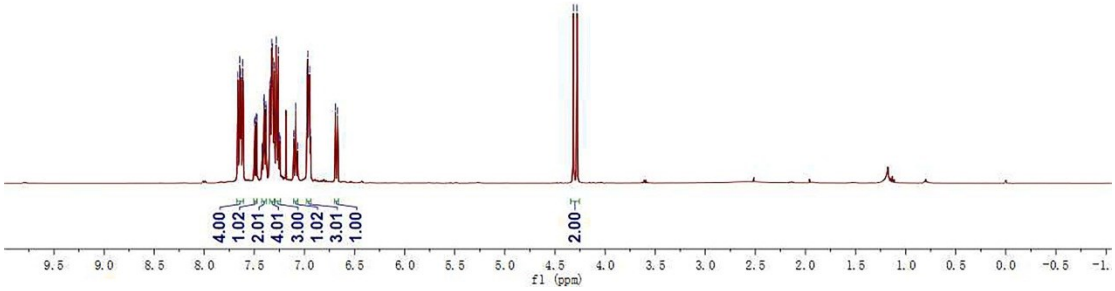


^{13}C NMR of **3q'** in $CDCl_3$ (101 MHz)

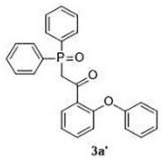


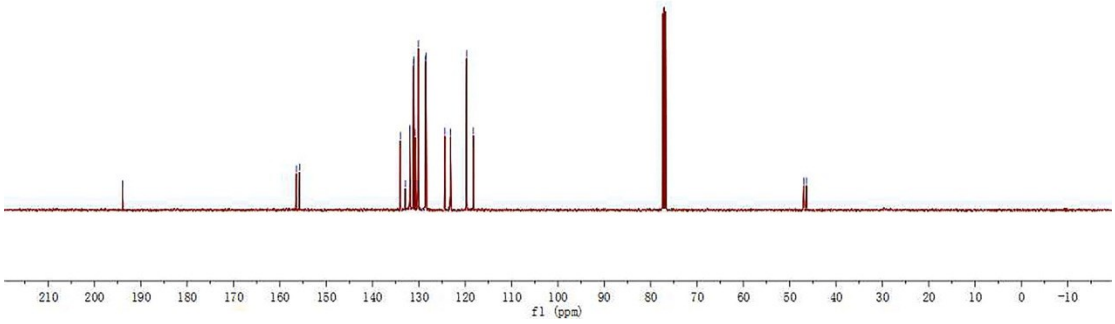
^{1}H NMR of **3a'** in $CDCl_3$ (400 MHz)



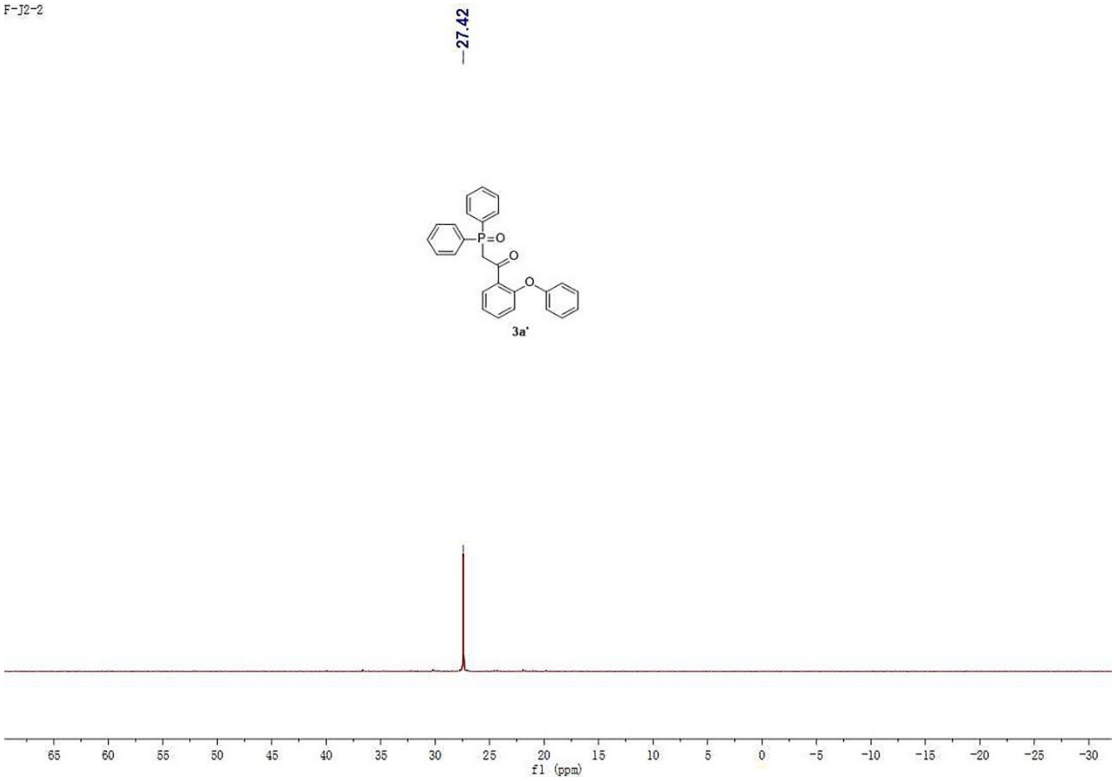


^{13}C NMR of **3a'** in $CDCl_3$ (101 MHz)

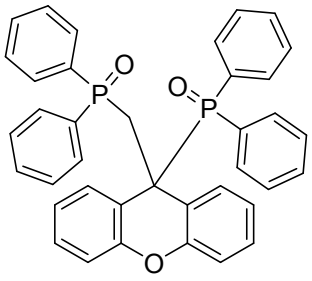




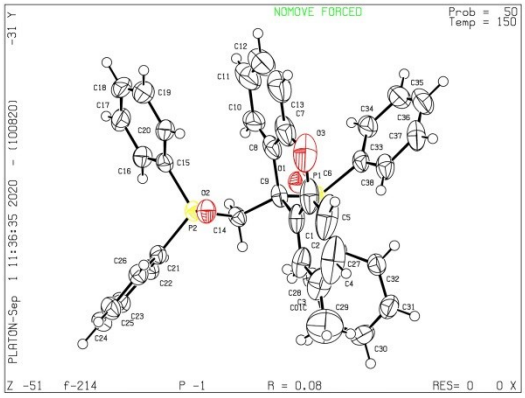
^{31}P NMR of **3a′** in $CDCl_3$ (162 MHz)



The X-ray crystal data of 3a



CCDC: 2079136



Bond precision: C-C = 0.0080 A Wavelength=0.71073

Cell: a=10.8036(9) b=11.4967(9) c=15.6103(14)
alpha=95.672(7) beta=91.026(7) gamma=113.558(8)
Temperature: 150 K

	Calculated	Reported
Volume	1765.1(3)	1765.1(3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C39 H32 O3 P2 [+ solvent]	C39 H32 O3 P2
Sum formula	C39 H32 O3 P2 [+ solvent]	C39 H32 O3 P2
Mr	610.59	610.58
Dx,g cm-3	1.149	1.149
Z	2	2
Mu (mm-1)	0.157	0.157
F000	640.0	640.0
F000'	640.66	
h,k,lmax	12,13,18	12,13,18
Nref	6216	6213
Tmin,Tmax	0.980,0.988	0.451,1.000
Tmin'	0.980	

Correction method= # Reported T Limits: Tmin=0.451 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.000 Theta(max)= 24.997

R(reflections)= 0.0787(4305) wR2(reflections)= 0.2200(6213)

S = 1.044 Npar= 398