Supporting Information

For

Copper Mediated C(sp^2)–H Amination and Hydroxylation of Phosphinamides

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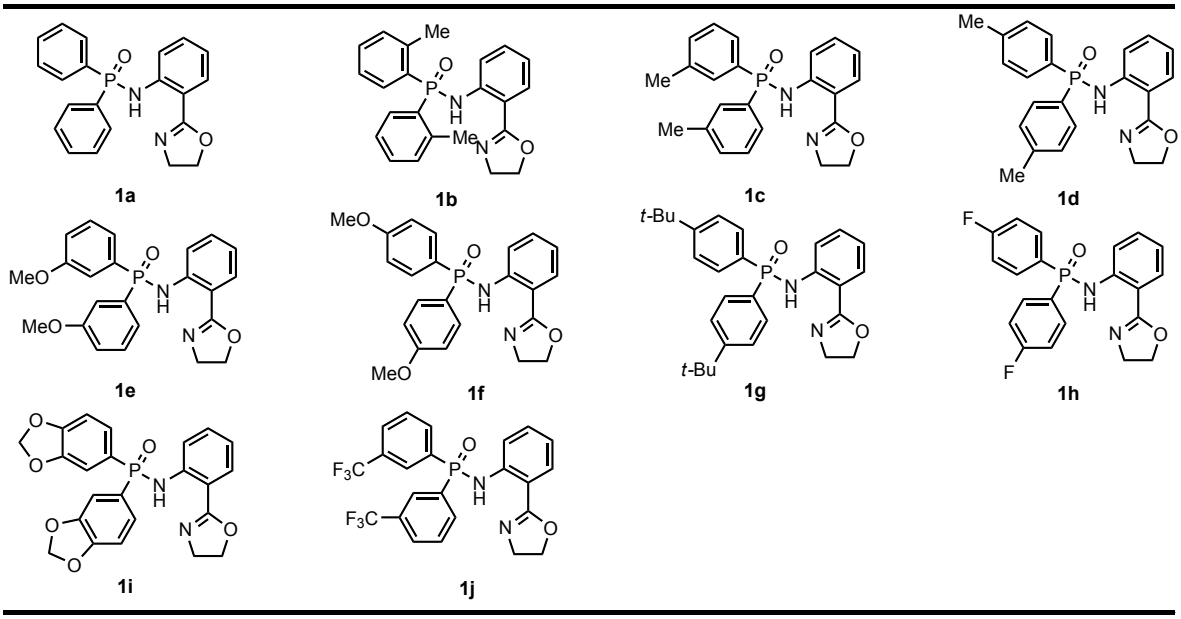
1. General Information

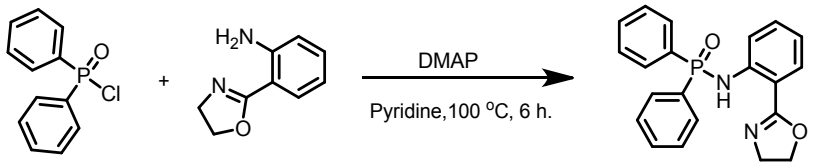
All commercial reagents were purchased from Alfa Aesar, TCI, Acros and Energy Chemical of the highest purity grade. They were used without further purification unless specified. ^{1}H and ^{13}C NMR spectra were recorded on Agilent AV 400, Varian Inova 400 (400 MHz and 100 MHz, respectively) instruments. The peaks were internally referenced to TMS (0.00 ppm) or residual undeuterated solvent signal. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. High resolution mass spectra were recorded at the Center for Mass Spectrometry, Shanghai Institute of Organic Chemistry.

2. Experimental Section

2.1 Preparation of Substrates 1a-1l.

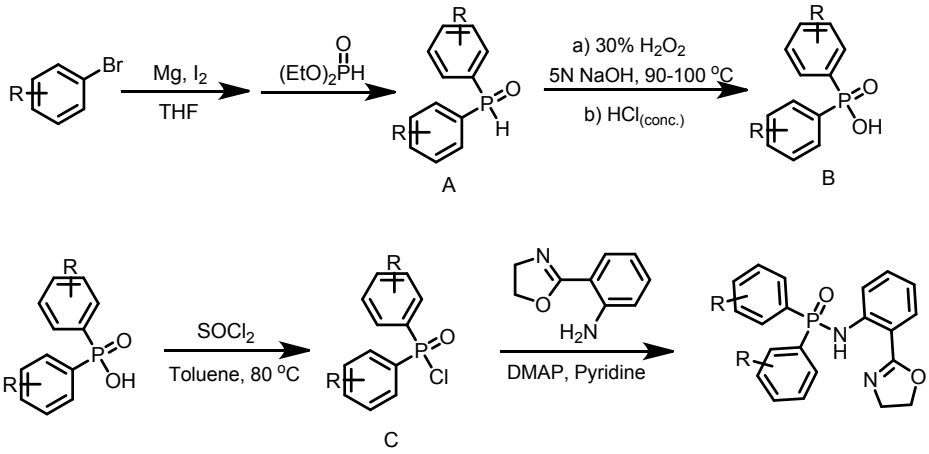


2.1.1 Preparation of Substrates 1a;



An diphenylphosphinyl chloride (10 mmol, 1.9 mL), 2-(4,5-dihydrooxazol-2-yl) aniline (12 mmol, 1.94 g) and DMAP (12 mmol, 1.46 g) were added to a 100 mL flask, then dissolved with pyridine (30 mL). The reaction mixture was stirred at 100 ^{o}C for 6 h. The solvent was removed in a rotary evaporator and the crude product was recrystallized from EtOAc/Hexane to give colorless crystals of the product.

2.1.2 Preparation of Substrates 1b-1j[1];



Aryl bromide (50 mmol) in THF (30 mL) was added slowly to a stirred THF (100 mL) solution of I_2 (cat.) containing magnesium turnings (1.2 g, 50 mmol), and heated under reflux for 1 hour. Then diethyl phosphate (1.93 ml, 15 mmol) in THF (20 mL) was added slowly under the cooling of an ice-water bath. The obtained mixture was heated under reflux for 1 hour. The resulting reaction mixture was cooled to 0 ^{o}C, and hydrochloric acid (50 mL, 6 N) was added slowly upon stirring. The solution was evaporated under reduced pressure at 40 ^{o}C. The residue was extracted with EtOAc (100 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo to give crude product **A** which was used directly without purification.

Hydrogen peroxide (30%, 8 mL) was added dropwise to a suspension of **A** in aqueous NaOH (5 N, 15 mL) at 90–100 ^{o}C, and the mixture was stirred for 1 hour at 100 ^{o}C. After the solution was cooled to 0 ^{o}C, hydrochloric acid (conc.) was added dropwise until no white solid was precipitated out. The precipitate was collected by filtration

and washed consecutively with water and Et_2O. Then be dried in vacuo to give the phosphinic acid **B** which was used directly without purification.

A suspension of **B** and thionyl chloride (10 mL) in toluene (30 mL) was heated to 80 ^oC for 3h. After thionyl chloride and toluene was removed under reduced pressure, the residue was re-dissolved in toluene (50 mL) and evaporated to give phosphinic chloride **C**. **C** (10 mmol), 2-(4,5-dihydrooxazol-2-yl)aniline (12 mmol, 1.94g) and DMAP (12 mmol, 1.46g) were added to a 100 mL flask, then dissolved with Pyridine (30 mL). The reaction mixture was stirred at 100 ^oC for 6 h. The solvent was removed in a rotary evaporator and the crude product was recrystallized from EtOAc/Hexane to give colorless crystals of the product.

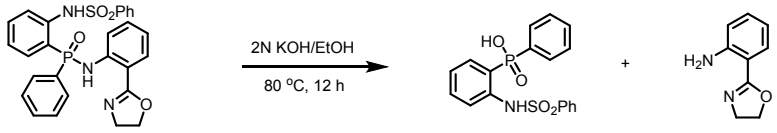
2.2 Typical Procedures for Cu(II)-Mediated Intermolecular C–N bond formation

To a 15 mL sealed tube was added substrates **1** (0.1 mmol, 1 equiv), $Cu(OAc)_2$ (0.1 mmol), amine (0.2 mmol), Na_2CO_3 (0.25 mmol), DMSO (1 mL). The reaction mixture was stirred at 100 ^oC for 6 h under air. After the completion, the mixture was diluted with ethyl acetate, then washed with ammonia water and saturated brine. The organic fraction was dried over Na_2SO_4, and concentrated in vacuo. The compounds were purified by flash column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate to give the product.

2.3 Typical Procedures for Cu(II)-Mediated Intermolecular C–O bond formation

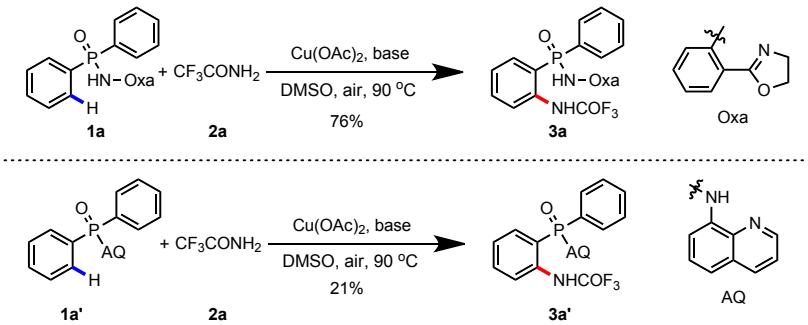
To a 25 mL Schlenk-type tube which has a Teflon high pressure valve and side arm was added substrates 1 (0.1 mmol, 1 equiv), $Cu(OAc)_2$ (0.1 mmol), Na_2CO_3 (0.1 mmol), DMSO (2 mL). The reaction tube was evacuated and back-filled with O_2 (6 times). Then the reaction mixture was stirred at 80 ^oC for 6 h. After the completion, the mixture was diluted with ethyl acetate, then washed with ammonia water and saturated brine. The organic fraction was dried over Na_2SO_4, and concentrated in vacuo. The compounds were purified by flash column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate to give the product.

2.4 The Procedure for Directing Group Removal.



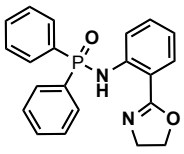
To a 15 mL sealed tube was added **4a** (0.1 mmol), KOH (224 mg, 4.0 mmol), EtOH (2 mL). The reaction mixture was stirred at 80 °C for 12 h under air. After the completion, the mixture was washed with H_2O and extracted with EtOAc (20 mL x 3).The organic phase was dried over Na_2SO_4 evaporated and purified by flash column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate to give the directing group with a yield of 93% (15 mg). The water fraction was soured with 1N HCl to PH 3~4, and extracted with EtOAc (20 ml x 3). The organic fraction was dried over Na_2SO_4 evaporated and purified by flash column chromatography on silica gel to get product with a yield of 75% (28 mg). **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 7.83 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.48 (td, *J* = 18.5, 11.1 Hz, 5H), 7.34 (dd, *J* = 8.3, 3.6 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 3H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.81 (t, *J* = 7.4 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 143.0 (d, *J* = 129.0 Hz), 140.9 (d, *J* = 4.8 Hz), 140.6, 134.3 (d, *J* = 6.9 Hz), 133.9, 133.1, 131.1 (d, *J* = 8.8 Hz), 130.0 (d, *J* = 125.8 Hz), 129.6, 128.2, 127.8 (d, *J* = 11.4 Hz), 127.2, 122.3 (d, *J* = 10.4 Hz), 116.2 (d, *J* = 7.7 Hz); **^{31}P NMR** (162 MHz, DMSO-*d6*) δ 19.7(s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{18}H_{17}NO_4PS$ $[M+H]^+$ 364.0610, found 364.0612.

2.5 Comparation of Different Directing Group

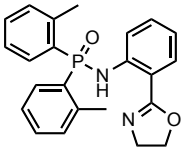


3. Analytical Data

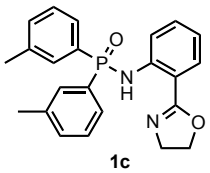
3.1 Characterization of Substrates 1a-1j;



N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-P,P-diphenylphosphinic amide (1a): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.96 (d, *J* = 13.2 Hz, 1H), 7.91 (dd, *J* = 12.1, 7.6 Hz, 4H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.57 – 7.40 (m, 6H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 6.86 (t, *J* = 7.5 Hz, 1H), 4.35 (t, *J* = 9.5 Hz, 2H), 4.04 (t, *J* = 9.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0, 143.0, 132.7 (d, *J* = 127.7 Hz), 132.2, 131.8 (d, *J* = 2.8 Hz), 131.6 (d, *J* = 10.2 Hz), 129.3, 128.6 (d, *J* = 12.9 Hz), 119.8, 118.2 (d, *J* = 5.1 Hz), 112.6 (d, *J* = 7.8 Hz), 66.0, 54.5; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.89 (d, *J* = 12.2 Hz). **HRMS** (ESI-TOF) m/z Calcd for $C_{21}H_{20}N_2O_2P$ $[M+H]^+$ 363.1257, found 363.1259.

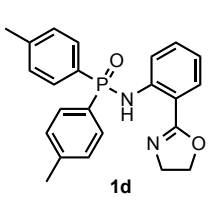


N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-P,P-di-o-tolylphosphinic amide (1b): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.80 (d, *J* = 13.6 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.73 (dd, *J* = 14.4, 7.6 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.16 (m, 5H), 6.86 (t, *J* = 7.6 Hz, 1H), 4.30 (t, *J* = 9.5 Hz, 2H), 3.93 (t, *J* = 9.5 Hz, 2H), 2.52 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.9, 143.5, 142.1 (d, *J* = 10.0 Hz), 133.1 (d, *J* = 11.5 Hz), 132.2, 131.9 (d, *J* = 2.7 Hz), 131.7 (d, *J* = 11.8 Hz), 130.6(d, *J* = 123.6 Hz), 129.3, 125.4 (d, *J* = 13.1 Hz), 119.5, 118.2 (d, *J* = 4.3 Hz), 112.1 (d, *J* = 7.8 Hz), 65.9, 54.3, 21.4 (d, *J* = 4.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.6 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{24}N_2O_2P$ $[M+H]^+$ 391.1570, found 391.1571.



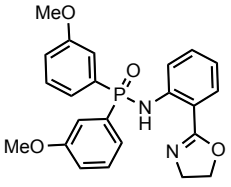
N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-P,P-di-m-tolylphosphinic amide (1c): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.96 (d, *J* = 12.9 Hz, 1H), 7.79 (d, *J* = 12.9 Hz, 3H), 7.65 (dd, *J* = 12.3, 6.8 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.33 – 7.24 (m, 4H), 7.14 (t, *J* = 7.3 Hz, 1H), 6.82 (t, *J* = 7.5 Hz, 1H), 4.30 (t, *J* = 9.4 Hz, 2H), 4.01 (t, *J* = 9.4 Hz, 2H), 2.34 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.9, 143.0, 138.3 (d, *J* = 12.9 Hz), 132.5 (d, *J* = 2.9 Hz), 132. 48 (d, *J* = 127.1 Hz), 132.1, 132.0, 129.2, 128.4, 128.3 (d, *J* = 4.6 Hz), 119.6, 118.0 (d, *J* = 5.1 Hz), 112.4 (d, *J* = 7.8 Hz), 65.9, 54.3, 21.3; **^{31}P**

NMR (162 MHz, $CDCl_3$) δ 19.5 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{24}N_2O_2P$ $[M+H]^+$ 391.1570, found 391.1571.



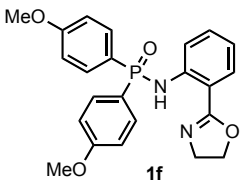
1d

N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-P,P-di-p-tolylphosphinic amide (1d): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.85 (d, *J* = 12.6 Hz, 1H), 7.78 (dd, 12.0, 8.0 Hz, 4H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.24 (dd, *J* = 8.1, 2.8 Hz, 4H), 7.17 (t, *J* = 7.8 Hz, 1H), 6.85 (t, *J* = 7.6 Hz, 1H), 4.36 (t, *J* = 9.4 Hz, 2H), 4.05 (t, *J* = 9.5 Hz, 2H), 2.38 (d, *J* = 9.7 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.8, 143.1, 142.1 (d, *J* = 2.9 Hz), 132.0, 131.5 (d, *J* = 10.6 Hz), 129.6 (d, *J* = 130.2 Hz), 129.2 (d, *J* = 13.3 Hz), 129.2, 119.5, 118.1 (d, *J* = 5.1 Hz), 112.4 (d, *J* = 7.6 Hz), 65.9, 54.4, 21.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 19.3 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{24}N_2O_2P$ $[M+H]^+$ 391.1570, found 391.1572.



1e

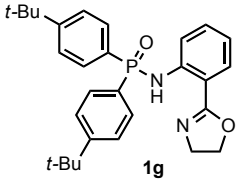
N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-P,P-bis(3-methoxyphenyl)phosphinic amide (1e): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.88 (d, *J* = 13.1 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.47 – 7.28 (m, 5H), 7.21 (s, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 7.4 Hz, 2H), 6.72 (t, *J* = 7.4 Hz, 1H), 4.17 (t, *J* = 9.3 Hz, 2H), 3.88 (t, *J* = 9.3 Hz, 2H), 3.65 (s, 6H)； **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.7, 159.4 (d, *J* = 16.2 Hz), 142. 8, 133.7 (d, *J* = 127.1 Hz), 133.6, 131.9, 129.6 (d, *J* = 15.3 Hz), 129.2, 127.4, 123.4 (d, *J* = 10.0 Hz), 119.7, 117.9, 116.1 (d, *J* = 11.3 Hz), 112.4 (d, *J* = 7.8 Hz), 65.8, 55.1, 54.3; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.9 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{24}N_2O_4P$ $[M+H]^+$ 423.1468, found 423.1467.



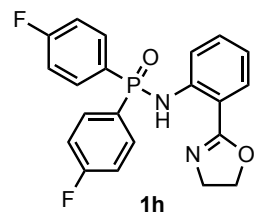
1f

N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-P,P-bis(4-methoxyphenyl)phosphinic amide (1f): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.77 (d, *J* = 12.8 Hz, 1H), 7.93 – 7.71 (m, 5H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.17 (t, *J* = 7.1 Hz, 1H), 6.94 (dd, *J* = 8.7, 2.4 Hz, 4H), 6.85 (t, *J* = 7.6 Hz, 1H), 4.36 (t, *J* = 9.5 Hz, 2H), 4.04 (t, *J* = 9.5 Hz, 2H), 3.83 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.9, 162.3 (d, *J* = 2.9 Hz),

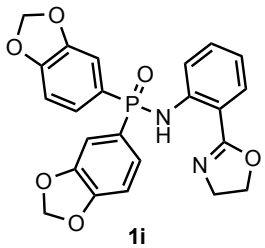
143.2, 133.4 (d, J = 11.6 Hz), 132.1, 129.3, 124.2 (d, J = 135.4 Hz), 119.6, 118.1 (d, J = 5.4 Hz), 114.1 (d, J = 14.0 Hz), 112.4 (d, J = 7.9 Hz), 66.0, 55.2, 54.5; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 19.2 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{24}N_2O_4P$ $[M+H]^+$ 423.1468, found 423.1468.



P,P-bis(4-(tert-butyl)phenyl)-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)phosphinic amide (1g): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.86 (d, J = 12.1 Hz, 1H), 7.81 (d, J = 9.5 Hz, 5H), 7.44 (s, 5H), 7.17 (t, J = 6.0 Hz, 1H), 6.84 (t, J = 7.5 Hz, 1H), 4.34 (t, J = 8.5 Hz, 2H), 4.06 (t, J = 8.8 Hz, 2H), 1.29 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0, 155.1, 143.3, 132.2, 131.4 (d, J = 10.8 Hz), 129.7(d, J = 130.0 Hz), 129.3, 125.6 (d, J = 13.0 Hz), 119.6, 118.3, 112.5 (d, J = 7.7 Hz), 66.0, 54.6, 34.9, 31.1; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.7 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{29}H_{36}N_2O_2P$ $[M+H]^+$ 475.2509, found 475.2510.

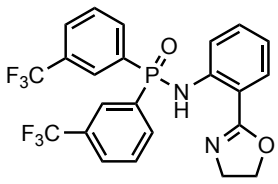


N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-P,P-bis(4-fluorophenyl)phosphinic amide (1h): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.97 (d, J = 13.2 Hz, 1H), 7.89 (ddd, J = 12.0, 8.7, 5.6 Hz, 4H), 7.80 (d, J = 7.9 Hz, 1H), 7.29 (t, J = 8.6 Hz, 1H), 7.19 (t, J = 8.4 Hz, 1H), 7.15 (td, J = 8.7, 2.3 Hz, 4H), 6.89 (t, J = 7.6 Hz, 1H), 4.38 (t, J = 9.5 Hz, 2H), 4.05 (t, J = 9.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.2 (dd, J = 252.2, 3.4 Hz), 165.1 (d, J = 1.5 Hz), 142.7, 134.1 (dd, J = 11.7, 8.8 Hz), 132.3, 129.5, 128.5 (dd, J = 132.8, 3.2 Hz), 120.2, 118.1 (d, J = 5.0 Hz), 116.1 (dd, J = 21.4, 14.3 Hz), 112.6 (d, J = 7.9 Hz), 66.1, 54.4; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -69.01 – -136.05 (m, 2F); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.4 (s, 1p). **HRMS** (ESI-TOF) m/z Calcd for $C_{21}H_{18}F_2N_2O_2P$ $[M+H]^+$ 399.1068, found 399.1070.



P,P-bis(benzo[d][1,3]dioxol-5-yl)-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)phosphinic amide (1i): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.81 (d, J = 13.2 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.44 (dd, J = 12.6, 8.1 Hz, 2H), 7.36 (d, J = 8.1 Hz, 1H),

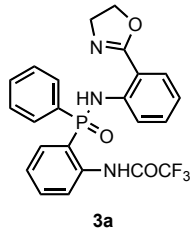
7.28 (d, *J* = 12 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 4.7 Hz, 3H), 5.99 (s, 4H), 4.36 (t, *J* = 9.3 Hz, 2H), 4.06 (t, *J* = 9.3 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0, 150.7, 147.9 (d, *J* = 19.7 Hz), 143.0, 132.1, 129.3, 127.0 (d, *J* = 11.2 Hz), 125.9 (d, *J* = 134.2 Hz), 119.8, 118.2 (d, *J* = 5.2 Hz), 112.5 (d, *J* = 7.7 Hz), 110.9 (d, *J* = 13.0 Hz), 108.7 (d, *J* = 16.3 Hz), 101.5, 66.0, 54.5; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.7 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{20}N_2O_6P$ $[M+H]^+$ 451.1053, found 451.1056.



1j

N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-P,P-bis(3-(trifluoromethyl)phenyl)phosphinic amide (1j): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.36 (d, *J* = 13.6 Hz, 1H), 8.28 (d, *J* = 12.4 Hz, 2H), 8.07 (dd, *J* = 12.3, 7.8 Hz, 2H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 2H), 7.61 (td, *J* = 7.7, 2.9 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 4.43 (t, *J* = 9.5 Hz, 2H), 4.11 (t, *J* = 9.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.3 (d, *J* = 1.4 Hz), 142.1, 134.9 (d, *J* = 10.1 Hz), 133.6 (d, *J* = 129.7 Hz), 132.4, 131.4 (dq, *J* = 32.7, 13.3 Hz), 129.6, 129.5 (d, *J* = 12.9 Hz), 129.0 – 128.9 (m), 128.5 (dq, *J* = 11.2, 3.7 Hz), 123.6 (dq, *J* = 270.7, 1.9 Hz), 120.7, 118.1 (d, *J* = 5.0 Hz), 112.9 (d, *J* = 7.9 Hz), 66.3, 54.2; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -62.8 (s, 6F); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 15.3 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{18}F_6N_2O_2P$ $[M+H]^+$ 499.1005, found 499.1006.

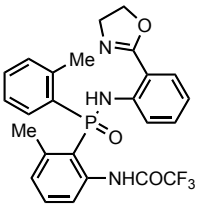
3.2 Characterization of products



3a

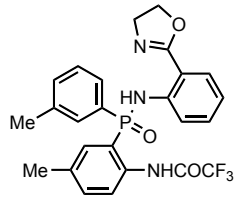
N-(2-(((2-(4,5-dihydrooxazol-2-yl)phenyl)amino)(phenyl)phosphoryl)phenyl)-2,2,2-trifluoroacetamide (3a): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.89 (s, 1H), 11.34 (d, *J* = 13.7 Hz, 1H), 8.59 (dd, *J* = 8.3, 5.1 Hz, 1H), 7.91(dd, *J* = 12.8, 6.8 Hz, 2H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.62 – 7.54 (m, 2H), 7.53 – 7.46 (m, 3H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.19 (td, *J* = 7.6, 1.2 Hz,

1H), 7.14 (td, *J* = 7.5, 1.6 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 4.39 (t, *J* = 9.4 Hz, 2H), 4.06 (td, *J* = 9.4, 3.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.1, 155.4 (q, *J* = 37.3 Hz), 141.9, 141.6 (d, *J* = 5.3 Hz), 133.6 (d, *J* = 2.3 Hz), 132.7 (d, *J* = 2.8 Hz), 132.4, 132.3, 131.3(d, *J* = 131.0 Hz), 131.1 (d, *J* = 10.5 Hz), 129.6, 129.0 (d, *J* = 13.3 Hz), 125.1 (d, *J* = 12.5 Hz), 121.6 (d, *J* = 8.7 Hz), 120.8, 119.3, 118.2 (d, *J* = 5.2 Hz), 115.8 (q, *J* = 287.2 Hz), 112.9 (d, *J* = 8.1 Hz), 66.2, 54.3; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -75.9 (s, 3F); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 23.7 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{20}F_3N_3O_3P$ $[M+H]^+$ 474.1189, found 474.1190.



3b

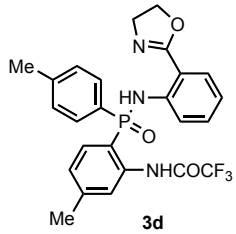
N-(2-(((2-(4,5-dihydrooxazol-2-yl)phenyl)amino)(o-tolyl)phosphoryl)-3-methylphenyl)-2,2,2-trifluoroacetamide (3b): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 14.17 (s, 1H), 11.40 (d, *J* = 14.3 Hz, 1H), 8.66 (dd, *J* = 8.4, 4.3 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.63 (dd, *J* = 15.1, 7.2 Hz, 1H), 7.53 – 7.40 (m, 3H), 7.35 – 7.17 (m, 3H), 6.95 (dd, *J* = 13.9, 6.1 Hz, 2H), 4.48 – 4.22 (m, 2H), 4.19 – 3.86 (m, 2H), 2.55 (s, 3H), 2.17 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.1, 155.6 (q, *J* = 36.9 Hz), 143.9 (d, *J* = 5.3 Hz), 142.3, 142.2, 141.7 (d, *J* = 8.6 Hz), 133.4 (d, *J* = 2.0 Hz), 132.6 (d, *J* = 2.8 Hz), 132.6, 132.4 (d, *J* = 12.4 Hz), 131.4 (d, *J* = 12.4 Hz), 130.9, 129.6, 128.7 (d, *J* = 11.1 Hz), 125.6 (d, *J* = 13.8 Hz), 120.5, 119.6 (d, *J* = 8.5 Hz), 117.6 (d, *J* = 4.6 Hz), 116.0(q, *J* = 287.0 Hz), 115.9 (d, *J* = 115.7 Hz), 112.4 (d, *J* = 8.2 Hz), 66.2, 54.3, 22.7(d, *J* = 5.2 Hz), 21.0 (d, *J* = 5.1 Hz); **^{19}F NMR** (375 MHz, $CDCl_3$) δ -75.8 (s, 3F); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.3 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{25}H_{24}F_3N_3O_3P$ $[M+H]^+$ 502.1502, found 502.1504.



3c

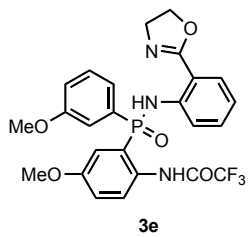
N-(2-(((2-(4,5-dihydrooxazol-2-yl)phenyl)amino)(m-tolyl)phosphoryl)-4-methylphenyl)-2,2,2-trifluoroacetamide (3c): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.82 (s, 1H), 11.30 (d, *J* = 13.3 Hz, 1H), 8.47 (dd, *J* = 8.5, 5.3 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 13.1 Hz, 1H), 7.64 (dt, *J* = 9.0, 4.0 Hz, 1H), 7.36 (ddd, *J* = 11.0, 6.0, 2.2 Hz, 3H), 7.29 – 7.18 (m, 2H), 6.93 (ddd, *J* = 8.2,

6.9, 1.6 Hz, 1H), 4.41 (t, *J* = 9.5 Hz, 2H), 4.17 – 4.02 (m, 2H), 2.40 (s, 3H), 2.26 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.1 (d, *J* = 1.4 Hz), 155.2 (q, *J* = 37.4 Hz), 142.0, 139.1 (d, *J* = 5.4 Hz), 138.9 (d, *J* = 13.2 Hz), 134.8 (d, *J* = 12.3 Hz), 134.3 (d, *J* = 2.4 Hz), 133.5 (d, *J* = 3.0 Hz), 132.4, 132.3, 131.3 (d, *J* = 130.3 Hz), 131.7 (d, *J* = 10.4 Hz), 129.5, 128.9 (d, *J* = 14.1 Hz), 128.1 (d, *J* = 10.5 Hz), 121.5 (d, *J* = 9.3 Hz), 120.6, 119.3, 118.1 (d, *J* = 5.3 Hz), 115.9 (q, *J* = 288.5 Hz), 112.9 (d, *J* = 8.0 Hz), 66.2, 54.3, 21.5, 21.0; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -75.9 (s, 3F); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.9 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{25}H_{24}F_3N_3O_3P$ $[M+H]^+$ 502.1502, found 502.1503.



3d

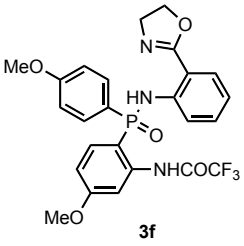
N-(2-(((2-(4,5-dihydrooxazol-2-yl)phenyl)amino)(p-tolyl)phosphoryl)-5-methylphenyl)-2,2,2-trifluoroacetamide (3d): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.86 (s, 1H), 11.20 (d, *J* = 13.4 Hz, 1H), 8.42 (d, *J* = 4.6 Hz, 1H), 7.81(d, 10.0 Hz, 1H), 7.78 (dd, 12.4, 8.0 Hz, 2H), 7.42 (dd, *J* = 14.1, 7.9 Hz, 1H), 7.30 – 7.26(m, 3H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.98 – 6.88 (m, 2H), 4.38 (t, *J* = 9.4 Hz, 2H), 4.19 – 3.93 (m, 2H), 2.37 (d, *J* = 12.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0, 155.3 (q, *J* = 37.3 Hz), 144.5 (d, *J* = 2.4 Hz), 143.3 (d, *J* = 2.9 Hz), 142.1, 141.5 (d, *J* = 5.7 Hz), 132.3, 132.2 (d, *J* = 8.8 Hz), 131.1 (d, *J* = 10.8 Hz), 129.7 (d, *J* = 13.7 Hz), 129.5, 128.4 (d, *J* = 134.5 Hz), 125.9 (d, *J* = 12.8 Hz), 122.1 (d, *J* = 9.1 Hz), 120.6, 118.2 (d, *J* = 5.3 Hz), 115.9 (q, *J* = 287.1 Hz), 115.8 (d, *J* = 124.2 Hz), 112.9 (d, *J* = 8.0 Hz), 66.2, 54.4, 21.9, 21.6; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -76.0 (s, 3F); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.0 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{25}H_{24}F_3N_3O_3P$ $[M+H]^+$ 502.1502, found 502.1503.



3e

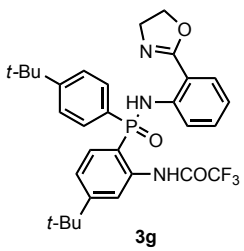
N-(2-(((2-(4,5-dihydrooxazol-2-yl)phenyl)amino)(3-methoxyphenyl)phosphoryl)-4-methoxyphenyl)-2,2,2-trifluoroacetamide (3e): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.05 (s, 1H), 11.11 (d, *J* = 13.2 Hz, 1H), 8.25 (dd, *J* = 4.2, 2.4 Hz, 1H), 7.81 (ddd, *J* = 12.2, 6.2, 2.0 Hz, 3H), 7.43 (dd, *J* = 13.7, 8.7 Hz, 1H),

7.28 (d, *J* = 8.4 Hz, 1H), 7.22 (dt, *J* = 7.8, 1.6 Hz, 1H), 6.98 (dd, *J* = 8.8, 2.7 Hz, 2H), 6.92 (dt, 7.9, 1.2 Hz, 1H), 6.66 (dt, *J* = 8.7, 2.1 Hz, 1H), 4.39 (t, *J* = 9.5 Hz, 2H), 4.06 (dd, *J* = 14.0, 6.0 Hz, 2H), 3.84 (d, *J* = 3.9 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0 (d, *J* = 1.5 Hz), 163.4 (d, *J* = 2.6 Hz), 162.9 (d, *J* = 3.0 Hz), 155.5 (q, *J* = 37.9 Hz), 143.4 (d, *J* = 6.7 Hz), 142.2, 133.6 (d, *J* = 9.8 Hz), 133.1, 133.0, 132.4, 129.5, 123.1 (d, *J* = 139.6 Hz), 120.5, 118.2 (d, *J* = 5.4 Hz), 115.8 (q, *J* = 287.1 Hz), 114.5 (d, *J* = 14.3 Hz), 112.8 (d, *J* = 8.0 Hz), 112.0 (d, *J* = 13.2 Hz), 110.7 (d, *J* = 91.5 Hz), 110.0(d, *J* = 128.6 Hz), 106.1 (d, *J* = 9.8 Hz), 66.2, 55.5, 55.4, 54.4; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -76.0 (s, 3F); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.7 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{25}H_{24}F_3N_3O_5P$ $[M+H]^+$ 534.1400, found 534.1402.



3f

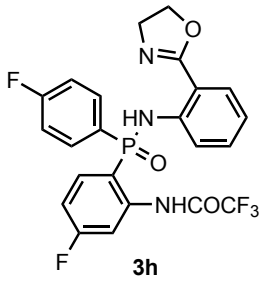
N-(2-(((2-(4,5-dihydrooxazol-2-yl)phenyl)amino)(4-methoxyphenyl)phosphoryl)-5-methoxyphenyl)-2,2,2-trifluoroacetamide (3f): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.05 (s, 1H), 11.12 (d, *J* = 13.3 Hz, 1H), 8.25 (s, 1H), 7.85 – 7.76 (m, 3H), 7.43 (dd, *J* = 13.7, 8.7 Hz, 1H), 7.28 (t, *J* = 6.8 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 6.98 (dd, *J* = 8.3, 1.9 Hz, 2H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 8.6 Hz, 1H), 4.37 (t, *J* = 9.5 Hz, 2H), 4.05 (t, *J* = 9.8 Hz, 2H), 3.83 (d, *J* = 3.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0 , 163.3 (d, *J* = 2.6 Hz), 162.9 (d, *J* = 3.0 Hz), 155.5 (q, *J* = 3.0 Hz), 143 (d, *J* = 6.7 Hz), 142.1, 133.6 (d, *J* = 9.8 Hz), 133.0 (d, *J* = 11.9 Hz), 132.3, 129.5, 1232.0 (d, *J* = 139.6 Hz), 120.5, 118.1 (d, *J* = 5.4 Hz), 115.8 (q, *J* = 286.9 Hz), 114.5 (d, *J* = 14.4 Hz), 112.8 (d, *J* = 8.0 Hz), 111.9 (d, *J* = 13.2 Hz), 110.0(d, *J* = 129.2 Hz), 106.2 (d, *J* = 9.7 Hz), 66.2, 55.5, 55.3, 54.4; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -24.7 (s, 3F); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.15 – 24.30 (m, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{25}H_{24}F_3N_3O_5P$ $[M+H]^+$ 534.1400, found 534.1401.



3g

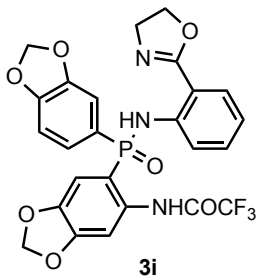
N-(5-(tert-butyl)-2-((4-(tert-butyl)phenyl)((2-(4,5-dihydrooxazol-2-yl)phenyl)amino)phosphoryl)phenyl)-2,2,2-trifluoroacetamide (3g): white solid. **^{1}H NMR** (400 MHz,

$CDCl_3$) δ 12.89 (s, 1H), 11.21 (d, *J* = 13.6 Hz, 1H), 8.68 (dd, *J* = 4.7, 1.5 Hz, 1H), 7.84 (t, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.51 (dd, *J* = 8.4, 3.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.23 (td, *J* = 7.8, 1.6 Hz, 1H), 7.15 (td, *J* = 2.0, 8.4 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 4.40 (t, *J* = 9.3 Hz, 2H), 4.12 – 4.07 (m, 2H), 1.31 (d, *J* = 9.5 Hz, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.1 (d, *J* = 1.5 Hz), 157.5 (d, *J* = 2.4 Hz), 156.2 (d, *J* = 2.9 Hz), 155.4 (q, *J* = 37.4 Hz), 142.2, 141.5 (d, *J* = 5.7 Hz), 132.4, 132.0 (d, *J* = 8.8 Hz), 131.0 (d, *J* = 10.8 Hz), 129.5, 128.5 (d, *J* = 134.3 Hz), 126.0 (d, *J* = 13.5 Hz), 122.2 (d, *J* = 12.6 Hz), 120.6, 118.9 (d, *J* = 8.9 Hz), 118.3 (d, *J* = 5.2 Hz), 115.9 (q, *J* = 287.2 Hz), 115.9 (d, *J* = 123.9 Hz), 112.9 (d, *J* = 8.0 Hz), 66.2, 54.5, 35.3, 35.1 (d, *J* = 0.9 Hz), 31.0, 30.9; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.0 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{31}H_{36}F_3N_3O_3P$ $[M+H]^+$ 586.2441, found 586.2442.



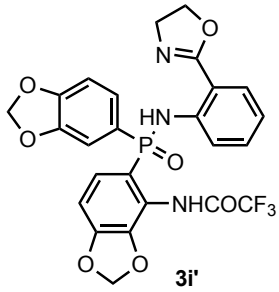
3h

N-(2-(((2-(4,5-dihydrooxazol-2-yl)phenyl)amino)(4-fluorophenyl)phosphoryl)-5-fluorophenyl)-2,2,2-trifluoroacetamide (3h): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.04 (s, 1H), 11.37 (d, *J* = 13.9 Hz, 1H), 8.43 (ddd, *J* = 11.3, 4.0, 2.5 Hz, 1H), 7.91 (ddd, *J* = 12.2, 8.7, 5.4 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.61 – 7.50 (m, 1H), 7.29 – 7.14 (m, 4H), 6.96 (ddd, *J* = 8.2, 6.0, 2.5 Hz, 1H), 6.91 – 6.83 (m, 1H), 4.41 (t, *J* = 9.5 Hz, 2H), 4.16 – 3.99 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5 (dd, *J* = 253.9, 3.5 Hz), 165.4 (dd, *J* = 252.4, 3.0 Hz), 165.1 (d, *J* = 1.5 Hz), 155.5 (q, *J* = 38.3 Hz), 143.6 (dd, *J* = 12.4, 6.9 Hz), 141.5, 134.3 (d, *J* = 20.0 Hz), 134.3, 133.8 (d, *J* = 8.9 Hz), 133.7 (d, *J* = 9.0 Hz), 132.5, 129.7, 127.2 (dd, *J* = 136.6, 3.4 Hz), 121.1, 118.1 (d, *J* = 5.3 Hz), 116.6 (dd, *J* = 21.4, 14.6 Hz), 115.6 (q, *J* = 287.0 Hz), 114.1 (dd, *J* = 125.3, 3.4 Hz), 113.0 (d, *J* = 8.3 Hz), 112.5 (dd, *J* = 21.9, 13.5 Hz), 109.4 (dd, *J* = 27.8, 9.9 Hz), 66.3, 54.3; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -76.00 (s, 3F), -101.35 – -101.87 (m, 1F), -104.81 (ddd, *J* = 7.0, 3.2, 1.5 Hz, 1F); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 23.0 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{18}F_5N_3O_3P$ $[M+H]^+$ 510.1000, found 510.1003.



3i

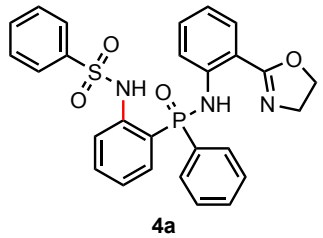
N-(6-(benzo[d][1,3]dioxol-5-yl((2-(4,5-dihydrooxazol-2-yl)phenyl)amino)phosphoryl)benzo[d][1,3]dioxol-5-yl)-2,2,2-trifluoroacetamide (3i): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.91 (s, 1H), 11.16 (d, *J* = 13.6 Hz, 1H), 8.18 (d, *J* = 4.4 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.43 (dd, *J* = 13.5, 8.0 Hz, 1H), 7.27 (m, 3H), 7.02 – 6.86 (m, 3H), 6.03 (s, 2H), 5.98 (d, *J* = 5.6 Hz, 2H), 4.40 (t, *J* = 9.4 Hz, 2H), 4.19 – 3.99 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.1, 155.1 (q, *J* = 38.4 Hz), 151.6 (d, *J* = 2.7 Hz), 151.5 (d, *J* = 3.1 Hz), 148.4 (d, *J* = 20.4 Hz), 144.8 (d, *J* = 18.5 Hz), 141.9, 137.8 (d, *J* = 5.8 Hz), 132.5, 129.6, 126.9 (d, *J* = 11.5 Hz), 124.4 (d, *J* = 138.4 Hz), 120.8, 118.2 (d, *J* = 5.2 Hz), 115.9(q, *J* = 288.0 Hz), 113.0 (d, *J* = 8.1 Hz), 111.1 (d, *J* = 127.1 Hz), 110.3 (d, *J* = 13.3 Hz), 110.3 (d, *J* = 10.9 Hz), 109.1 (d, *J* = 16.7 Hz), 103.4 (d, *J* = 11.5 Hz), 102.2, 101.8, 66.3, 54.4; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -75.9 (s, 3F); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 23.7 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{25}H_{20}F_3N_3O_7P$ $[M+H]^+$ 562.0985, found 562.0987.



3i'

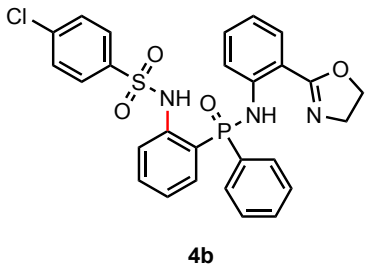
N-(6-(benzo[d][1,3]dioxol-5-yl((2-(4,5-dihydrooxazol-2-yl)phenyl)amino)phosphoryl)benzo[d][1,3]dioxol-5-yl)-2,2,2-trifluoroacetamide (3i'): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.0 (s, 1H), 11.0 (d, *J* = 13.6 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.40 (ddd, *J* = 13.7, 8.0, 1.3 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.28 – 7.19 (m, 2H), 7.08 (dd, *J* = 14.3, 8.0 Hz, 1H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.90 (dd, *J* = 8.0, 2.9 Hz, 1H), 6.70 (dd, *J* = 8.0, 2.1 Hz, 1H), 6.11 (dd, *J* = 11.0, 0.9 Hz, 2H), 6.03 (dd, *J* = 4.3, 1.0 Hz, 2H), 4.38 (t, *J* = 9.5 Hz, 2H), 4.14 – 3.95 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.1, 154.1 (q, *J* = 37.9 Hz), 152.7 (d, *J* = 2.7 Hz), 151.5 (d, *J* = 3.1 Hz), 148.3 (d, *J* = 20.3 Hz), 142.2, 142.0 (d, *J* = 15.3 Hz), 132.3, 129.6, 127.1 (d, *J* = 9.5 Hz), 127.0 (d, *J* = 11.8 Hz), 124.1 (d, *J* = 137.1 Hz), 120.7 (d, *J* = 8.3 Hz), 120.6, 118.4 (d, *J* = 4.9 Hz), 117.6 (d, *J* = 129.2 Hz), 115.8 (q, *J* = 288.4 Hz), 112.8 (d, *J* = 8.1 Hz), 110.5 (d, *J* = 13.6 Hz), 109.0 (d, *J* =

16.8 Hz), 106.6 (d, *J* = 15.4 Hz), 102.5, 101.8, 66.3, 54.4; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -75.4 (s, 3F); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 22.4 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{25}H_{20}F_3N_3O_7P$ $[M+H]^+$ 562.0985, found 562.0988.



4a

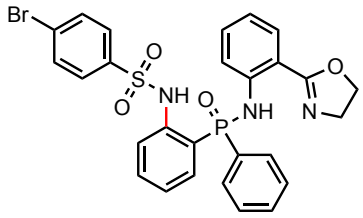
N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-2-(2-nitrophenylsulfonamido)benzamide (4a): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.45 (s, 1H), 11.07 (d, *J* = 13.6 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.84 (dd, *J* = 8.3, 5.2 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.70 (dd, *J* = 12.7, 8.0 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.46 – 7.27 (m, 7H), 7.16 – 7.07 (m, 2H), 6.91 (ddd, *J* = 12.0, 11.0, 4.9 Hz, 2H), 4.36 (t, *J* = 9.4 Hz, 2H), 4.00 (t, *J* = 9.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.9, 143.4 (d, *J* = 5.7 Hz), 142.0, 139.6, 133.6 (d, *J* = 2.2 Hz), 132.7 (d, *J* = 9.2 Hz), 132.6, 132.4 (d, *J* =11.5 Hz), 132.4 (d, *J* =2.7 Hz), 132.2，131.1, 131.0 (d, *J* = 10.6 Hz), 129.4, 129.0, 128.9 (d, *J* = 14.2 Hz), 128.7, 127.3, 126.3, 123.4 (d, *J* = 12.7 Hz), 120.5, 119.8 (d, *J* = 8.9 Hz), 118.0 (d, *J* = 5.3 Hz), 117.0 (d, *J* = 123.0 Hz), 112.8 (d, *J* = 8.0 Hz), 66.2, 54.3; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.3 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{27}H_{25}N_3O_4PS$ $[M+H]^+$ 518.1298, found 518.1298.



4b

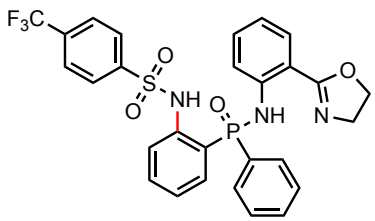
N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-2-(4-nitrophenylsulfonamido)benzamide (4b): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.39 (s, 1H), 10.99 (d, *J* = 13.3 Hz, 1H), 7.87 (dd, *J* = 8.2, 5.3 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.62 (dd, *J* = 12.7, 7.2 Hz, 2H), 7.56 (t, *J* = 7.0 Hz, 1H), 7.48 – 7.38 (m, 3H), 7.34 (dd, *J* = 14.3, 7.7 Hz, 1H), 7.20 – 7.10 (m, 4H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.91 (dd, *J* = 10.3, 4.1 Hz, 1H), 4.36 (t, *J* = 9.1 Hz, 2H), 3.97 (t, *J* = 9.5 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.0, 143.2 (d, *J* = 5.7 Hz), 142.1, 139.0, 138.2, 133.7, 132.8 (d, *J* = 9.1 Hz), 132.5 (d, *J* = 2.8 Hz), 132.3, 131.6 (d, *J* = 131.3 Hz), 131.0 (d, *J* = 10.5 Hz), 129.5, 129.0, 128.8 (d, *J* = 13.4 Hz), 128.7, 123.9 (d, *J* = 12.5

Hz), 129.0 (d, *J* = 9.0 Hz), 120.6, 118.0 (d, *J* = 5.2 Hz), 117.8 (d, *J* = 122.7 Hz), 112.8 (d, *J* = 8.1 Hz), 66.2, 54.3; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.7 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{27}H_{24}ClN_3O_4PS$ $[M+H]^+$552.0908, found 552.0908.



4c

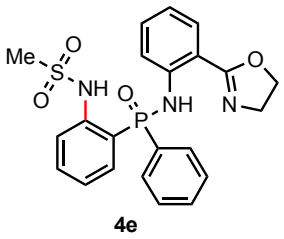
2-(4-bromophenylsulfonamido)-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)benzamide (4c): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.39 (s, 1H), 10.99 (d, *J* = 13.8 Hz, 1H), 7.87 (dd, *J* = 8.1, 4.9 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.70 – 7.53 (m, 5H), 7.47 – 7.38 (m, 3H), 7.38 – 7.30 (m, 3H), 7.19 – 7.10 (m, 2H), 7.04 – 6.96 (m, 1H), 6.91 (ddd, *J* = 8.3, 6.3, 2.1 Hz, 1H), 4.50 – 4.19 (m, 2H), 3.97 (t, *J* = 9.5 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.0, 143.1 (d, *J* = 5.6 Hz), 142.0, 138.7, 133.6, 132.8 (d, *J* = 9.0 Hz), 132.5 (d, *J* = 2.8 Hz), 132.3, 132.0, 131.9, 131.0 (d, *J* = 10.6 Hz), 129.5, 128.9, 128.8, 127.6, 123.9 (d, *J* = 12.5 Hz), 121.0 (d, *J* = 8.8 Hz), 120.6, 118.2, 118.0 (d, *J* = 5.2 Hz), 104.1, 66.2, 54.3; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.3 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{27}H_{24}BrN_3O_4PS$ $[M+H]^+$ 596.0403, found 596.0402.



4d

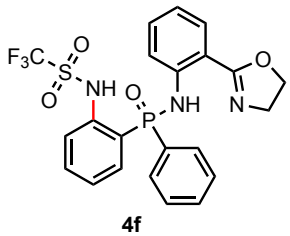
2-(3-(1-benzyl-1H-pyrazol-4-yl)phenylsulfonamido)-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)benzamide (4d): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.57 (s, 1H), 11.05 (d, *J* = 12.5 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.89 (dd, *J* = 8.2, 5.2 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.62 (dd, *J* = 12.8, 7.7 Hz, 2H), 7.55 – 7.32 (m, 7H), 7.13 (q, *J* = 8.4 Hz, 2H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.90 (t, *J* = 7.2 Hz, 1H), 4.35 (t, *J* = 9.5 Hz, 2H), 3.96 (t, *J* = 9.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.9, 143.2, 142.8 (d, *J* = 5.6 Hz), 141.9, 134.0 (d, *J* = 33.0 Hz), 133.7 (d, *J* = 2.2 Hz), 132.8 (d, *J* = 9.0 Hz), 132.6 (d, *J* = 2.8 Hz), 132.2, 132.1, 130.9 (d, *J* = 10.6 Hz), 129.5, 128.7 (d, *J* = 13.3 Hz), 127.7, 125.8 (q, *J* = 3.5 Hz), 124.0 (d, *J* = 12.5 Hz), 123.1 (q, *J* = 271.6 Hz), 120.7, 120.6 (d, *J* = 9.1 Hz), 117. 9 (d, *J* = 5.2 Hz), 117.7 (d, *J* = 121.8 Hz)，112.8 (d, *J* = 8.2 Hz), 66.2, 54.3; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -63.1 (s, 3F); **^{31}P**

NMR (162 MHz, $CDCl_3$) δ 25.1 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{28}H_{24}F_3N_3O_4PS$ $[M+H]^+$ 586.1172, found 586.1174.



4e

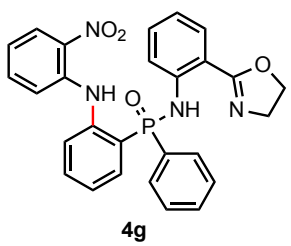
N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-2-(2,2,2-trifluoroacetamido)benzamide (4e): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.23 (d, *J* = 13.8 Hz, 1H), 10.93 (s, 1H), 7.91 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.75 (dd, *J* = 8.3, 5.2 Hz, 1H), 7.60 – 7.42 (m, 5H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.25 – 7.18 (td, *J* = 7.8, 1.6 Hz, 1H), 7.06 (td, *J* = 7.6, 2.4 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 4.38 (t, *J* = 9.4 Hz, 2H), 4.04 (td, *J* = 9.4, 2.9 Hz, 2H), 2.89 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0, 143.3 (d, *J* = 5.8 Hz), 142.0, 133.8 (d, *J* = 2.2 Hz), 132.8 (d, *J* = 8.9 Hz), 132.6 (d, *J* = 2.9 Hz), 132.3, 131.6 (d, *J* = 130.3 Hz), 131.2 (d, *J* = 10.4 Hz), 129.5, 128.9 (d, *J* = 13.3 Hz), 123.5 (d, *J* = 12.5 Hz), 120.7, 119.7 (d, *J* = 8.9 Hz), 118.2 (d, *J* = 5.2 Hz), 117.8 (d, *J* = 122.5 Hz), 112.8 (d, *J* = 8.0 Hz), 66.2, 54.3, 39.7; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.3 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{22}H_{23}N_3O_4PS$ $[M+H]^+$ 456.1141, found 456.1142.



4f

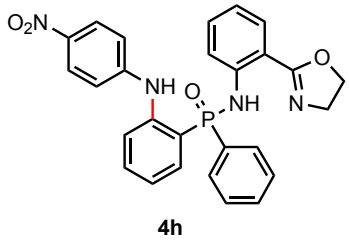
N-(2-((2-(4,5-dihydrooxazol-2-yl)phenyl)carbamoyl)phenyl)-2,3,4,5,6-pentafluorobenzamide (4f): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.54 (brs, 2H), 7.89 (dd, *J* = 12.7, 7.6 Hz, 2H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.78 (dd, *J* = 8.4, 5.2 Hz, 1H), 7.57 (dd, *J* = 10.5, 4.3 Hz, 1H), 7.46 (dt, *J* = 20.5, 7.9 Hz, 4H), 7.26 (t, *J* = 4.1 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 6.8 Hz, 1H), 6.91 (t, *J* = 7.6 Hz, 1H), 4.57 – 4.27 (m, 2H), 4.11 – 3.97 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0, 141.9, 133.8 (d, *J* = 2.2 Hz), 132.8, 132.7 (d, *J* = 4.8 Hz), 132.4 , 131.2 (d, *J* = 10.6 Hz), 131.0 (d, *J* = 131.7 Hz), 129.6, 128.9 (d, *J* = 13.4 Hz), 124.0 (q, *J* = 15.2 Hz), 124.0 (d, *J* = 8.2 Hz), 120.7, 120.0 (d, *J* = 321.8 Hz), 119.8 (d, *J* = 8.2 Hz), 118.0 (d, *J* = 5.3 Hz), 117.9, 112.9 (d, *J* = 8.2 Hz), 66.3, 54.3; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -76.4 (s,

3F); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.0 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{22}H_{20}F_3N_3O_4PS$ $[M+H]^+$ 510.0859, found 510.0860.



4g

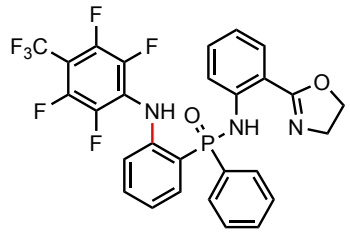
N-(2-((2-(4,5-dihydrooxazol-2-yl)phenyl)carbamoyl)phenyl)-3,5-dinitrobenzamide (4g): yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.20 (d, *J* = 13.6 Hz, 1H), 9.74 (s, 1H), 8.30-8.11 (m, 1H), 8.07 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.92 – 7.78 (m, 2H), 7.67 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.48-7.43 (m, 2H), 7.42 – 7.30 (m, 4H), 7.19 (td, *J* = 8.0, 1.6 Hz, 1H), 7.02 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 1H), 6.86 (td, *J* = 8.0, 1.2 Hz, 1H), 6.68 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 1H), 6.55 (dd, *J* = 8.8, 1.2 Hz, 1H), 4.38-4.25 (m, 2H), 4.05-3.88 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.9, 142.3 (d, *J* = 109.8 Hz), 142.2 (d, *J* = 5.5 Hz), 135.2 (d, *J* = 8.0 Hz), 134.7, 134.3, 133.2 (d, *J* = 2.0 Hz), 132.0 (d, *J* = 130.5 Hz), 132.1, 132.0 (d, *J* = 2.8 Hz), 131.0 (d, *J* = 10.8 Hz), 129.4, 128.7 (d, *J* = 13.3 Hz), 126.6 (d, *J* = 121.9 Hz), 125.9, 125.4 (d, *J* = 8.5 Hz), 125.2 (d, *J* = 12.1 Hz), 119.9, 117.88 (d, *J* = 4.9 Hz), 117.4 (d, *J* = 129.2 Hz), 112.5 (d, *J* = 8.0 Hz), 66.0, 54.3; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.1 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{27}H_{24}N_4O_4P$ $[M+H]^+$ 499.1530, found 499.1531.



4h

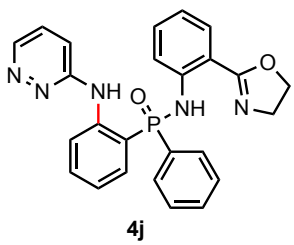
2-chloro-N-(2-((2-(4,5-dihydrooxazol-2-yl)phenyl)carbamoyl)phenyl)-6-nitrobenzamide (4h): yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.14 (d, *J* = 13.4 Hz, 1H), 9.75 (s, 1H), 8.09 (d, *J* = 9.1 Hz, 2H), 7.88 – 7.81 (m, 3H), 7.58 – 7.48 (m, 3H), 7.48 – 7.40 (m, 3H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.22 (dd, *J* = 11.4, 4.3 Hz, 1H), 7.09 (d, *J* = 9.2 Hz, 2H), 6.98 (td, *J* = 7.2, 1.6 Hz, 1H), 6.92 (td, *J* = 7.6, 0.8 Hz, 1H), 4.37 (t, *J* = 9.5 Hz, 2H), 4.03 (t, *J* = 9.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0, 148.7, 145.6 (d, *J* = 6.2 Hz), 142.4, 140.3, 133.3 (d, *J* = 9.1 Hz), 133.3 (d, *J* = 2.2 Hz), 132.4(d, *J* = 2.8 Hz), 132.3, 131.7 (d, *J* = 129.3 Hz), 131.1 (d, *J* = 10.5 Hz), 129.6, 128.8 (d, *J* = 13.2 Hz), 125.9, 122.1 (d, *J* = 12.6 Hz), 120.4, 119.5 (d, *J* = 123.9 Hz), 119.2 (d, *J* = 9.2

Hz), 118.2 (d, J = 5.1 Hz), 115.6, 112.8, 66.2, 54.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.4 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{27}H_{24}N_4O_4P$ $[M+H]^+$ 499.1530, found 499.1530.



4i

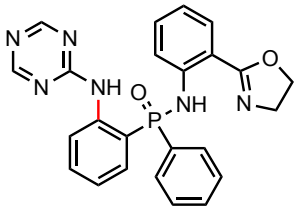
4-chloro-N-(2-((2-(4,5-dihydrooxazol-2-yl)phenyl)carbamoyl)phenyl)picolinamide (4i): red solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.16 (d, J = 13.4 Hz, 1H), 9.63 (s, 1H), 7.90 (dd, J = 12.8, 7.2 Hz, 2H), 7.82 (d, J = 7.9 Hz, 1H), 7.56 (t, J = 7.3 Hz, 1H), 7.53 – 7.42 (m, 3H), 7.39 (d, J = 8.1 Hz, 2H), 7.24 (dd, J = 13.2, 5.9 Hz, 1H), 6.94 (dd, J = 7.6, 2.4 Hz, 2H), 6.83 (dd, J = 8.3, 4.3 Hz, 1H), 4.37 (t, J = 9.4 Hz, 2H), 4.03 (t, J = 9.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0, 145.7 (d, J = 5.7 Hz), 142.5, 133.1 (d, J = 1.9 Hz), 132.7(d, J = 9.1 Hz), 132.4 (d, J = 2.7 Hz), 132.3, 131.6 (d, J = 130.1 Hz), 131.3 (d, J = 10.6 Hz), 129.5, 128.8 (d, J = 13.3 Hz), 121.5 (d, J = 12.8 Hz), 120.3, 118.2 (d, J = 5.2 Hz), 117.0 (d, J = 124.7 Hz), 116.9 (d, J = 9.2 Hz), 112.7 (d, J = 8.0 Hz), 66.2, 54.4; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -55.39 (t, J = 21.2 Hz, 3F), -138.59 – -144.28 (m, 2F), -146.60 (d, J = 15.9 Hz, 2F); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.2 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{28}H_{20}F_7N_3O_2P$ $[M+H]^+$ 594.1176, found 594.1178.



4j

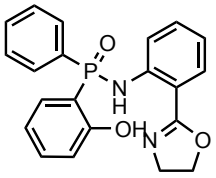
N-(2-((2-(4,5-dihydrooxazol-2-yl)phenyl)carbamoyl)phenyl)isonicotinamide (4j): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.18 (d, J = 13.3 Hz, 1H), 10.85 (s, 1H), 8.94 (dd, J = 8.2, 5.9 Hz, 1H), 8.70 (d, J = 4.2 Hz, 1H), 7.89 (dd, J = 6.8, 1.2 Hz, 2H), 7.82 (d, J = 7.9 Hz, 1H), 7.56 – 7.41 (m, 5H), 7.39 (d, J = 8.3 Hz, 1H), 7.24 (ddd, J = 15.4, 6.4, 1.7 Hz, 2H), 7.02 (d, J = 9.0 Hz, 1H), 6.96 – 6.87 (m, 2H), 4.37 (t, J = 9.4 Hz, 2H), 4.03 (t, J = 9.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0, 157.0, 145.8 (d, J = 5.7 Hz), 145.3, 142.4, 133.7 (d, J = 2.2 Hz), 132.6 (d, J = 9.4 Hz), 132.3, 132.3 (d, J = 129.7 Hz), 132.3 (d, J = 2.8 Hz), 131.1 (d, J = 10.5 Hz), 129.5, 128.8 (d, J = 13.1 Hz), 127.4,

121.1 (d, *J* = 13.0 Hz), 120.4 (d, *J* = 8.5 Hz), 120.3, 118.1 (d, *J* = 5.2 Hz), 117.9, 115.3 (d, *J* = 124.2 Hz), 112.8 (d, *J* = 7.9 Hz), 66.2, 54.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.3 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{25}H_{23}N_5O_2P$ $[M+H]^+$ 456.1584, found 456.1585.



4k

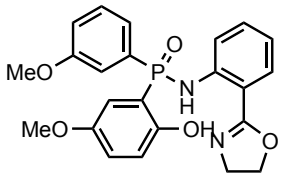
N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-2-((4-nitrophenyl)amino)benzamide (4k): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.45 (s, 1H), 11.18 (d, *J* = 13.6 Hz, 1H), 8.72 (s, 2H), 8.61 (dd, *J* = 8.1, 5.5 Hz, 1H), 7.92 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.58 (ddd, *J* = 14.5, 7.7, 1.4 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.47 – 7.40 (m, 3H), 7.22 (td, *J* = 7.8, 1.6 Hz, 1H), 7.05 (td, *J* = 7.5, 1.4 Hz, 1H), 6.92 (td, *J* = 7.8, 1.2 Hz, 1H), 4.38 (t, *J* = 9.5 Hz, 2H), 4.18 – 3.85 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.1, 165.1, 163.1, 143.2 (d, *J* = 5.3 Hz), 142.4, 133.2 (d, *J* = 2.2 Hz), 132.6 (d, *J* = 8.6 Hz), 132.4, 132.0 (d, *J* = 129.9 Hz), 131.8 (d, *J* = 10.3 Hz), 131.2 (d, *J* = 10.5 Hz), 129.5, 129.1 (d, *J* = 13.3 Hz), 128.8 (d, *J* = 13.2 Hz), 123.1 (d, *J* = 12.5 Hz), 121.7 (d, *J* = 8.6 Hz), 120.5, 118.6 (d, *J* = 121.6 Hz), 118.4 (d, *J* = 5.0 Hz), 112.8 (d, *J* = 7.9 Hz), 66.2, 54.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 23.8 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{24}H_{22}N_6O_2P$ $[M+H]^+$ 457.1536, found 457.1537.



5a

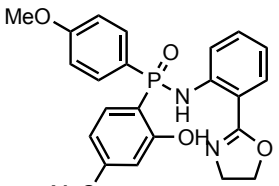
N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-2-((2-nitrophenyl)amino)benzamide (5a): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.33 (s, 1H), 11.28 (d, *J* = 13.5 Hz, 1H), 7.97 (dd, *J* = 12.7, 7.0 Hz, 2H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.55 (dd, *J* = 10.3, 4.3 Hz, 1H), 7.50 (td, *J* = 7.3, 3.4 Hz, 2H), 7.38 – 7.27 (m, 3H), 7.22 (t, *J* = 7.8 Hz, 1H), 6.96 (dd, *J* = 8.2, 5.5 Hz, 1H), 6.91 (t, *J* = 7.3 Hz, 1H), 6.78 (td, *J* = 7.3, 2.4 Hz, 1H), 4.38 (t, *J* = 9.5 Hz, 2H), 4.06 (dd, *J* = 13.9, 6.2 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0, 163.4 (d, *J* = 5.2 Hz), 142.1, 134.5 (d, *J* = 2.2 Hz), 132.4 (d, *J* = 2.8 Hz), 132.4, 132.0 (d, *J* = 131.0 Hz), 131.5 (d, *J* = 9.0 Hz), 131.1 (d, *J* = 10.5 Hz), 129.4, 128.8 (d, *J* = 13.2 Hz), 120.5, 119.5 (d, *J* = 12.8 Hz), 118.1 (d, *J* = 5.3 Hz),

118.0 (d, *J* = 1.4 Hz), 112.9 (d, *J* = 8.0 Hz), 111.6 (d, *J* = 126.9 Hz), 66.2, 54.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.7 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{21}H_{20}N_2O_3P$ $[M+H]^+$ 379.1206, found 379.1207.



5b

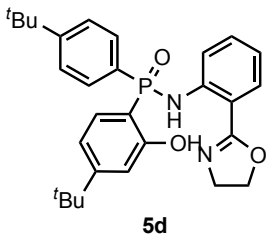
2-((4-cyanophenyl)amino)-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)benzamide (5b): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.22 (d, *J* = 13.4 Hz, 1H), 10.88 (s, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.52 (dd, *J* = 16.2, 8.6 Hz, 2H), 7.40 (td, *J* = 7.8, 4.5 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.23 (td, *J* = 8.0, 1.6 Hz, 1H), 7.08 (dd, *J* = 7.8, 2.4 Hz, 1H), 6.98 – 6.86 (m, 3H), 6.81 (dd, *J* = 15.1, 2.9 Hz, 1H), 4.38 (t, *J* = 9.4 Hz, 2H), 4.22 – 4.01 (m, 2H), 3.84 (s, 3H), 3.63 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.1, 159.7 (d, *J* = 16.5 Hz), 157.4 (d, *J* = 4.7 Hz), 152.2 (d, *J* = 15.8 Hz), 142.0, 133.2 (d, *J* = 131.0 Hz), 132.4, 130.1 (d, *J* = 15.6 Hz), 129.5, 123.2 (d, *J* = 10.2 Hz), 121.2 (d, *J* = 2.4 Hz), 120.6, 118.9 (d, *J* = 11.2 Hz), 118.7 (d, *J* = 3.0 Hz), 118.1 (d, *J* = 5.5 Hz), 115.8 (d, *J* = 11.6 Hz), 115.1 (d, *J* = 10.2 Hz), 112.9 (d, *J* = 8.0 Hz), 111.6 (d, *J* = 126.6 Hz), 66.2, 55.7, 55.4, 54.5; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.7 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{24}N_2O_5P$ $[M+H]^+$ 439.1417, found 439.1418.



5c

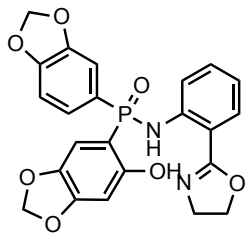
2-((3,5-bis(trifluoromethyl)phenyl)amino)-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)benzamide (5c): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.46 (s, 1H), 11.06 (d, *J* = 13.0 Hz, 1H), 7.86 (dd, *J* = 12.1, 8.7 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.16 (dd, *J* = 13.5, 8.6 Hz, 1H), 6.98 (dd, *J* = 8.7, 2.5 Hz, 2H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.46 (dd, *J* = 4.2, 2.3 Hz, 1H), 6.39 – 6.31 (m, 1H), 4.37 (t, *J* = 9.5 Hz, 2H), 4.07 (t, *J* = 9.5 Hz, 2H), 3.84 (s, 3H), 3.76 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.2 (d, *J* = 6.4 Hz), 165.0, 164.5 (d, *J* = 2.2 Hz), 162.7 (d, *J* = 3.1 Hz), 142.3, 132.9 (d, *J* = 11.8 Hz), 132.6 (d, *J* = 10.3 Hz), 132.3, 129.4, 123.8 (d, *J* = 138.9 Hz), 120.3, 118.0 (d, *J* = 5.8 Hz), 114.3 (d, *J* = 14.4 Hz), 112.8 (d, *J* = 7.5 Hz), 107.9 (d, *J* = 13.6 Hz), 103.6 (d, *J* = 134.4 Hz), 101.5 (d, *J* = 10.0 Hz), 66.1, 55.3, 55.2, 54.5; **^{31}P NMR** (162 MHz,

$CDCl_3$) δ 27.3 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{24}N_2O_5P$ $[M+H]^+$ 439.1417, found 439.1419.



5d

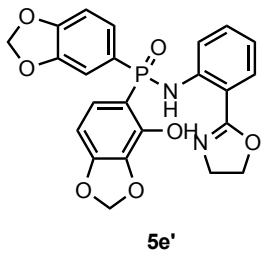
N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)benzamide (5d): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.25 (s, 1H), 11.14 (d, *J* = 13.3 Hz, 1H), 7.89 (dd, *J* = 12.3, 8.4 Hz, 2H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.50 (dd, *J* = 8.4, 3.1 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.21 (dd, *J* = 13.8, 8.2 Hz, 2H), 6.97 (dd, *J* = 5.0, 1.7 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.80 (dt, *J* = 8.2, 2.1 Hz, 1H), 4.39 (t, *J* = 9.5 Hz, 2H), 4.22 – 3.89 (m, 2H), 1.32 (s, 9H), 1.25 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0 (d, *J* = 1.4 Hz), 163.1 (d, *J* = 5.5 Hz), 158.4 (d, *J* = 2.5 Hz), 155.8 (d, *J* = 2.9 Hz), 142.4, 132.4, 131.1 (d, *J* = 9.4 Hz), 130.9 (d, *J* = 10.8 Hz), 129.4 (d, *J* = 0.5 Hz), 129.2 (d, *J* = 133.4 Hz), 125.8 (d, *J* = 13.4 Hz), 120.3, 118.2 (d, *J* = 5.5 Hz), 117.1 (d, *J* = 13.0 Hz), 114.9 (d, *J* = 9.4 Hz), 112.8 (d, *J* = 7.9 Hz), 108.8 (d, *J* = 129.4 Hz), 66.2, 54.5, 35.0 (d, *J* = 1.0 Hz), 35.0 (d, *J* = 0.7 Hz), 31.1, 30.9; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.4 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{29}H_{36}N_2O_3P$ $[M+H]^+$ 491.2458, found 491.2459.



5e

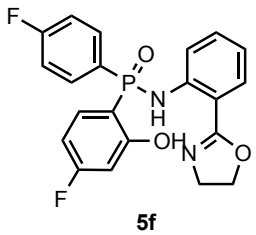
N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-2-(pyridin-3-ylamino)benzamide (5e): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.30 (s, 1H), 11.07 (d, *J* = 13.3 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.49 (dd, *J* = 13.3, 8.0 Hz, 1H), 7.35 (t, *J* = 6.8 Hz, 2H), 7.25 (dd, *J* = 9.4, 6.2 Hz, 1H), 6.92 (td, *J* = 7.8, 3.0 Hz, 2H), 6.61 (d, *J* = 13.4 Hz, 1H), 6.46 (d, *J* = 4.6 Hz, 1H), 6.03 (s, 2H), 5.86 (d, *J* = 5.0 Hz, 2H), 4.39 (t, *J* = 9.4 Hz, 2H), 4.09 (dd, *J* = 14.0, 5.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.1, 160.7 (d, *J* = 6.1 Hz), 152.8 (d, *J* = 2.7 Hz), 151.2 (d, *J* = 3.1 Hz), 148.2 (d, *J* = 20.1 Hz), 142.1, 141.0 (d, *J* = 19.1 Hz), 132.4, 129.5, 126.7 (d, *J* = 11.5 Hz), 125.4 (d, *J* = 138.0 Hz), 120.5, 118.1 (d, *J* = 5.5 Hz), 112.9 (d, *J* = 8.0 Hz), 110.4 (d, *J* = 13.3 Hz), 109.0 (d, *J* = 16.6 Hz), 108.1 (d, *J* = 11.6 Hz), 102.3, 101.6 (d,

J = 29.6 Hz), 100.9, 99.5 (d, *J* = 11.9 Hz), 66.5, 54.5; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.3 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{20}N_2O_7P$ $[M+H]^+$ 467.1003, found 467.1003.



5e'

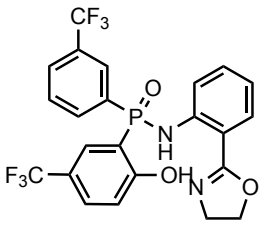
N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-2-((5-(trifluoromethyl)pyridin-2-yl)amino)benzamide (5e'): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.38 (s, 1H), 11.15 (s, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.50 (dd, *J* = 12.8, 7.4 Hz, 1H), 7.34 (dd, *J* = 16.6, 10.4 Hz, 2H), 7.25 (dd, *J* = 11.0, 5.1 Hz, 1H), 6.92 (dd, *J* = 10.8, 5.6 Hz, 2H), 6.85 (ddd, *J* = 14.4, 8.2, 2.7 Hz, 1H), 6.37 (dt, *J* = 8.2, 2.6 Hz, 1H), 6.03 (d, *J* = 2.5 Hz, 2H), 6.01 (dd, *J* = 14.1, 1.9 Hz, 2H), 4.39 (dd, *J* = 9.5, 7.3 Hz, 2H), 4.10 (dd, *J* = 14.3, 5.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.1 (d, *J* = 1.6 Hz), 152.5 (d, *J* = 2.8 Hz), 151.2 (d, *J* = 3.1 Hz), 148.2 (d, *J* = 20.1 Hz), 147.6 (d, *J* = 7.6 Hz), 142.1, 134.7 (d, *J* = 16.6 Hz), 132.4, 129.5, 126.8 (d, *J* = 11.6 Hz), 126.0 (d, *J* = 10.0 Hz), 125.4 (d, *J* = 137.4 Hz), 120.6, 118.2 (d, *J* = 5.4 Hz), 112.9 (d, *J* = 8.0 Hz), 110.5 (d, *J* = 13.4 Hz), 108.9 (d, *J* = 16.7 Hz), 107.5 (d, *J* = 132.2 Hz), 101.9, 101.7 (d, *J* = 12.8 Hz), 101.7, 66.2, 54.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.4 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{20}N_2O_7P$ $[M+H]^+$ 467.1003, found 467.1003.



5f

N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-2-(pyridazin-3-ylamino)benzamide (5f): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.54 (s, 1H), 11.29 (d, *J* = 13.0 Hz, 1H), 8.03 – 7.91 (m, 2H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.32 – 7.14 (m, 5H), 6.94 (ddd, *J* = 8.2, 6.8, 1.7 Hz, 1H), 6.66 (ddd, *J* = 10.7, 4.3, 2.4 Hz, 1H), 6.51 (tt, *J* = 8.4, 2.2 Hz, 1H), 4.39 (t, *J* = 9.5 Hz, 2H), 4.20 – 3.97 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3 (dd, *J* = 133.0, 3.3 Hz), 165.6 (d, *J* = 6.8 Hz), 165.5, 165.1 (d, *J* = 1.5 Hz), 164.8 (dd, *J* = 130.8, 3.5 Hz), 141.7, 133.7 (dd, *J* = 12.0, 9.0 Hz), 133.3 (d, *J* = 21.2 Hz), 133.3, 132.4, 129.6 (d, *J* = 0.5 Hz), 127.9 (dd, *J* = 136.4, 3.4 Hz), 120.9, 117.9 (d, *J* = 5.5 Hz), 116.3 (dd, *J* = 21.5, 14.5 Hz), 112.9 (d, *J* = 8.1

Hz), 108.3 (dd, *J* = 130.9, 3.0 Hz), 107.8 (dd, *J* = 22.3, 13.9 Hz), 105.1 (dd, *J* = 23.6, 10.4 Hz), 66.2, 54.3; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -103.38 (dd, *J* = 18.0, 7.5 Hz, 1F), -105.17 – -105.89 (m, 1F); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.4 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{21}H_{18}F_2N_2O_3P$ $[M+H]^+$ 415.1018, found 415.1017.



5g

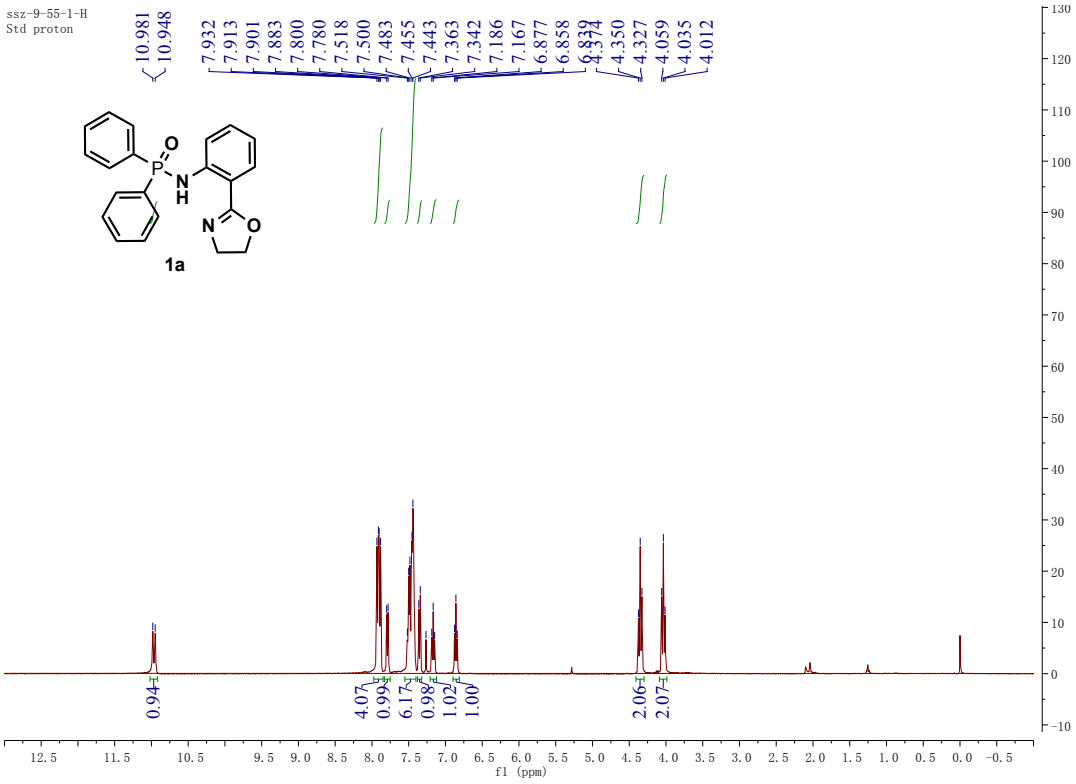
2-((1,3,5-triazin-2-yl)amino)-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)benzamide (5g): white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.69 (s, 2H), 8.34 (d, *J* = 12.9 Hz, 1H), 8.08 (dd, *J* = 12.6, 7.5 Hz, 1H), 7.85 (d, *J* = 7.4 Hz, 2H), 7.67 (td, *J* = 7.6, 2.8 Hz, 1H), 7.59 (t, *J* = 10.9 Hz, 2H), 7.31 – 7.18 (m, 2H), 7.06 (dd, *J* = 8.8, 5.2 Hz, 1H), 6.99 (t, *J* = 7.3 Hz, 1H), 4.46 (t, *J* = 9.5 Hz, 2H), 4.21 – 3.98 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.6 (d, *J* = 5.2 Hz), 164.8, 140.7, 134.1 (d, *J* = 11.0 Hz), 132.4 (d, *J* = 132.7 Hz), 132.1, 131.2 (d, *J* = 3.2 Hz), 129.3, 129.2 (d, *J* = 13.1 Hz), 129.0, 129.0 (d, *J* = 6.5 Hz), 128.3 (dq, *J* = 10.1, 3.9 Hz), 127.52 (dq, *J* = 11.6, 3.5 Hz), 121.0, 118.5 (d, *J* = 9.1 Hz), 117.6 (d, *J* = 5.2 Hz), 112.9 (d, *J* = 8.2 Hz), 111.2 (d, *J* = 128.3 Hz), 66.0, 53.6; **^{19}F NMR** (375 MHz, $CDCl_3$) δ -61.9 (s, 3F), -62.9 (s, 3F); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.6 (s, 1P). **HRMS** (ESI-TOF) m/z Calcd for $C_{23}H_{18}F_6N_2O_3P$ $[M+H]^+$ 515.0954, found 515.0955.

4. Reference

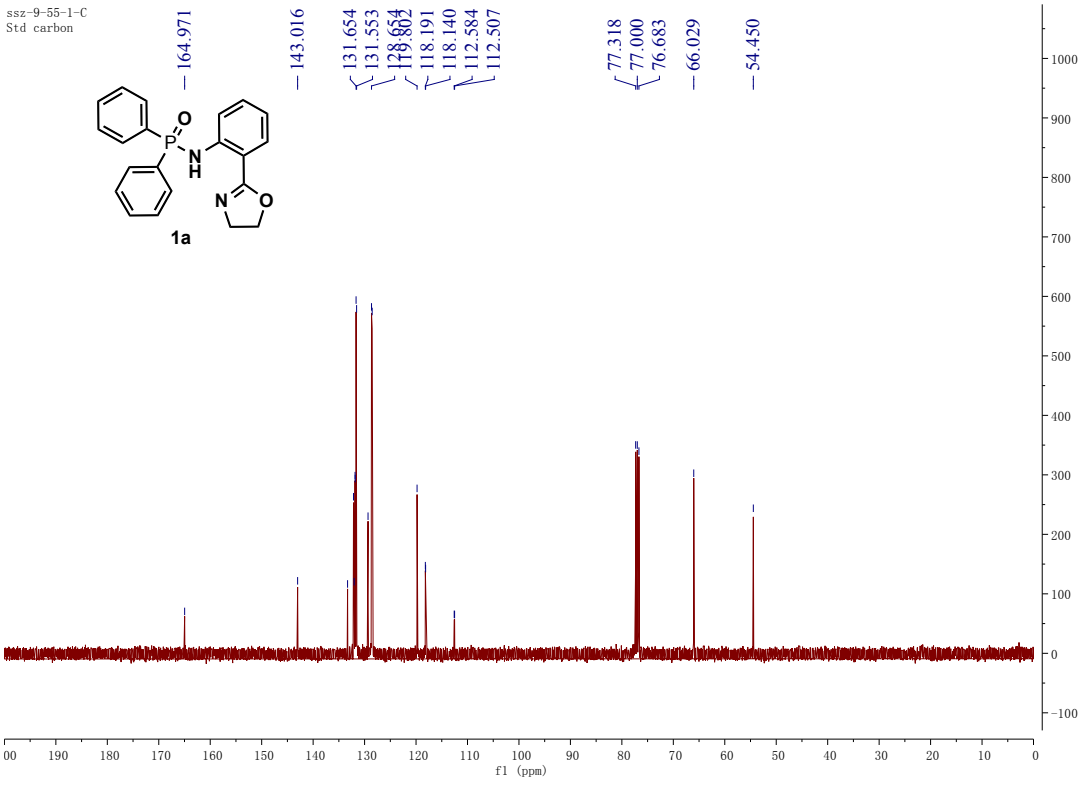
1. Guan, J.; Wu, G.-J.; Han, F.-S. *Chem. Eur. J.* **2014**, *20*, 3301.

5. NMR Spectra for New Compounds

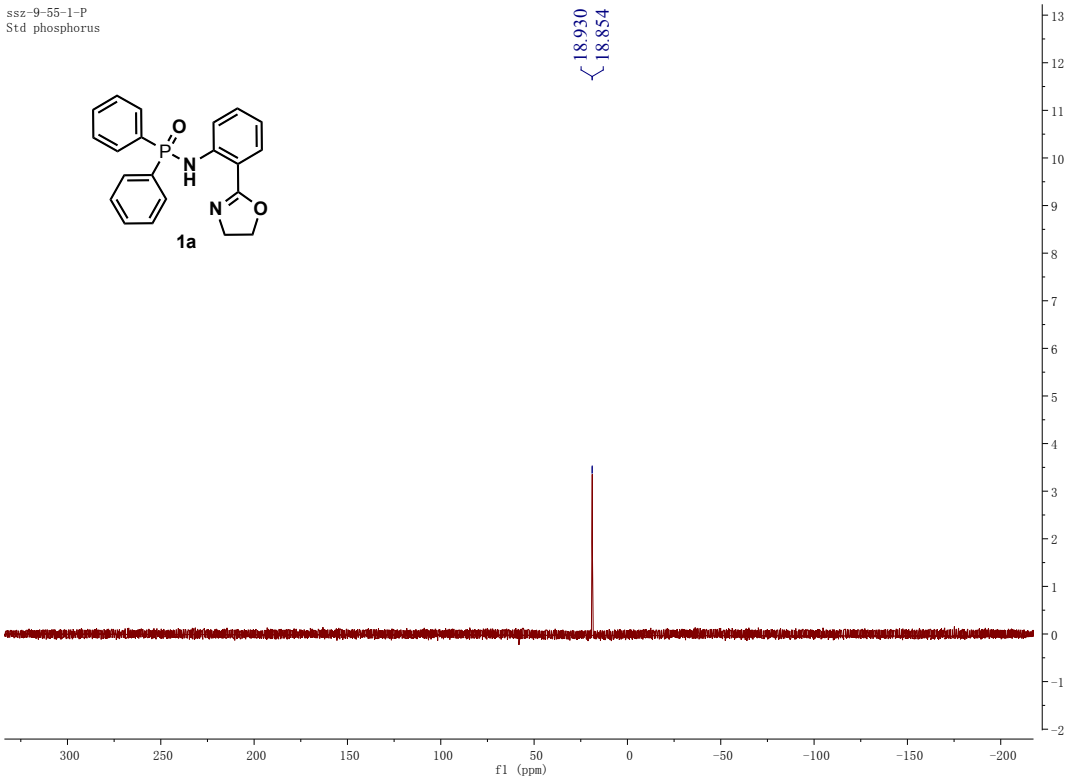
^{1}H NMR for Compound 1a



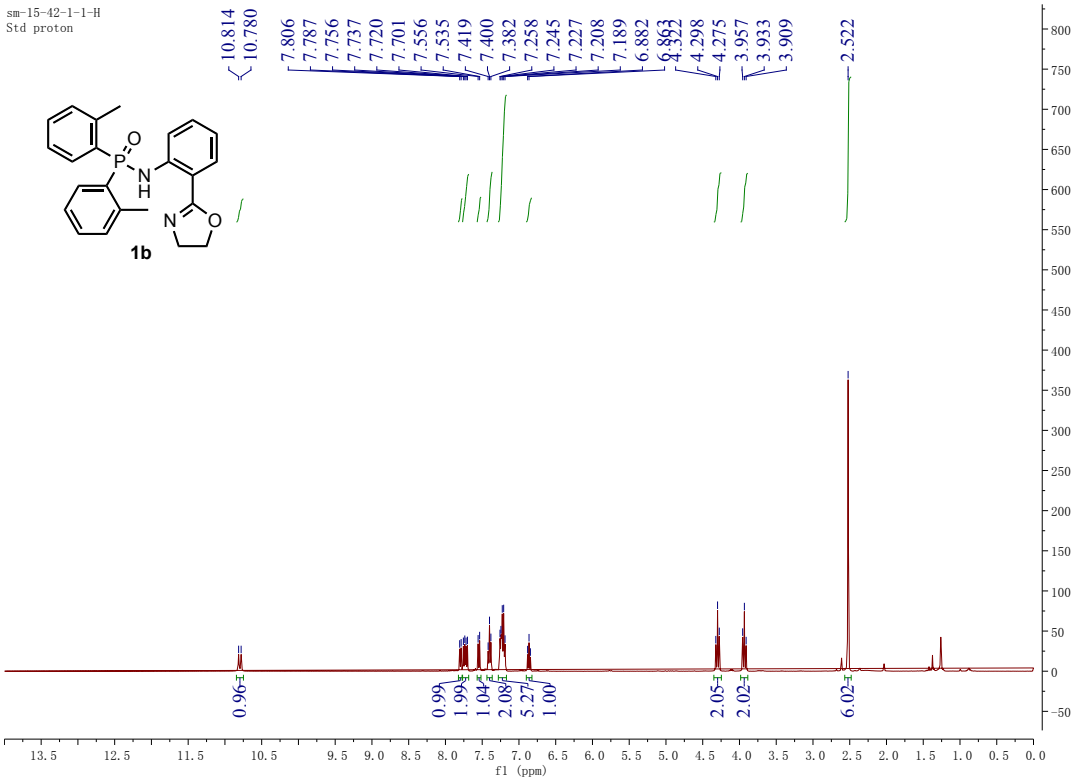
^{13}C NMR for Compound 1a



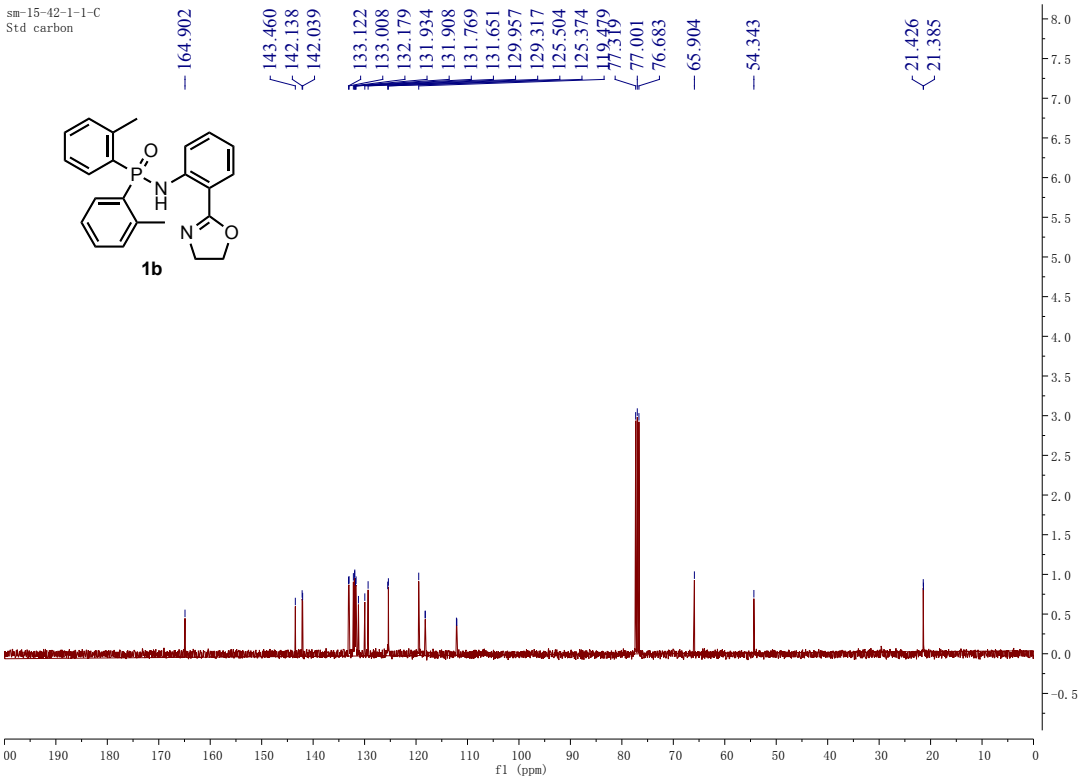
^{31}P NMR for Compound 1a



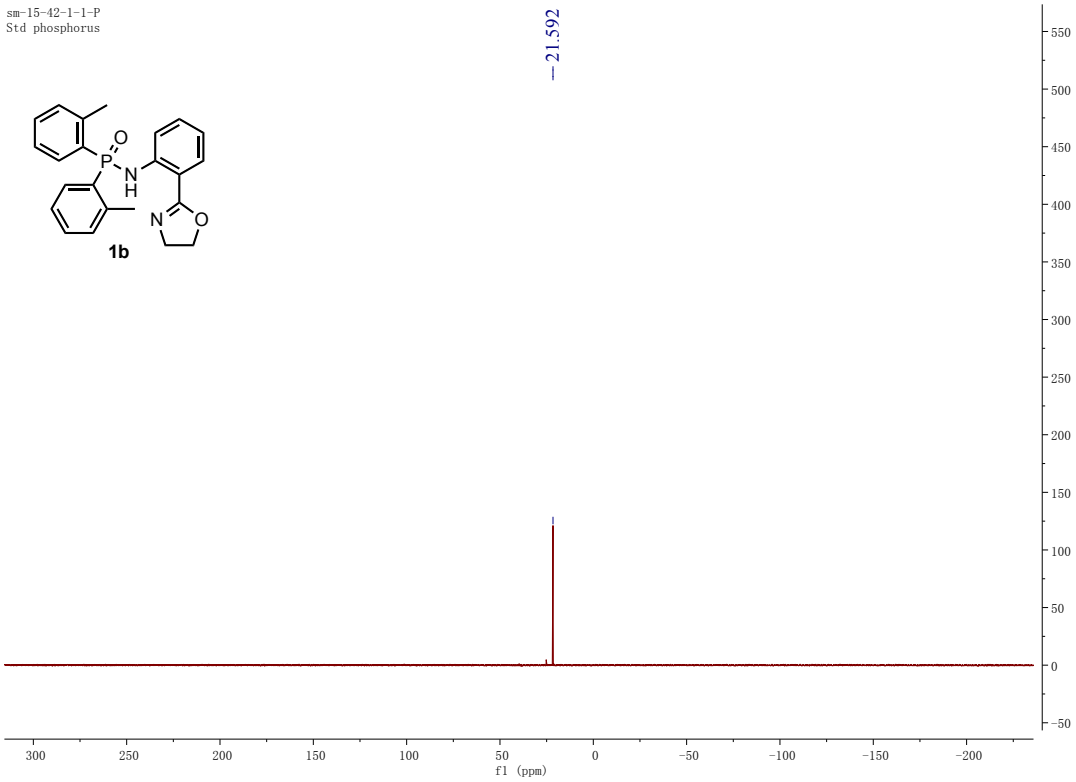
^{1}H NMR for Compound 1b



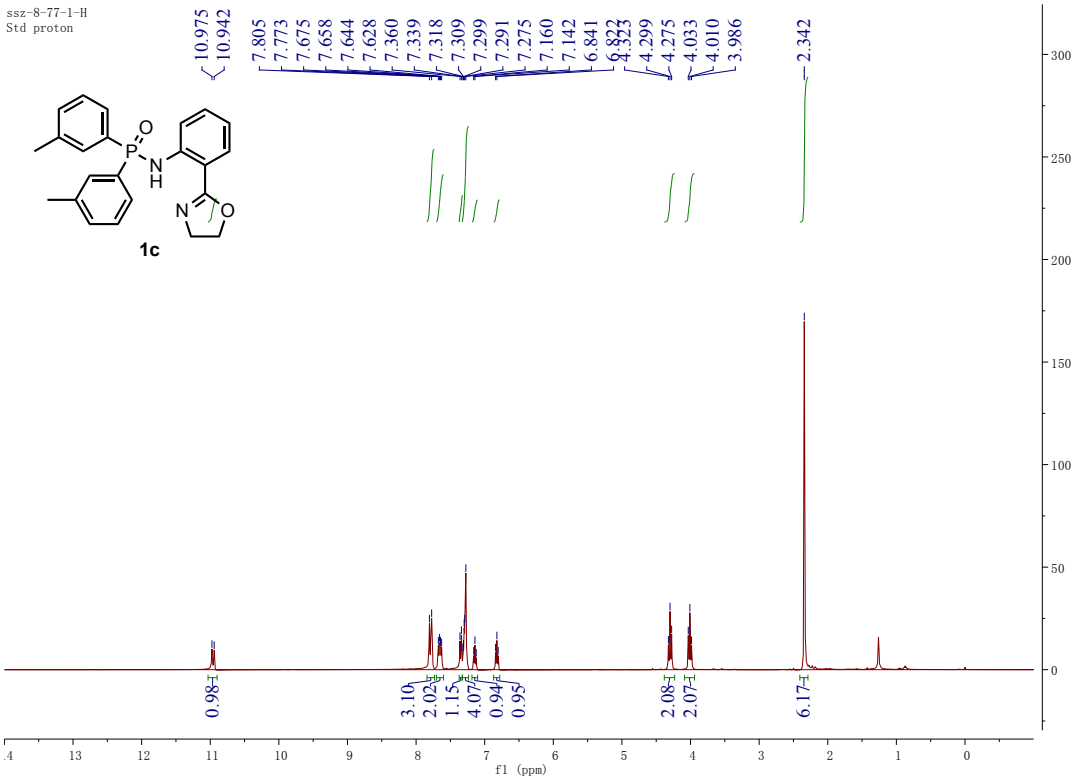
^{13}C NMR for Compound 1b



^{31}P NMR for Compound 1b



^{1}H NMR for Compound 1c



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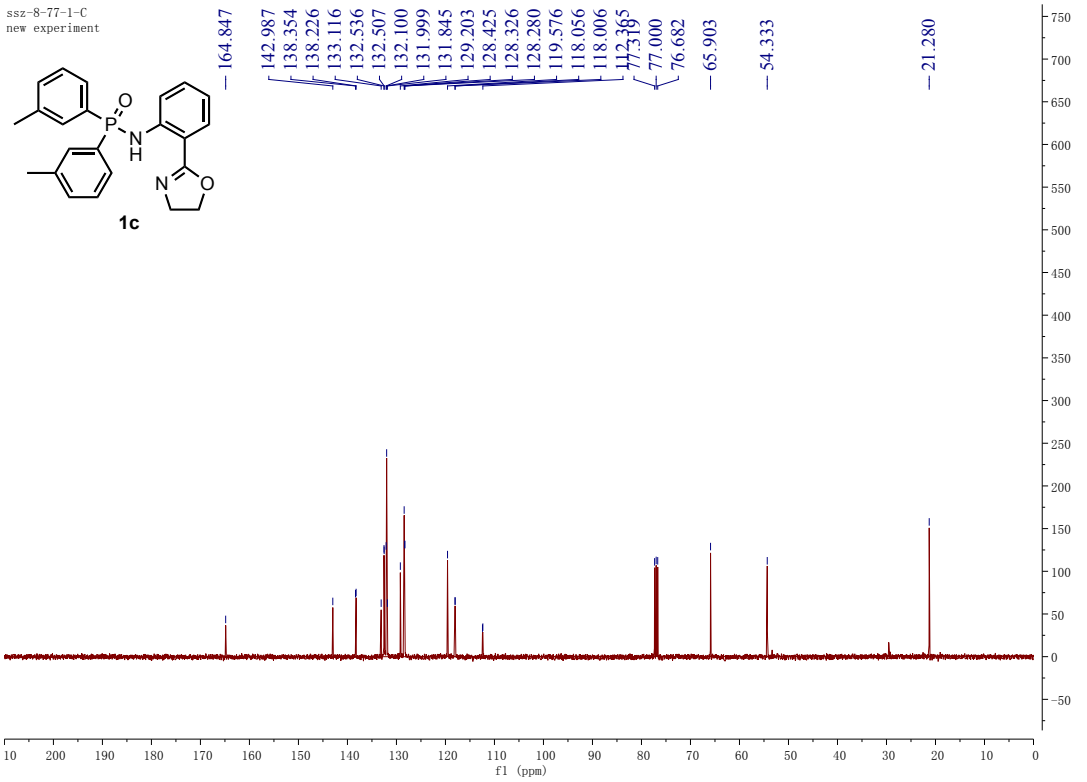

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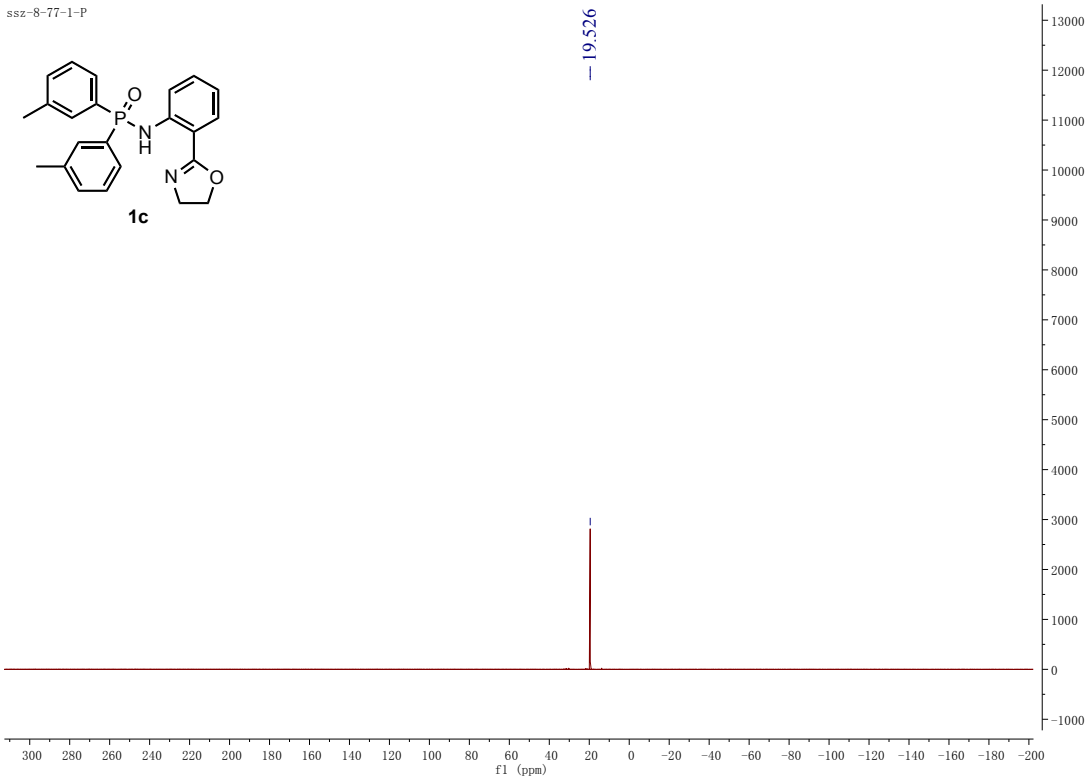
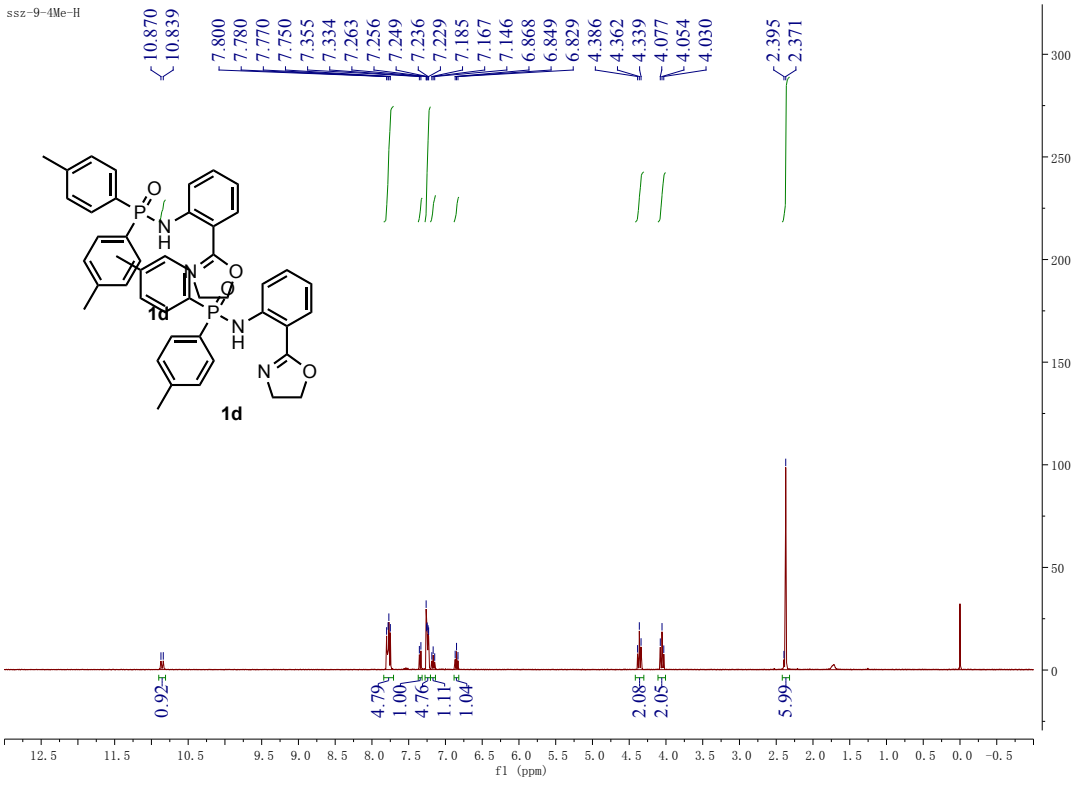
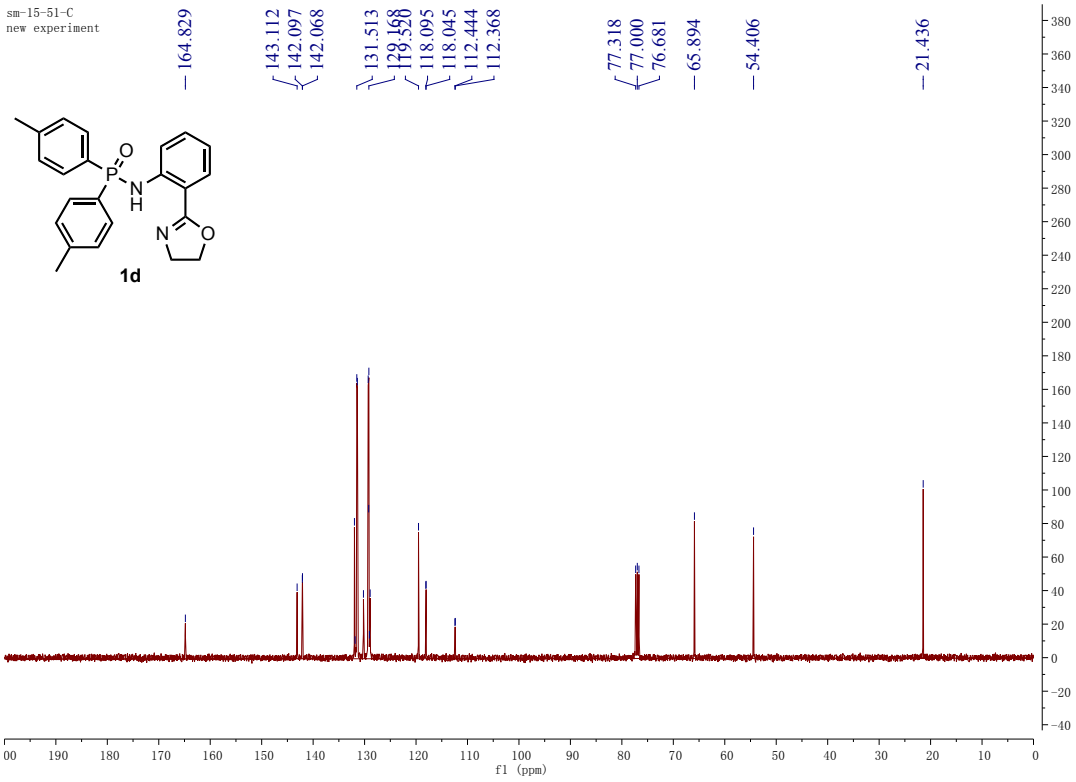


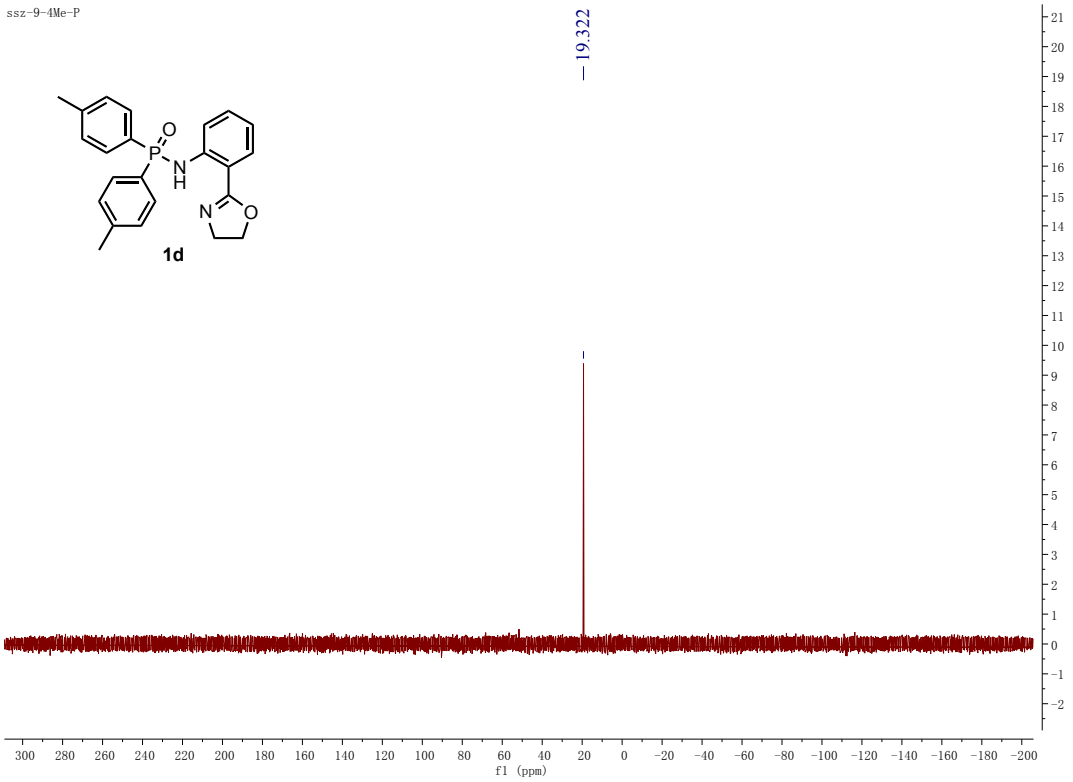
^{1}H NMR for Compound 1d



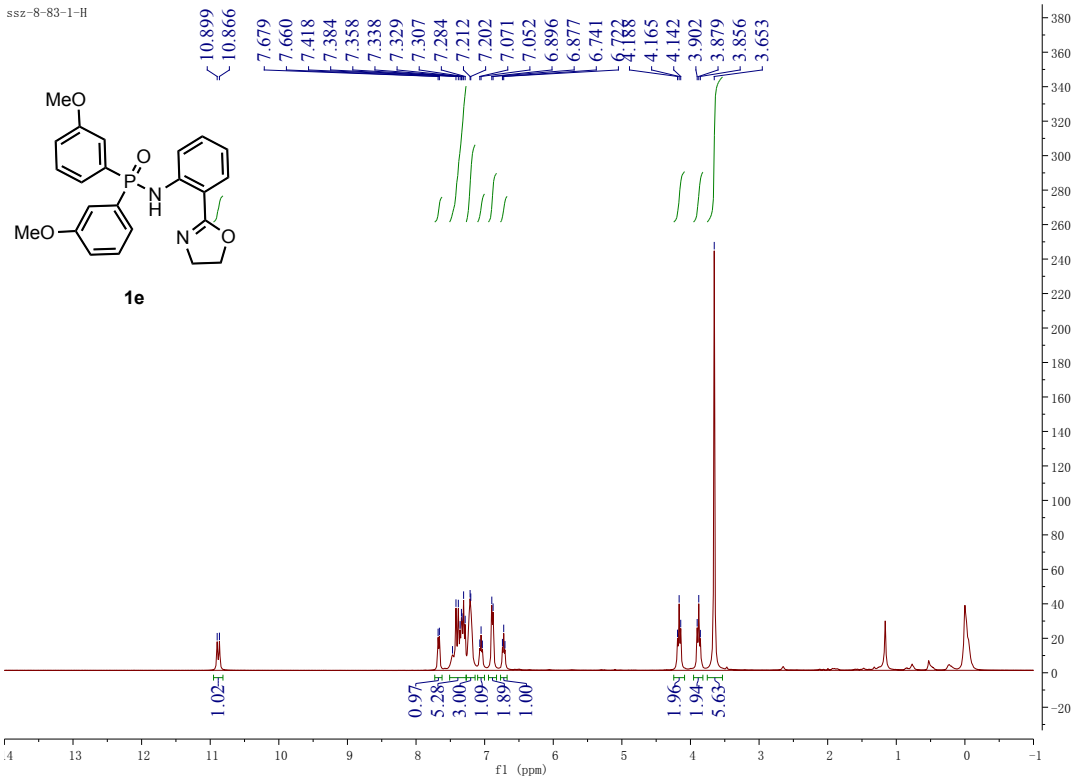
^{13}C NMR for Compound 1d



^{31}P NMR for Compound 1d



^{1}H NMR for Compound 1e



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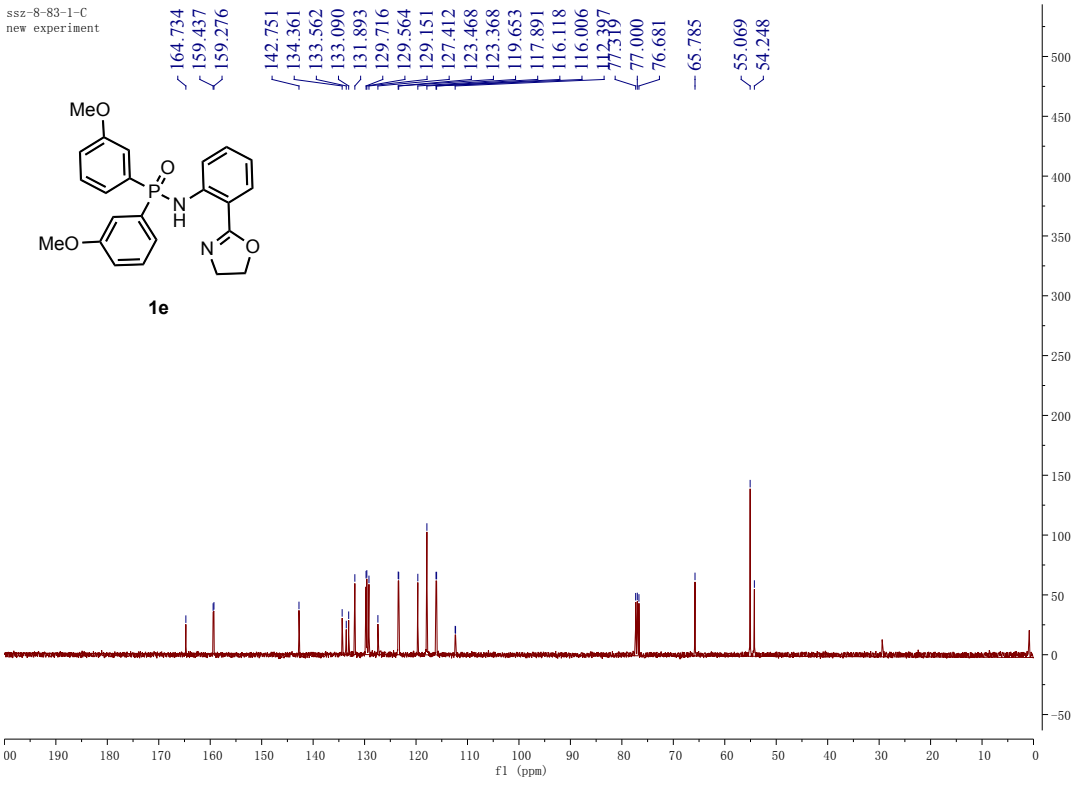
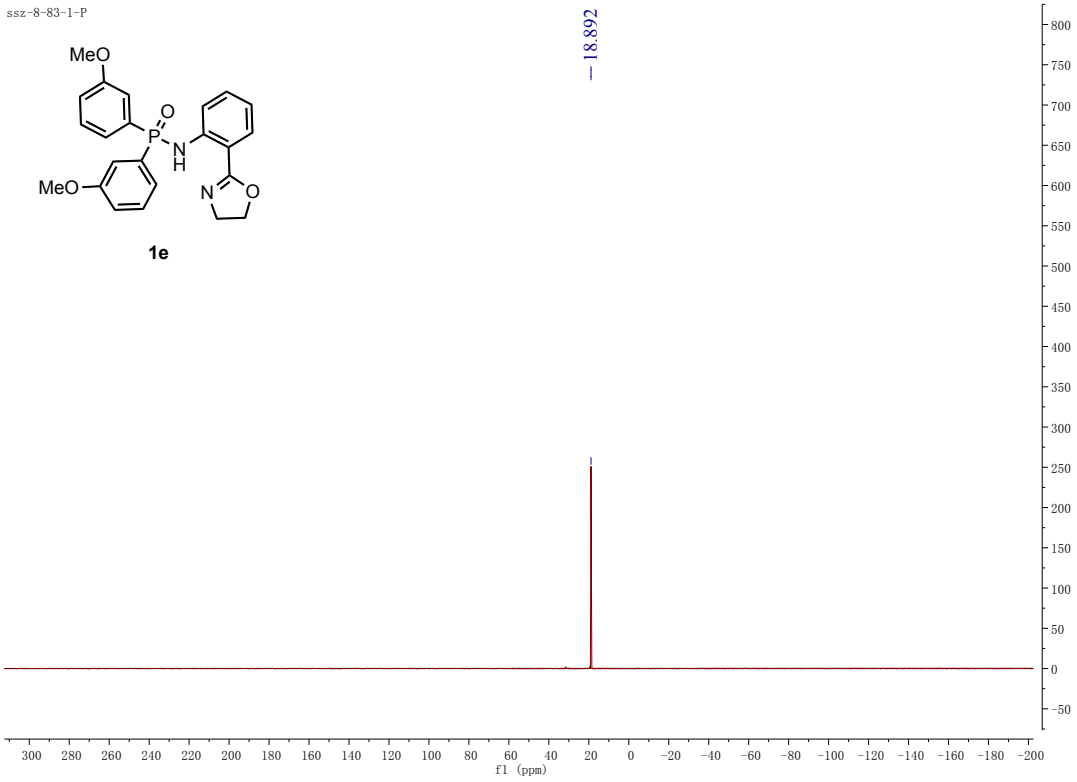


^{31}P NMR for Compound 1e



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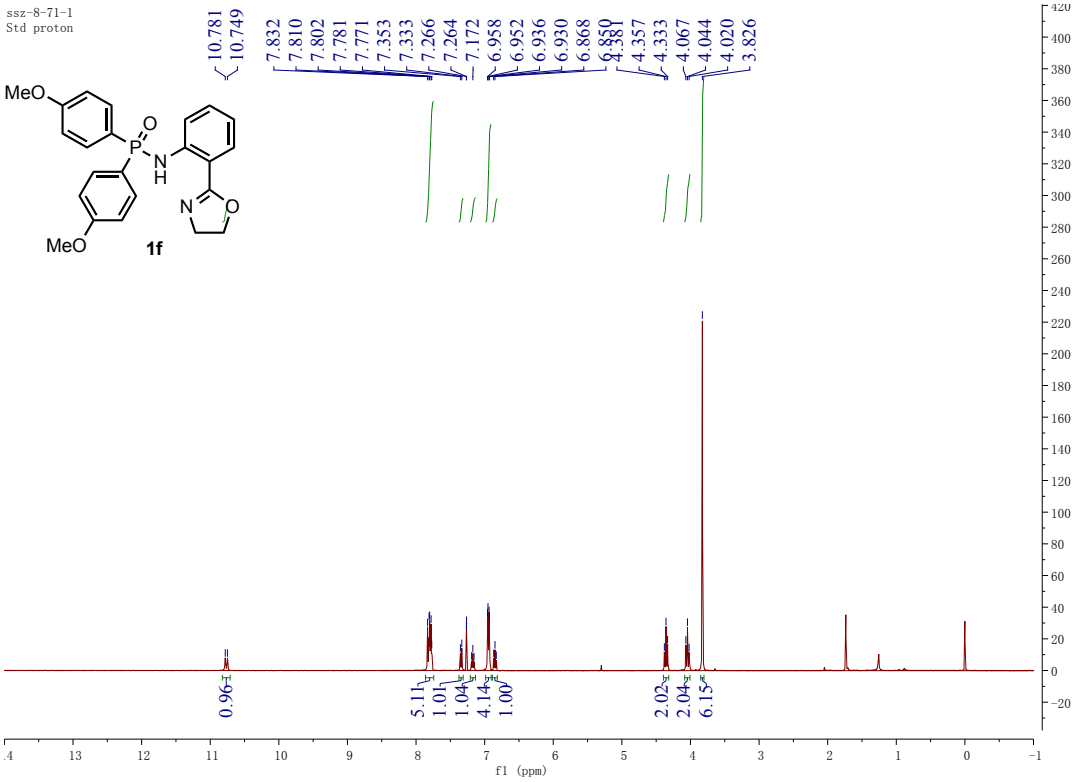

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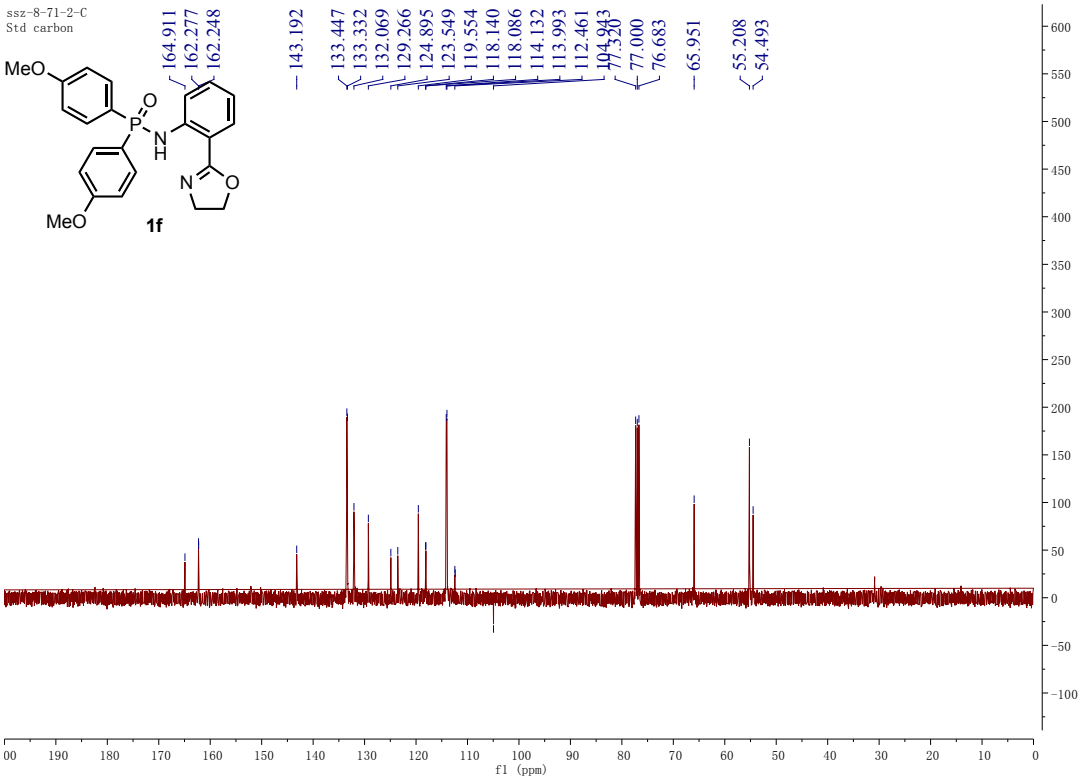
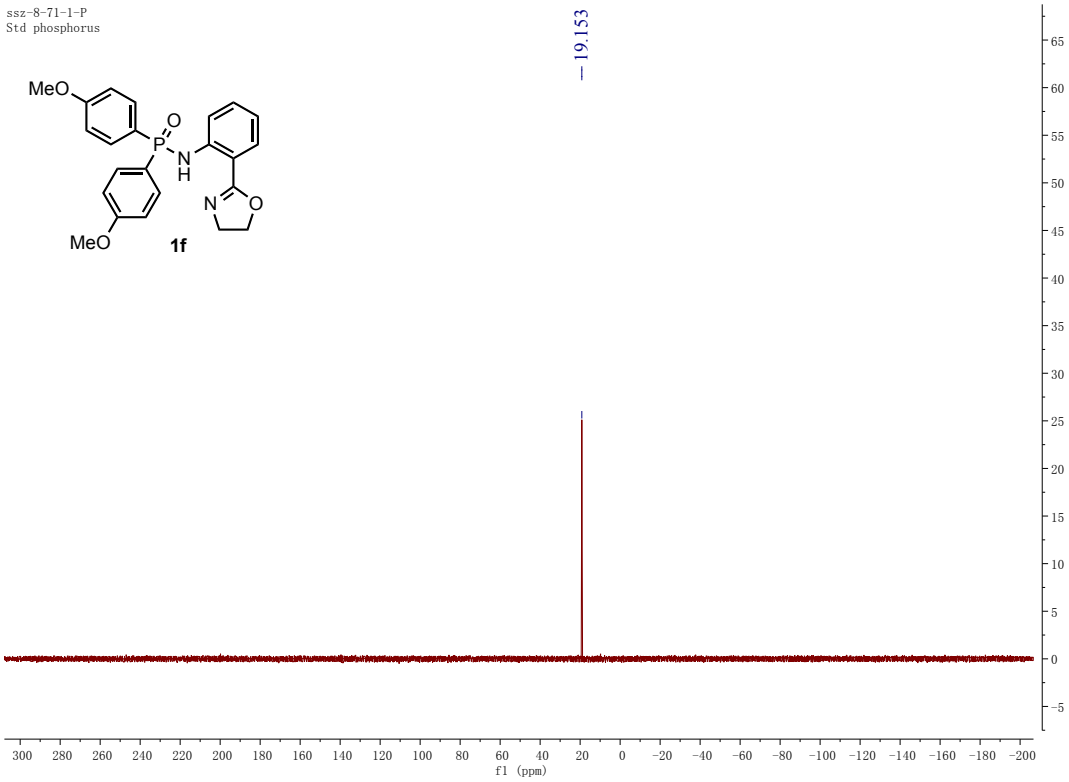
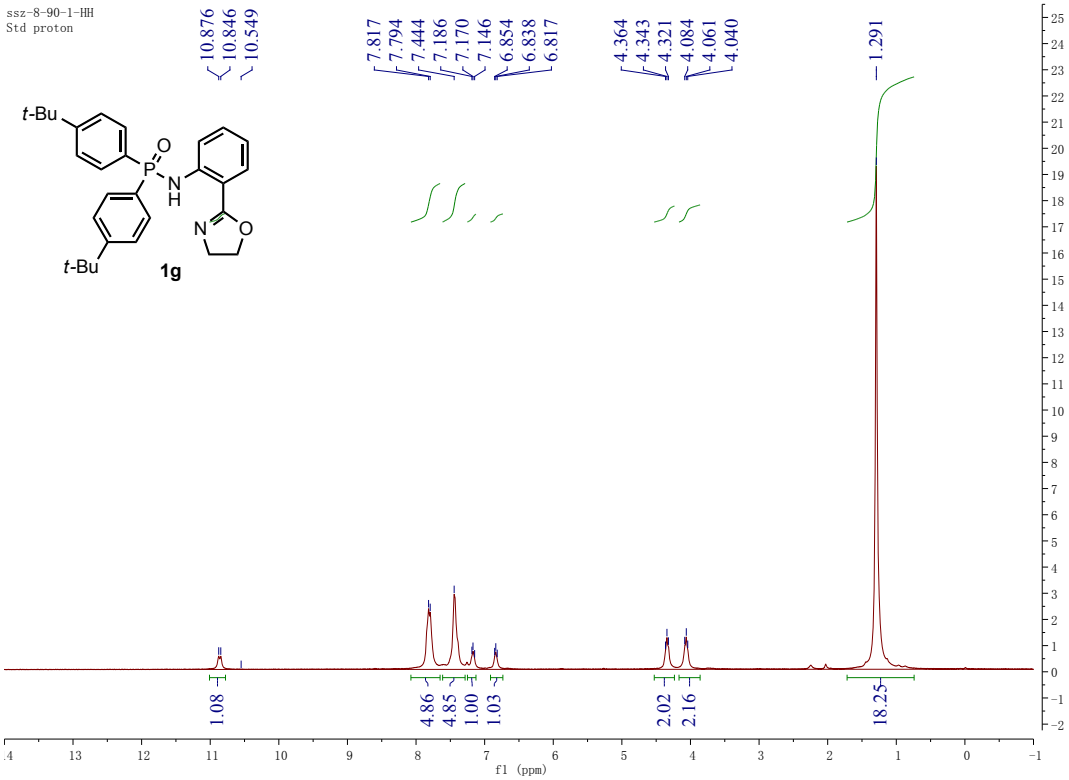


^{31}P NMR for Compound 1f



^{1}H NMR for Compound 1g



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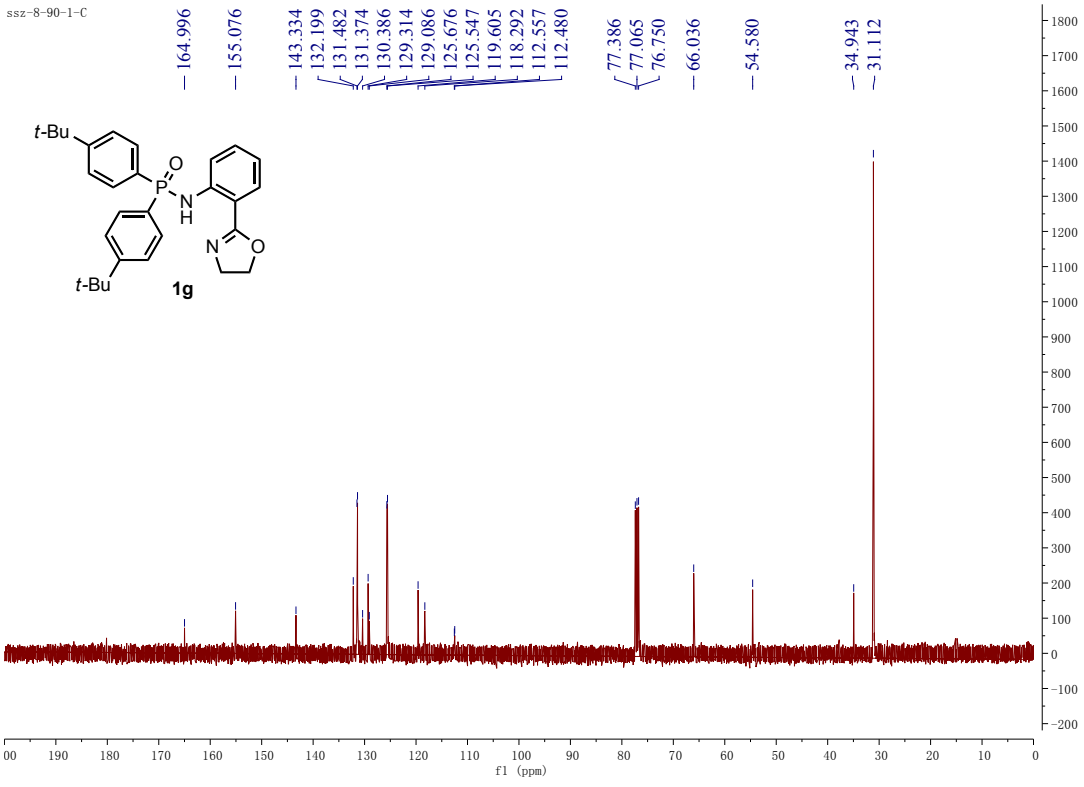

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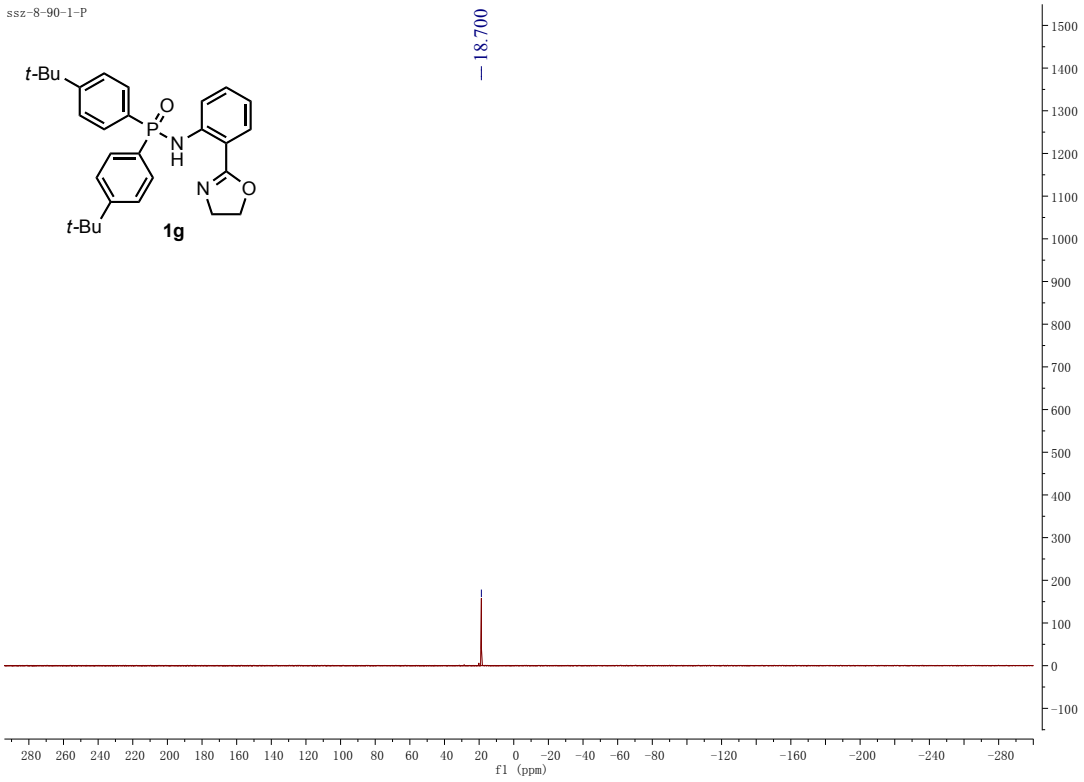
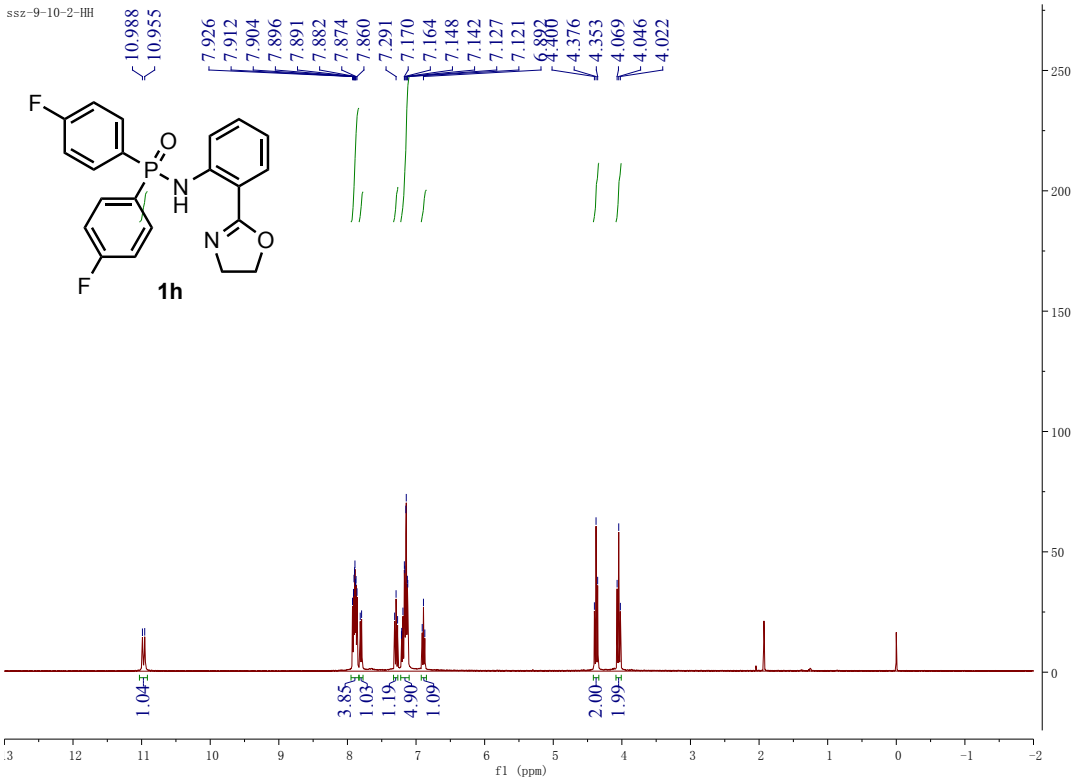
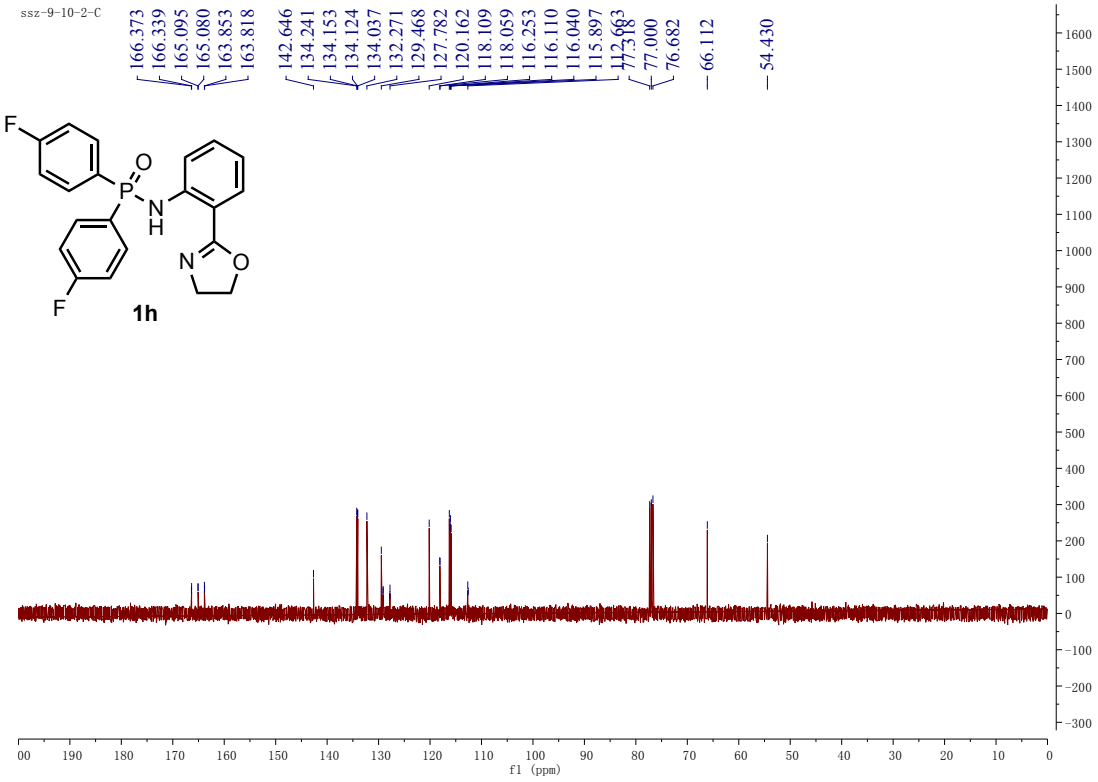


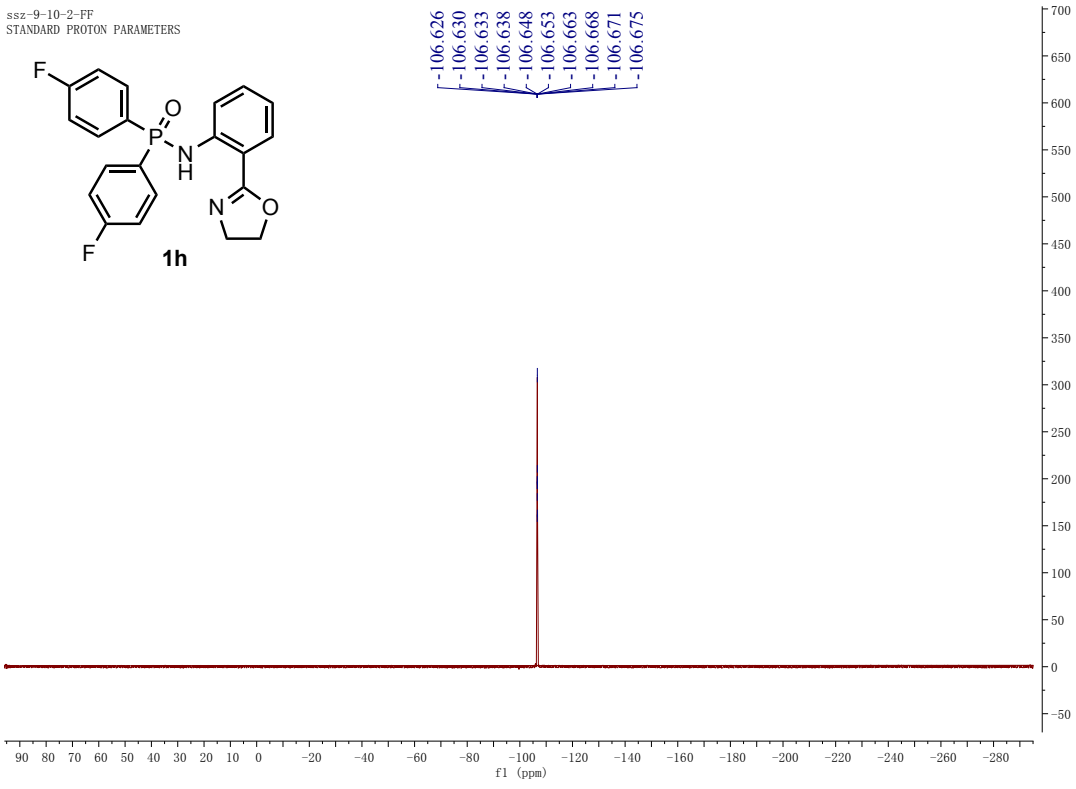
^{1}H NMR for Compound 1h



^{13}C NMR for Compound 1h



^{19}F NMR for Compound 1h



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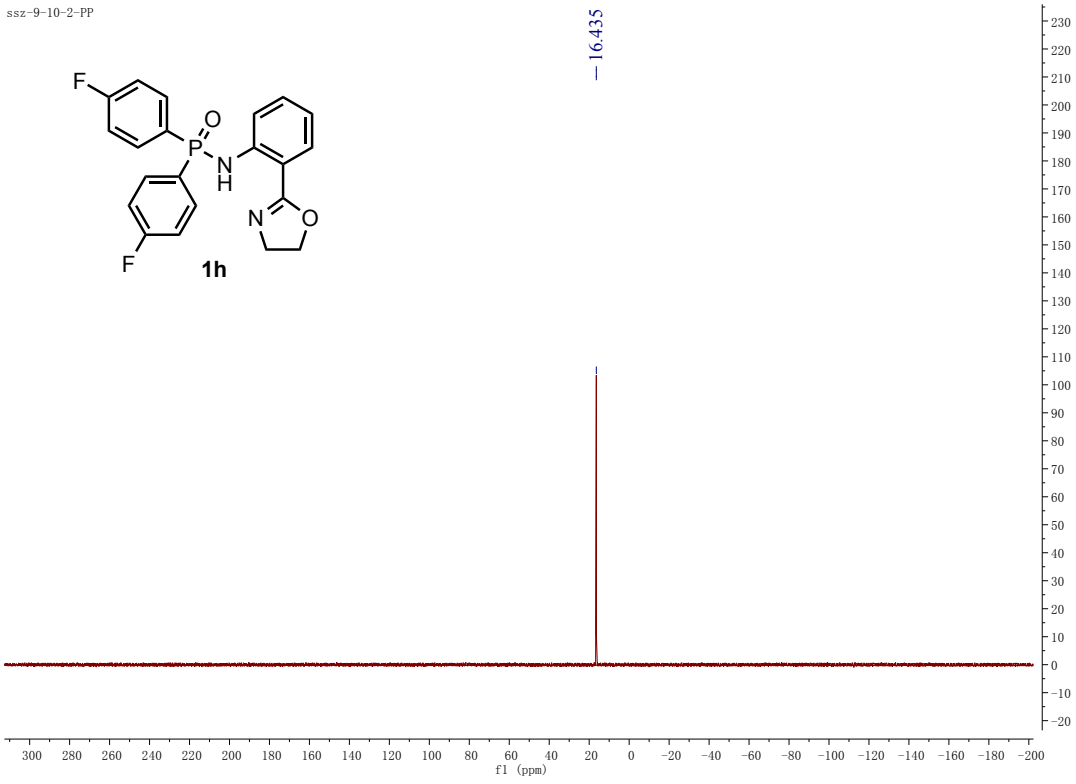
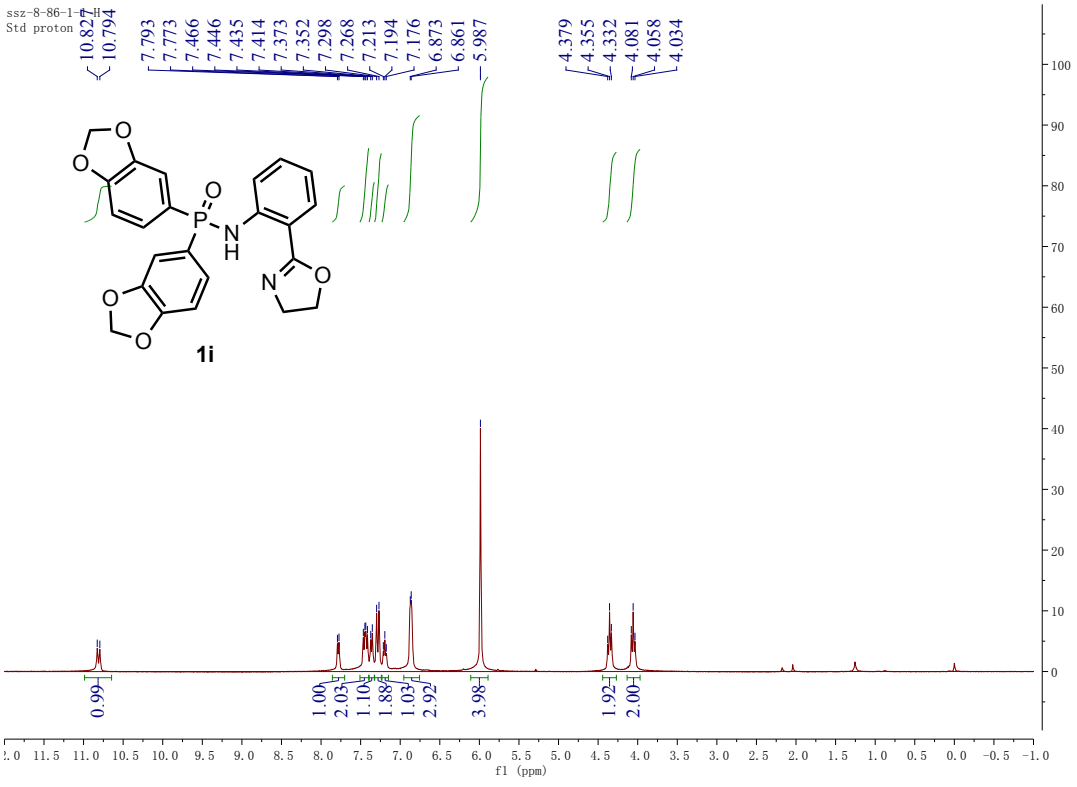


^{1}H NMR for Compound 1i



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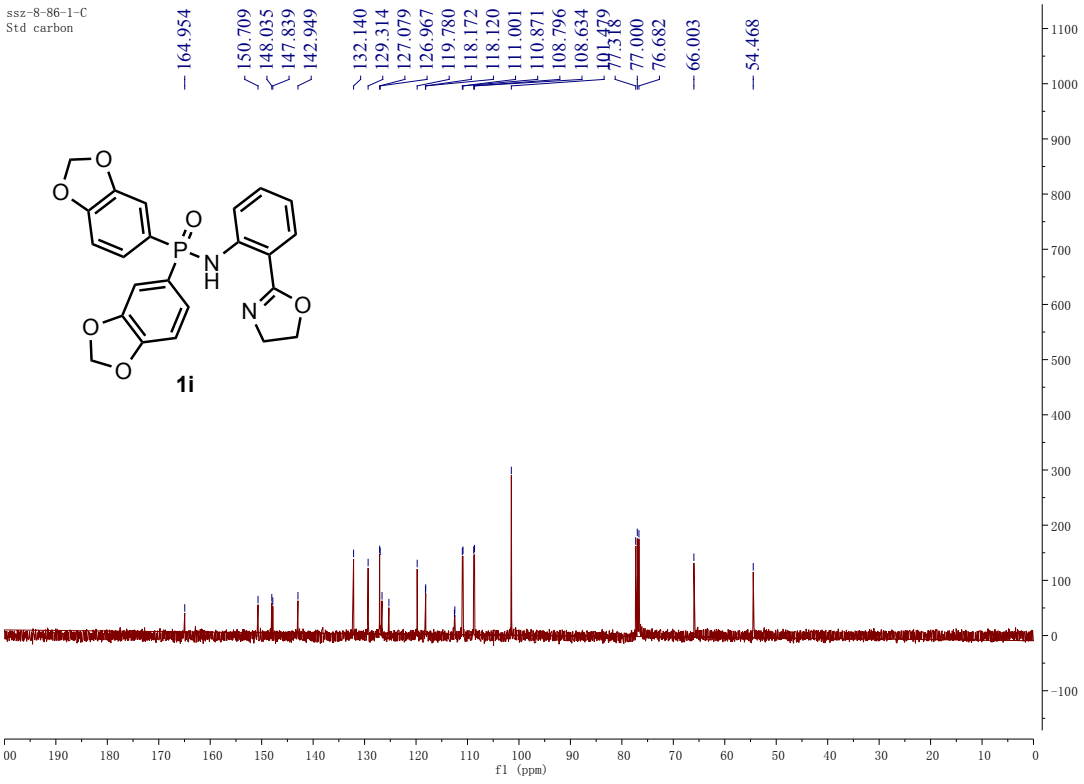

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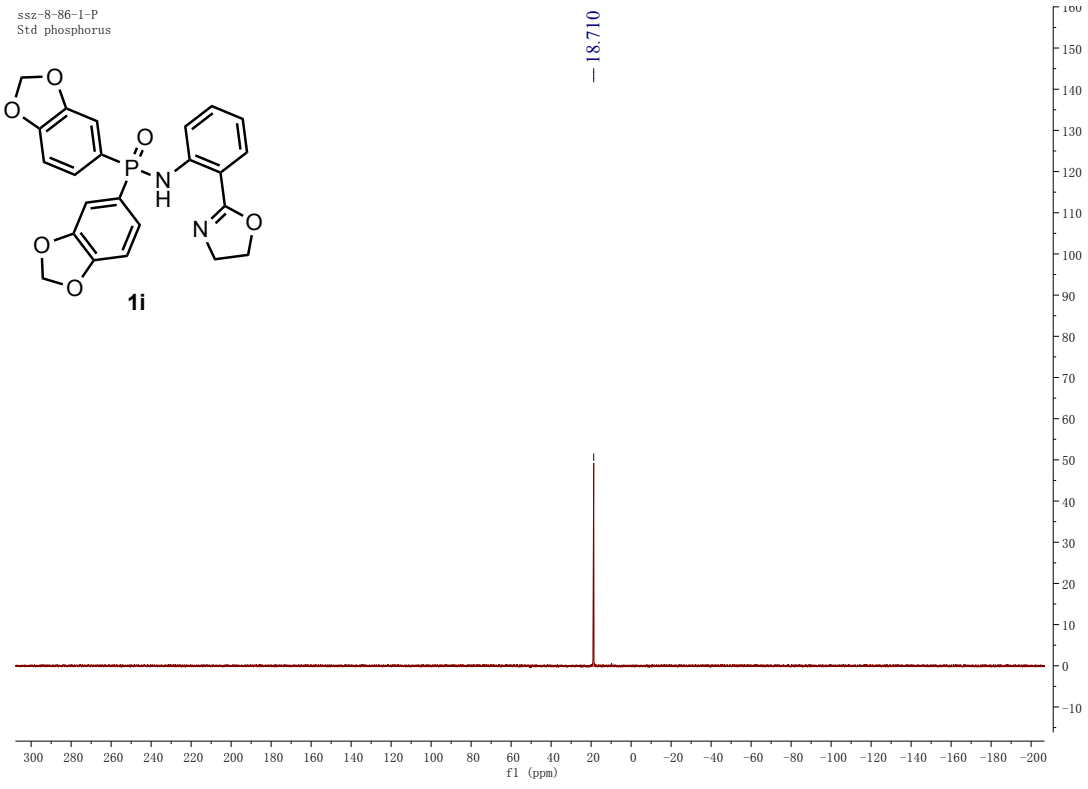

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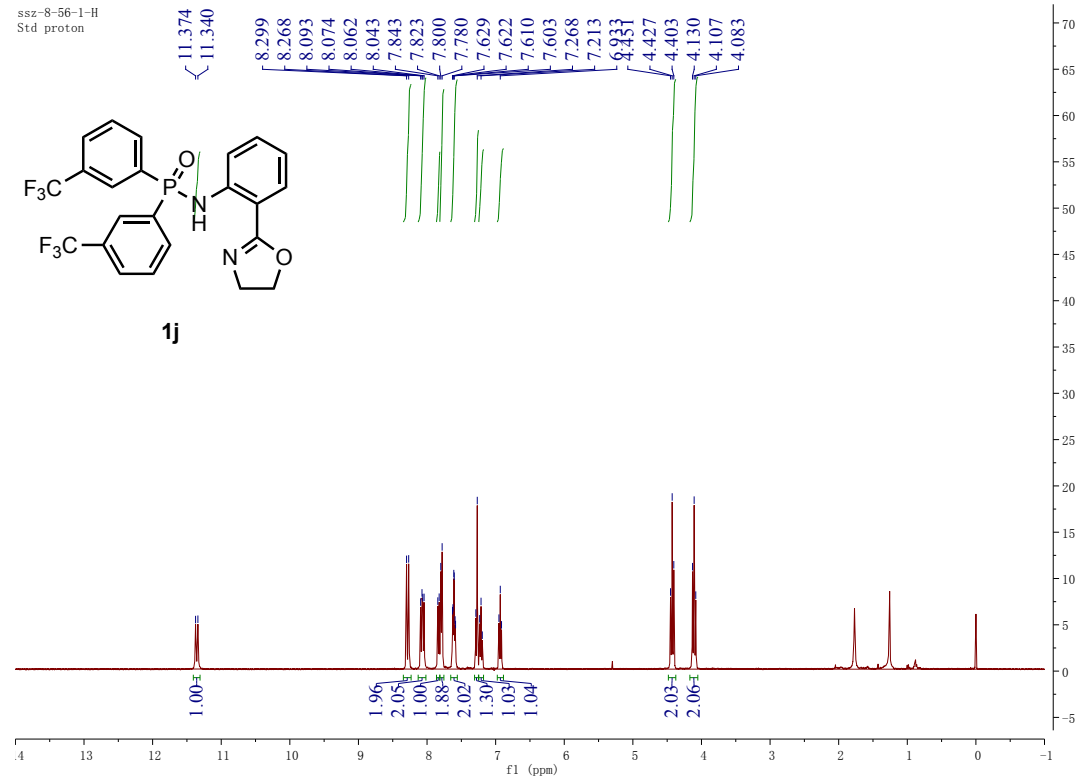
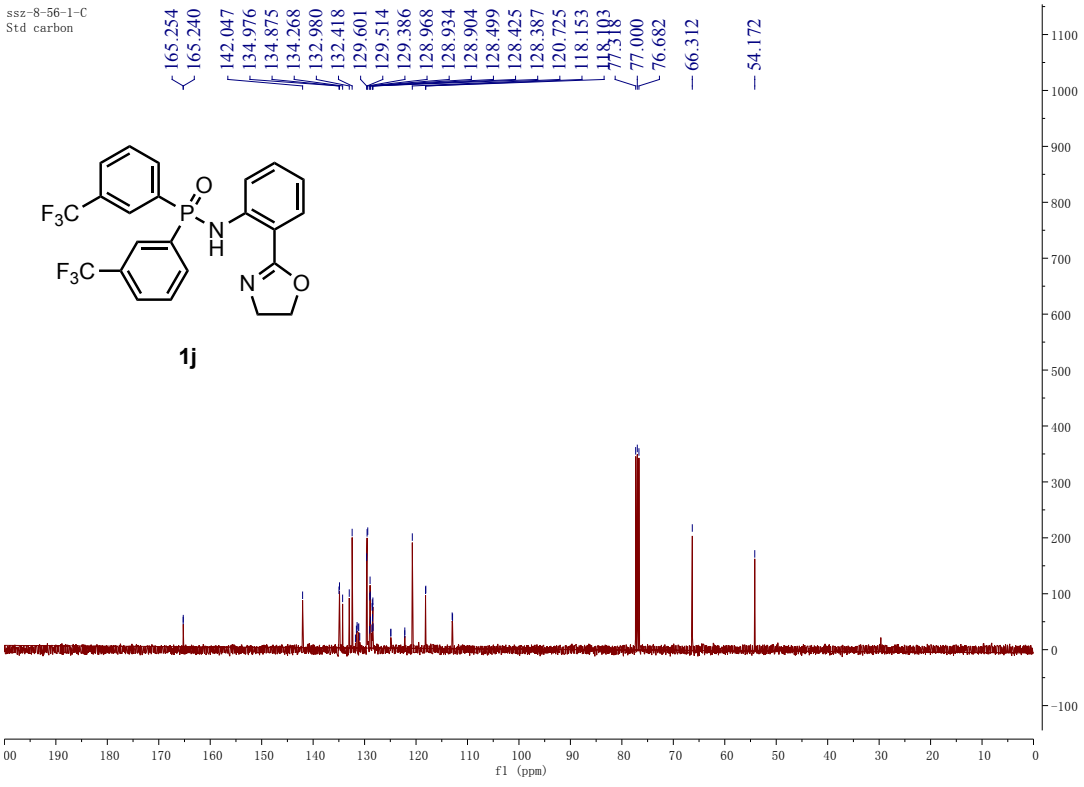
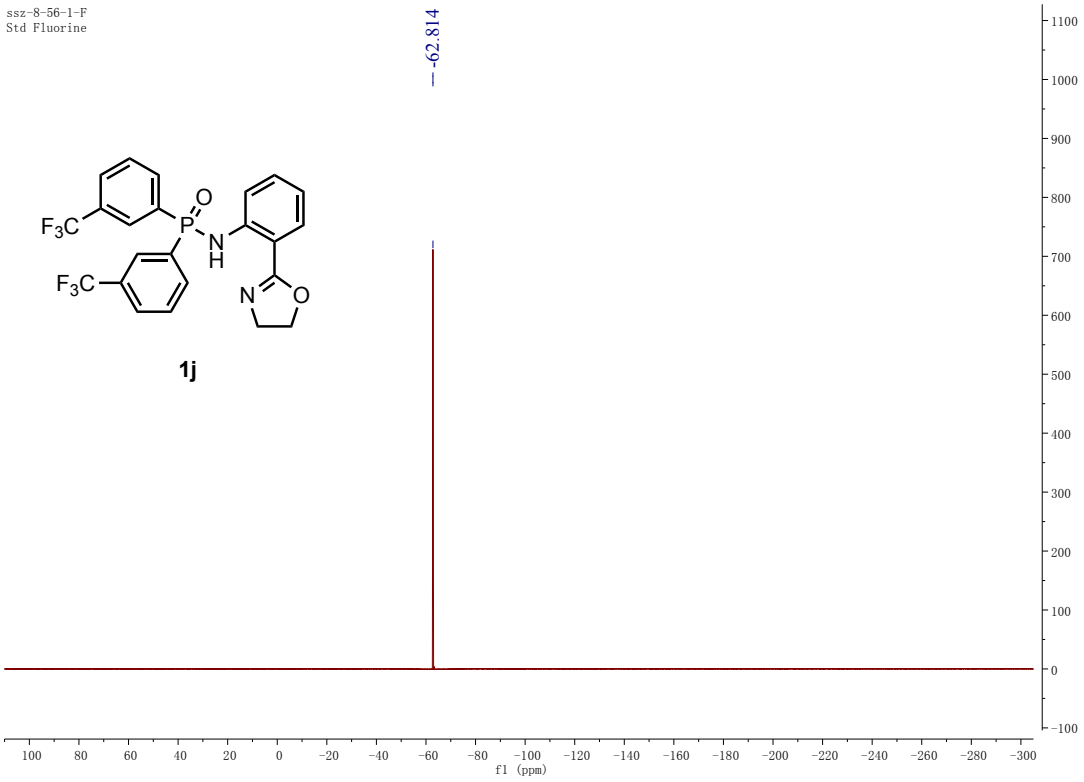


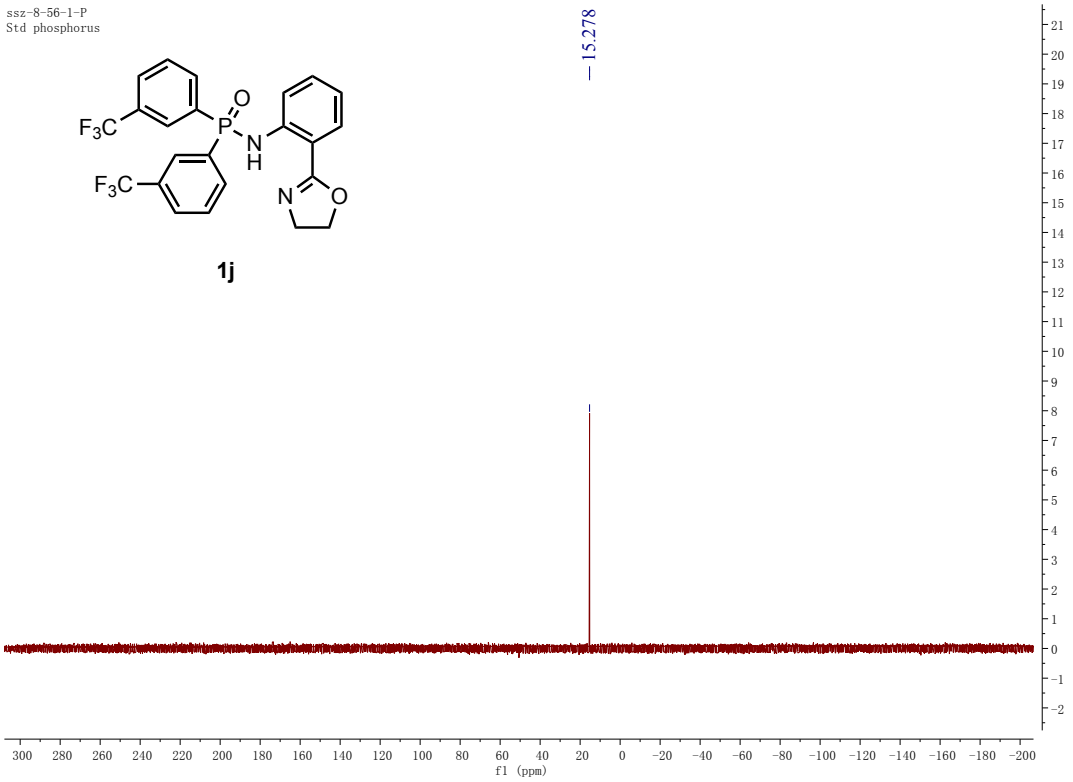
^{13}C NMR for Compound 1j



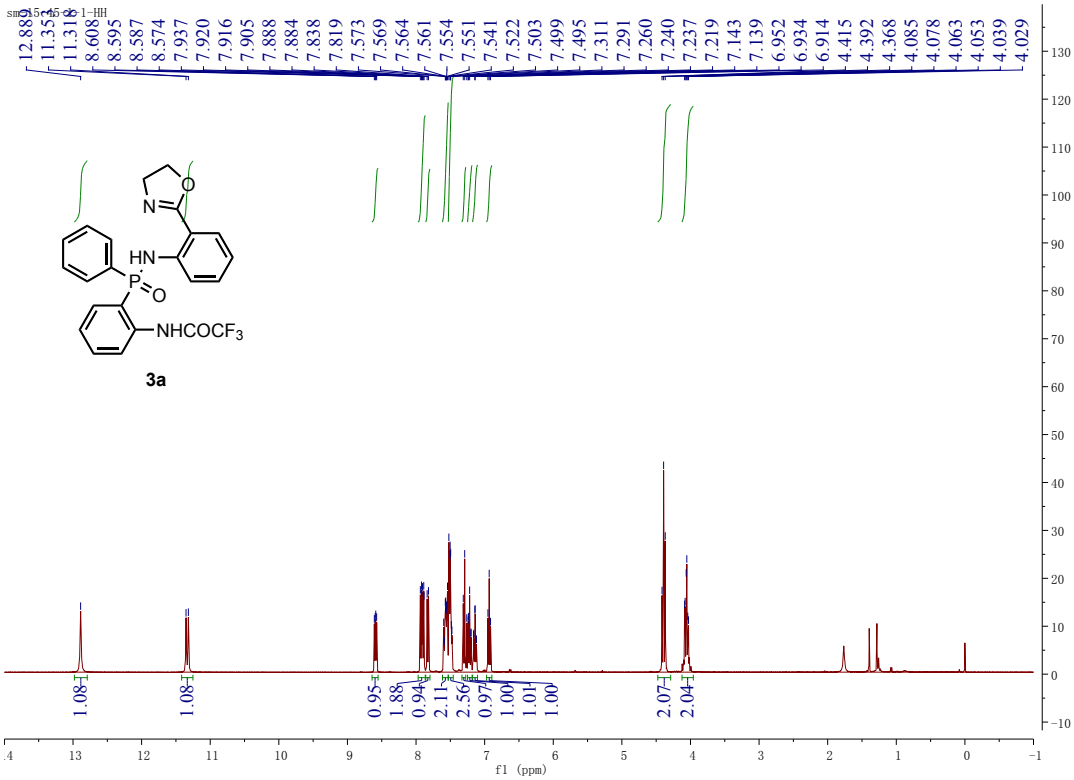
^{19}F NMR for Compound 1j



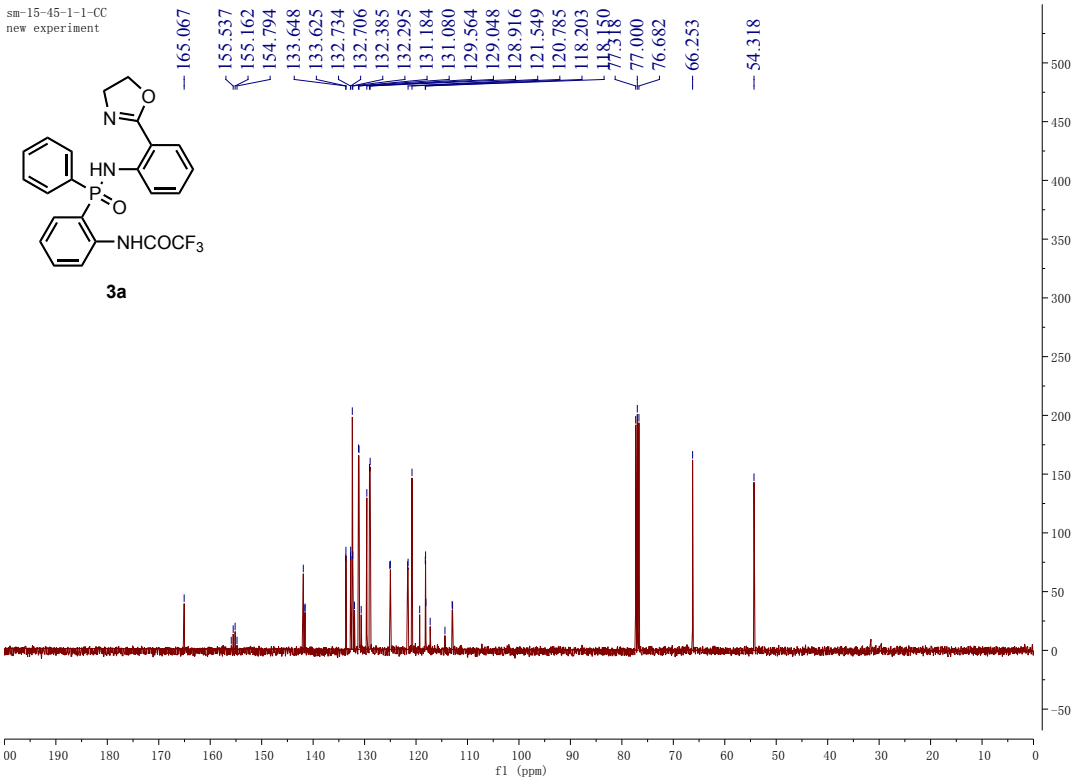
^{31}P NMR for Compound 1j



^{1}H NMR for Compound 3a



^{13}C NMR for Compound 3a



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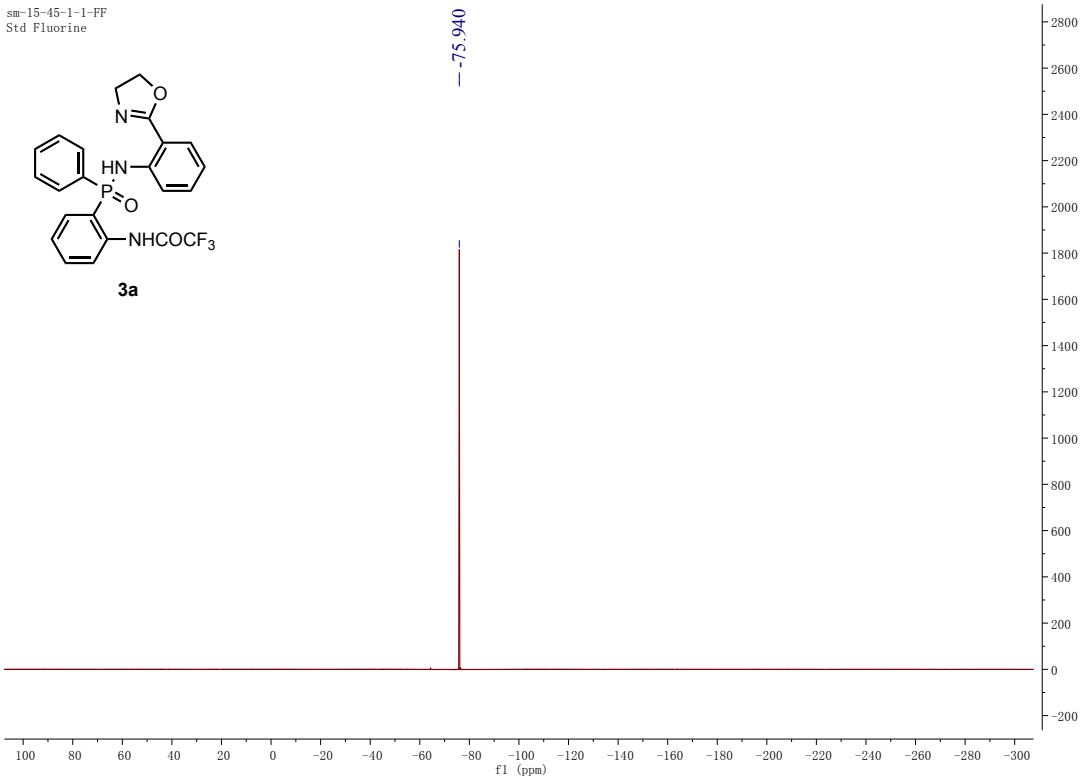
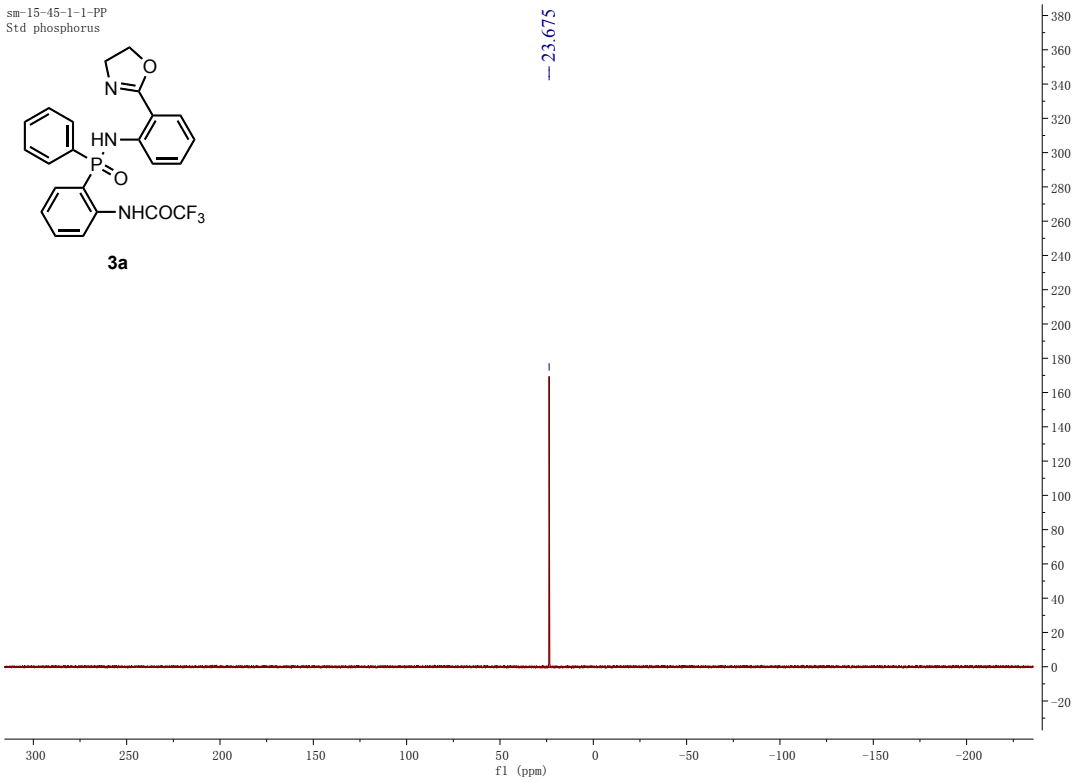
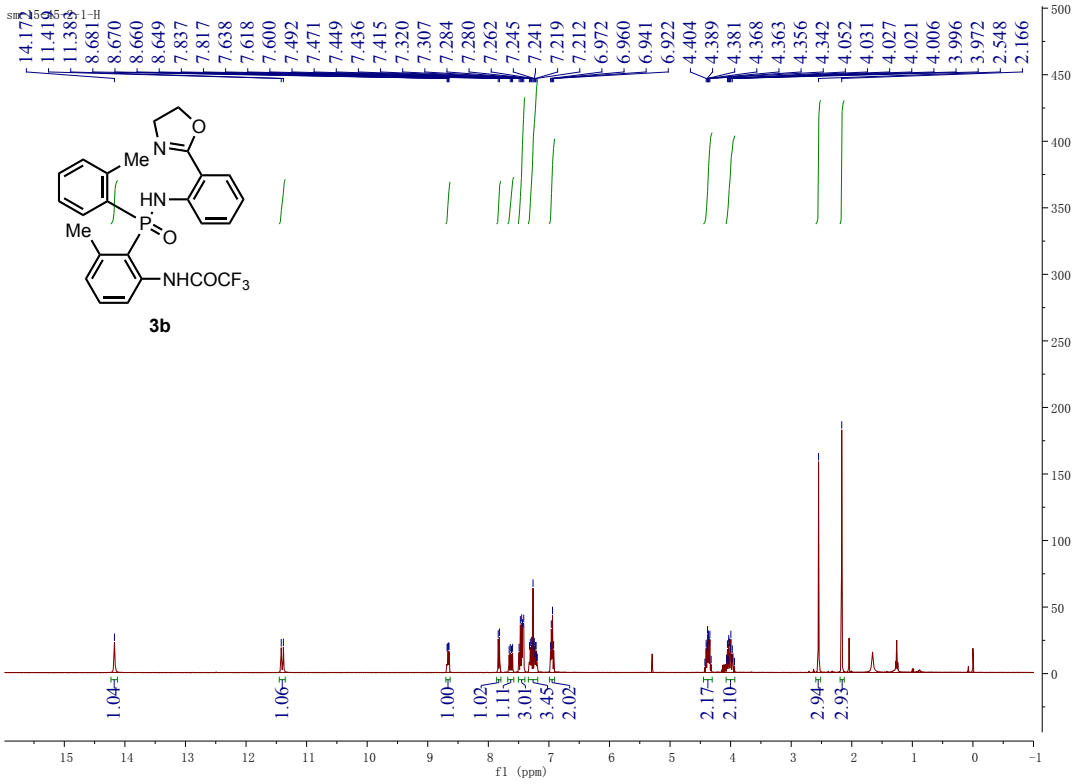


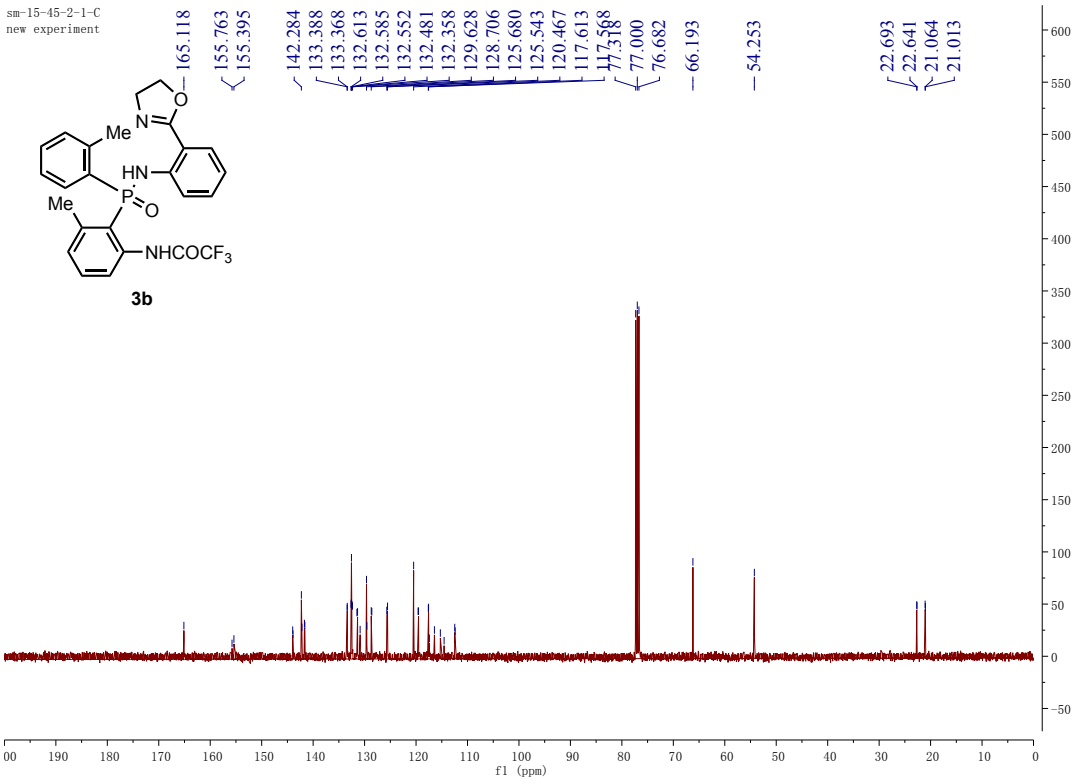
^{31}P NMR for Compound 3a



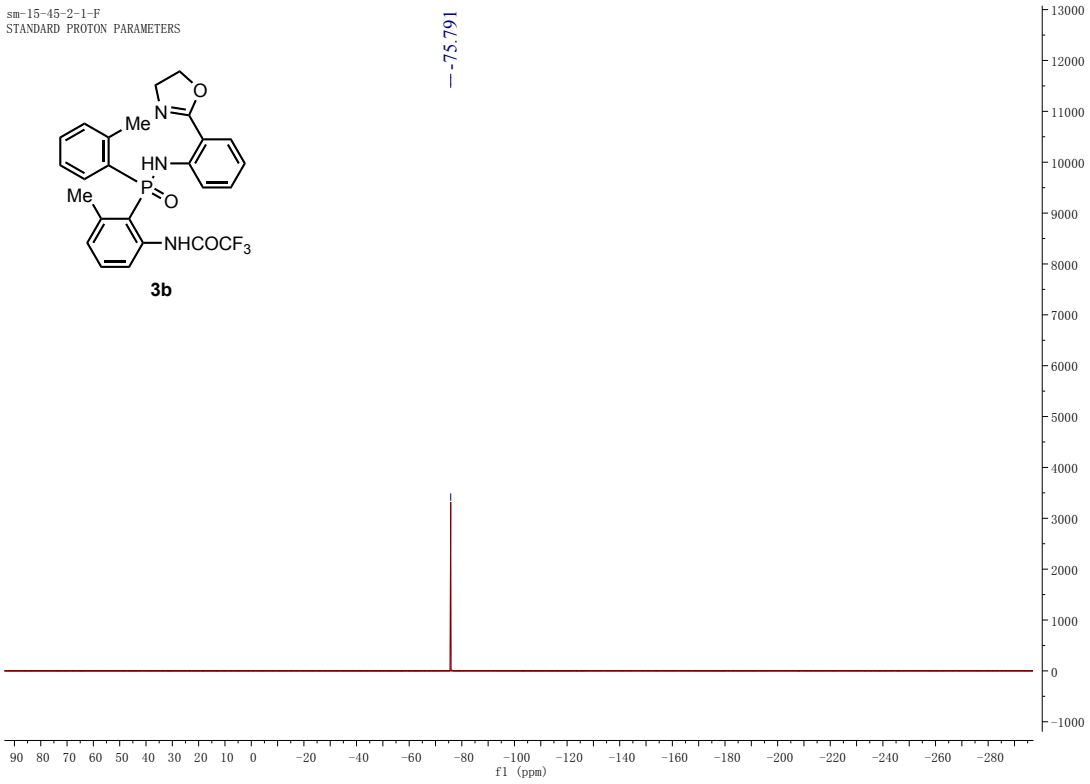
^{1}H NMR for Compound 3b



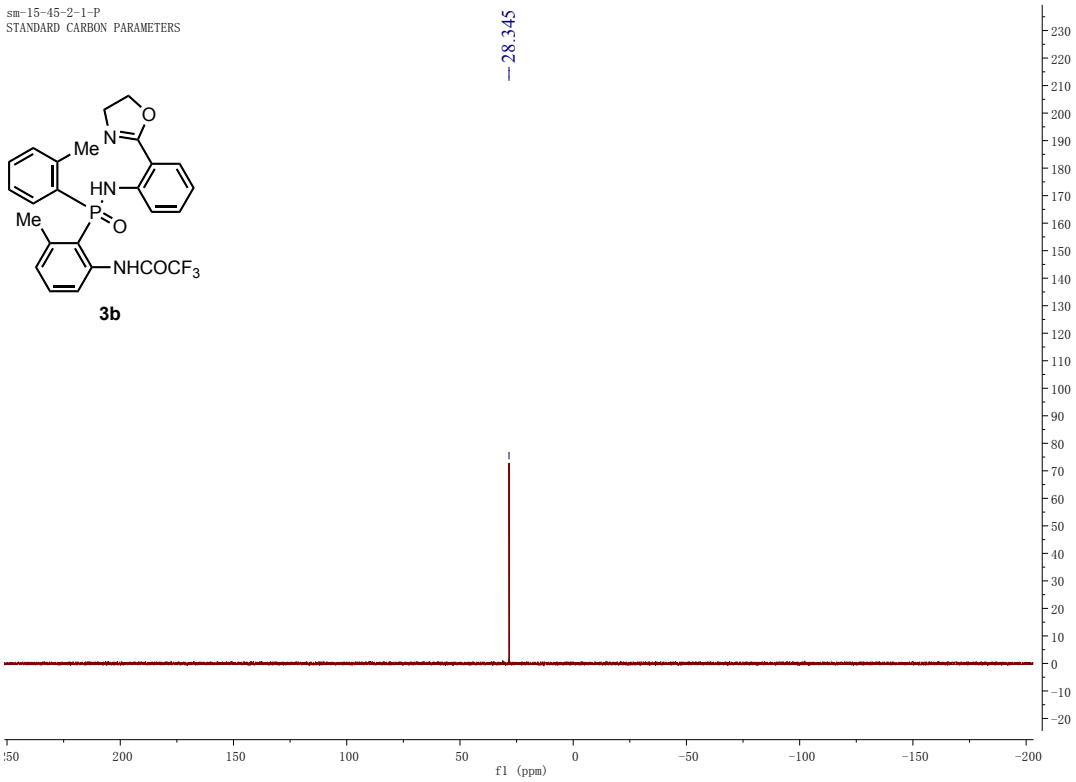
^{13}C NMR for Compound 3b



^{19}F NMR for Compound 3b

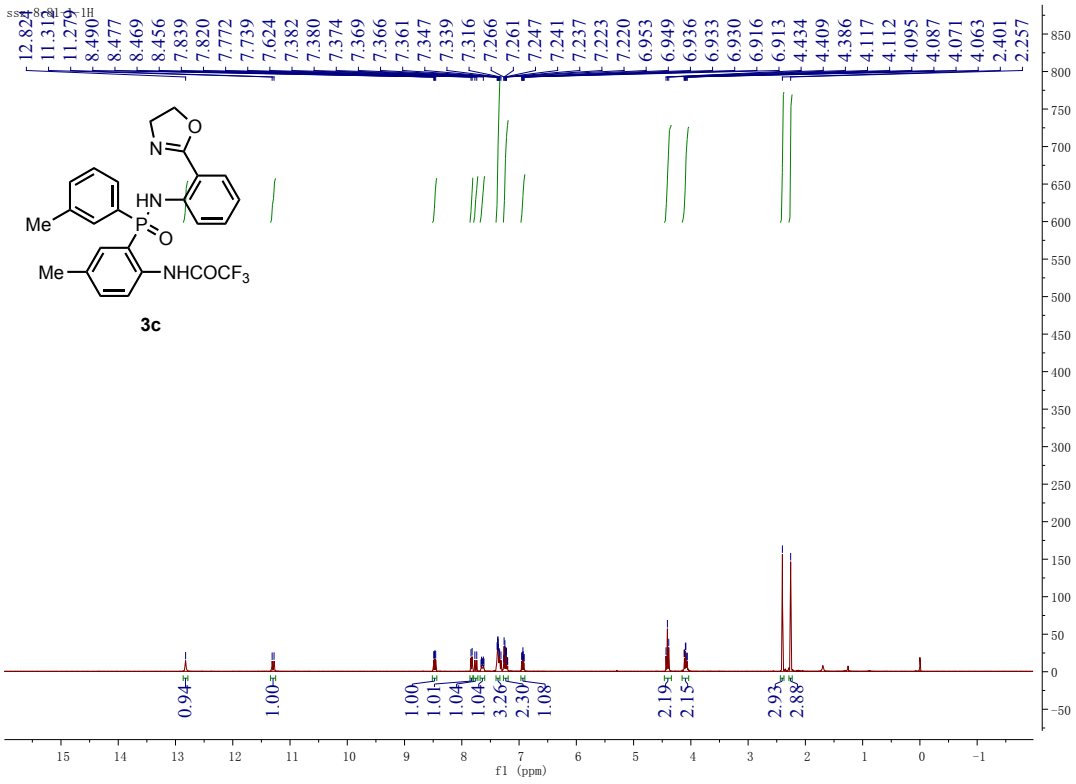


^{31}P NMR for Compound 3b



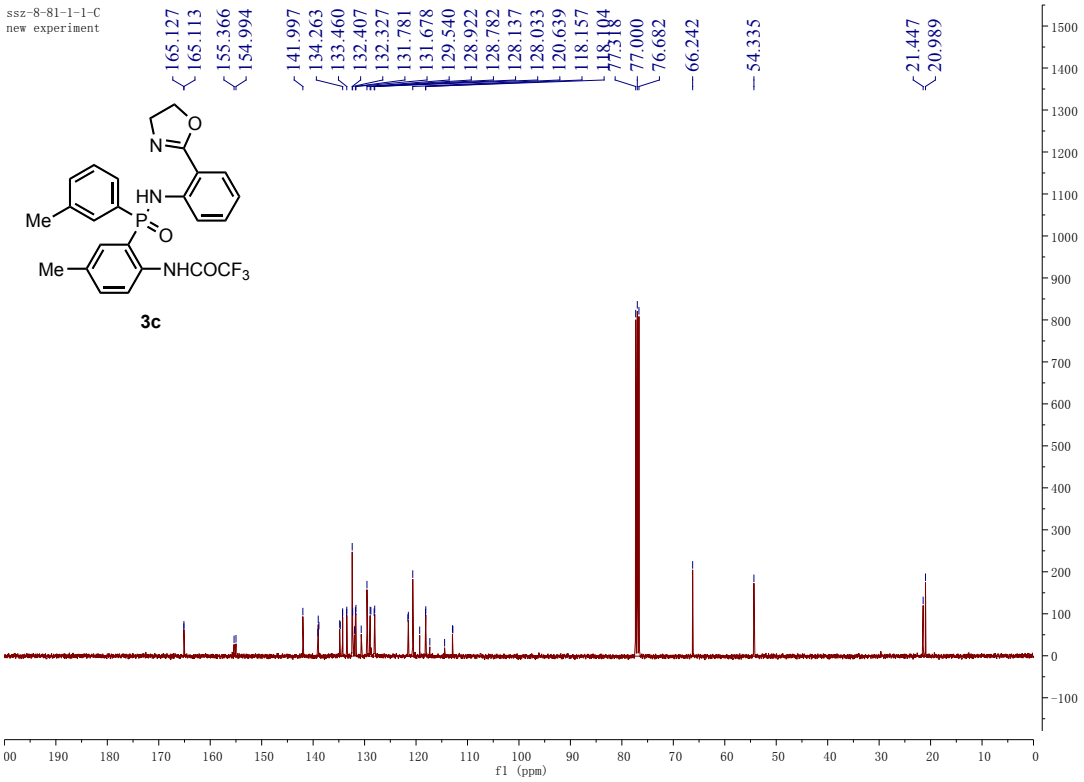
3b

^{1}H NMR for Compound 3c

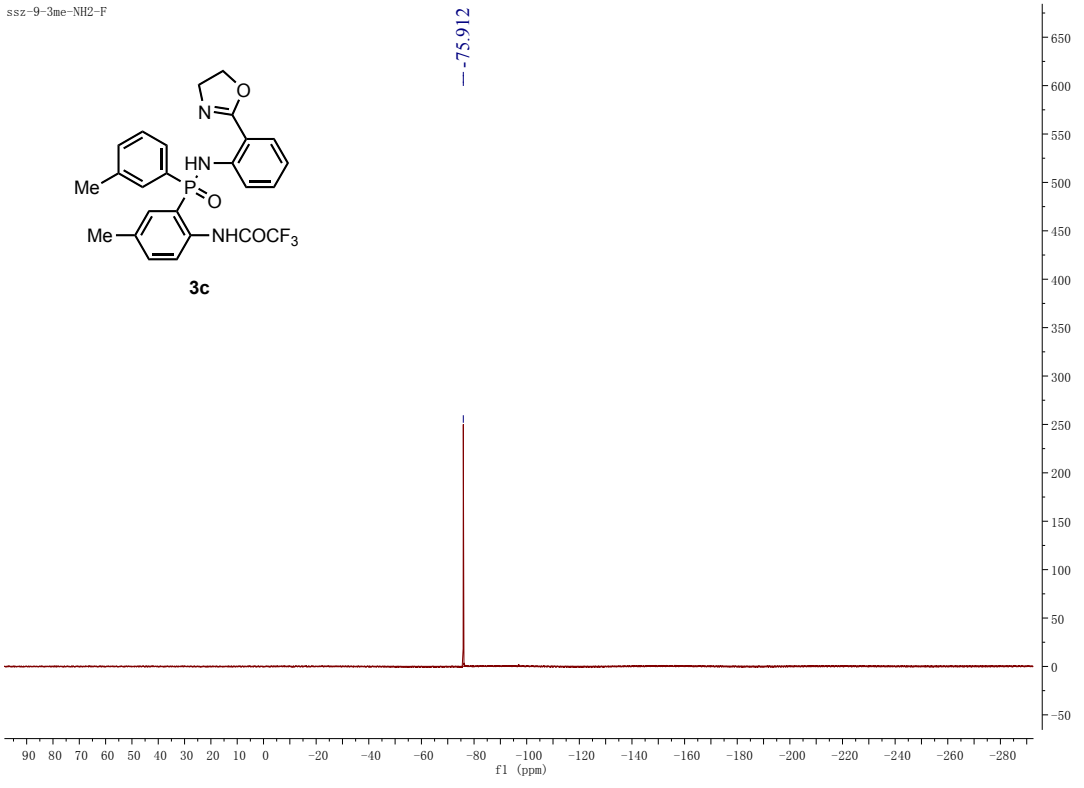


3c

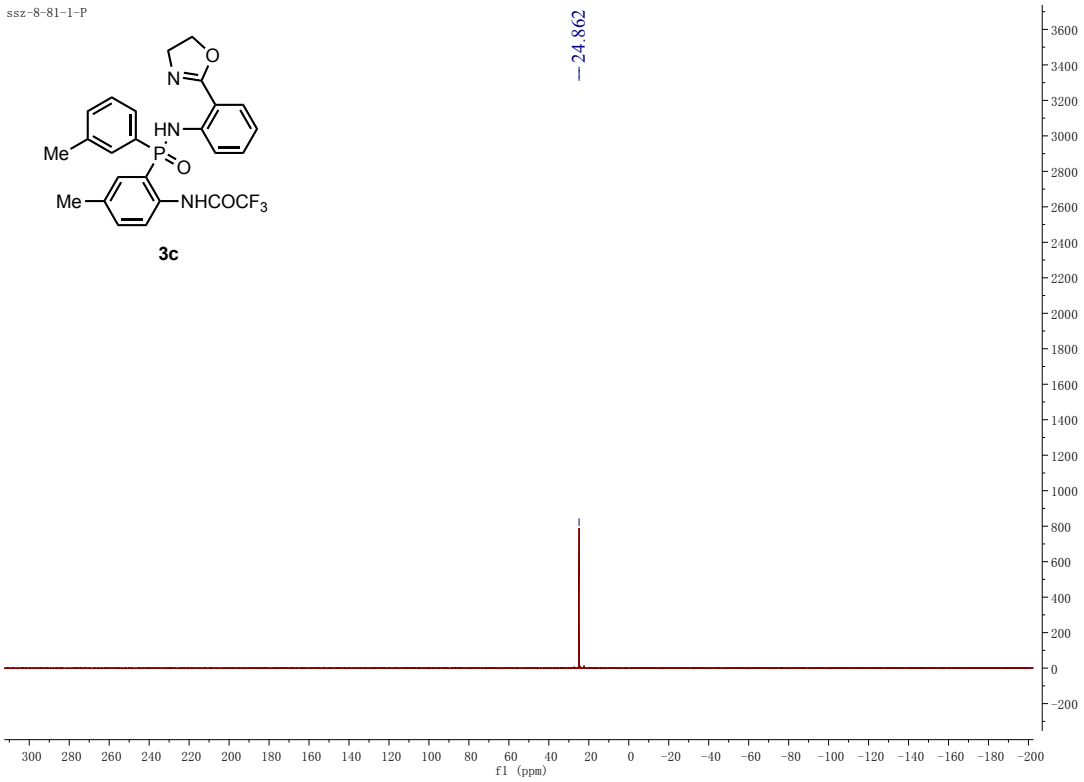
^{13}C NMR for Compound 3c



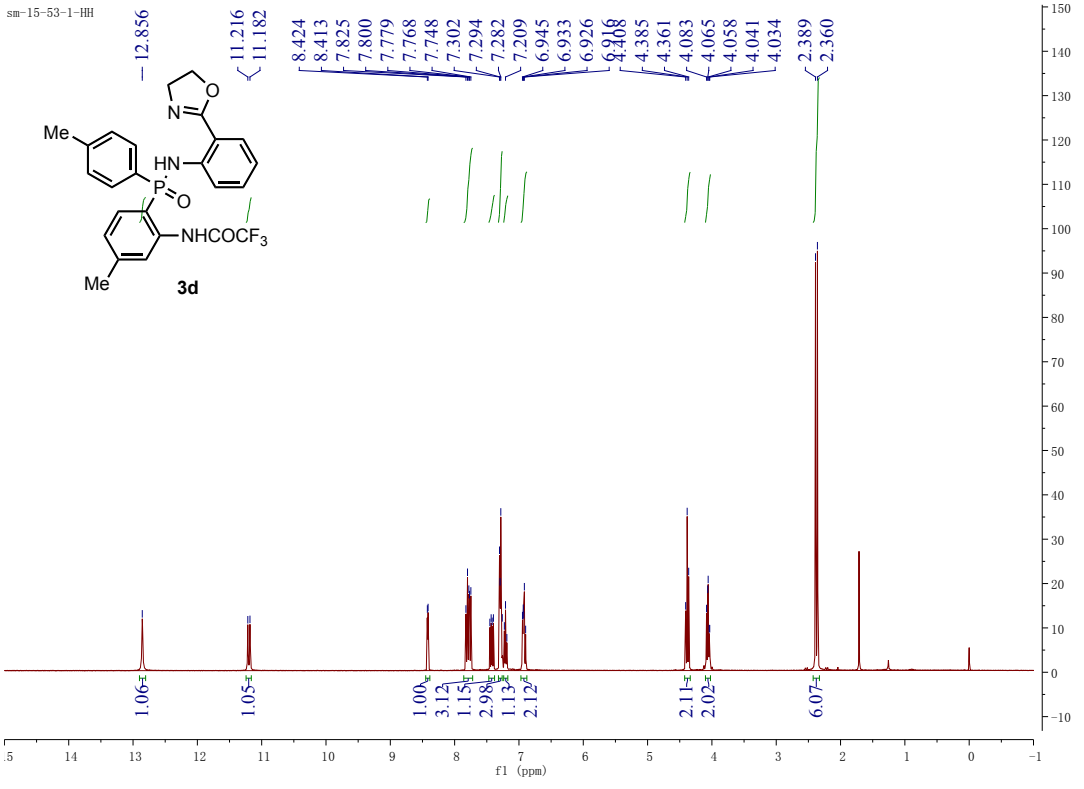
^{19}F NMR for Compound 3c



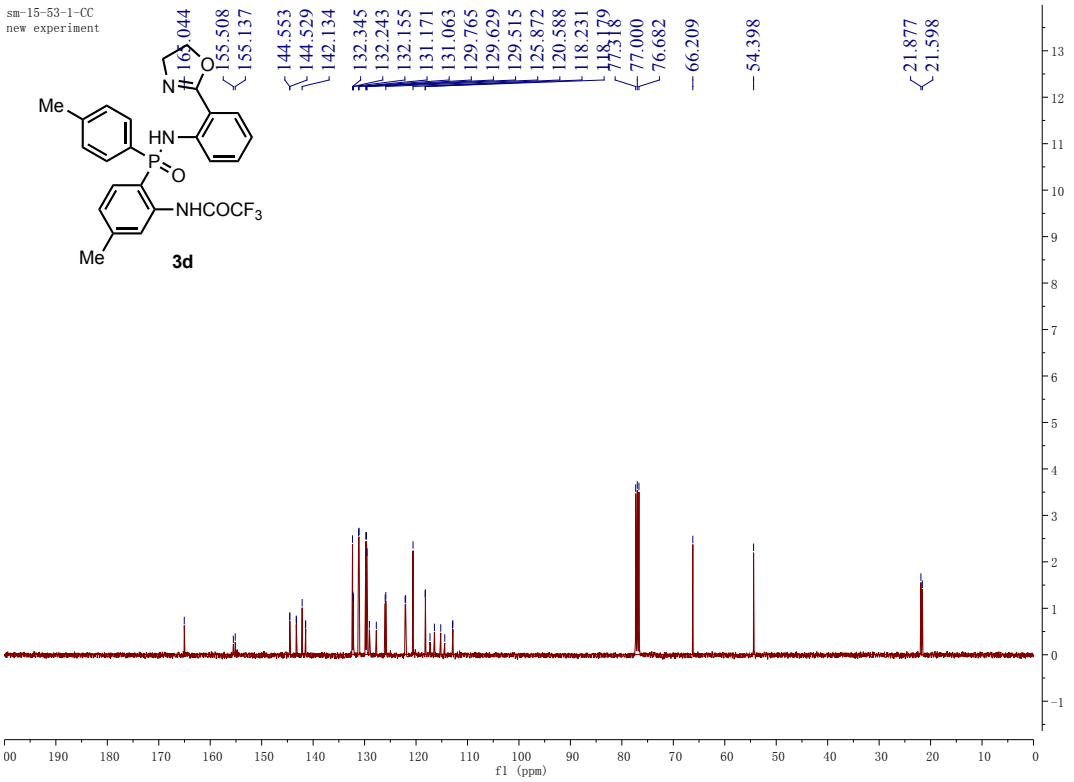
^{31}P NMR for Compound 3c



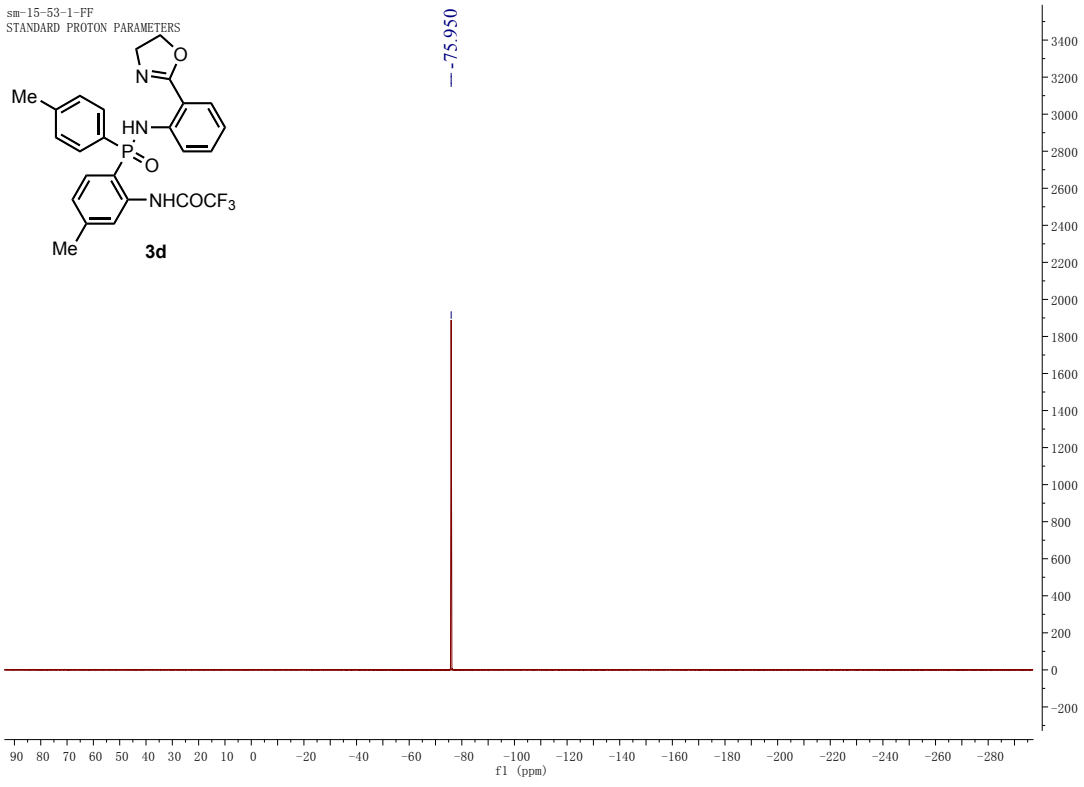
^{1}H NMR for Compound 3d



^{13}C NMR for Compound 3d



^{19}F NMR for Compound 3d



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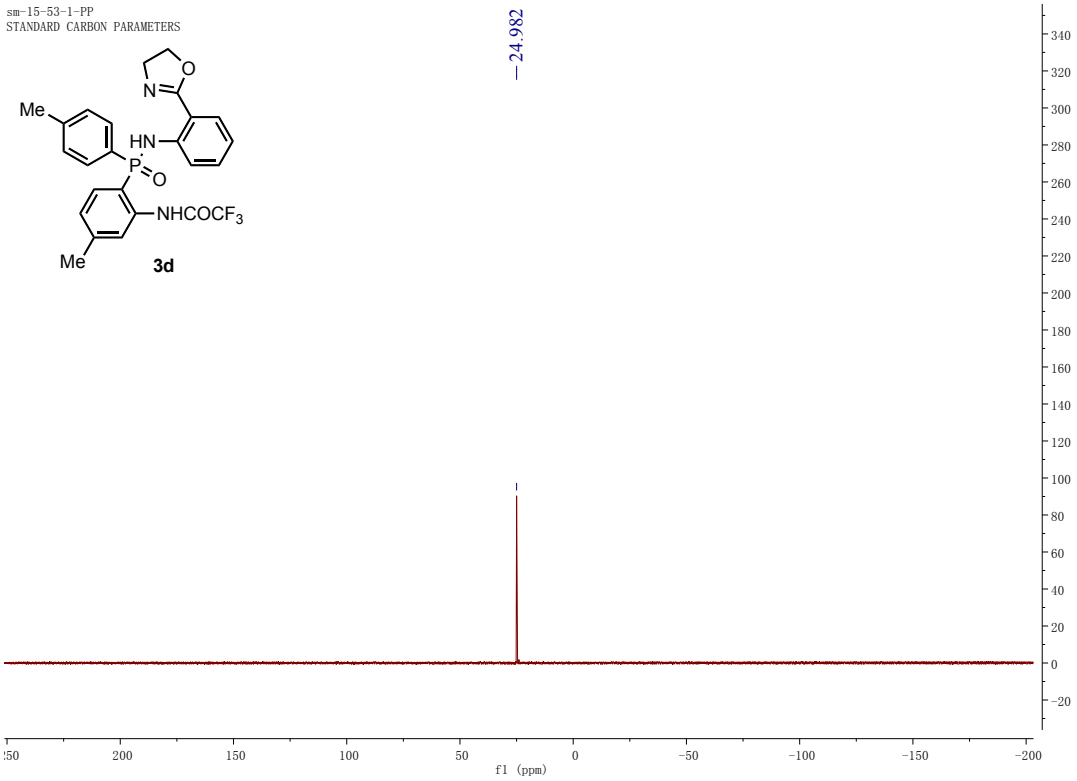

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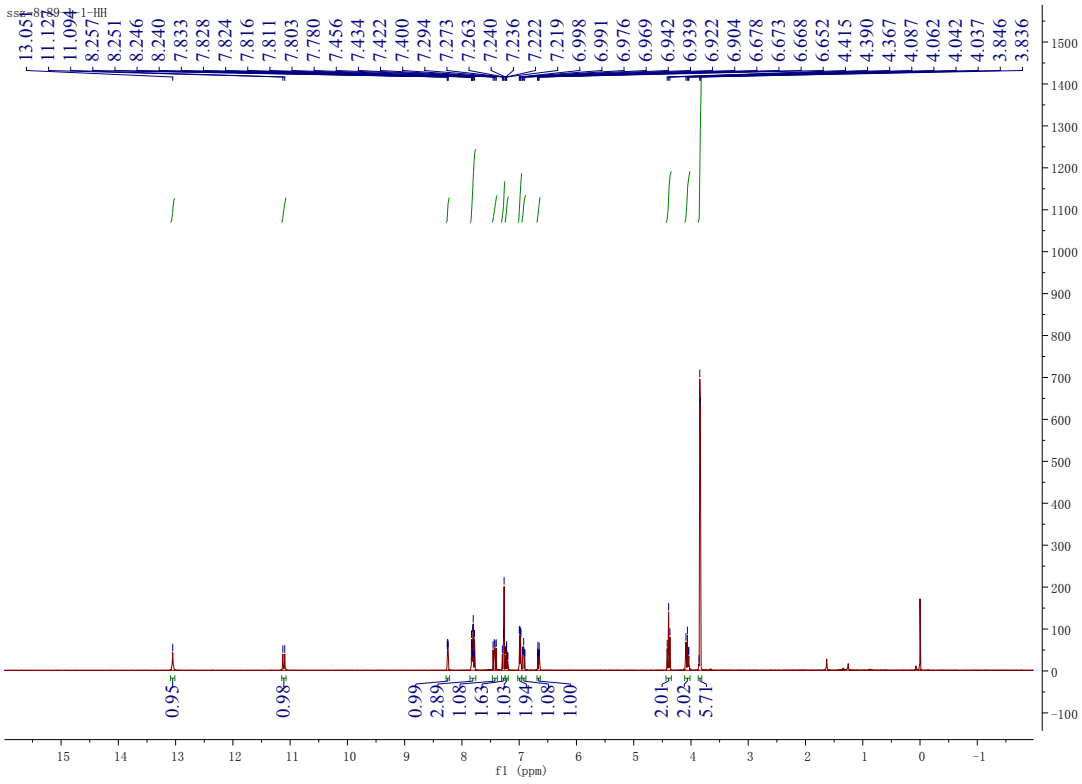

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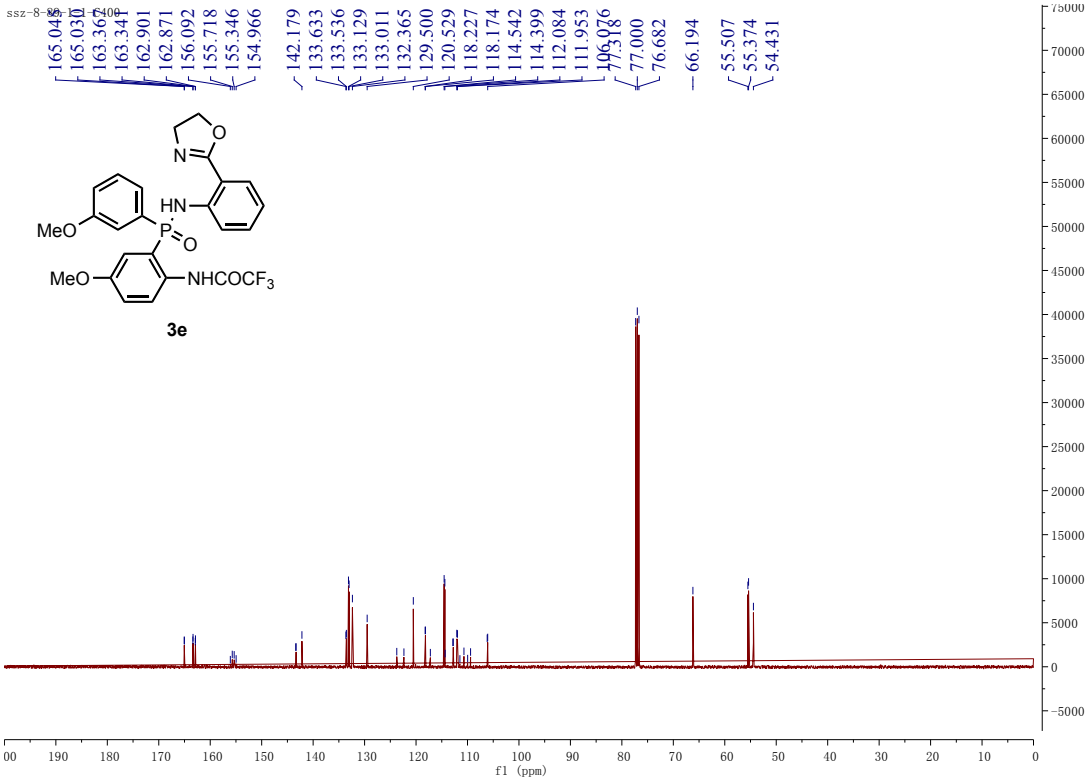
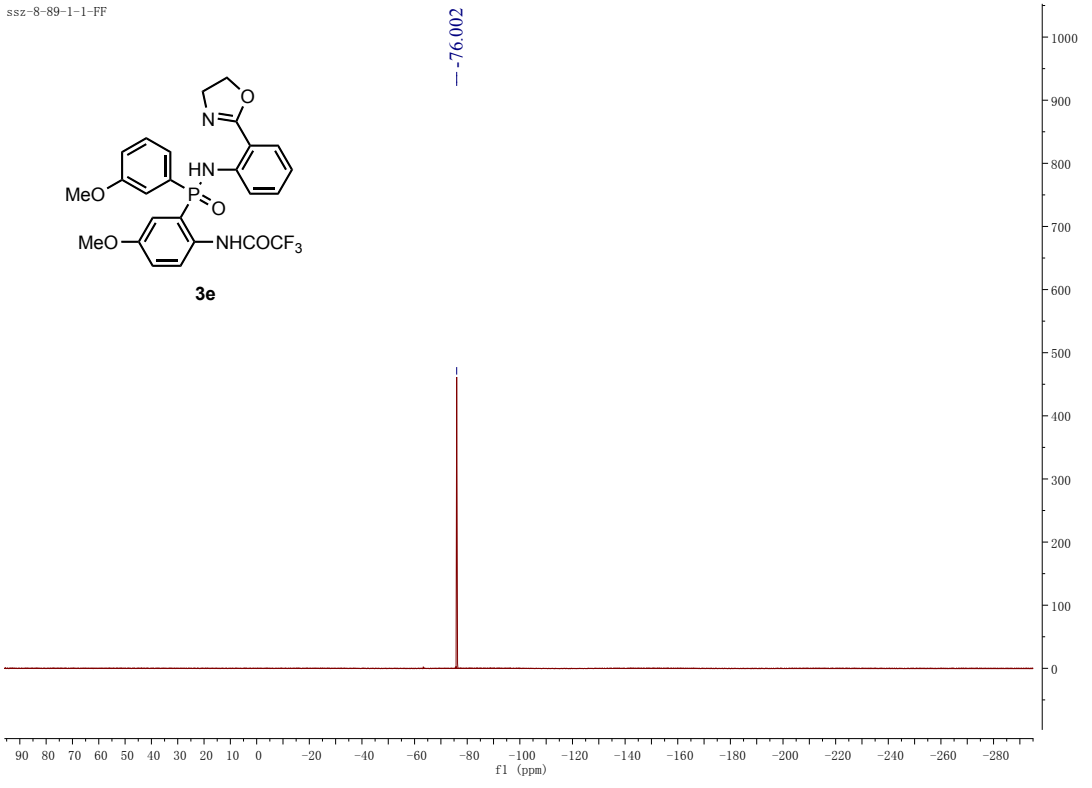
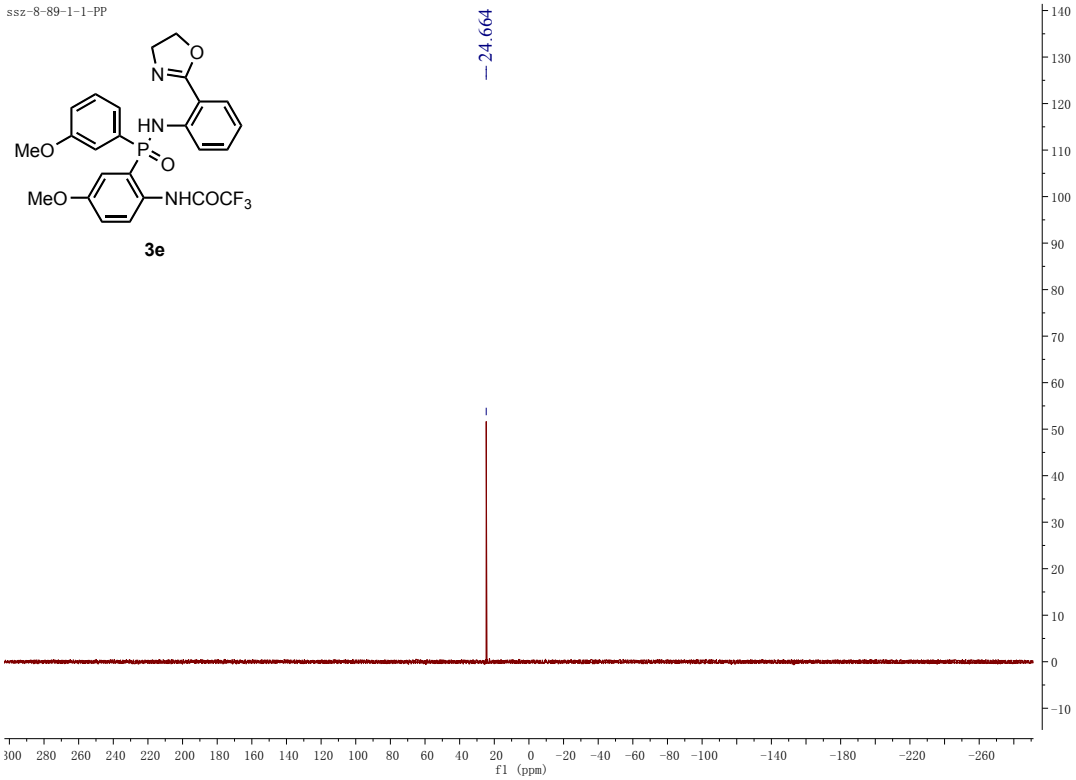


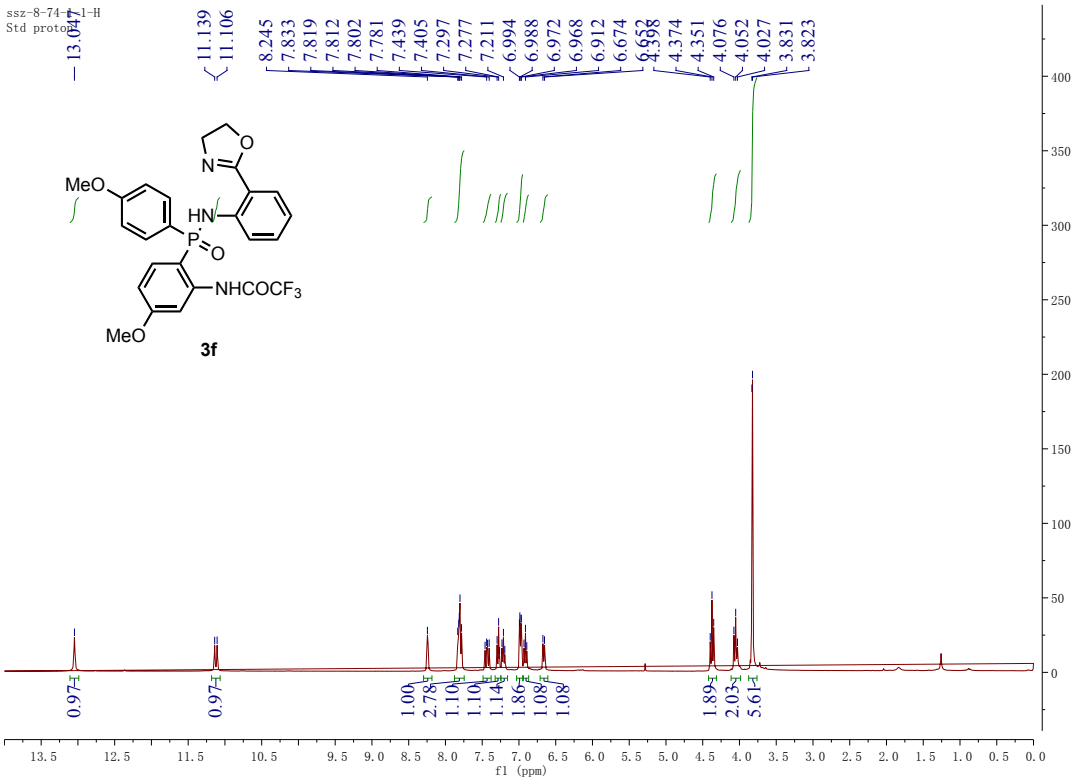
^{19}F NMR for Compound 3e



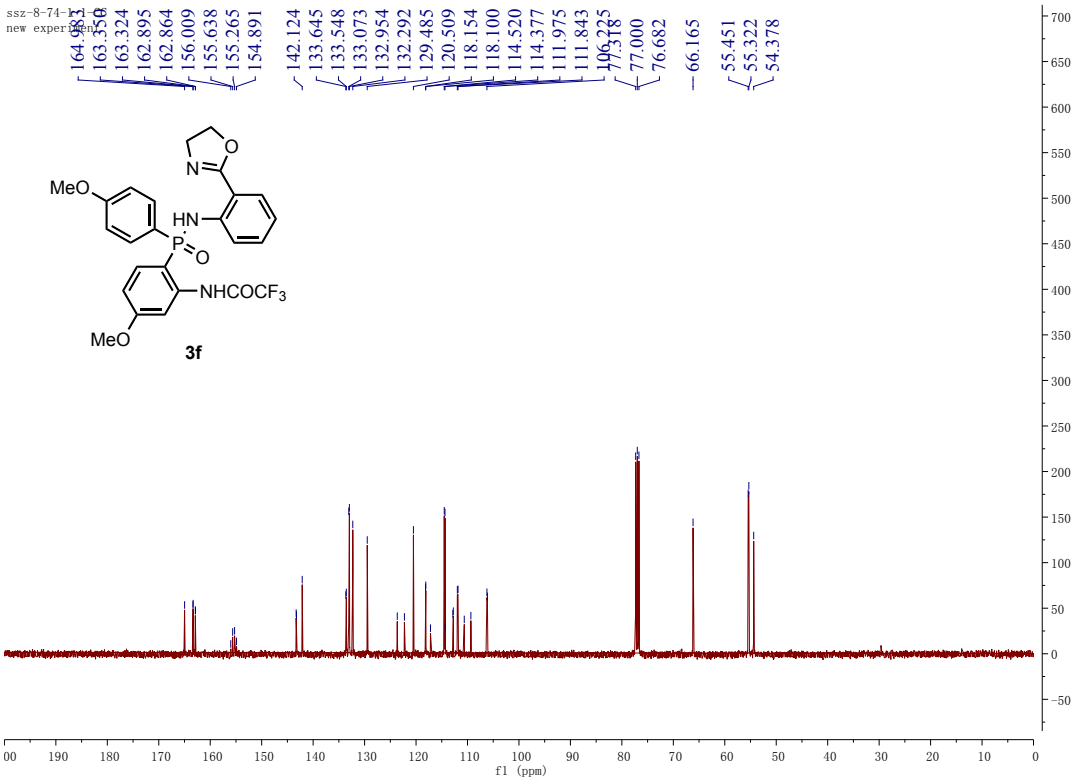
^{31}P NMR for Compound 3e



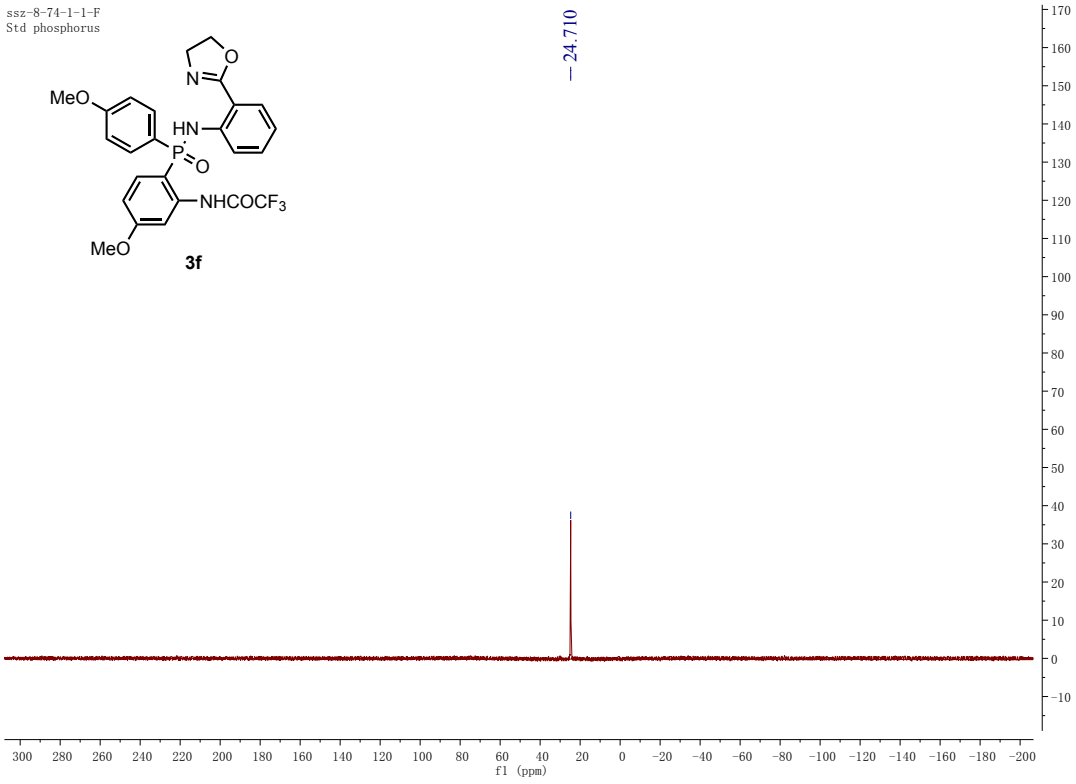
^{1}H NMR for Compound 3f



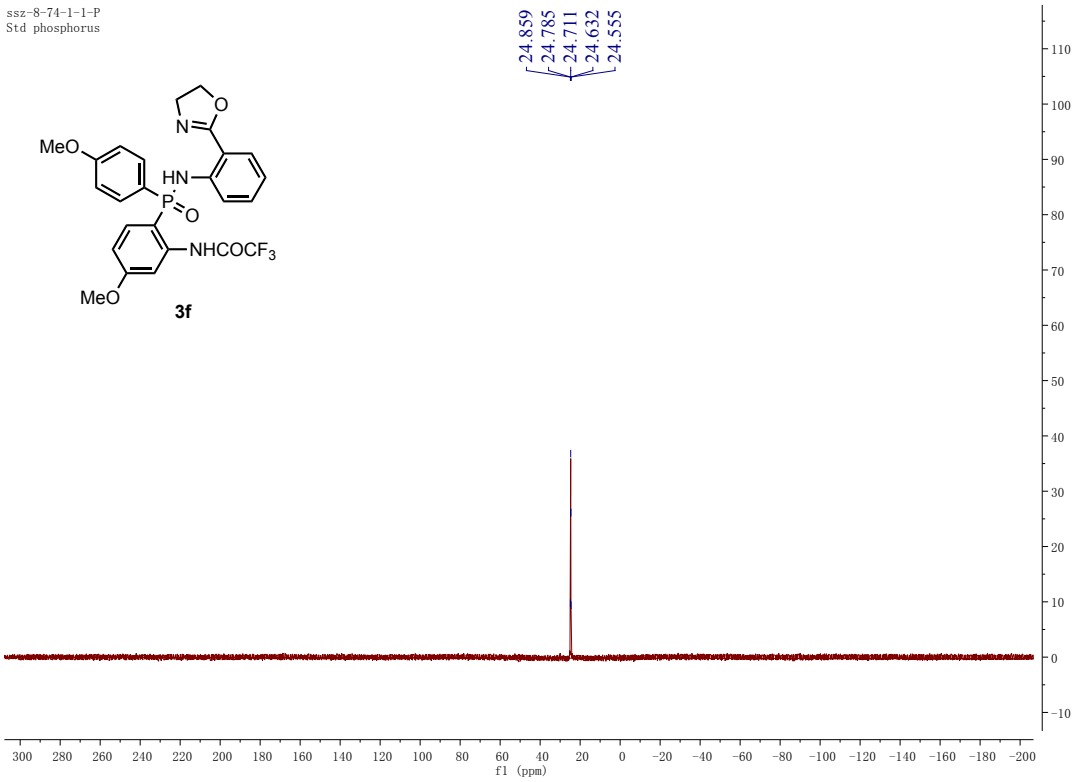
^{13}C NMR for Compound 3f



^{19}F NMR for Compound 3f



^{31}P NMR for Compound 3f



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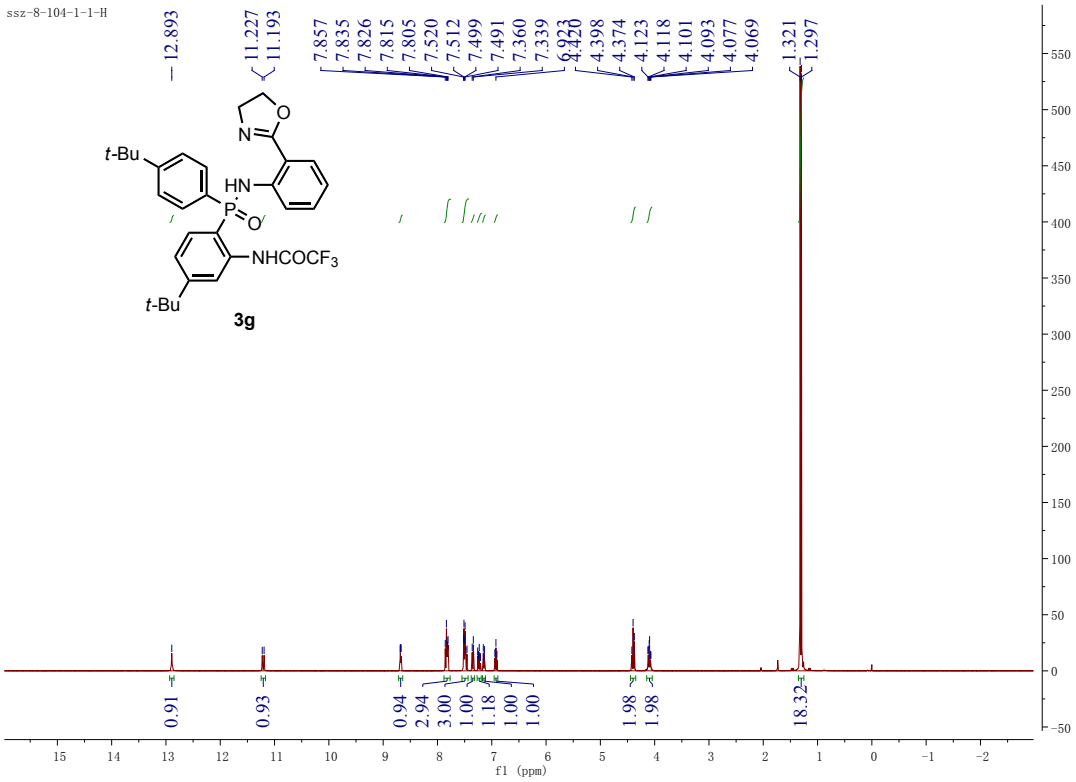

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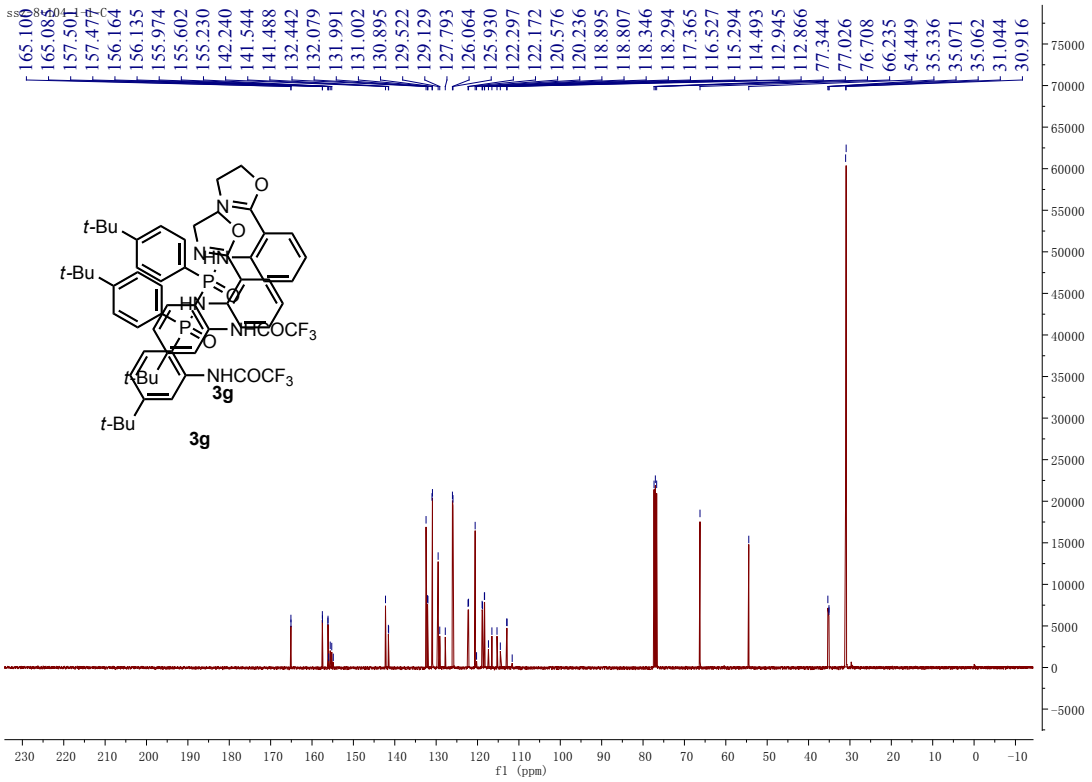

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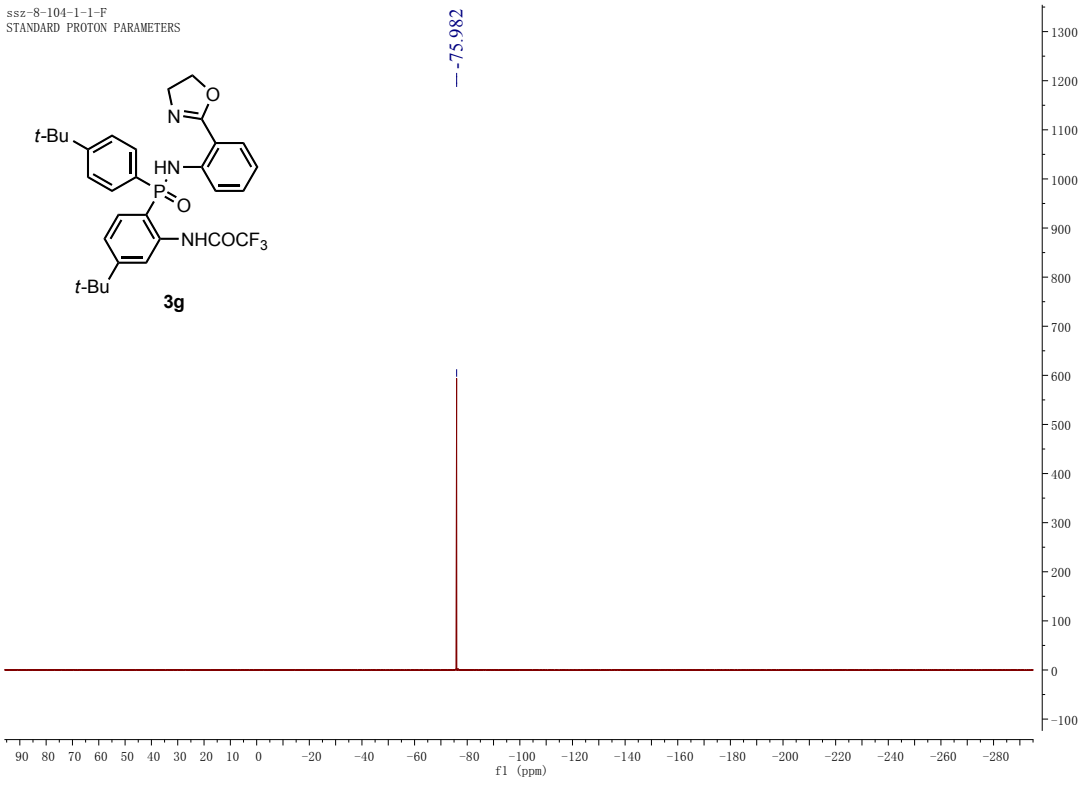

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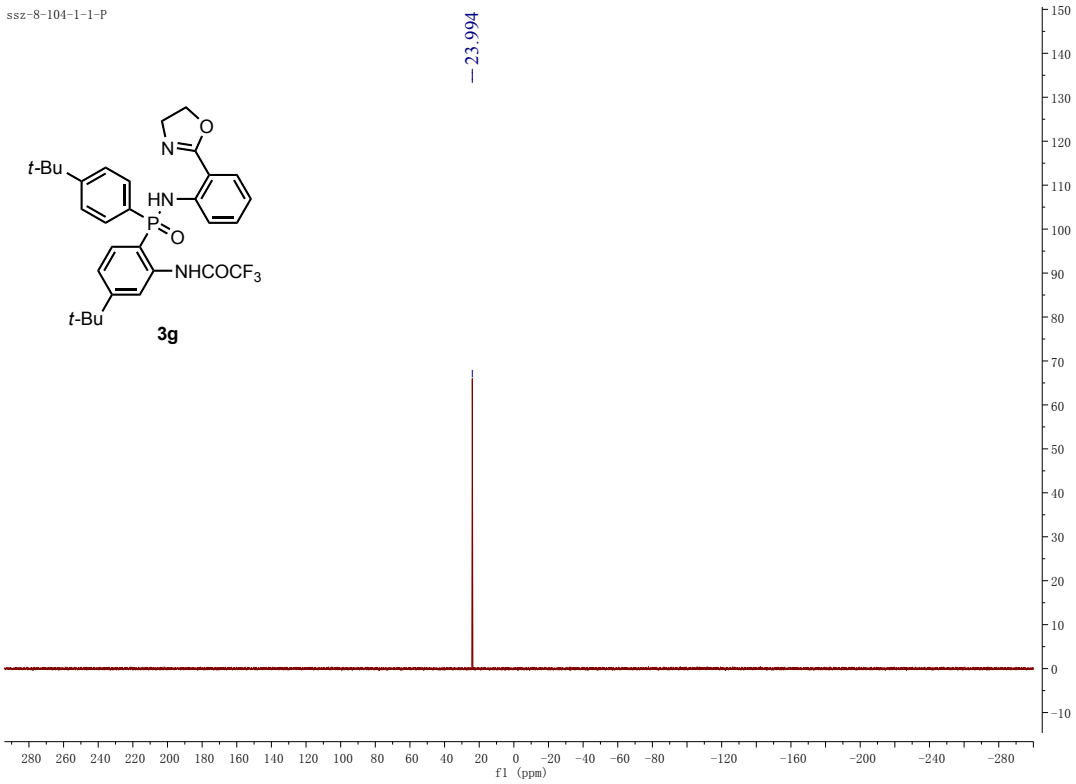
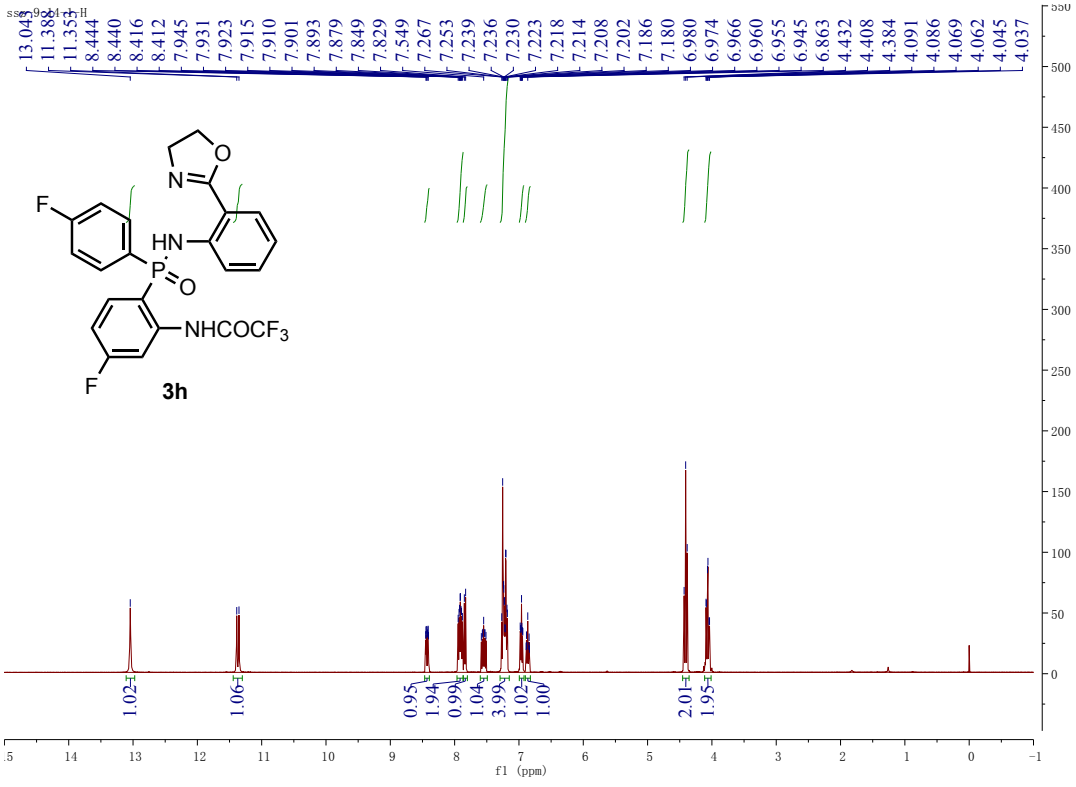
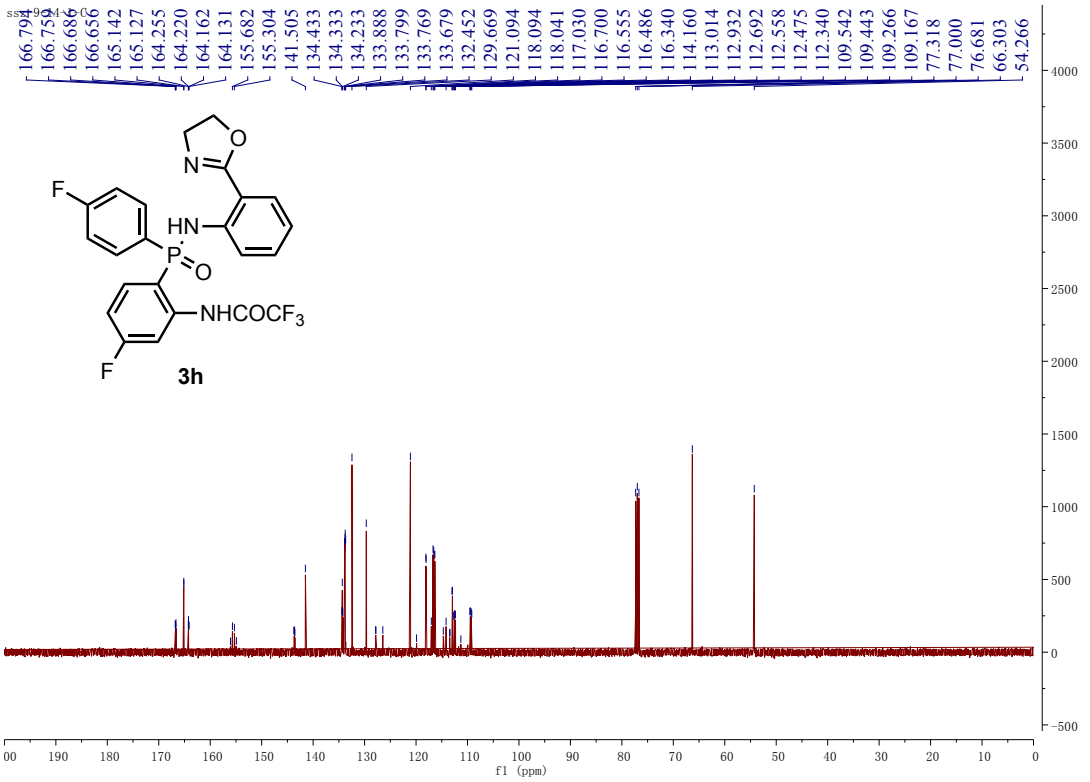
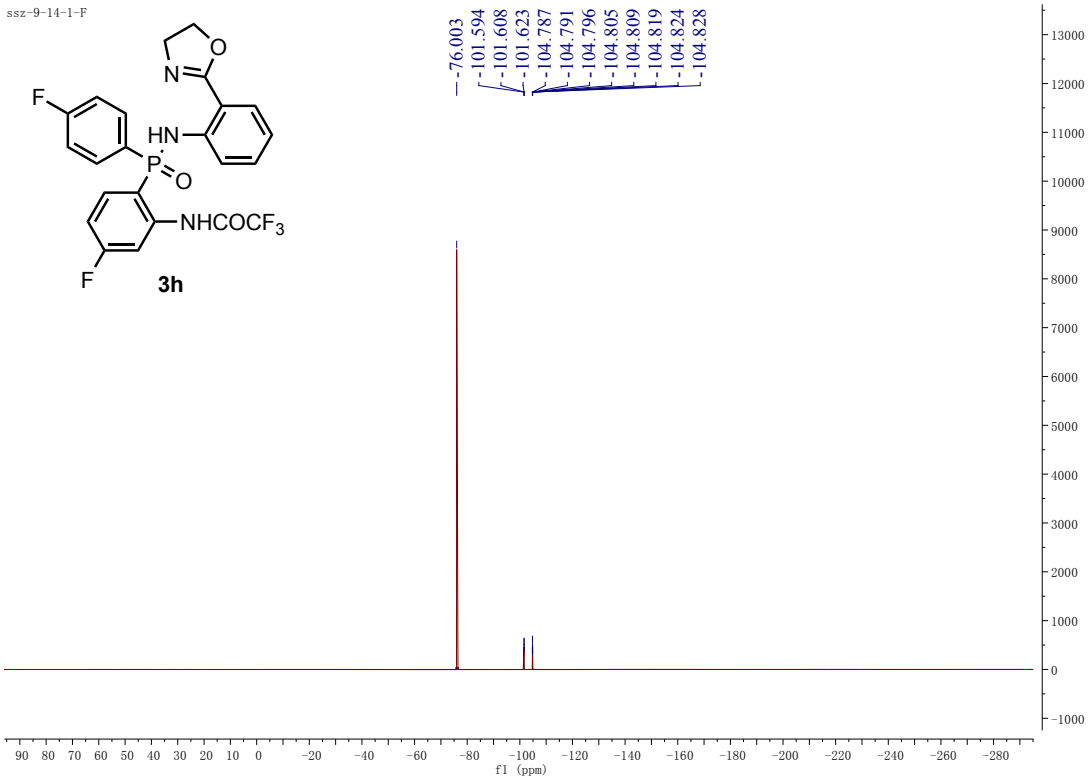


^{1}H NMR for Compound 3h

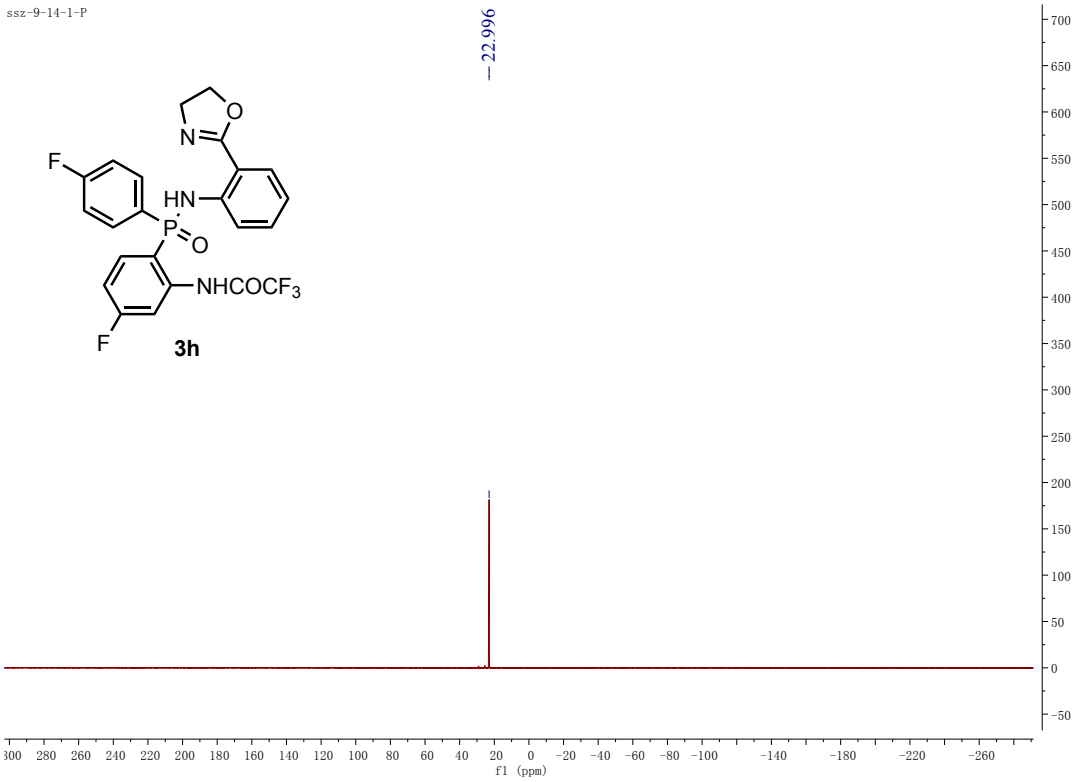


^{13}C NMR for Compound 3h

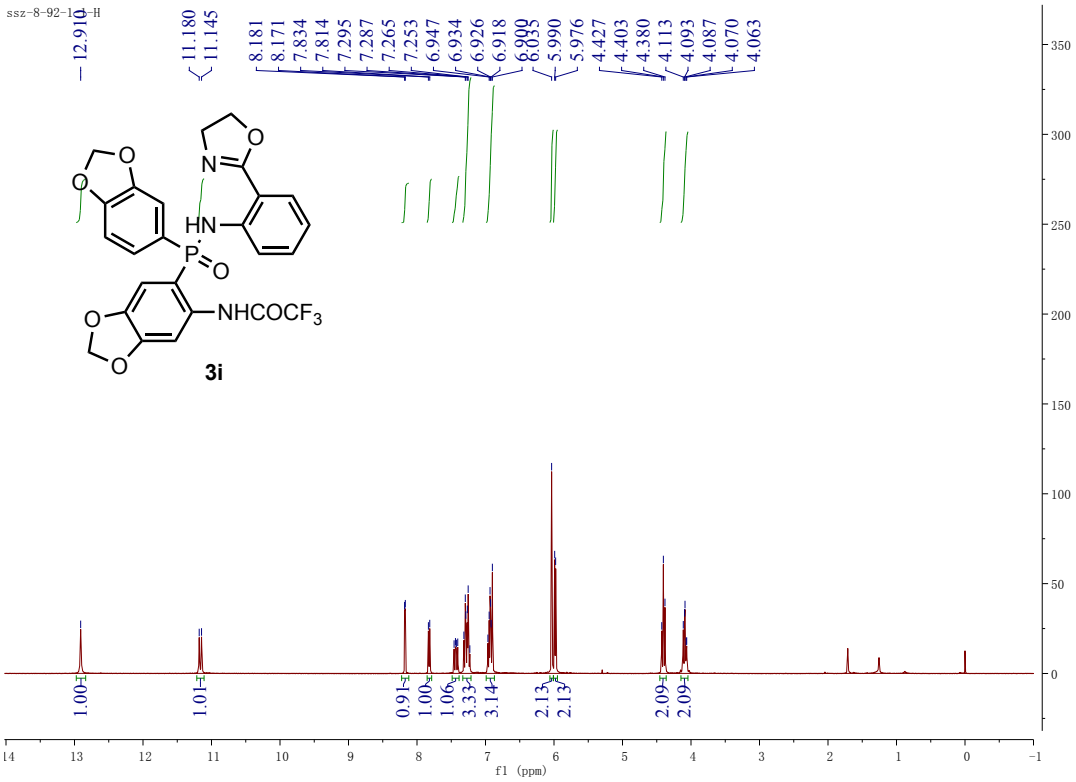




^{31}P NMR for Compound 3h



^{1}H NMR for Compound 3i



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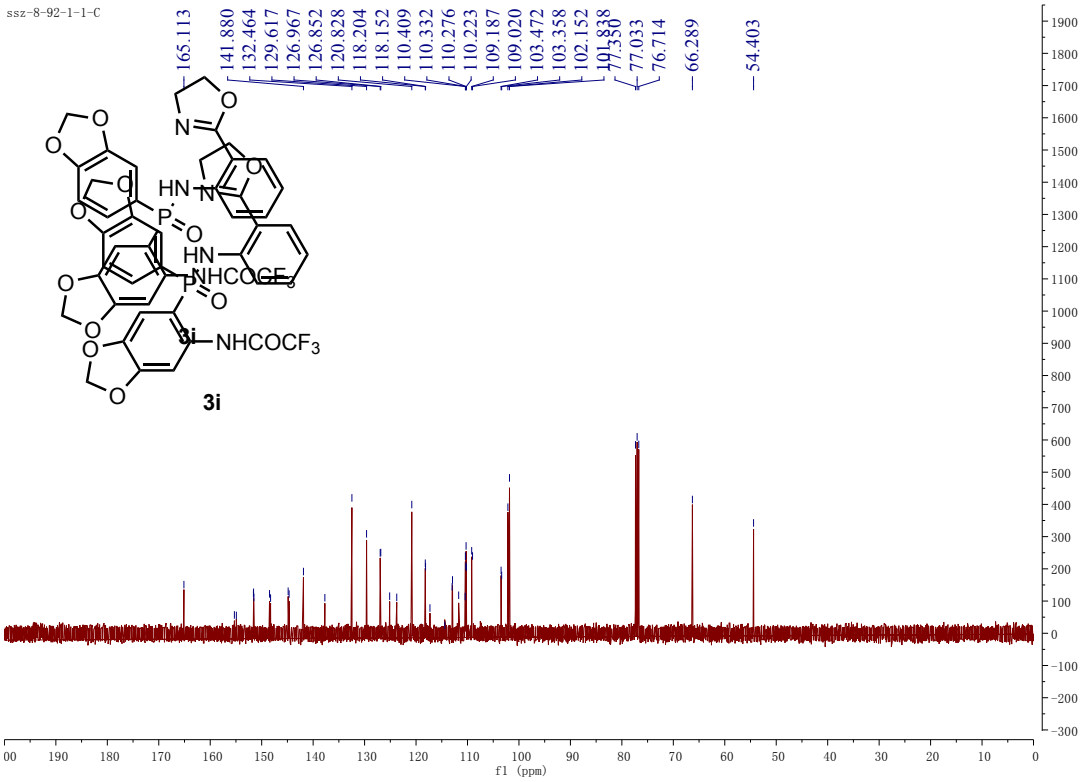
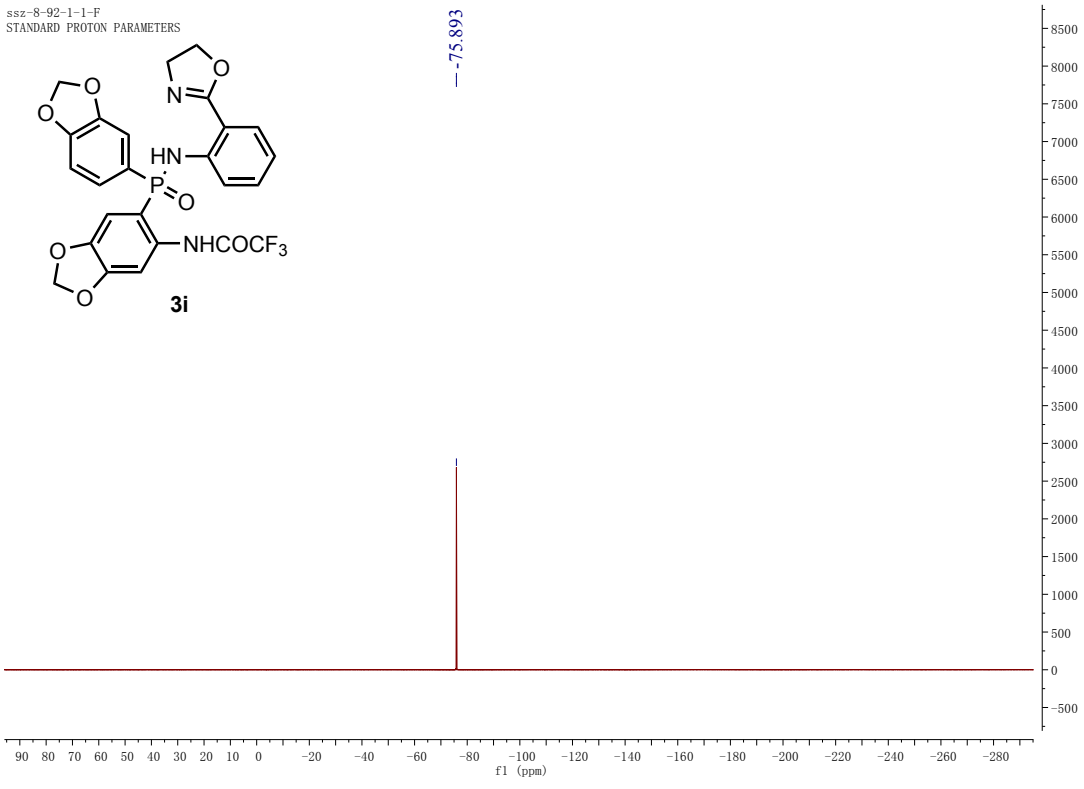
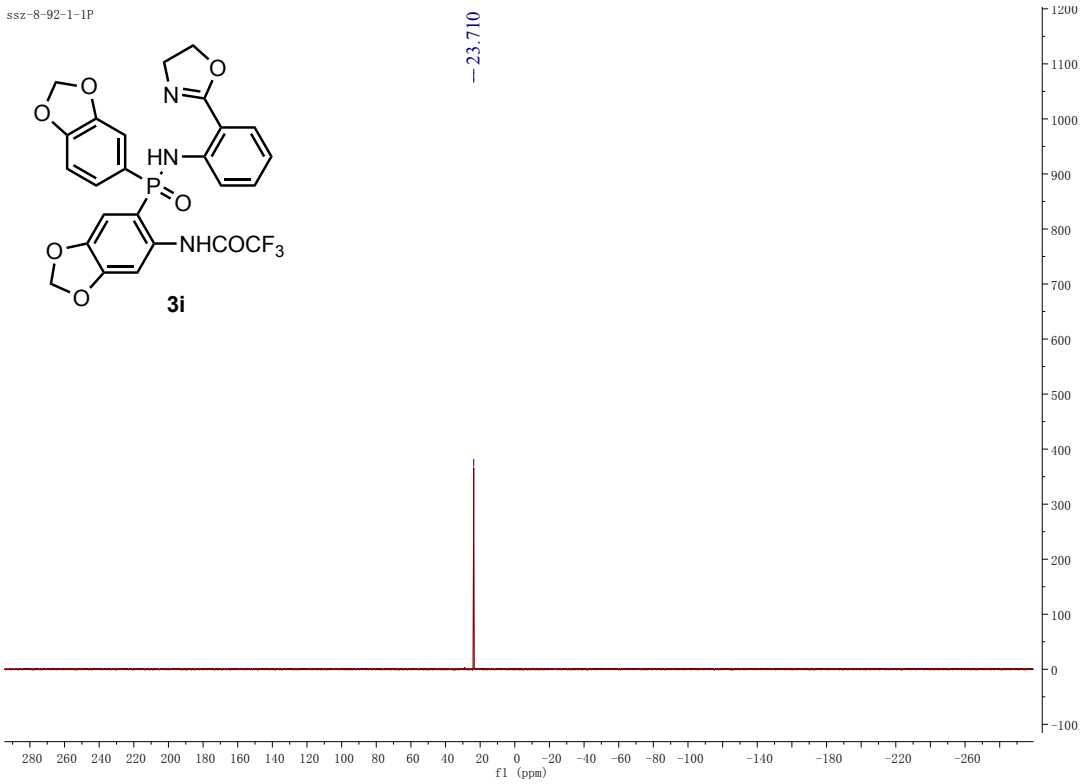


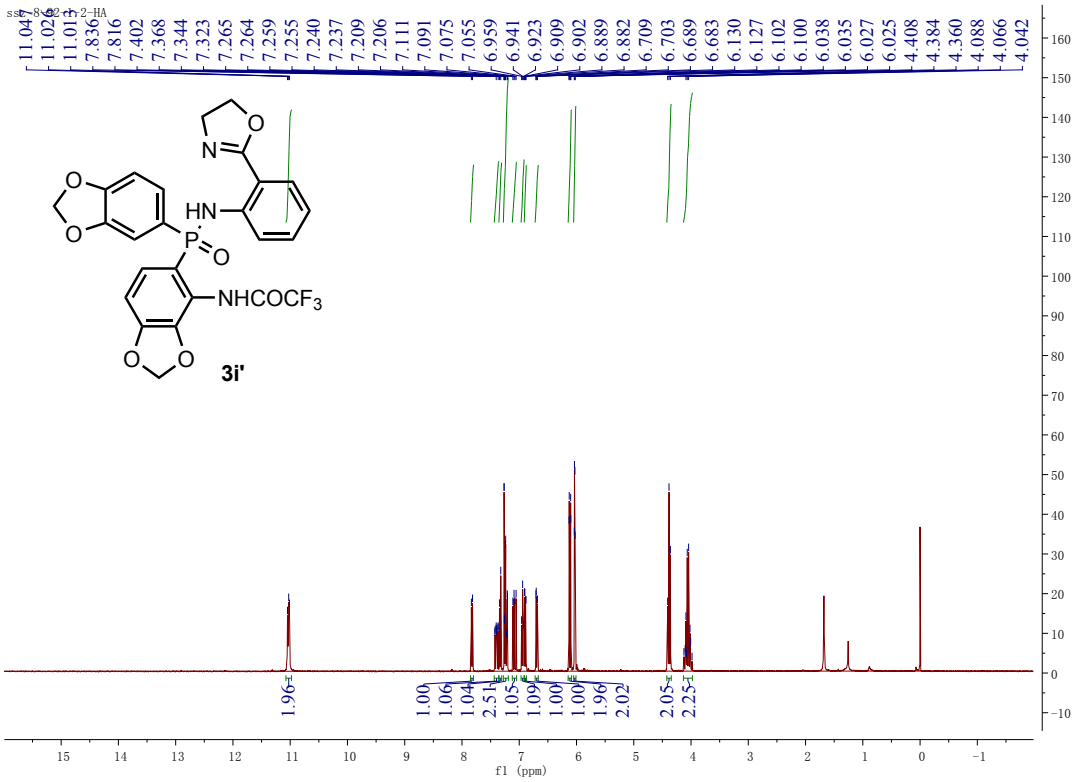
^{19}F NMR for Compound 3i



^{31}P NMR for Compound 3i



^{1}H NMR for Compound 3i'



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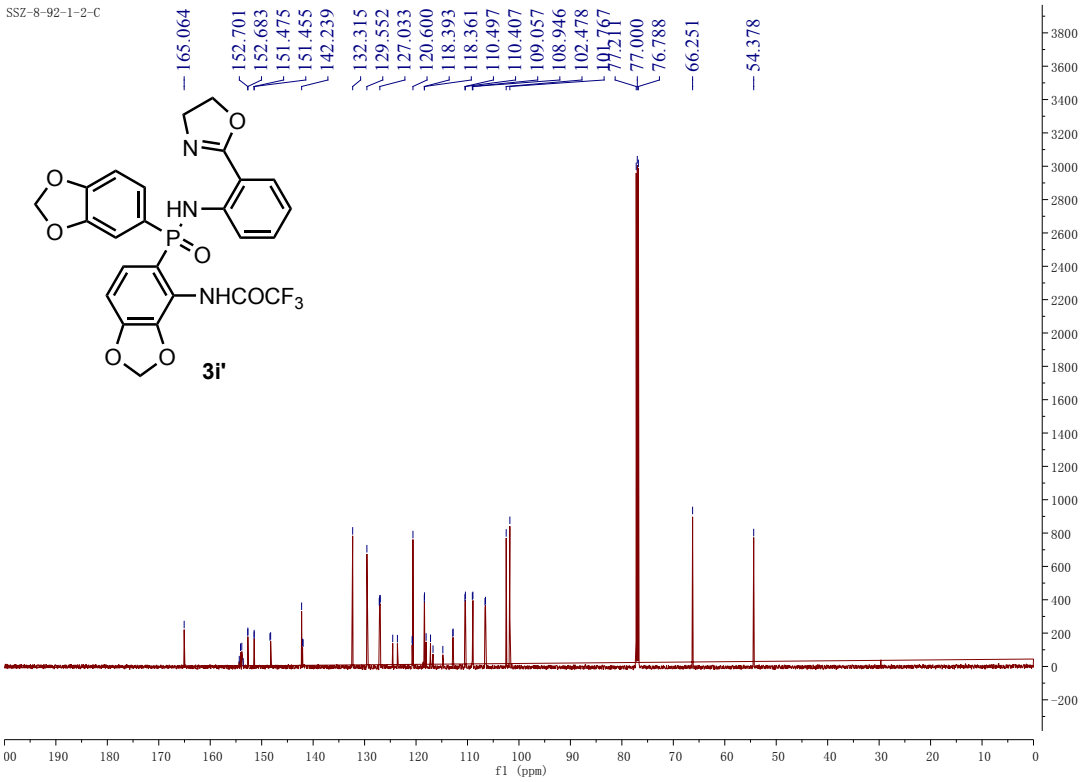

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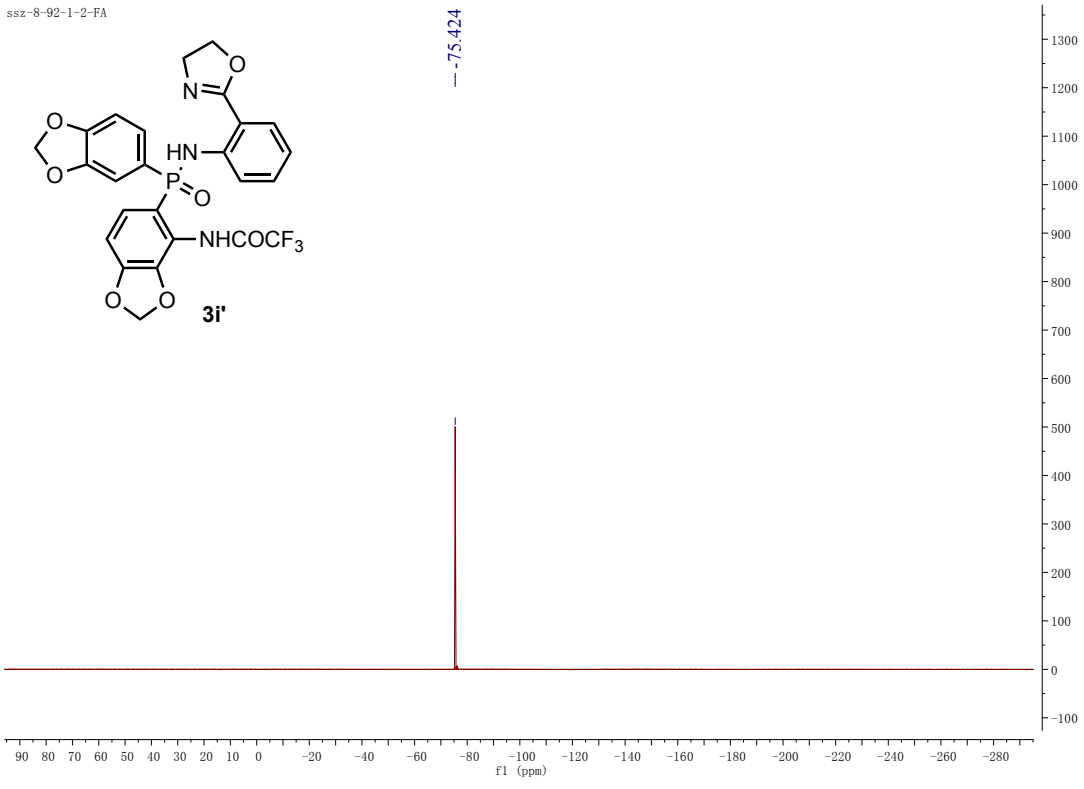

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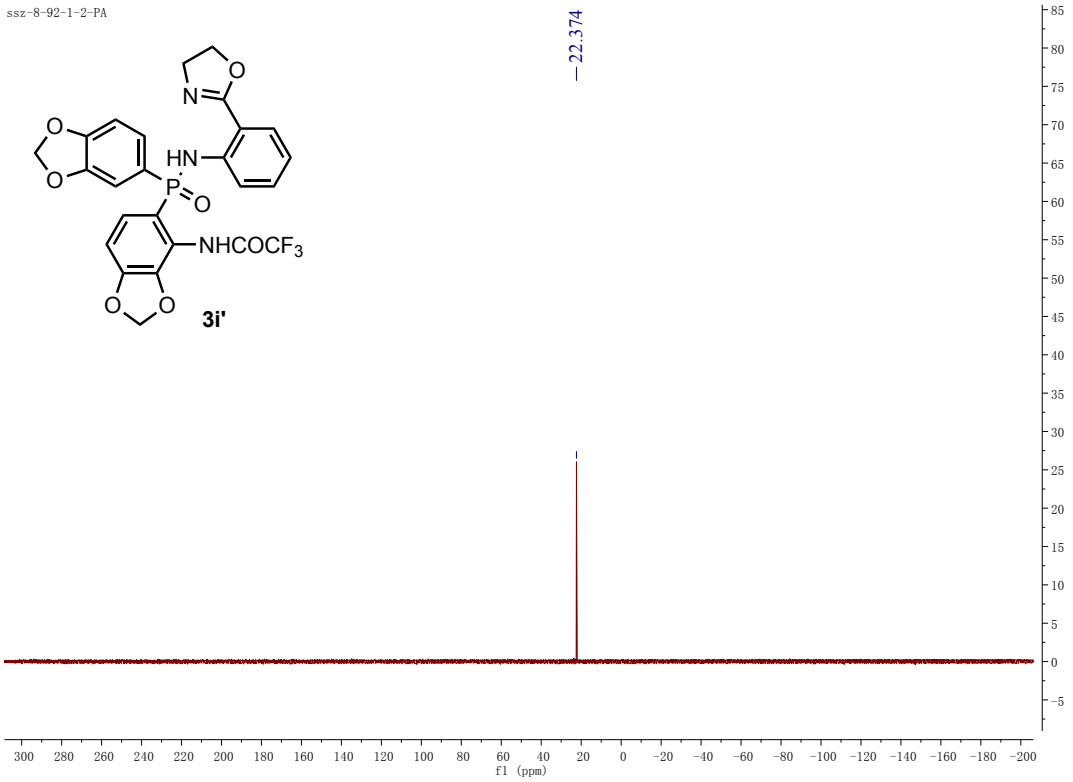
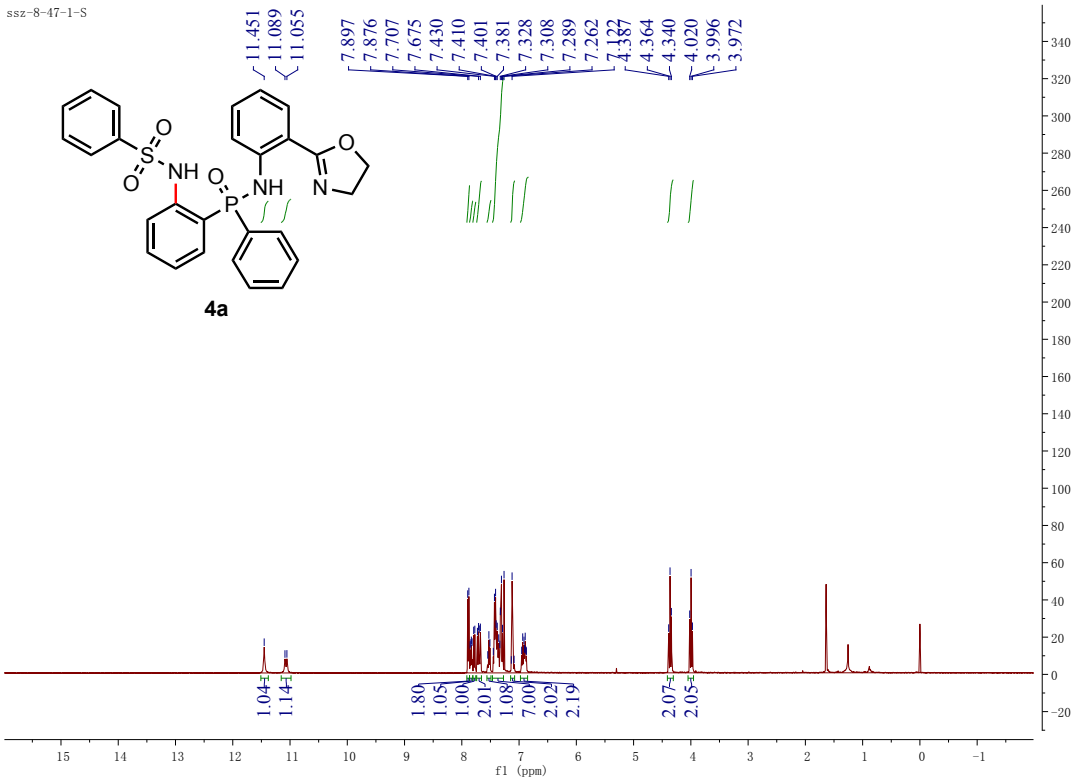
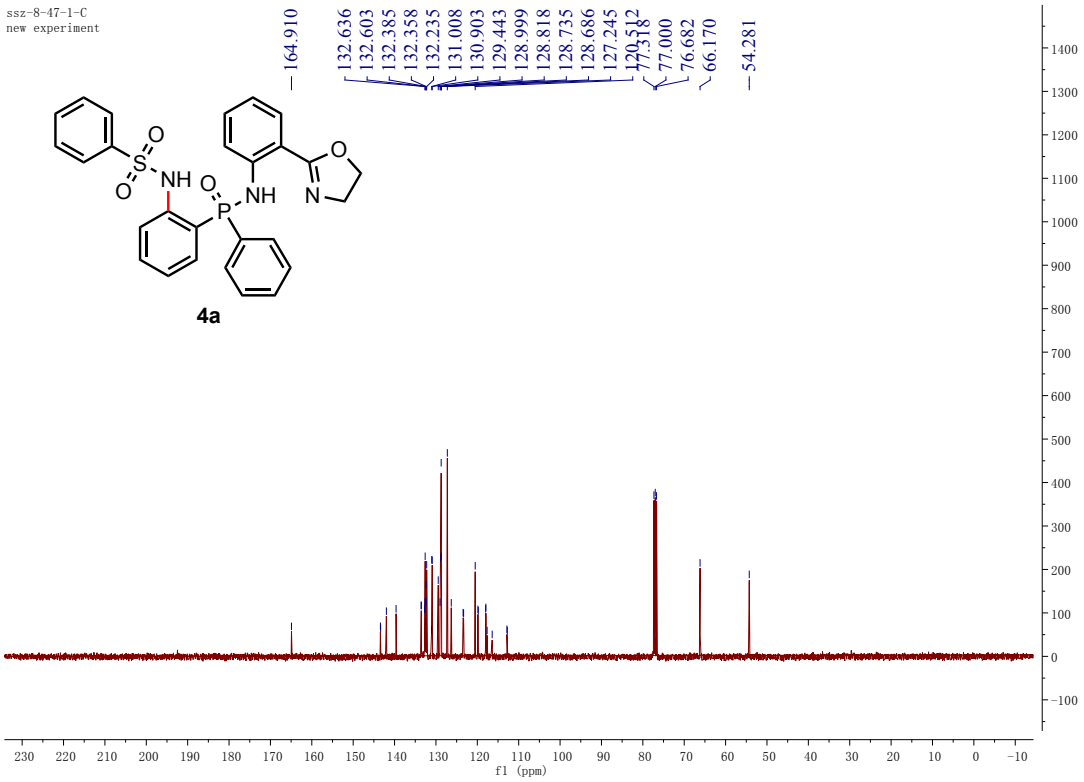


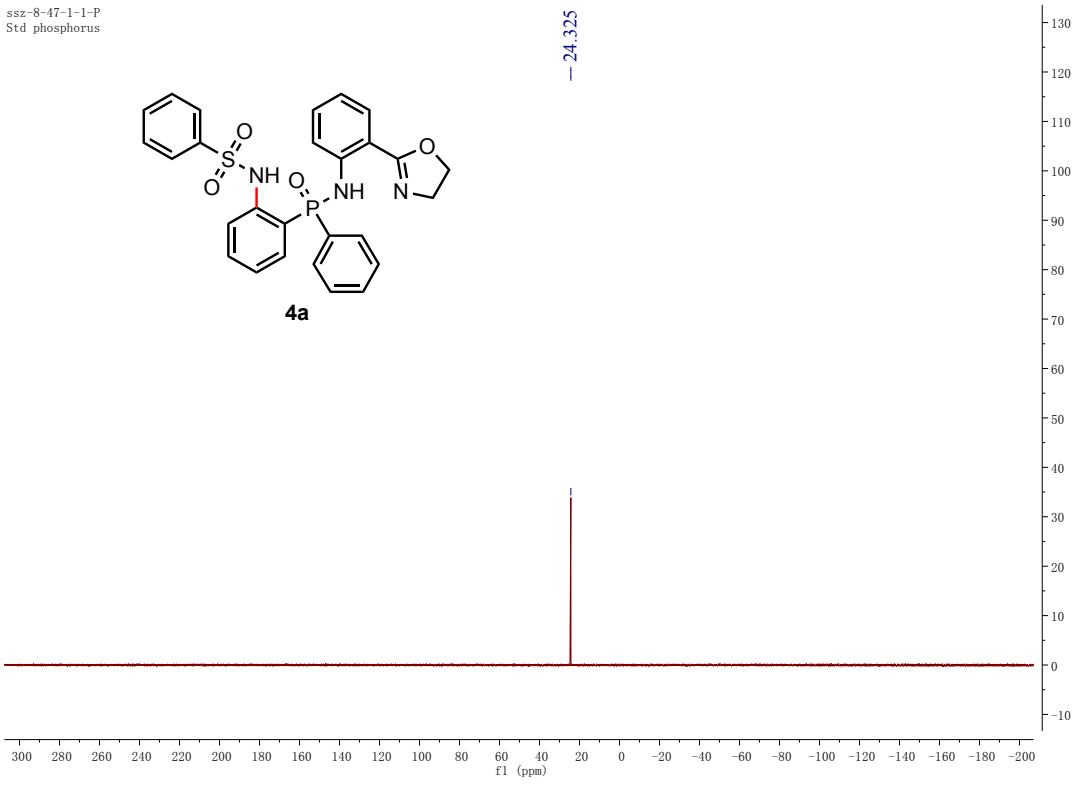
^{1}H NMR for Compound 4a



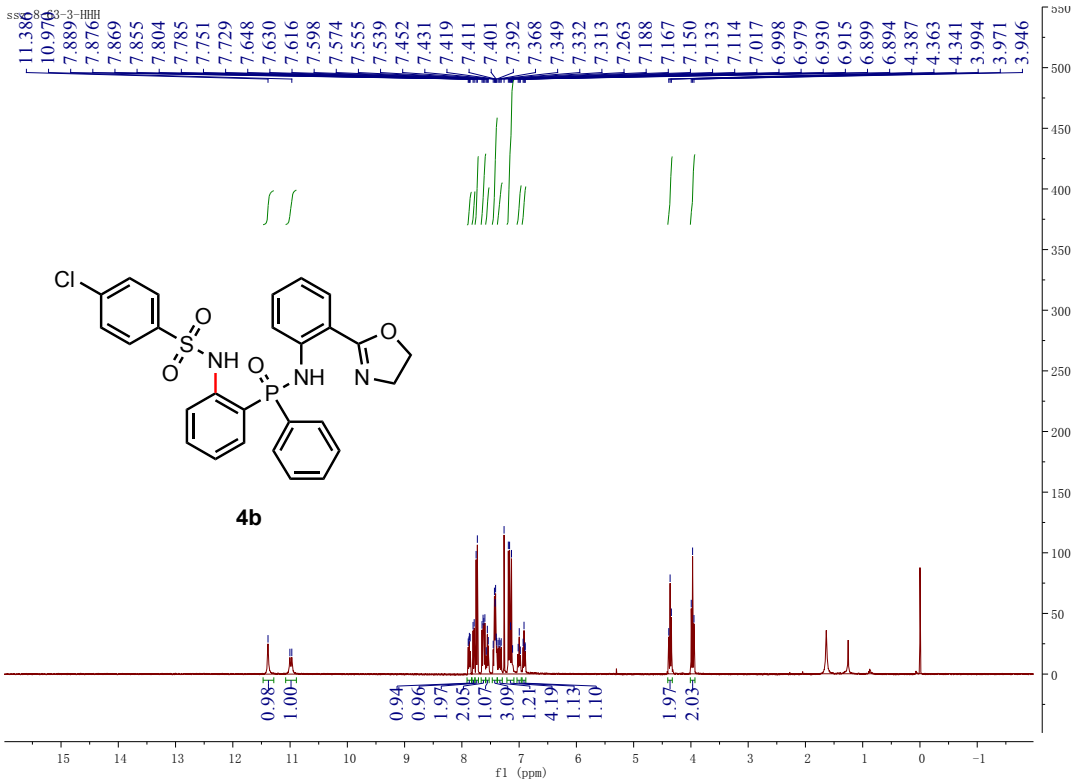
^{13}C NMR for Compound 4a



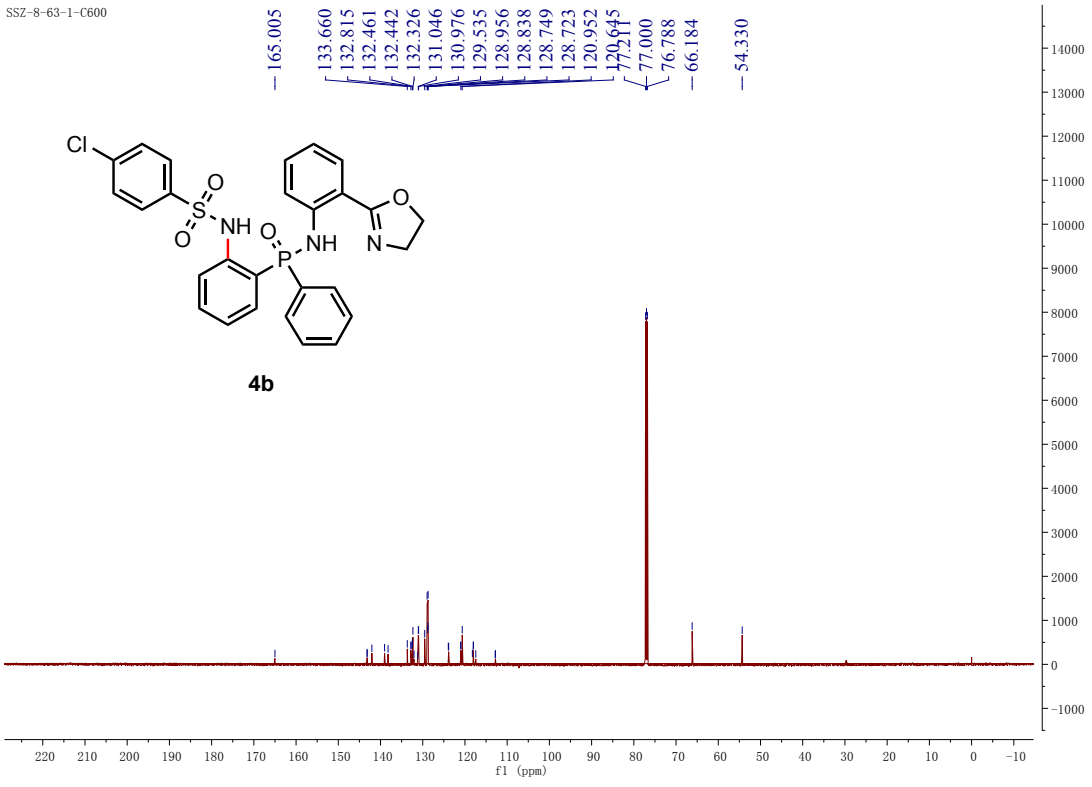
^{31}P NMR for Compound 4a



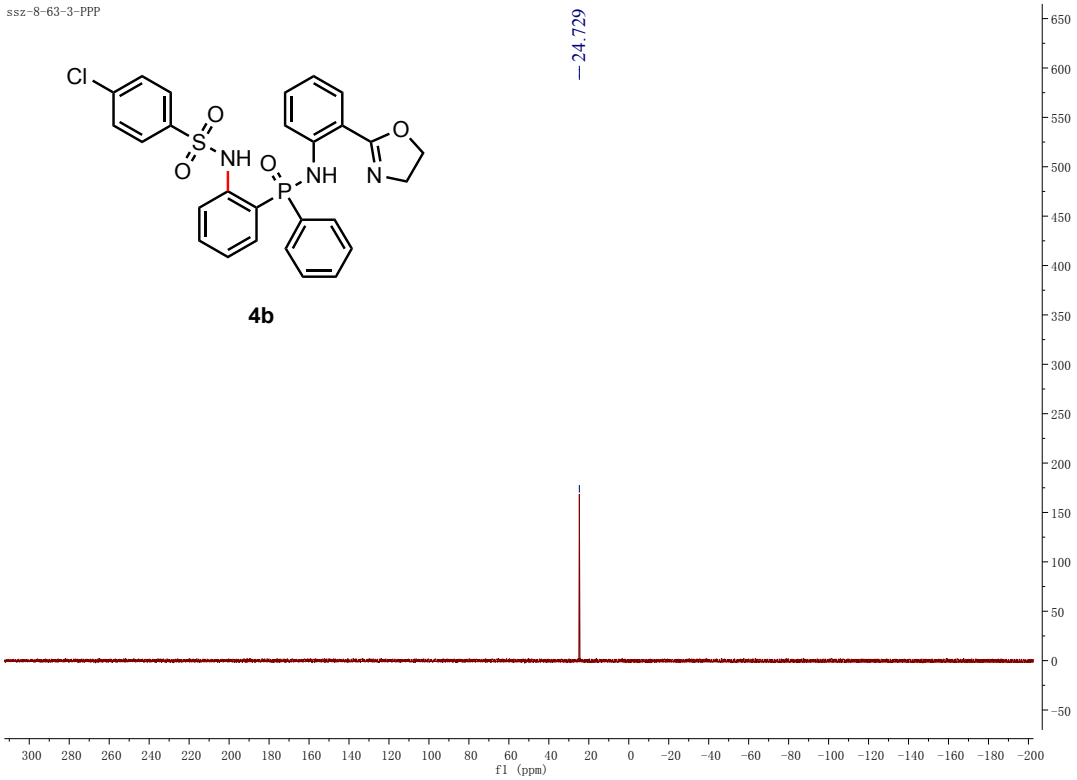
^{1}H NMR for Compound 4b



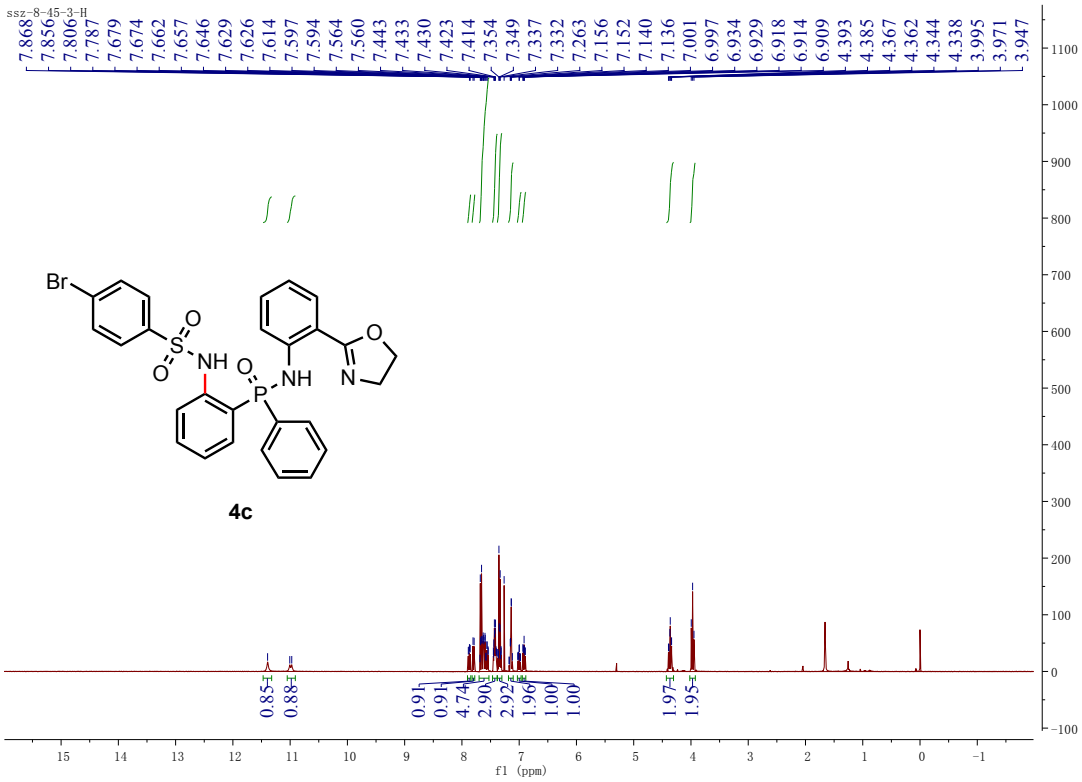
^{13}C NMR for Compound 4b



^{31}P NMR for Compound 4b



^{1}H NMR for Compound 4c



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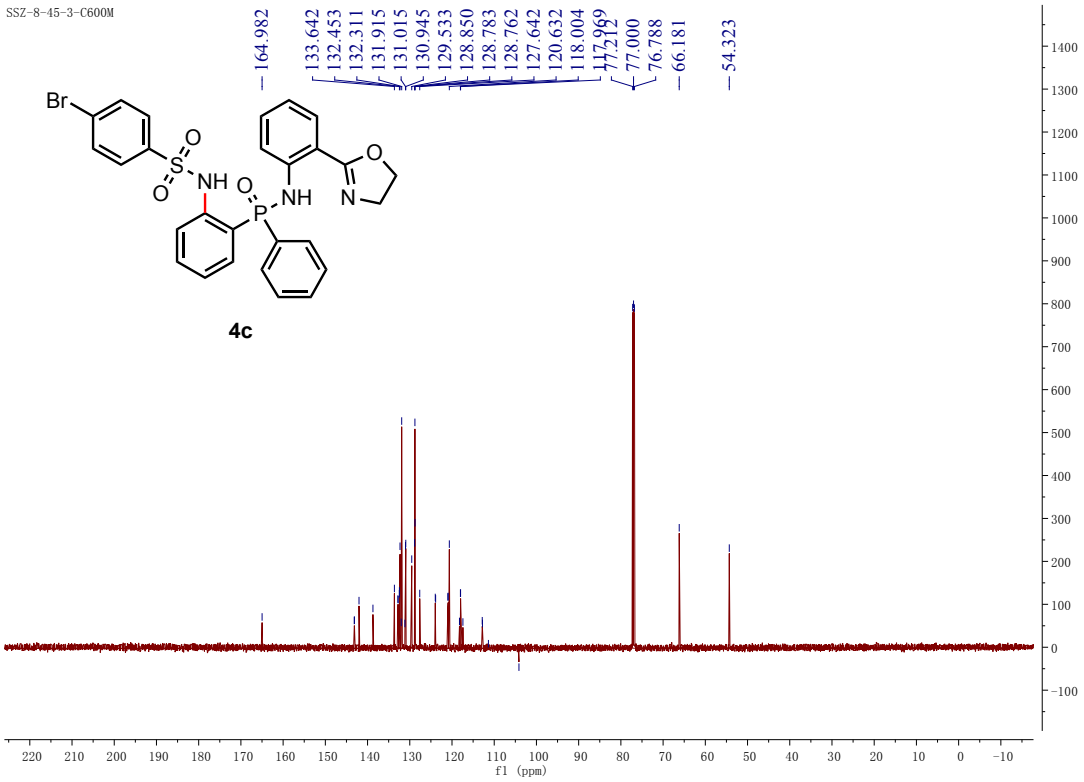

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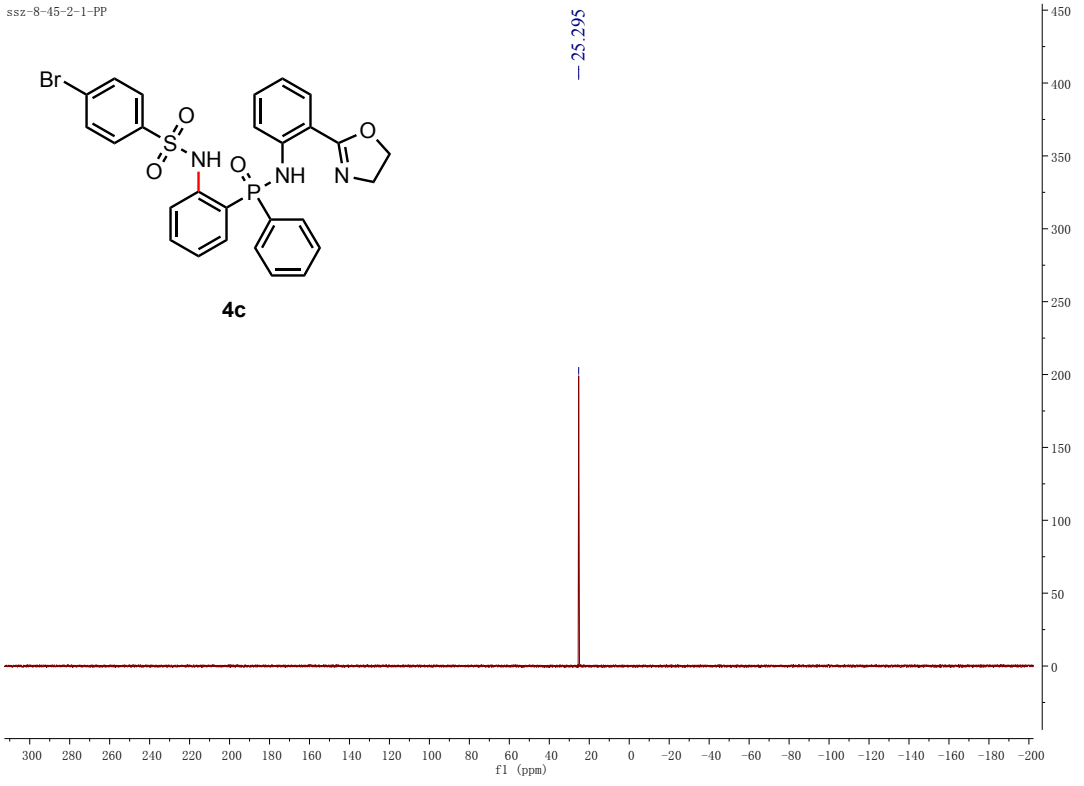
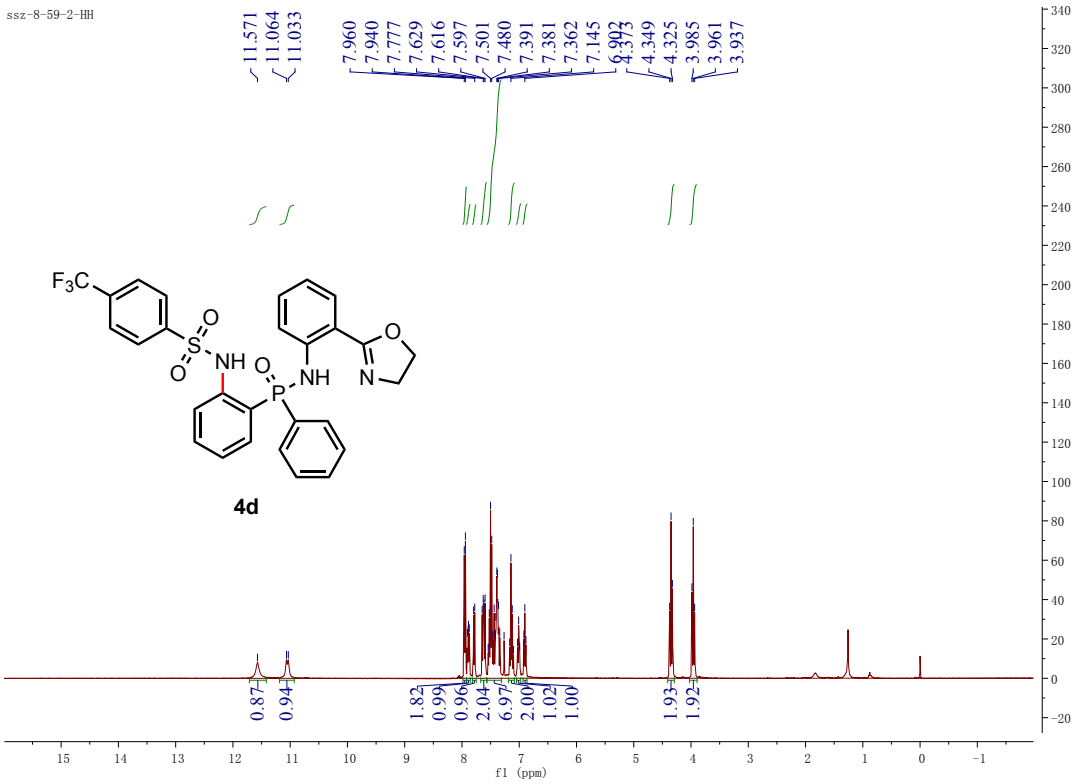
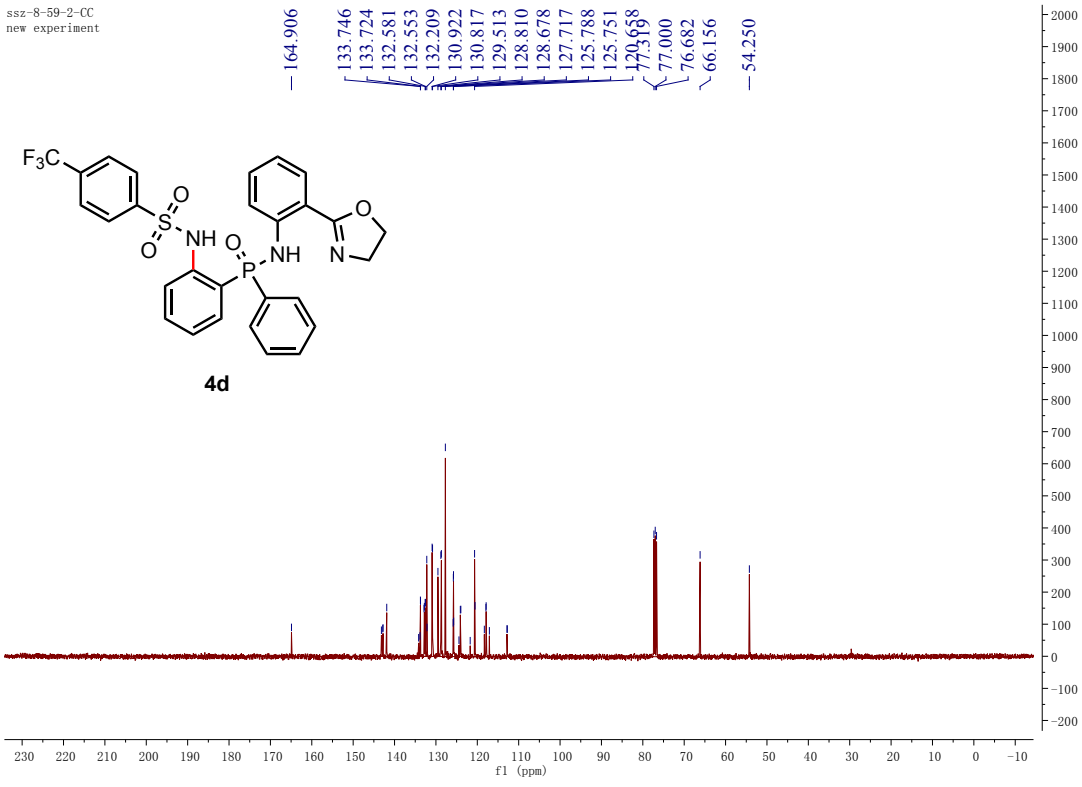


^{1}H NMR for Compound 4d



^{13}C NMR for Compound 4d



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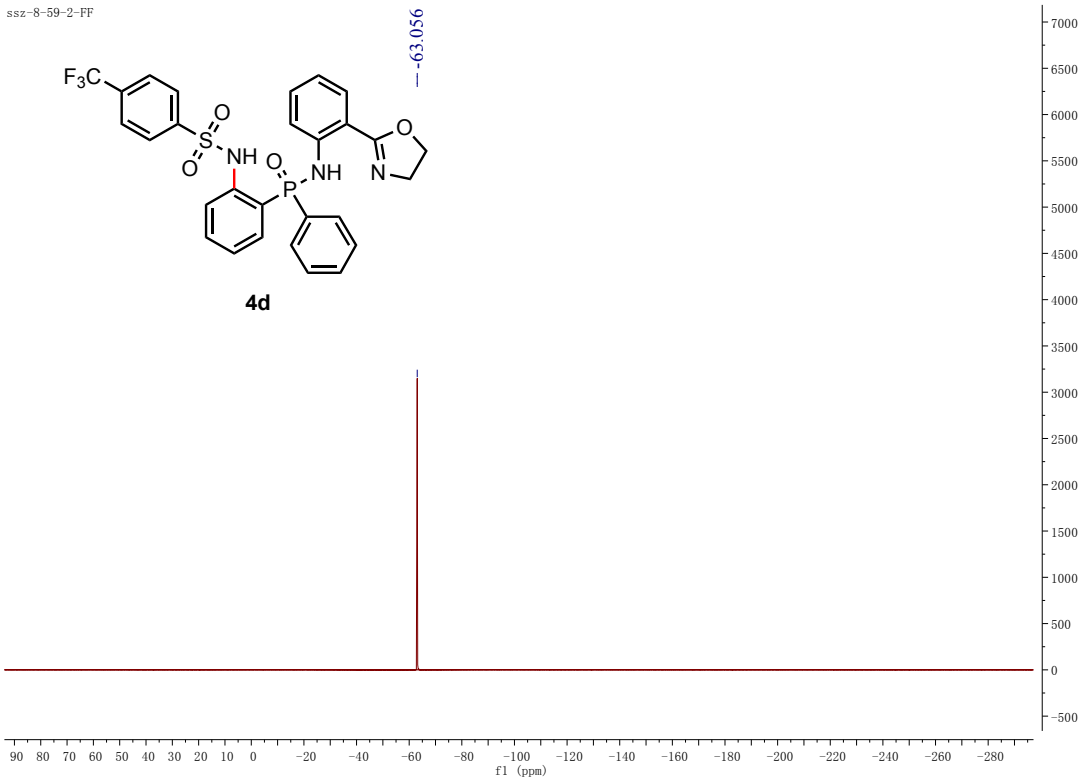
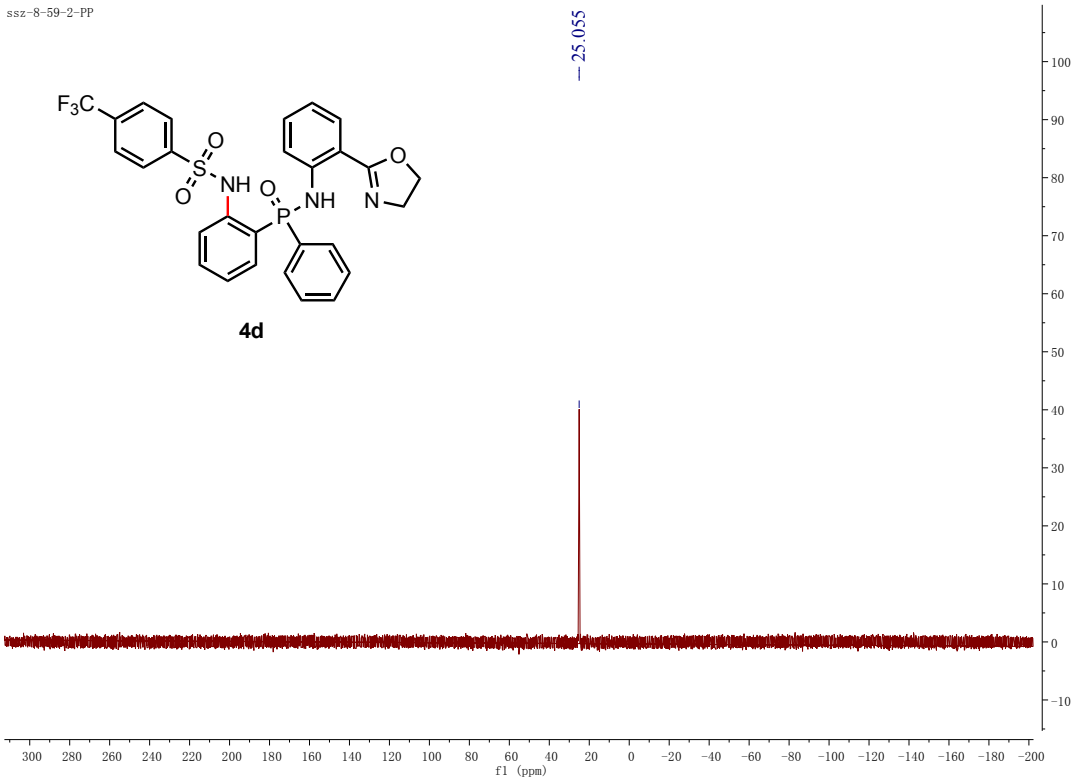


^{31}P NMR for Compound 4b



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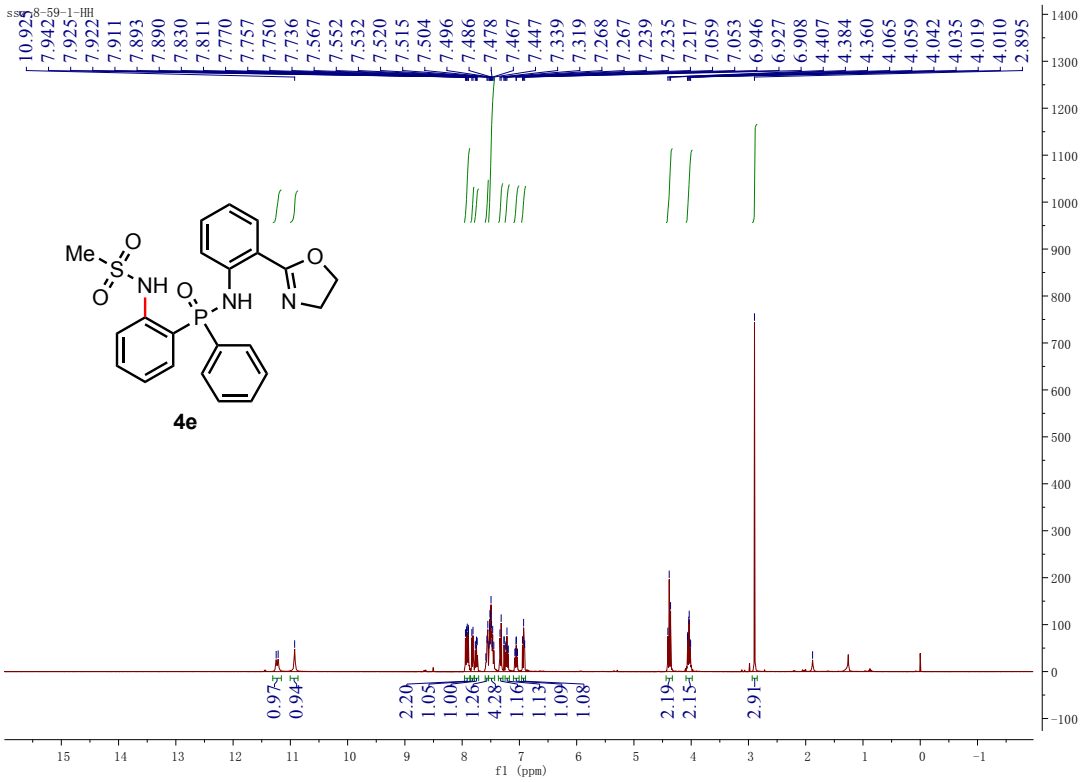

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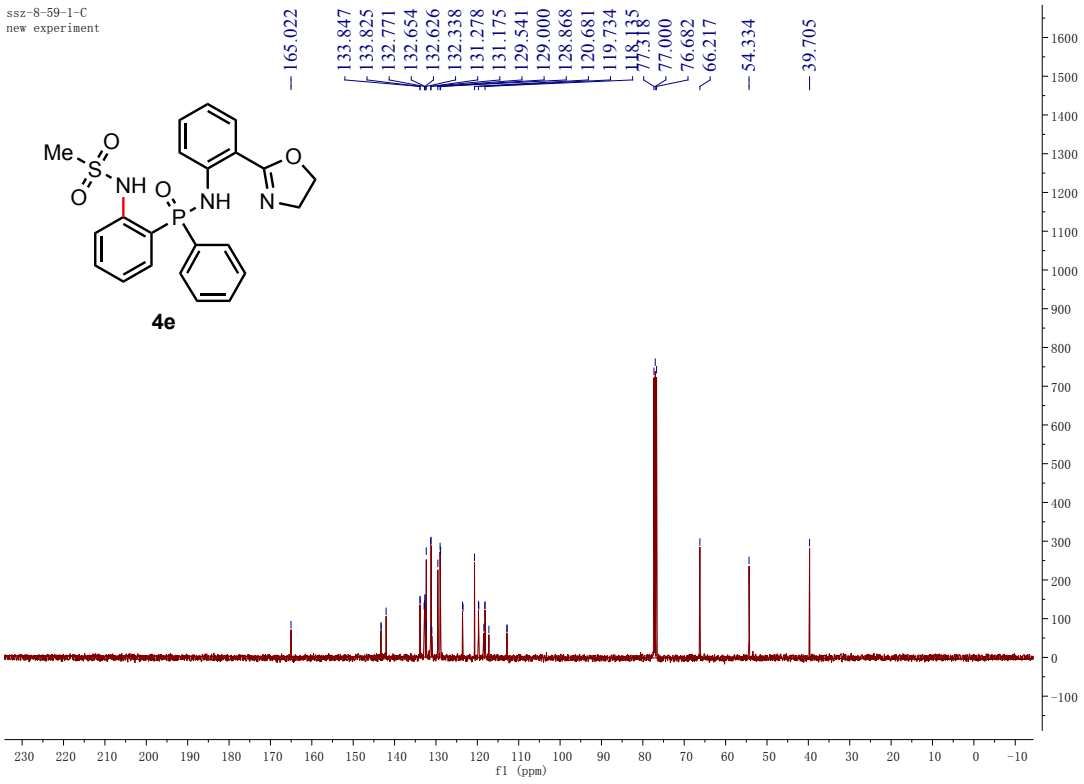
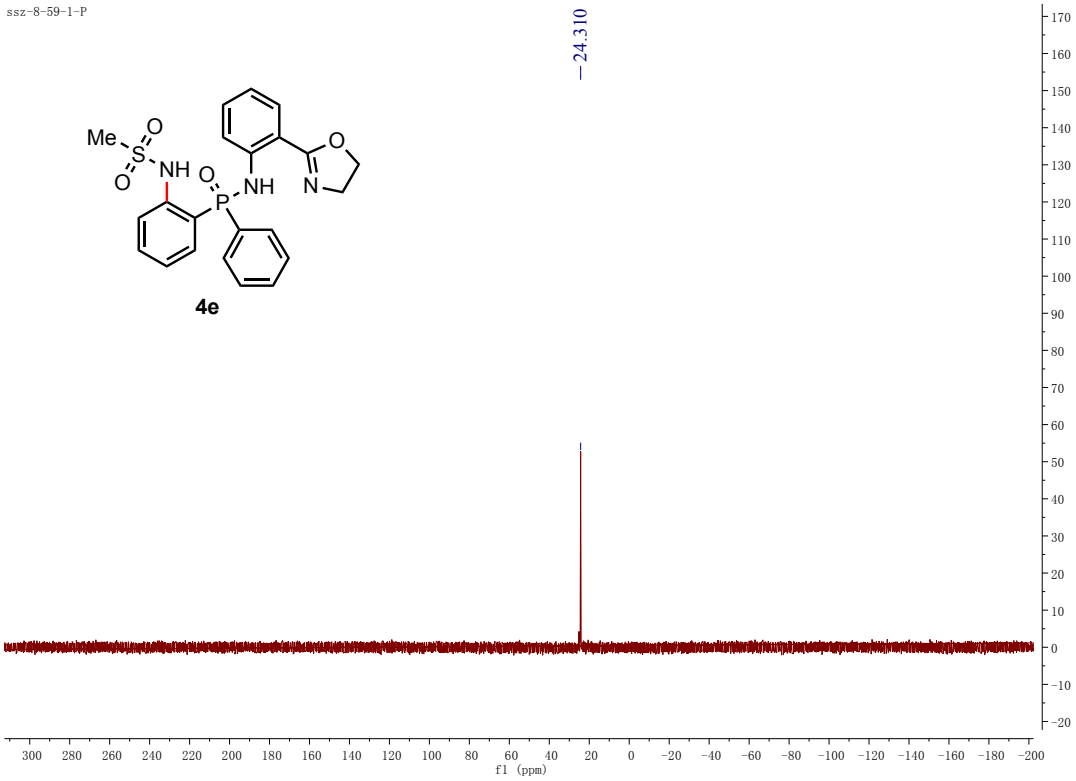
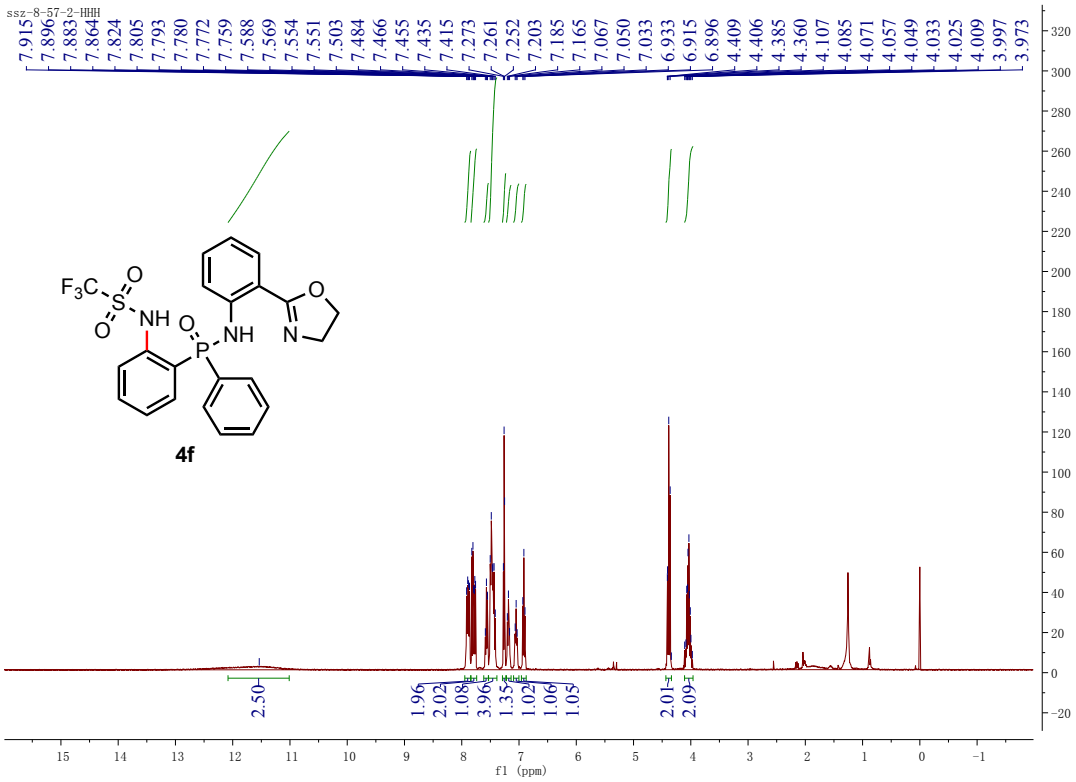


^{31}P NMR for Compound 4e



^{1}H NMR for Compound 4f



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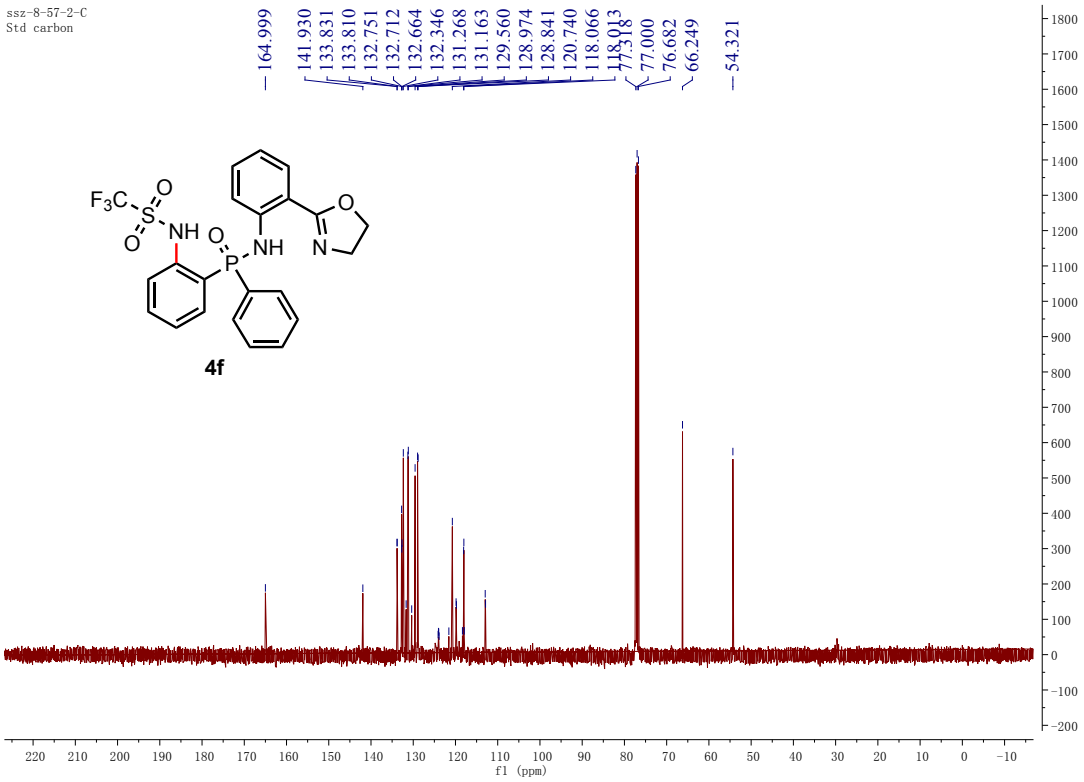
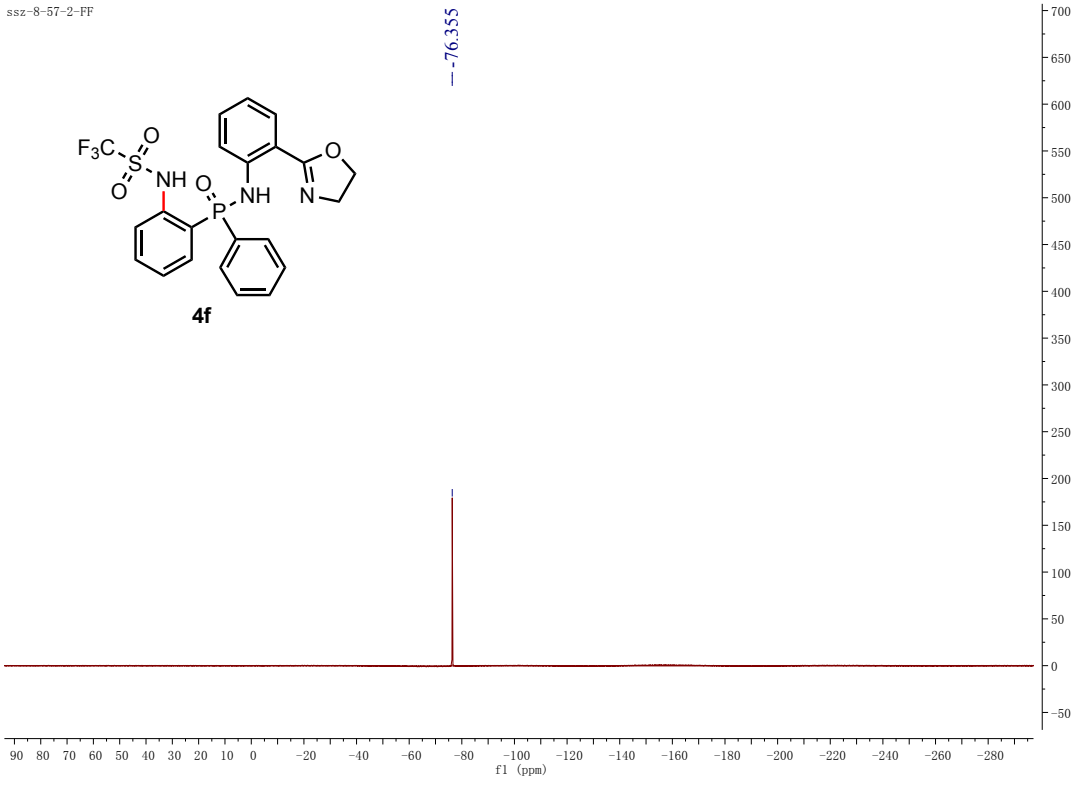
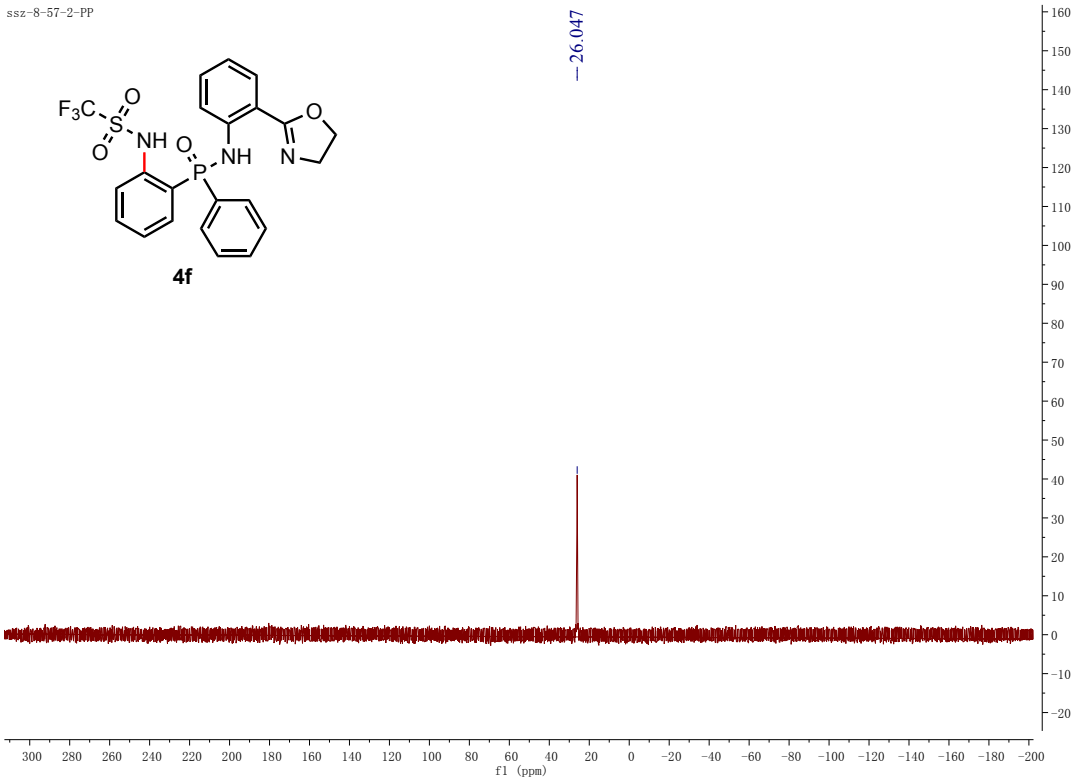


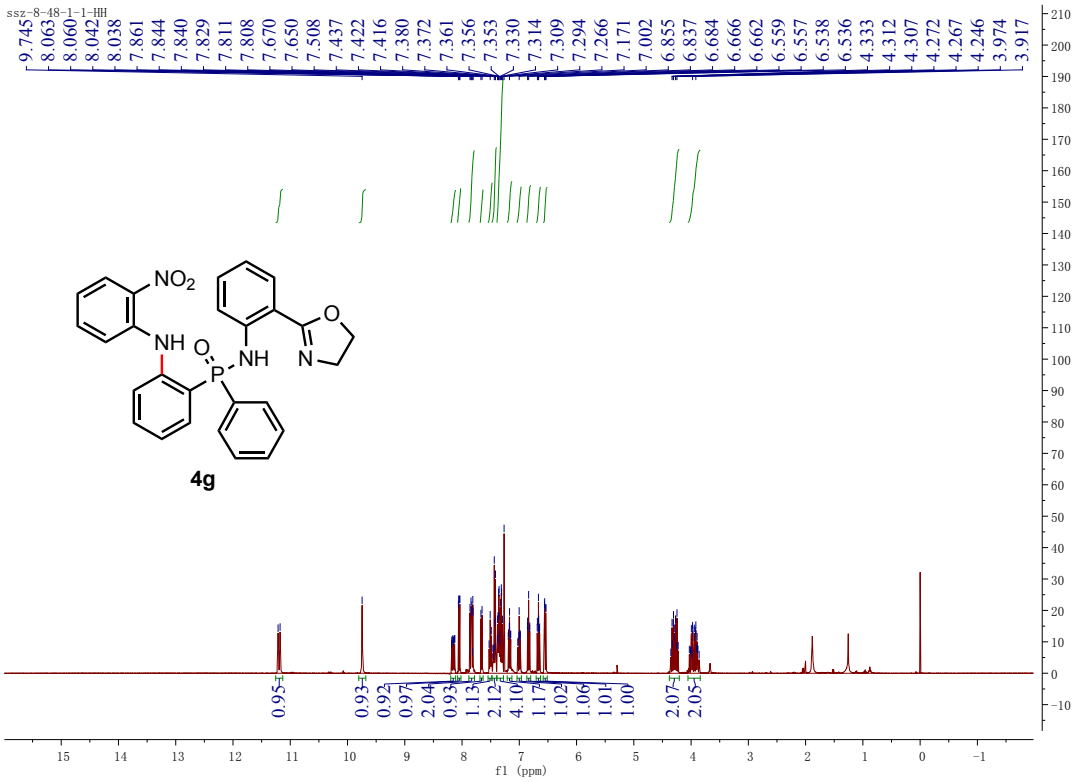
^{19}F NMR for Compound 4f



^{31}P NMR for Compound 4f



^{1}H NMR for Compound 4g



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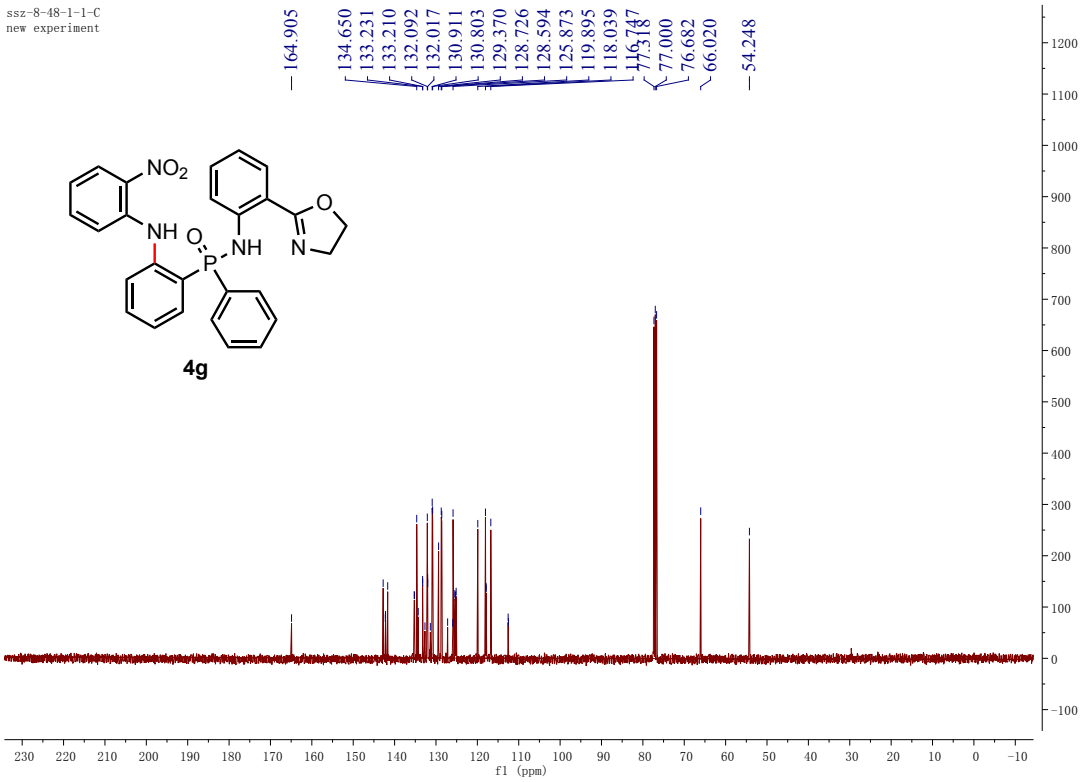

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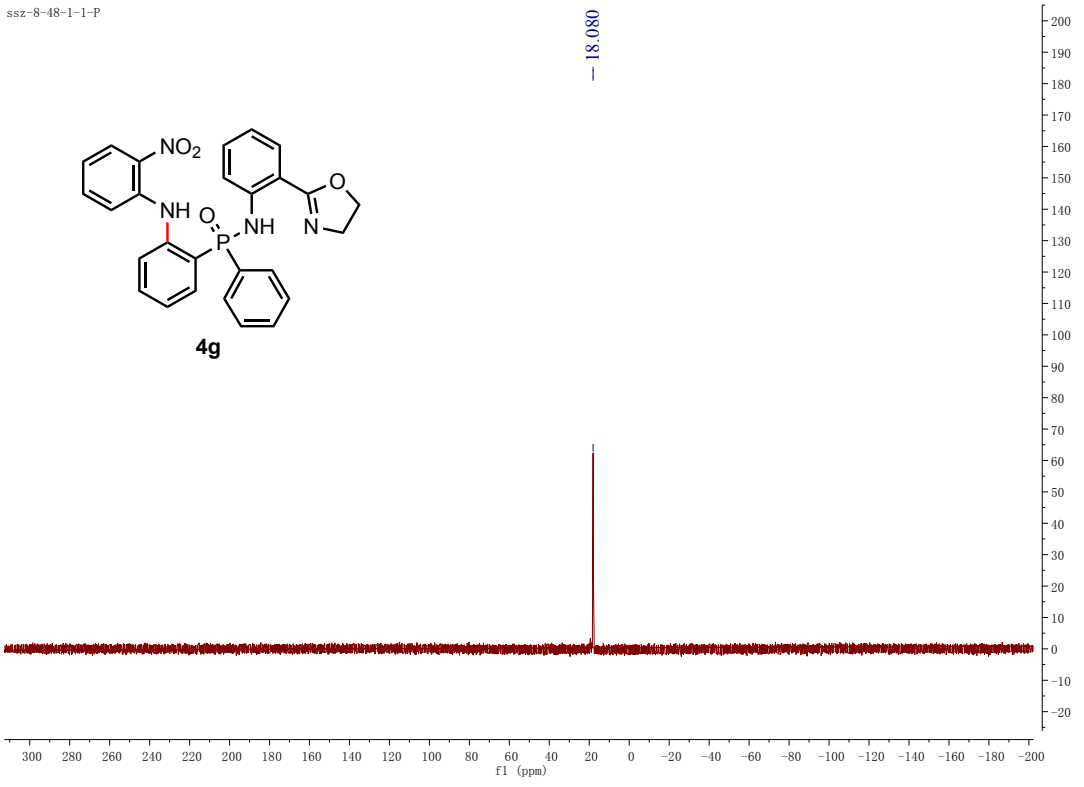
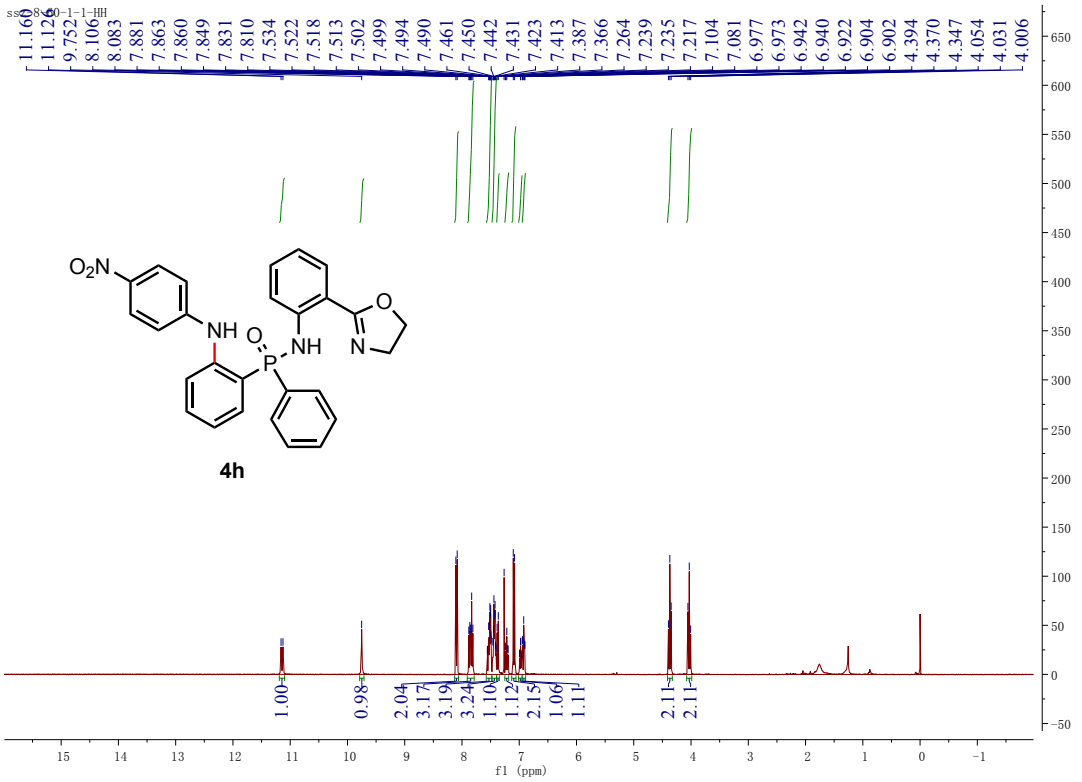


^{1}H NMR for Compound 4h



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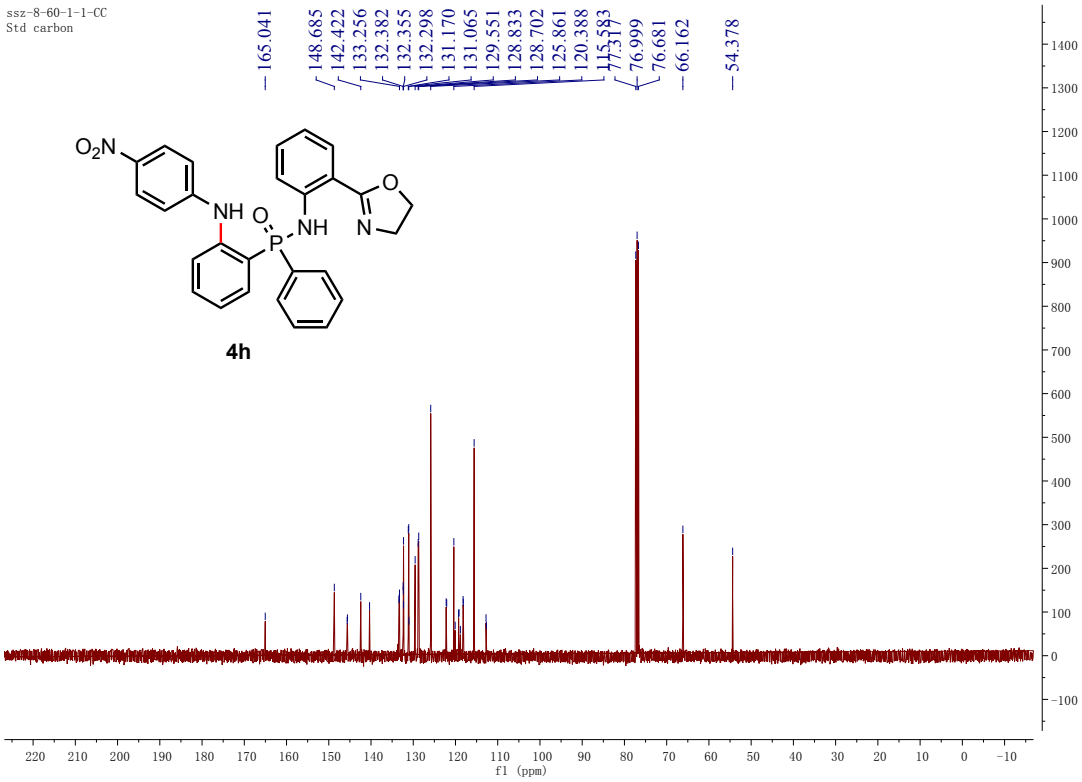

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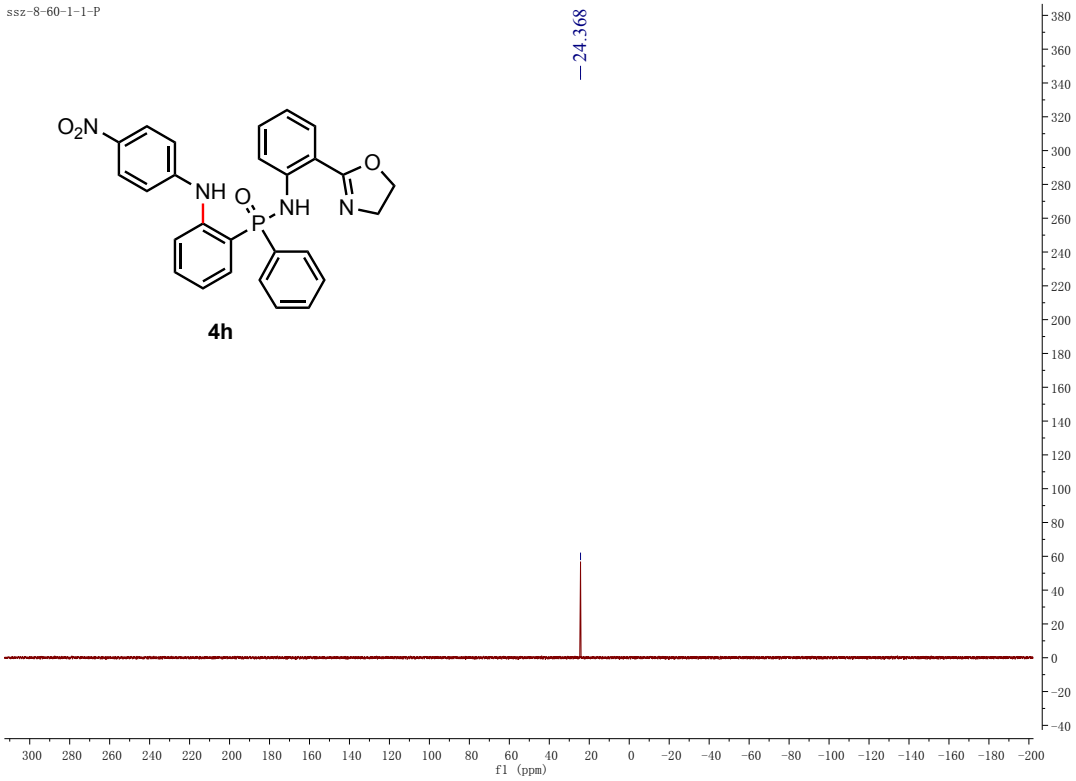
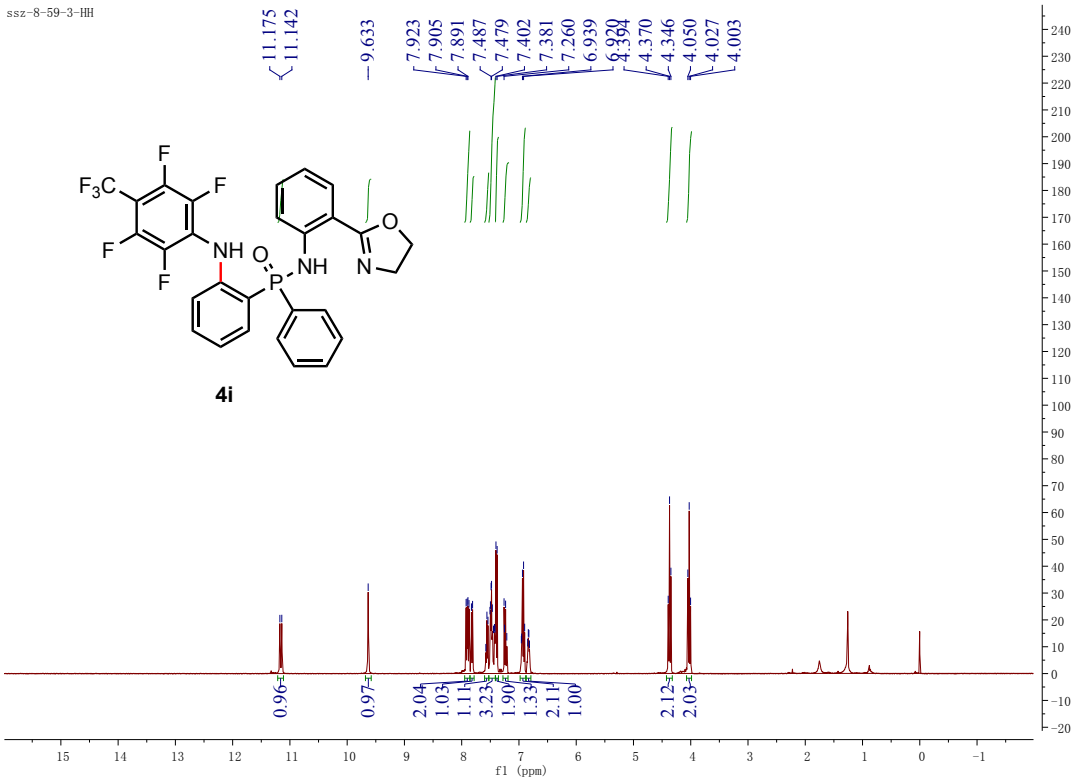
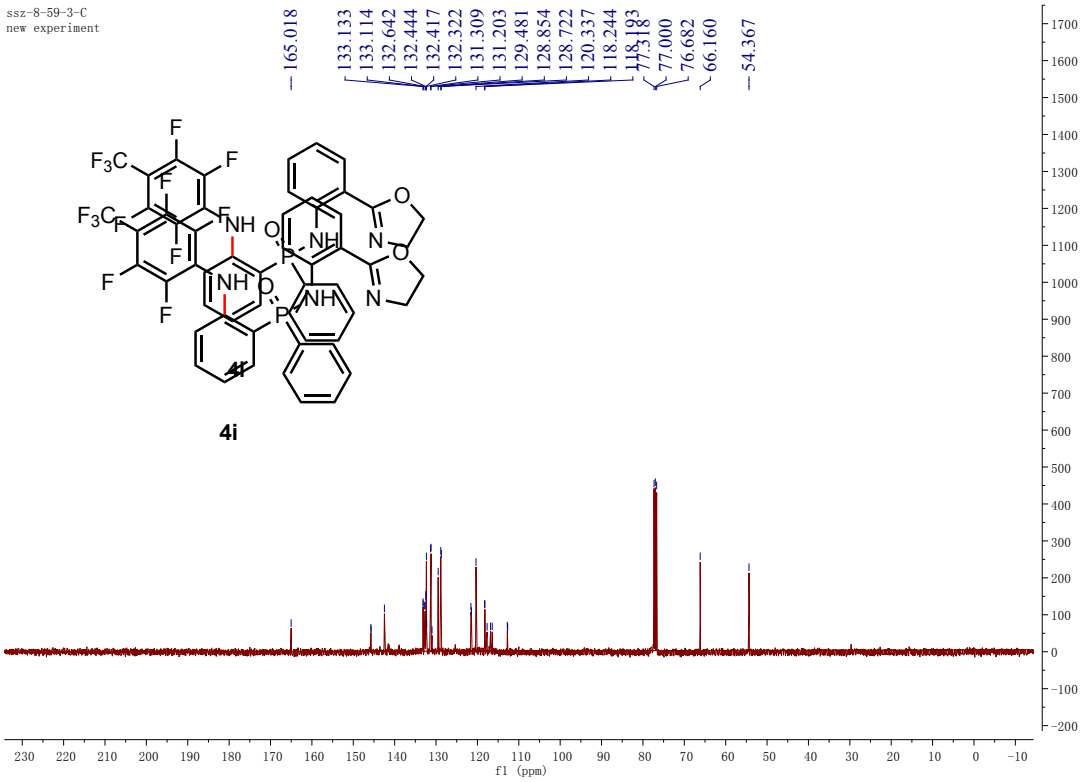


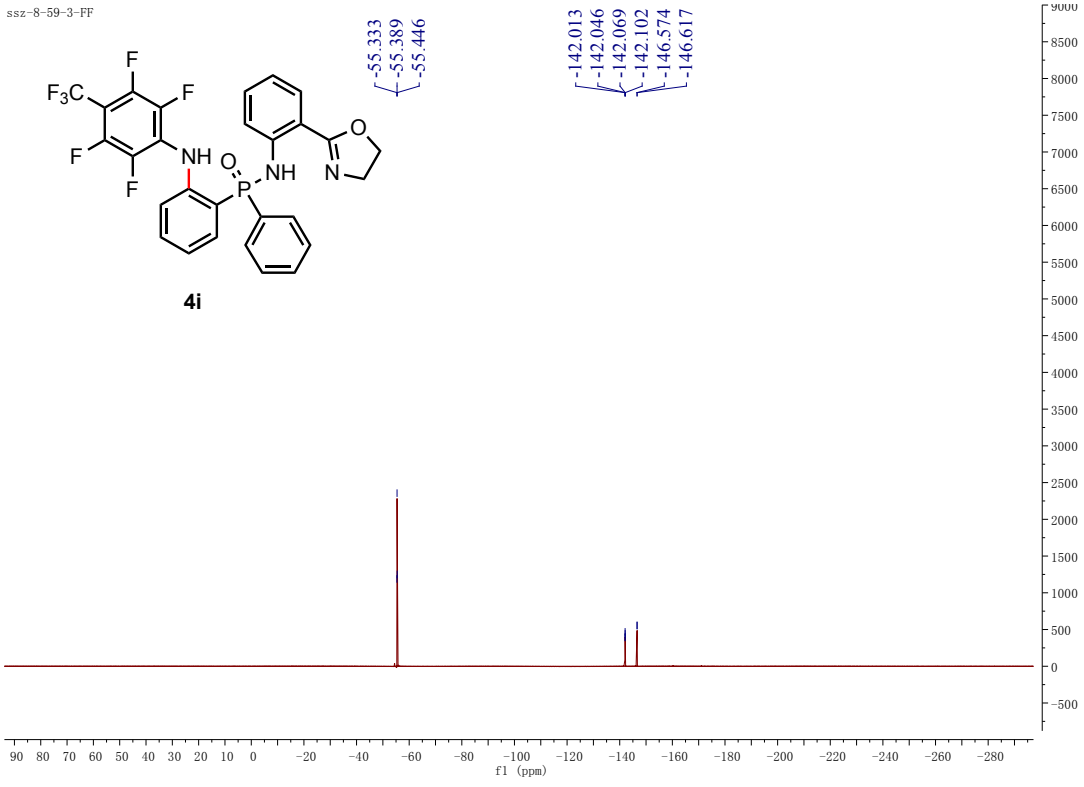
^{1}H NMR for Compound 4i



^{13}C NMR for Compound 4i



^{19}F NMR for Compound 4i



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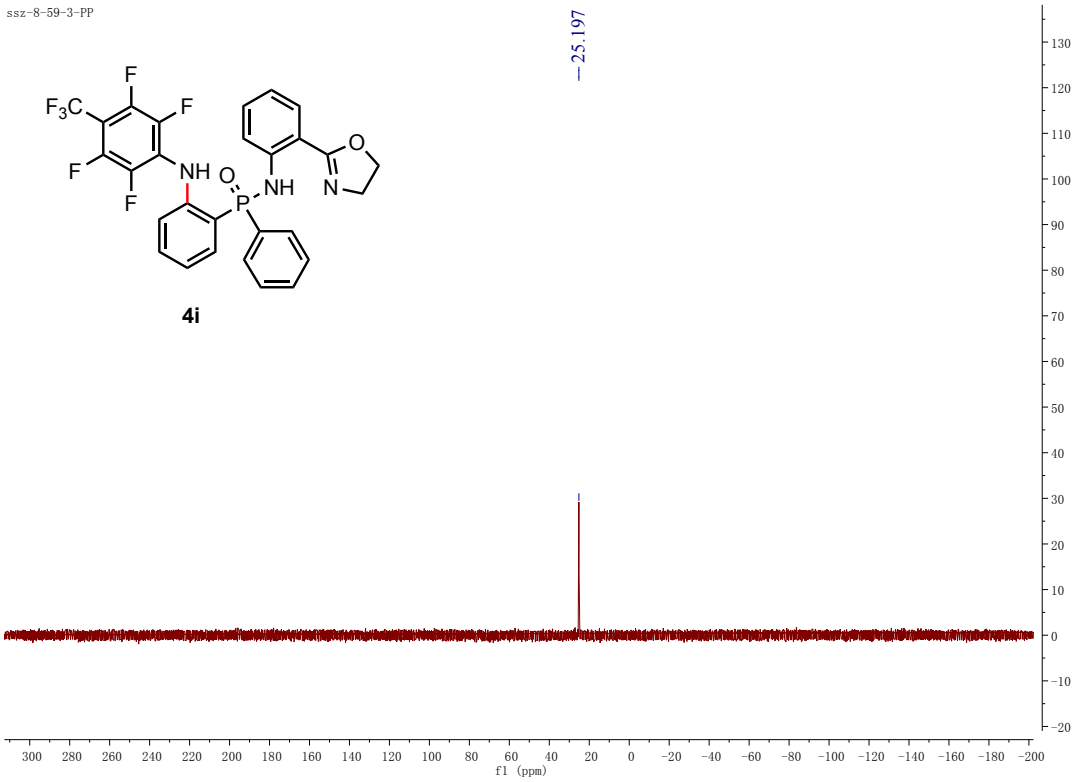

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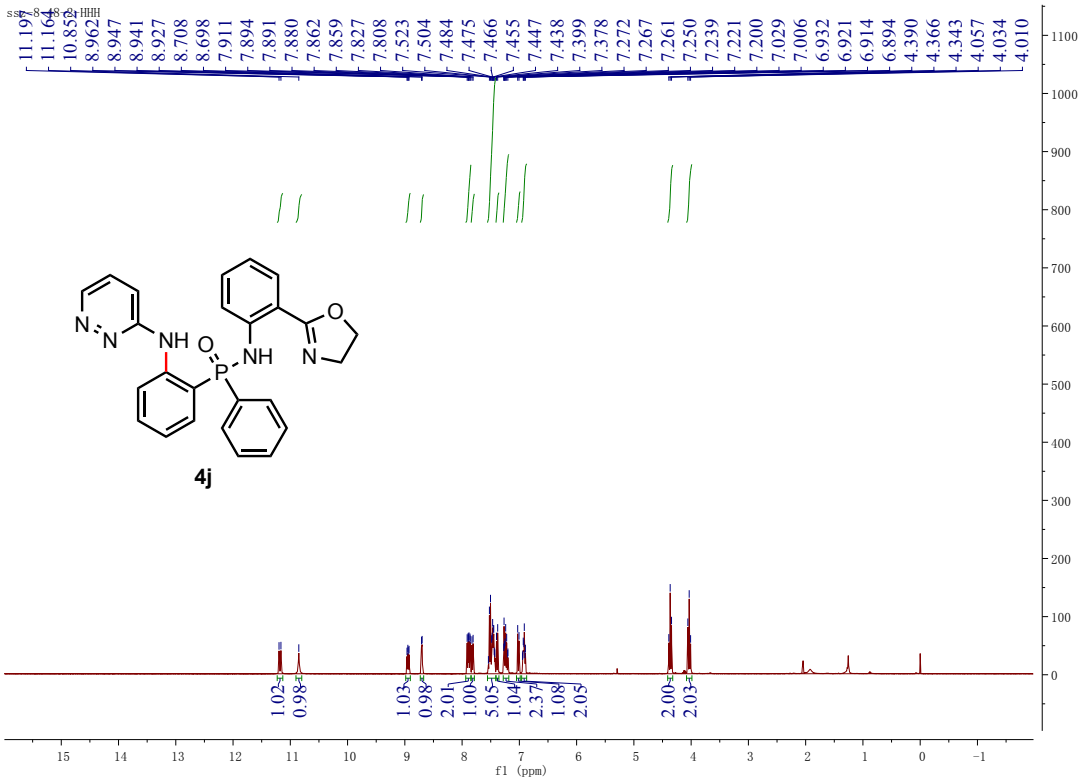

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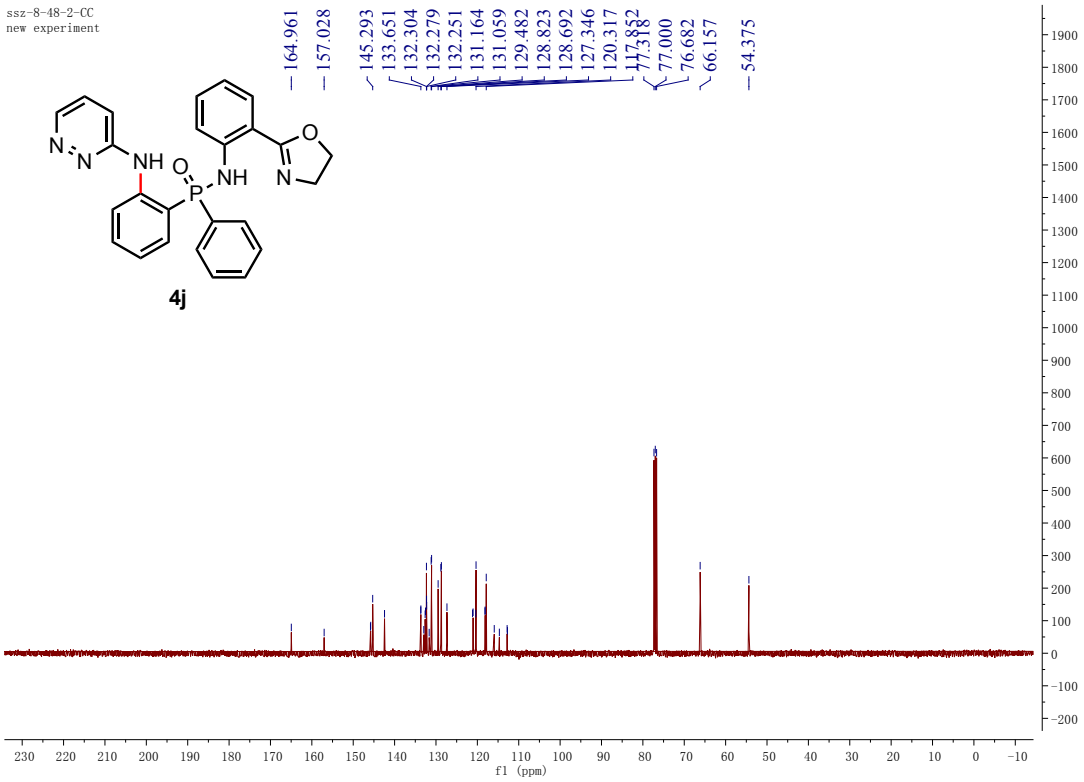

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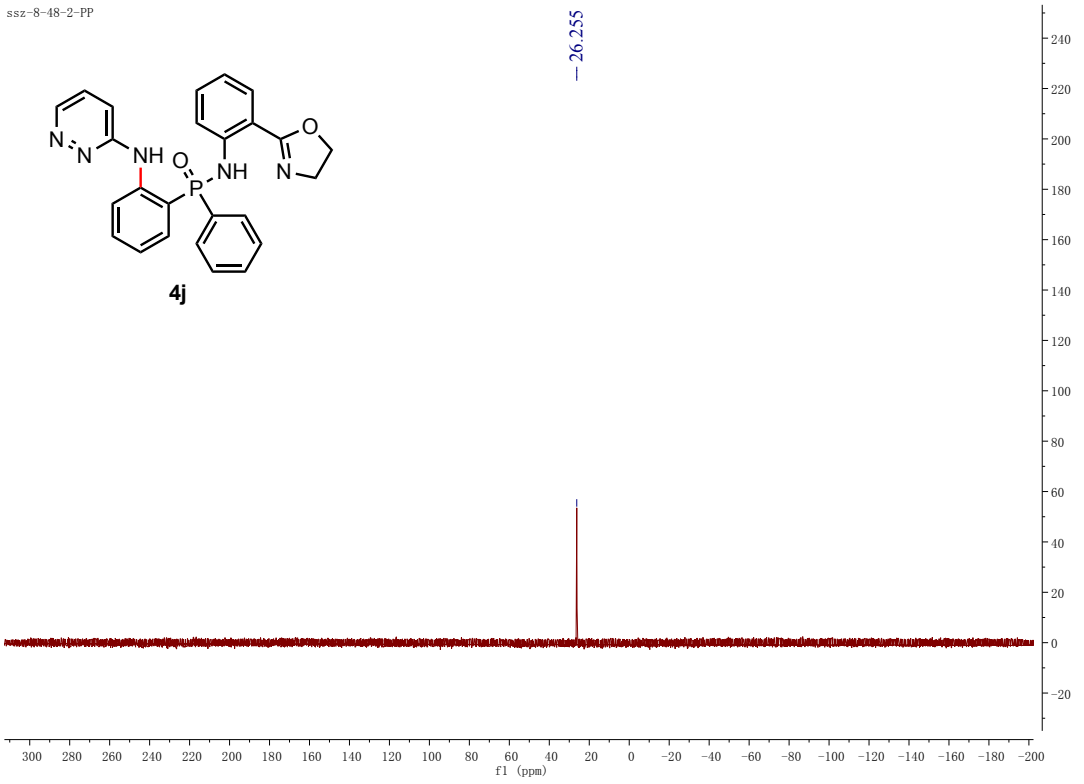
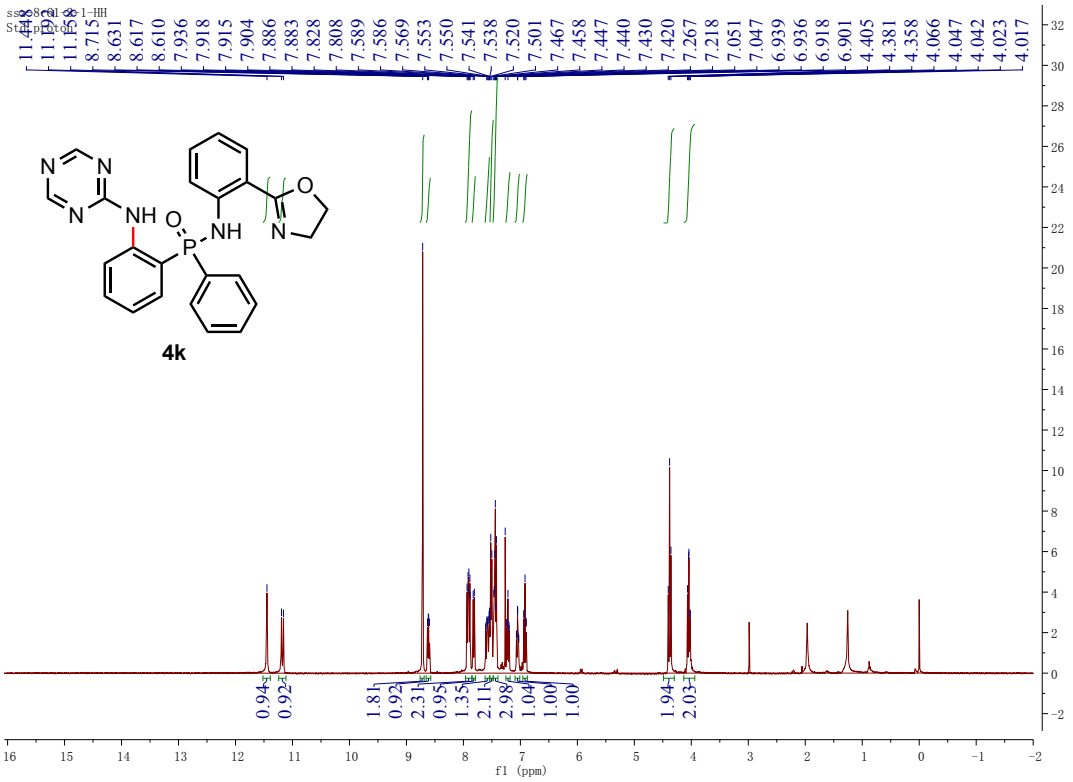


^{1}H NMR for Compound 4k



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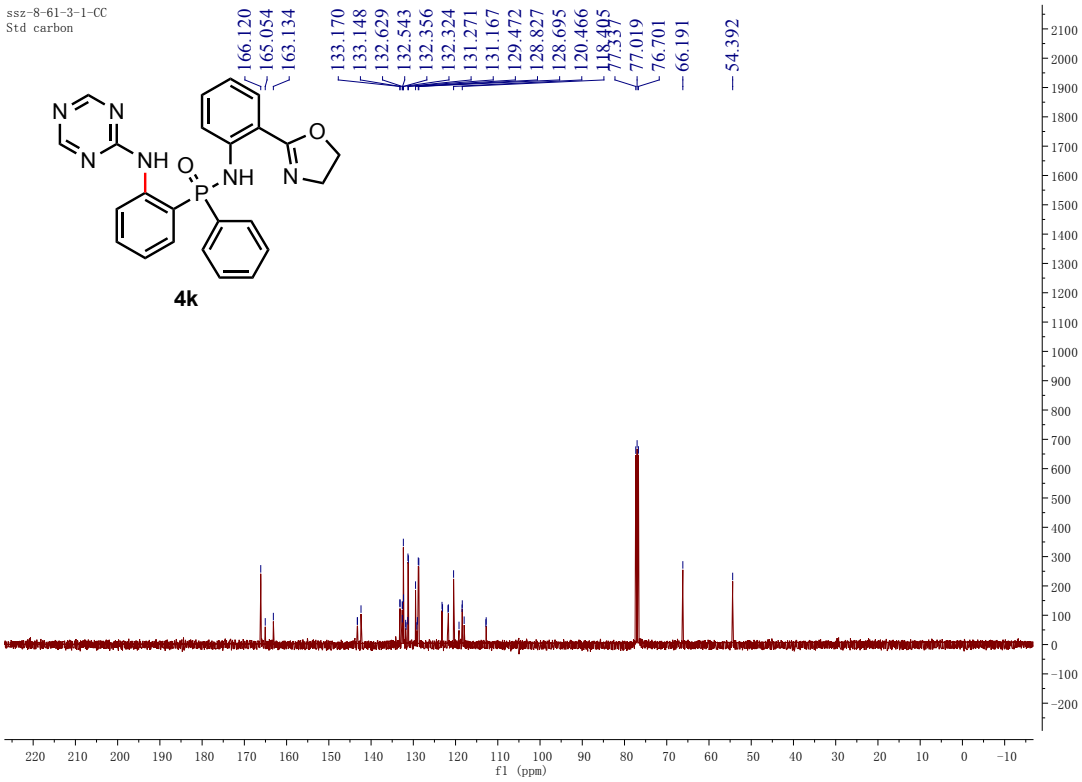
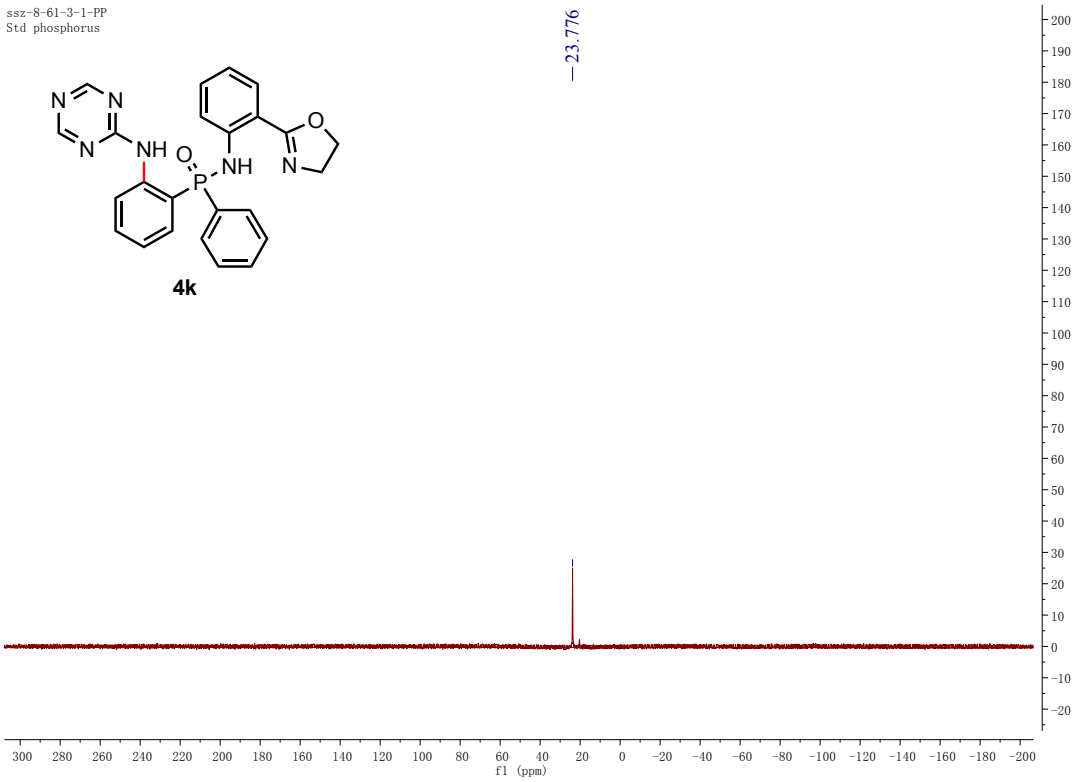
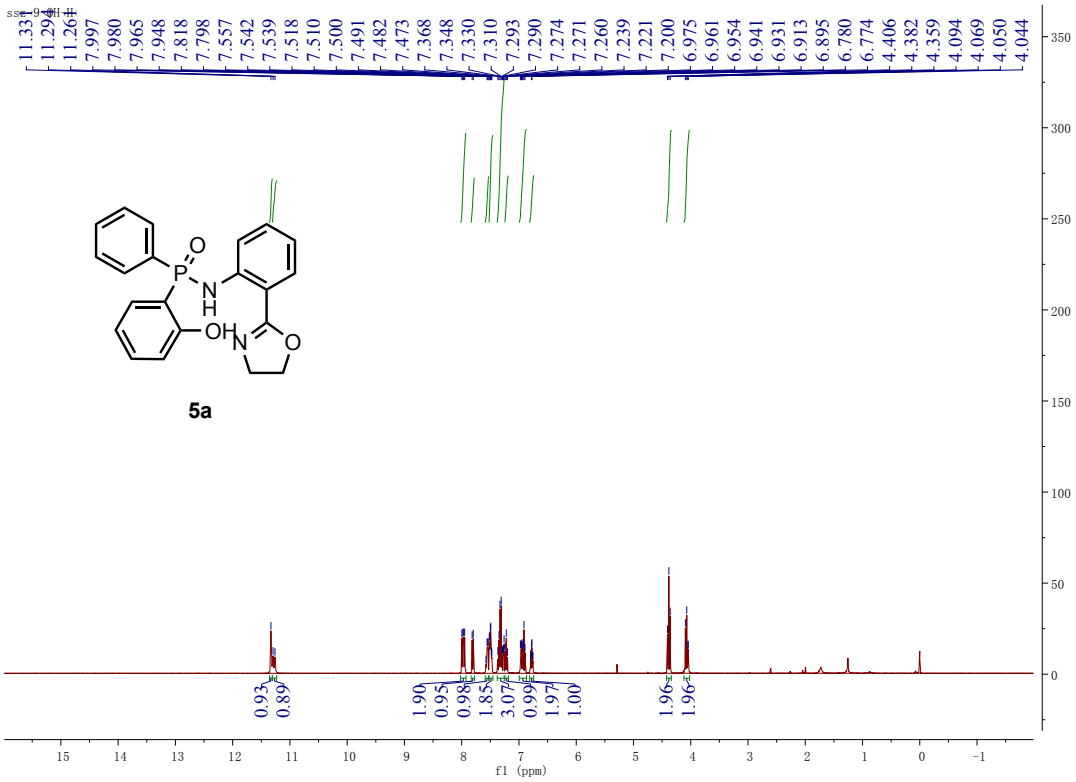


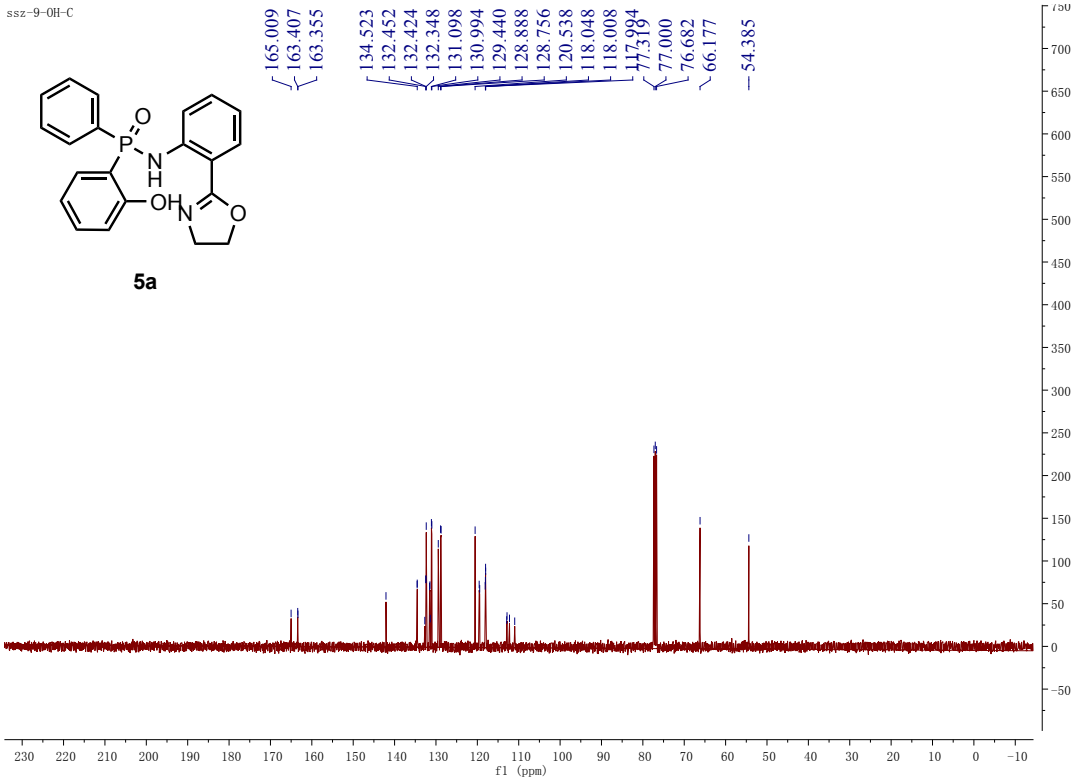
^{31}P NMR for Compound 4k



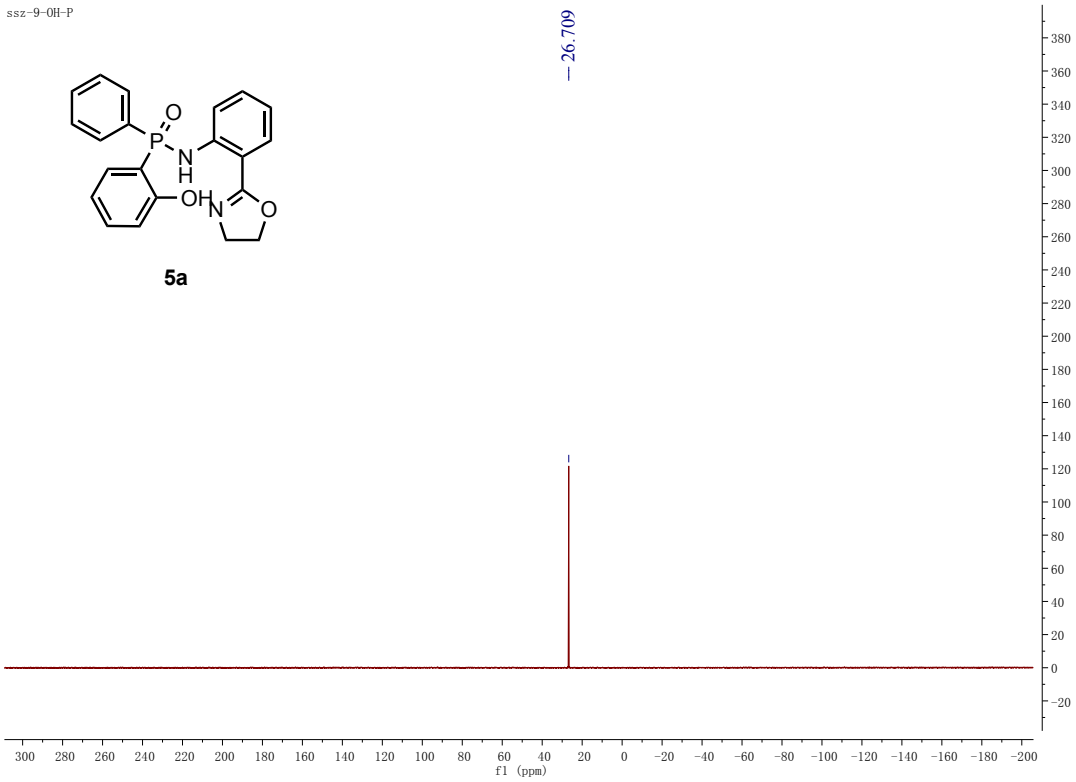
^{1}H NMR for Compound 5a



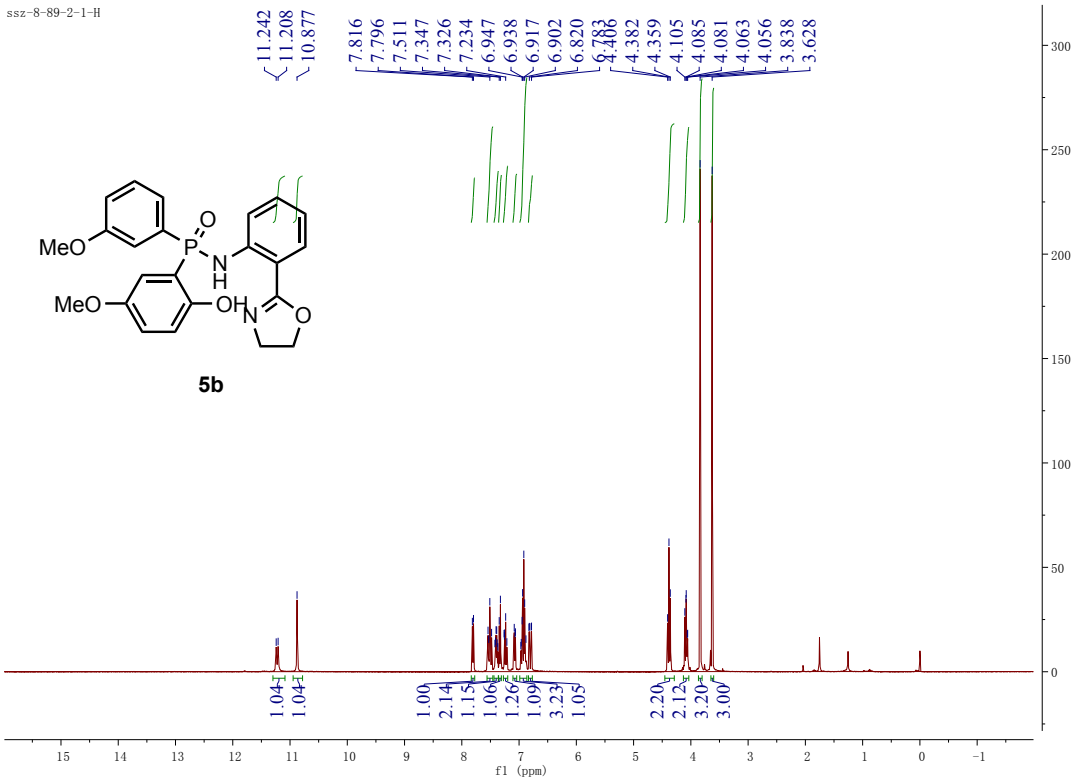
^{13}C NMR for Compound 5a



^{31}P NMR for Compound 5a



^{1}H NMR for Compound 5b



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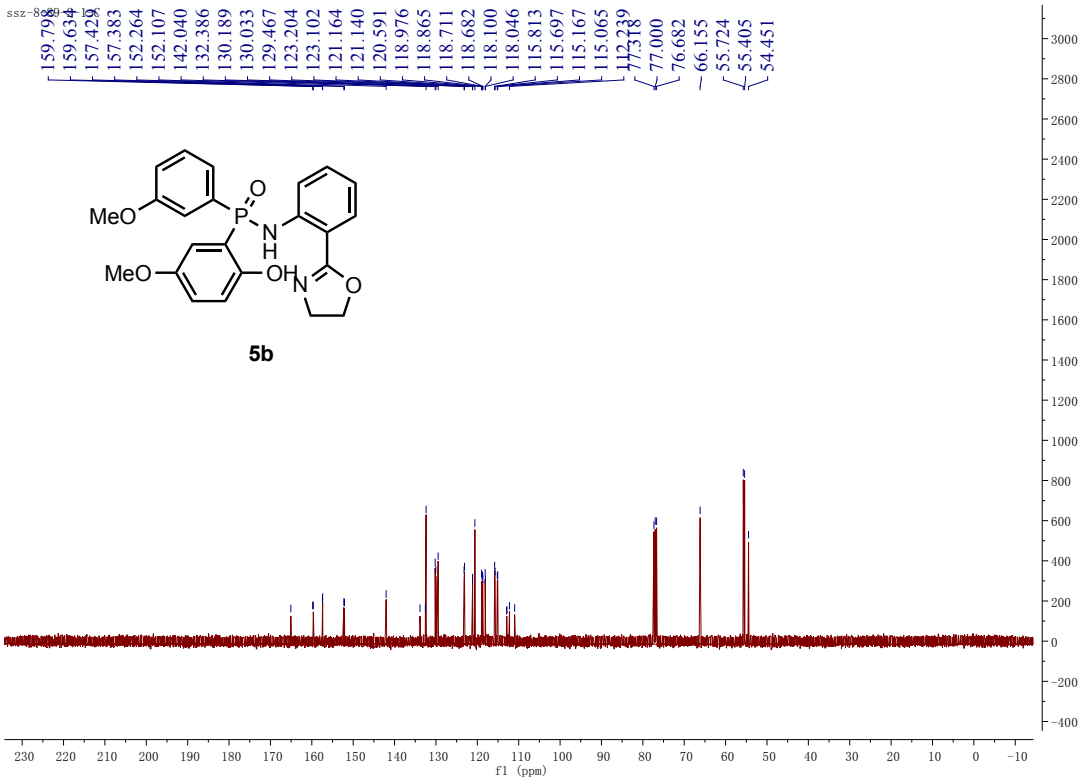
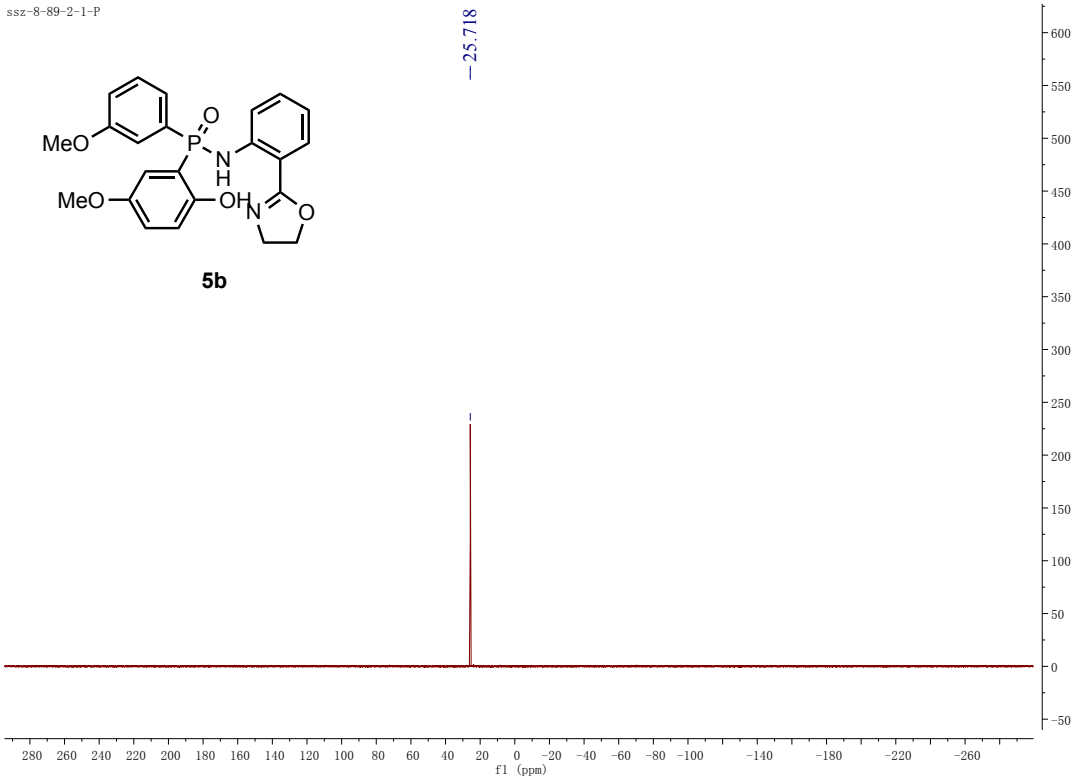
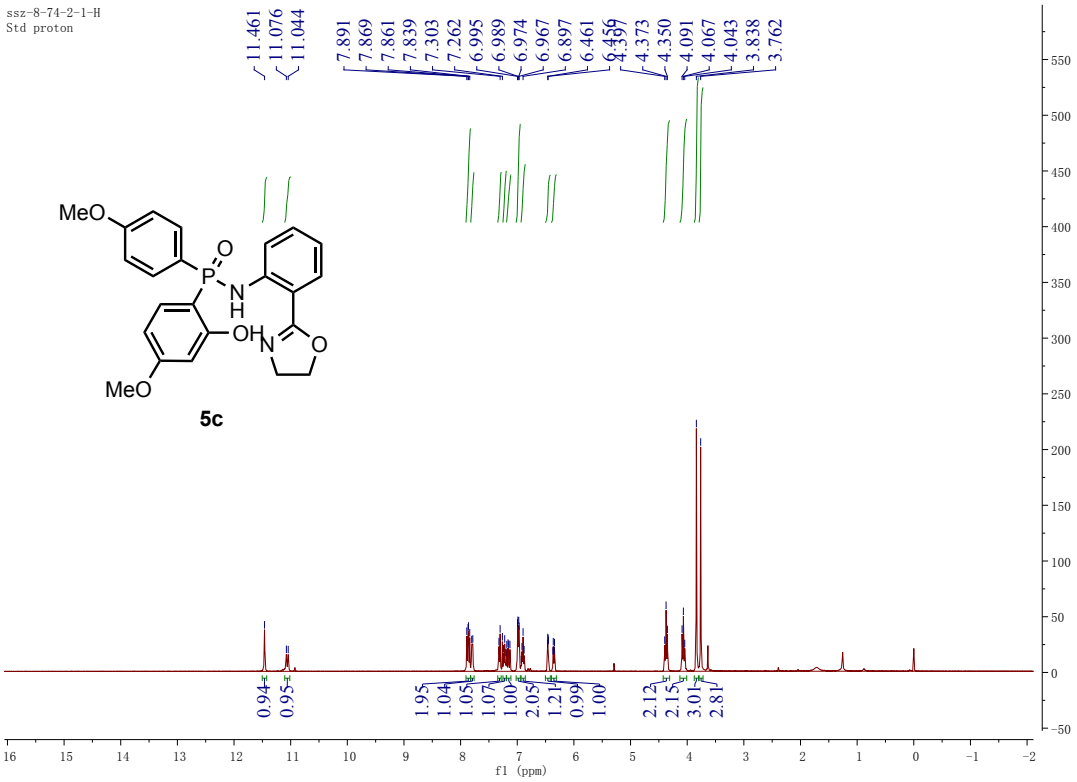


^{31}P NMR for Compound 5b



^{1}H NMR for Compound 5c



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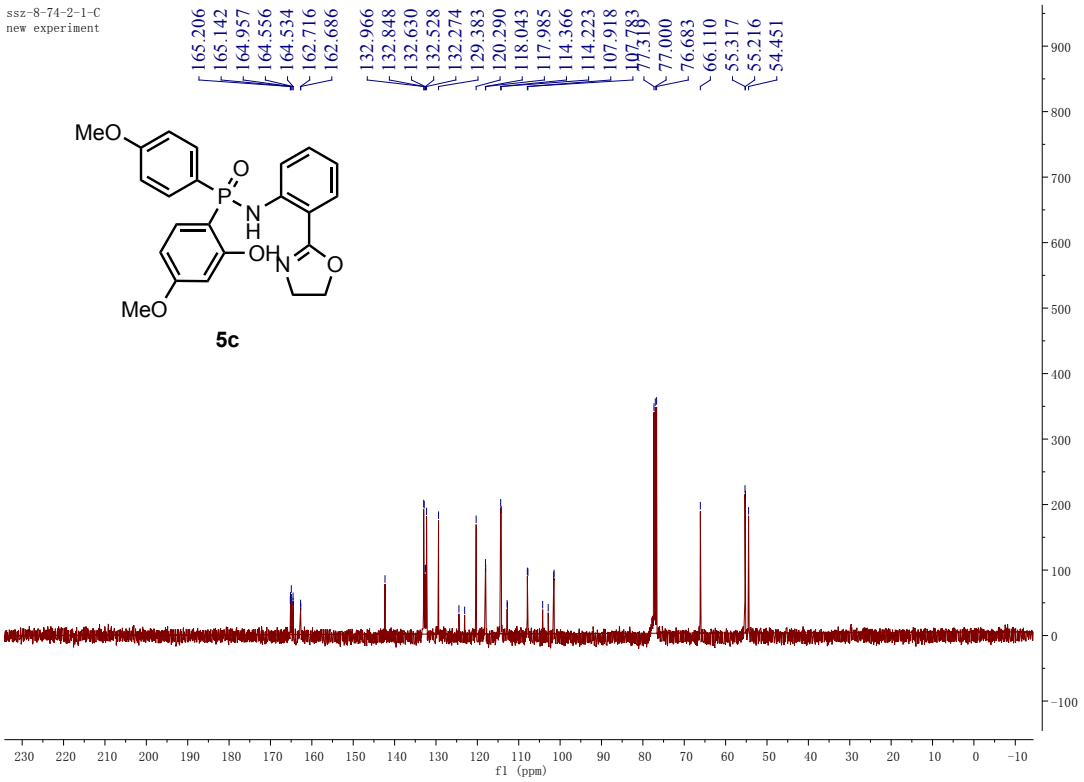

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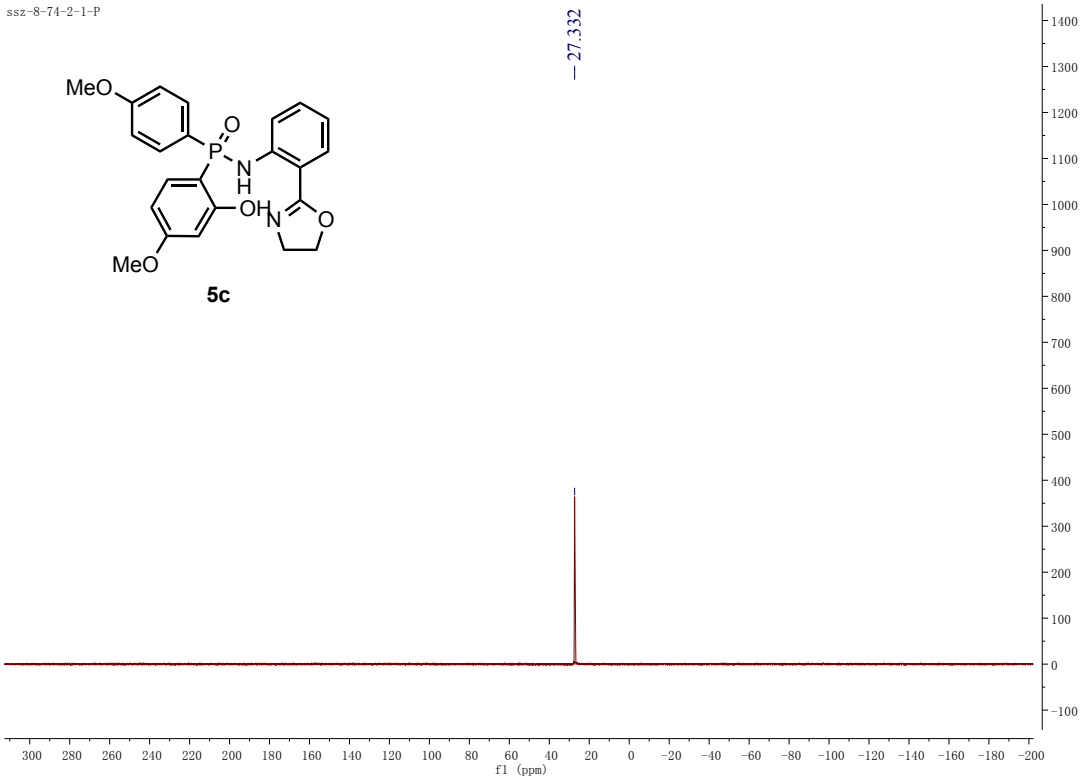
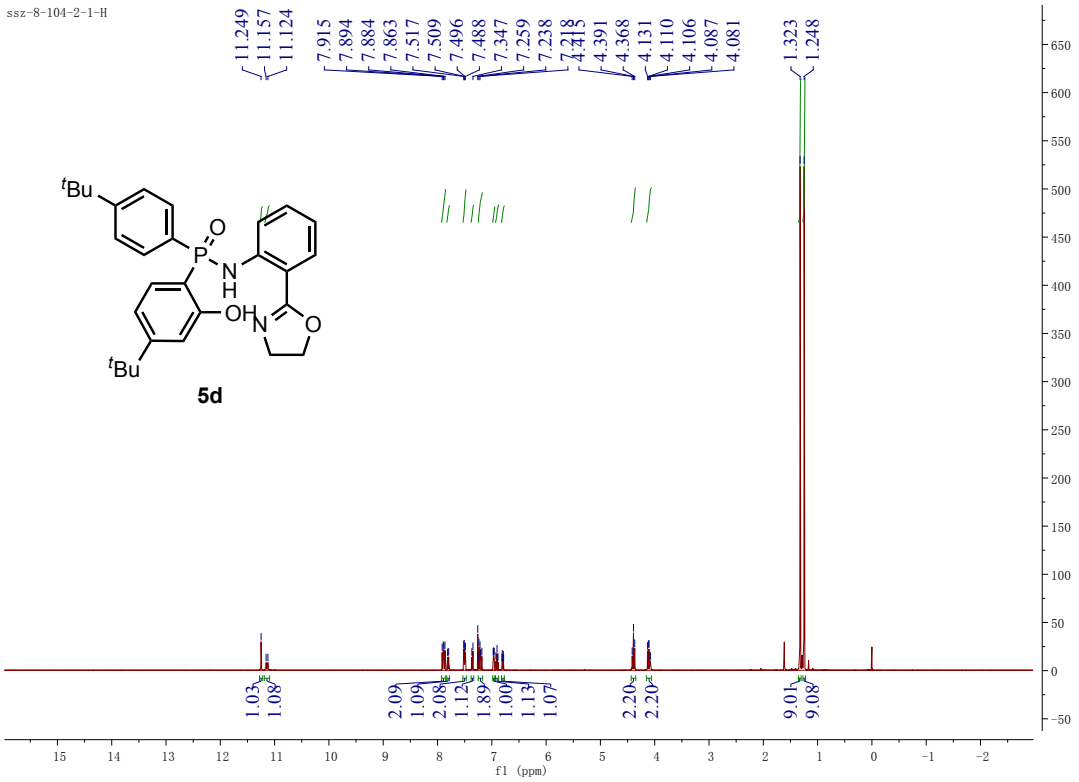
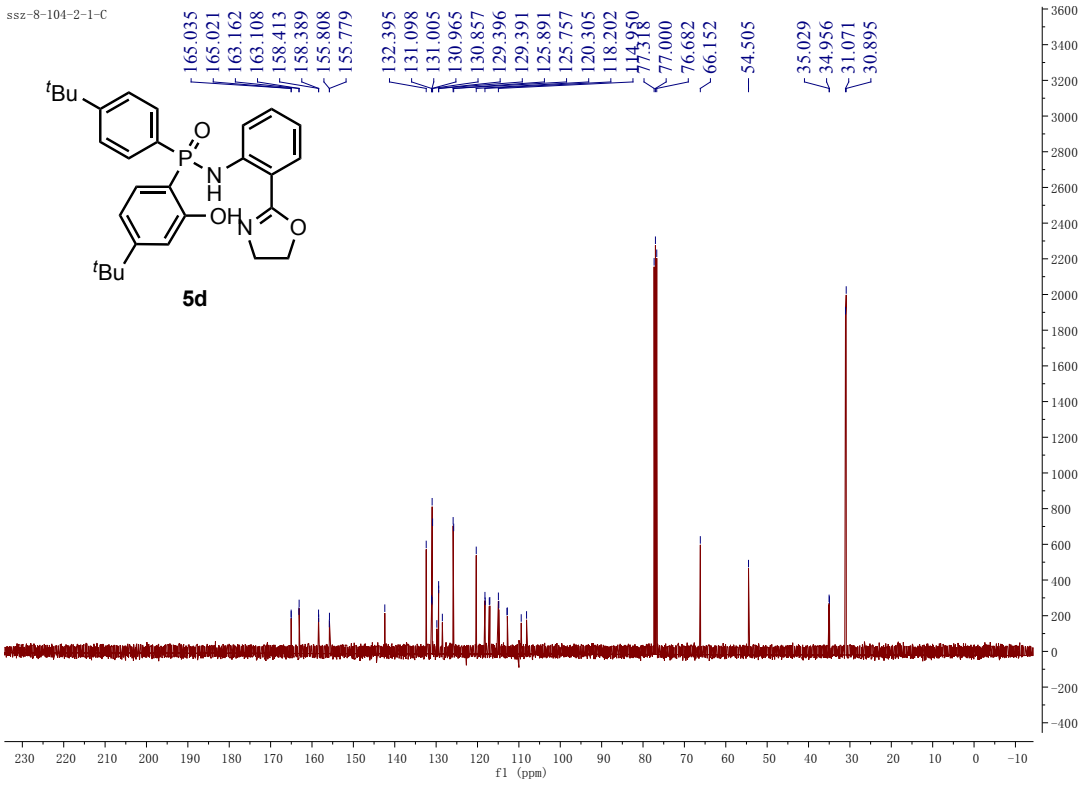


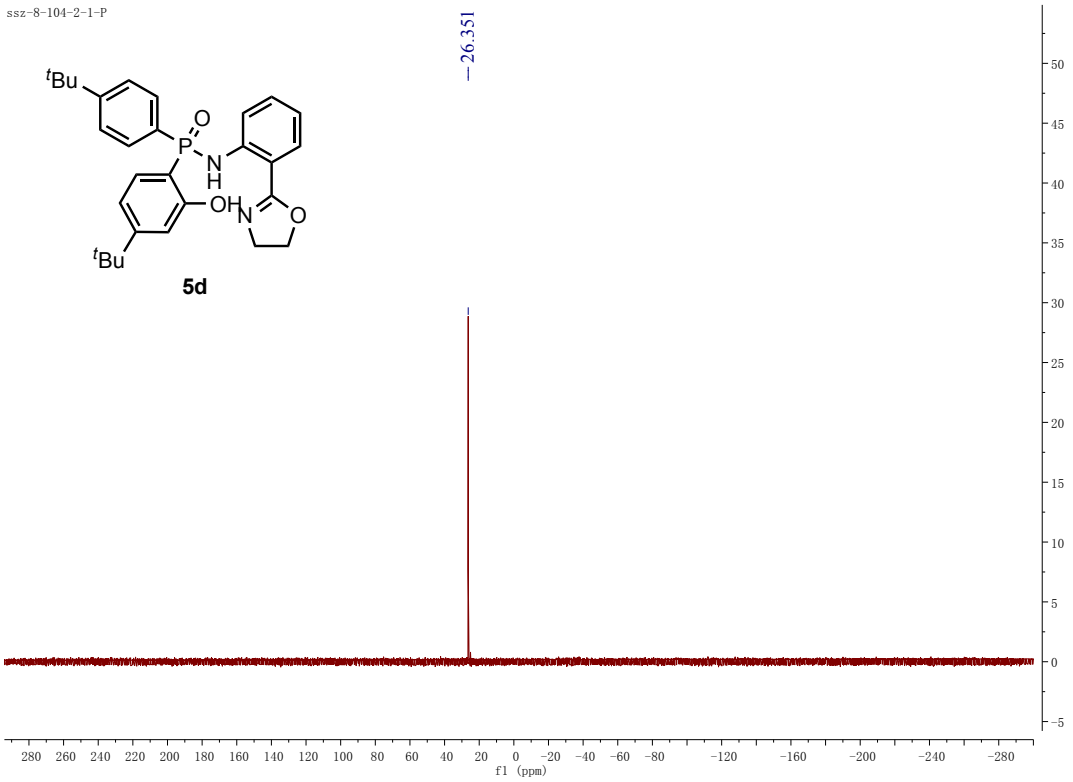
^{1}H NMR for Compound 5d



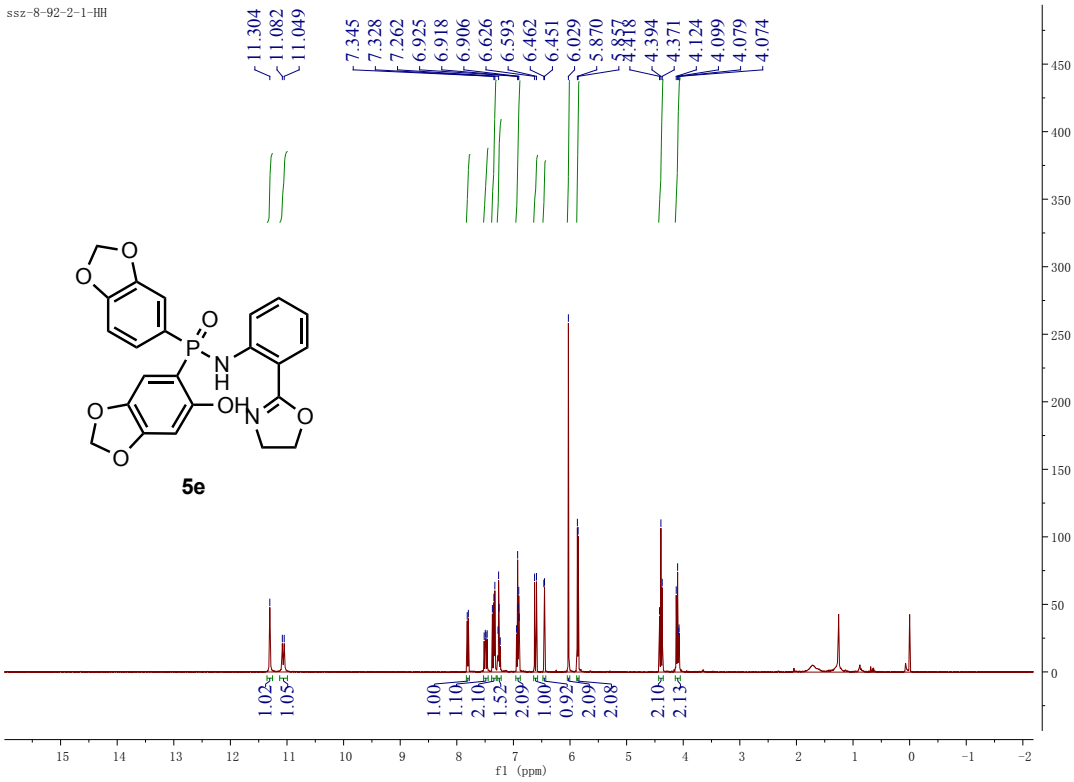
^{13}C NMR for Compound 5d



^{31}P NMR for Compound 5d



^{1}H NMR for Compound 5e



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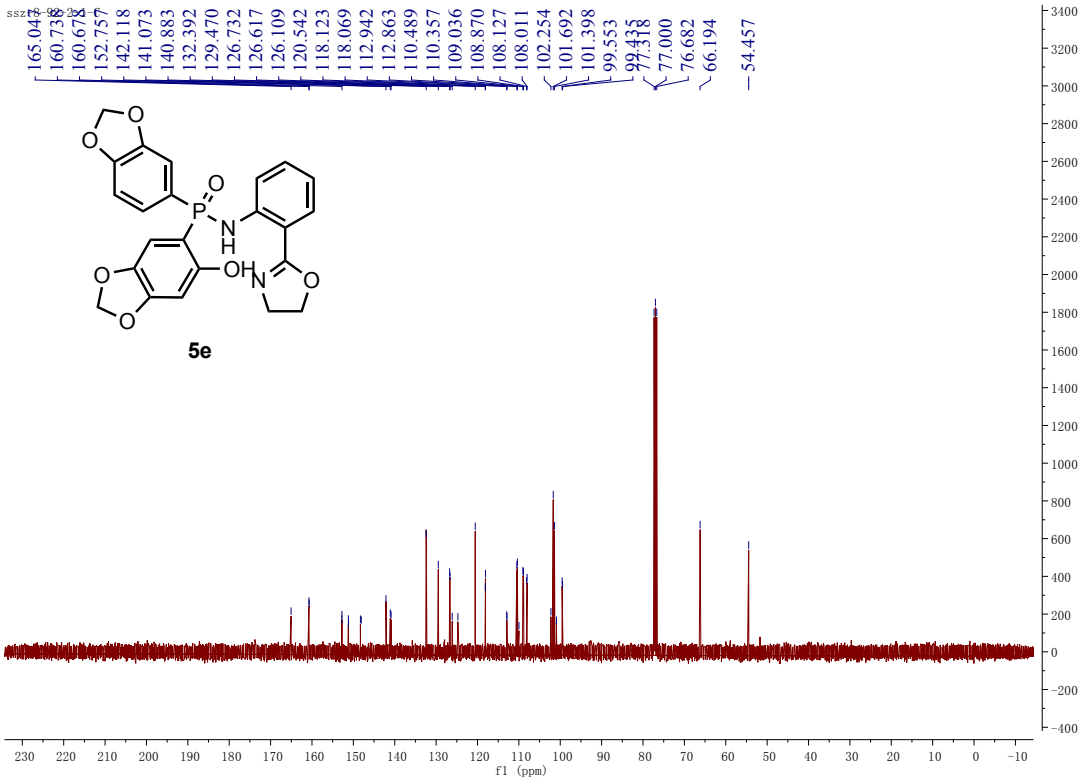
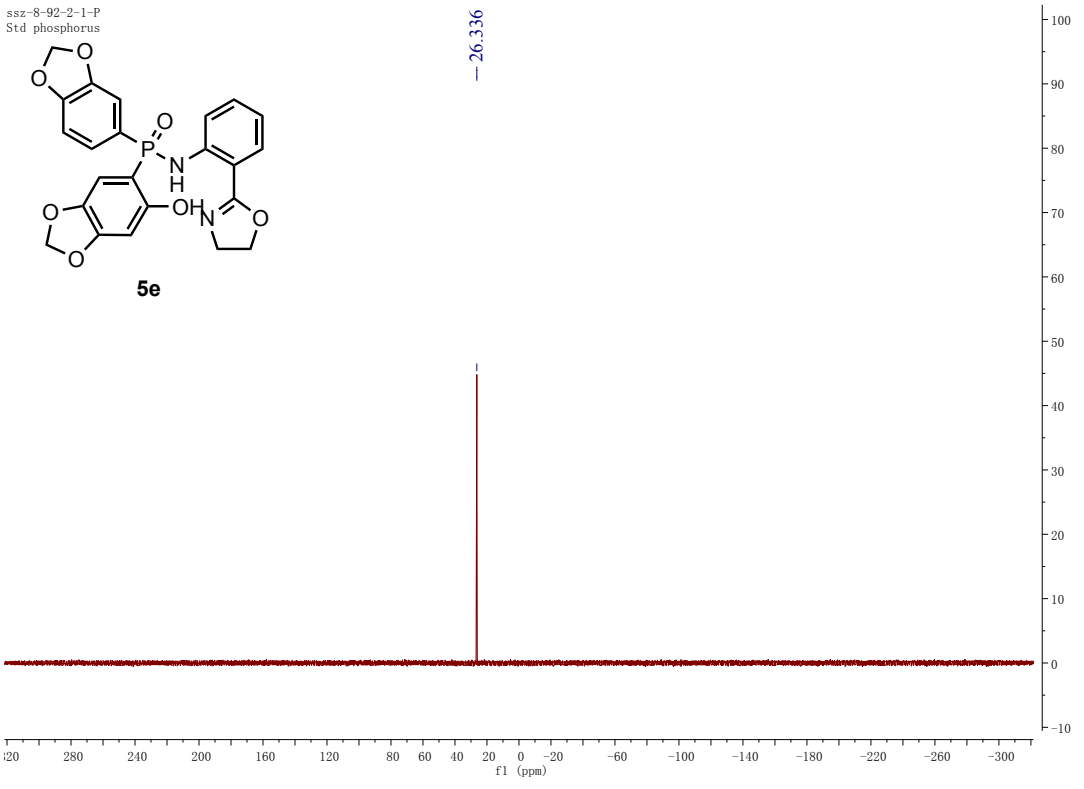
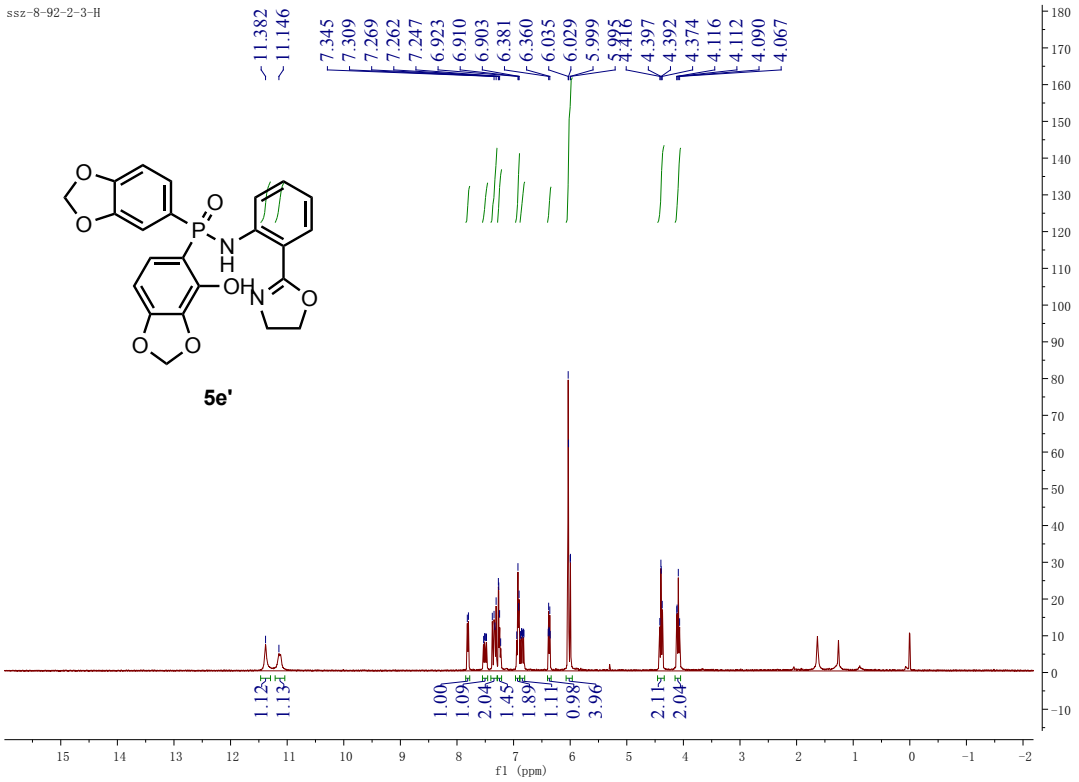


^{31}P NMR for Compound 5e

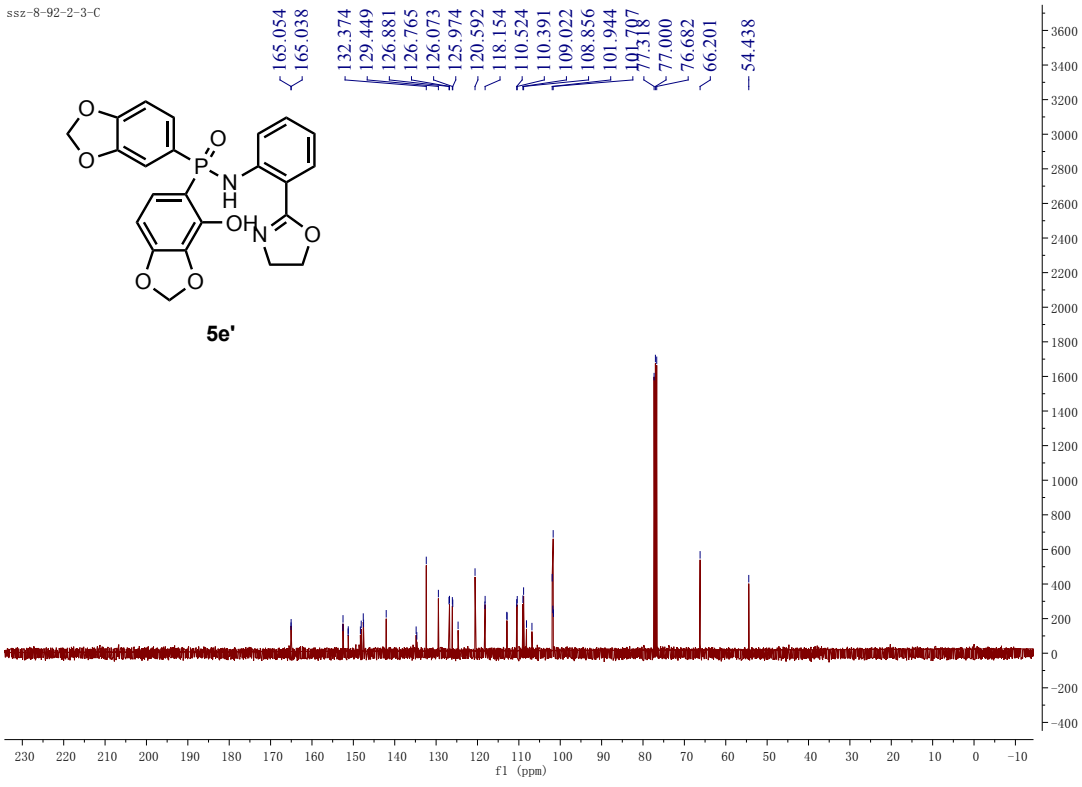


^{1}H NMR for Compound 5e'



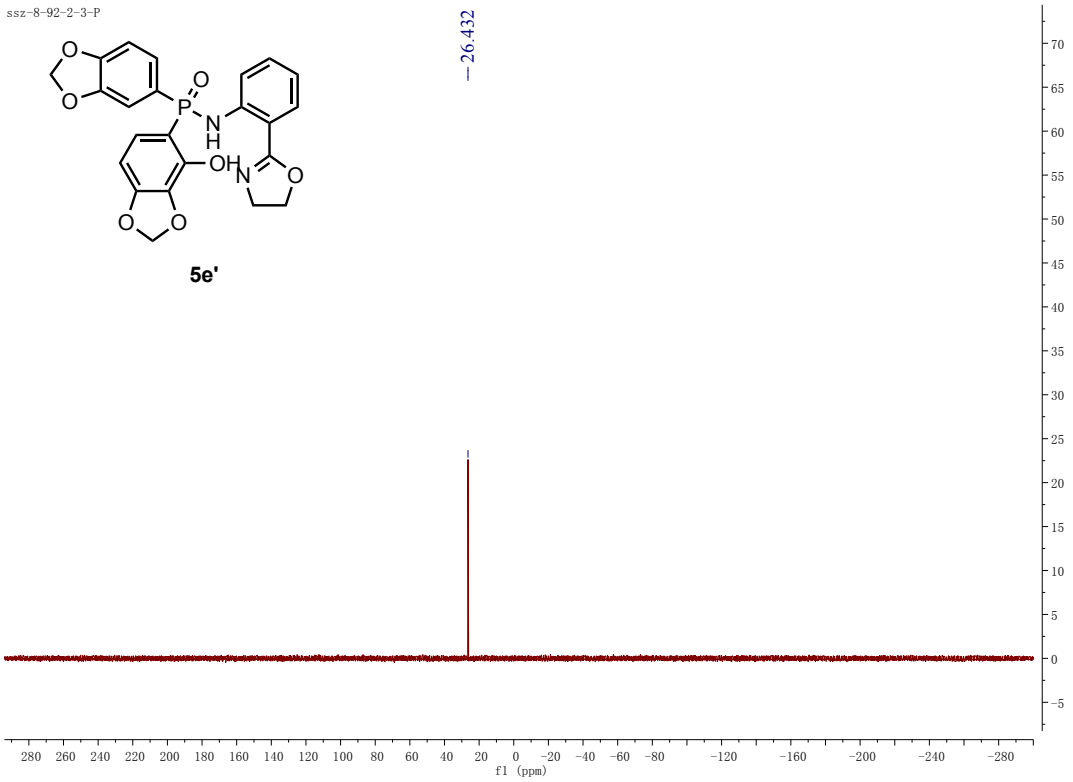
5e'

^{13}C NMR for Compound 5e'

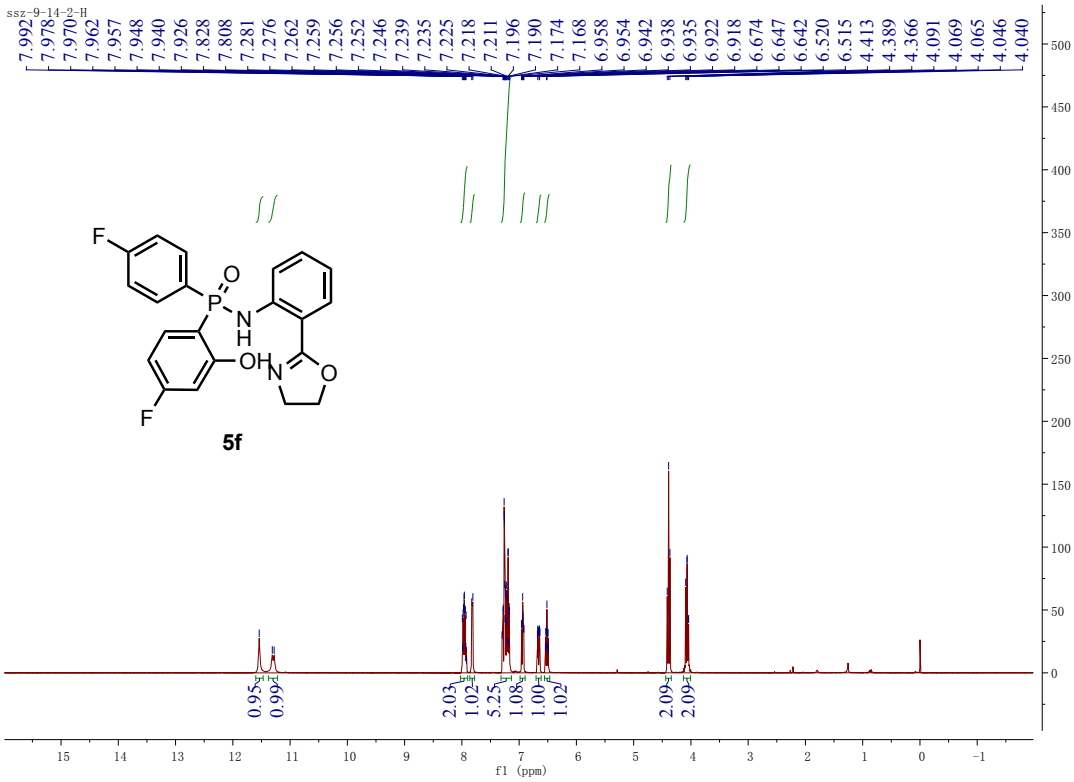


5e'

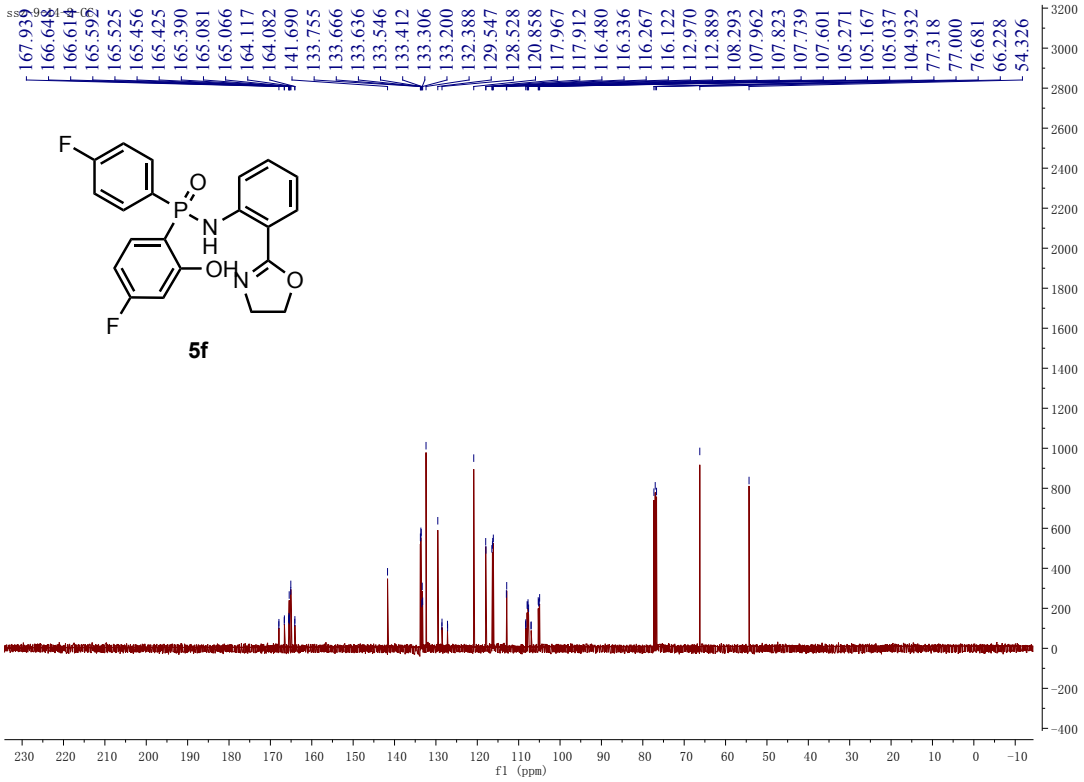
^{31}P NMR for Compound 5e’



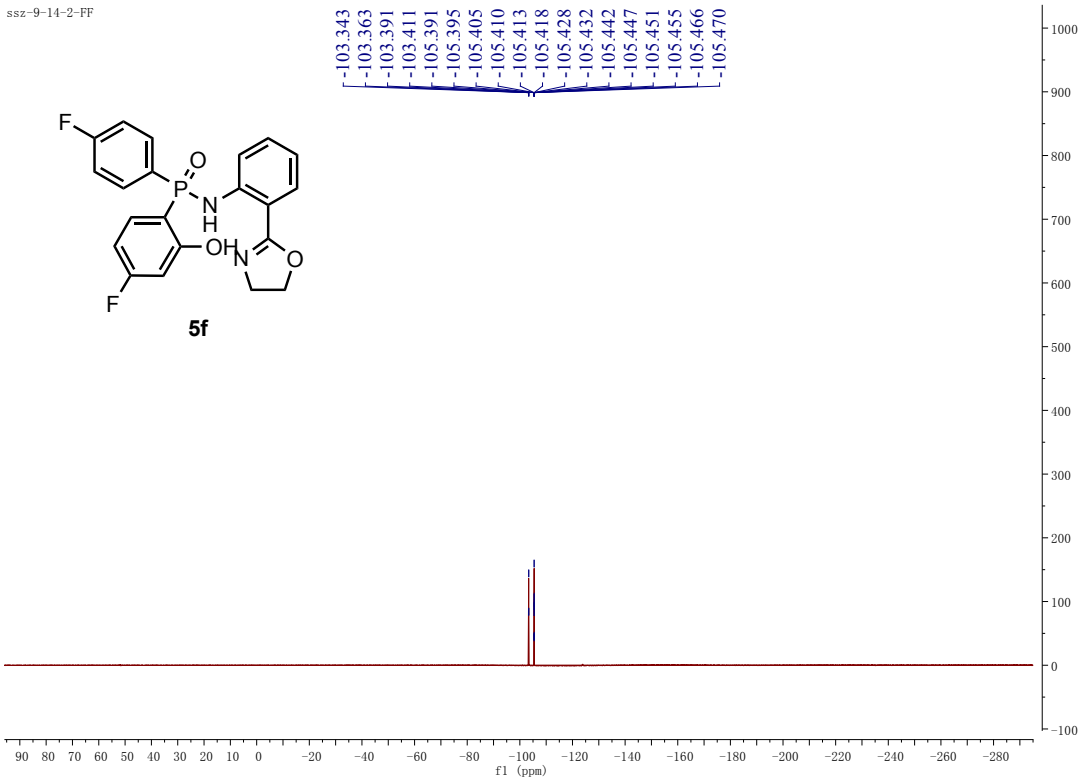
^{1}H NMR for Compound 5f



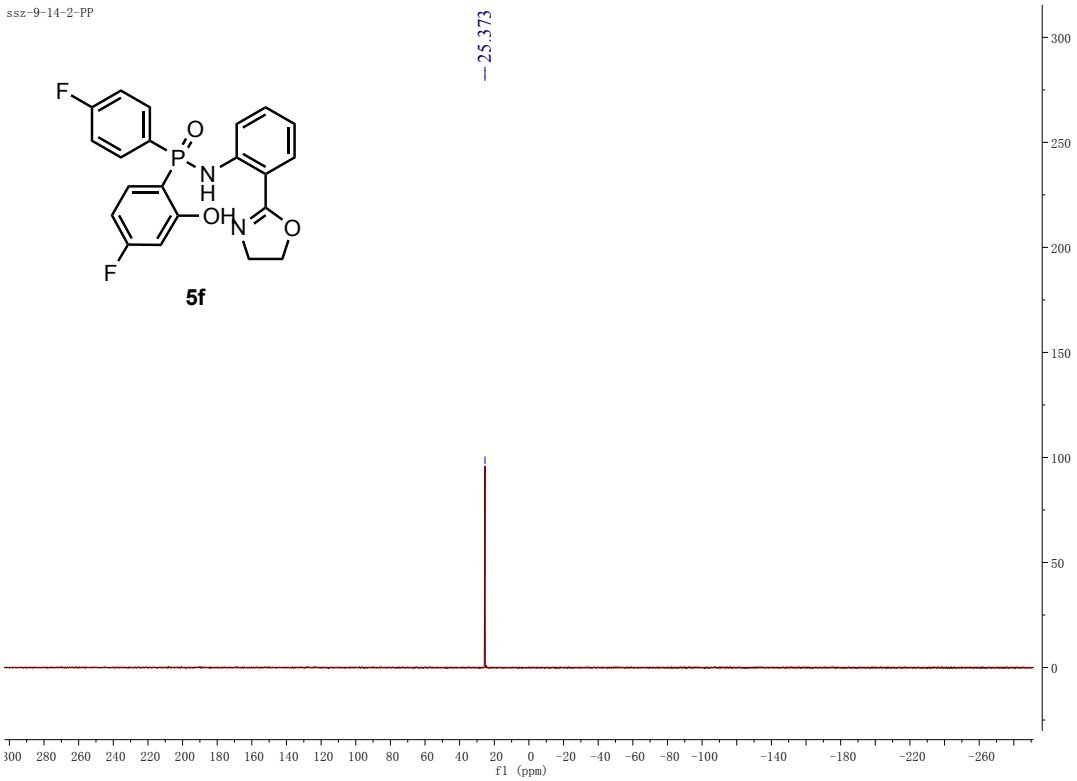
^{13}C NMR for Compound 5f



^{19}F NMR for Compound 5f

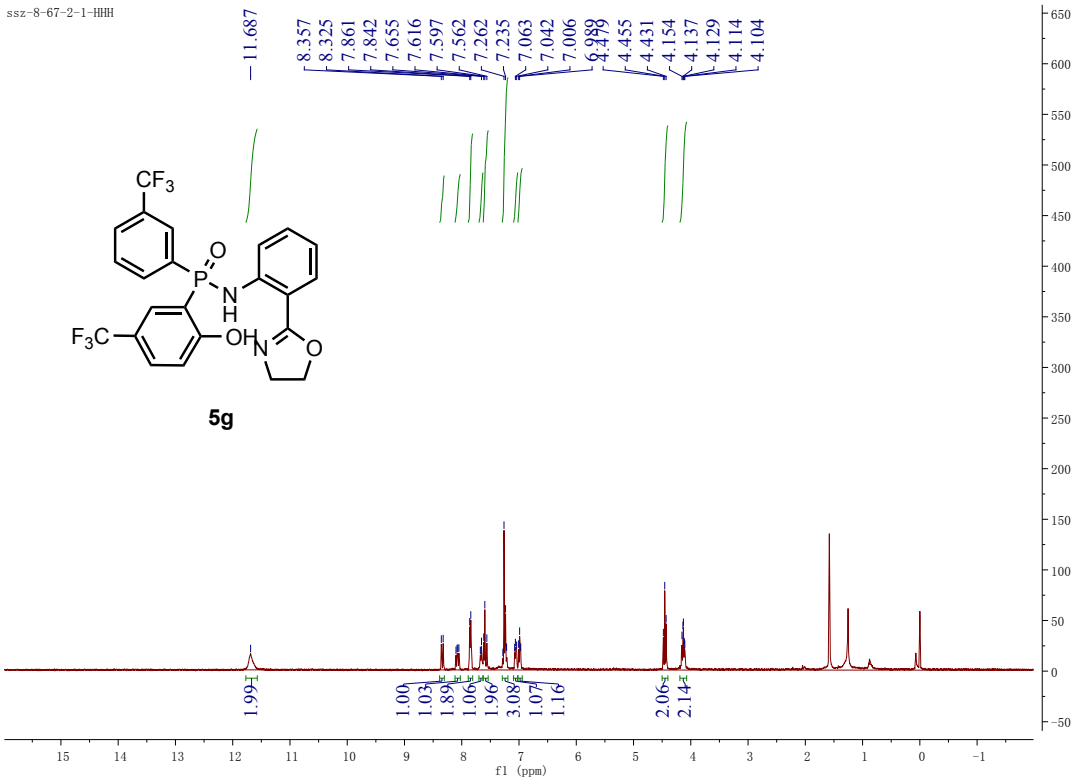


^{31}P NMR for Compound 5f



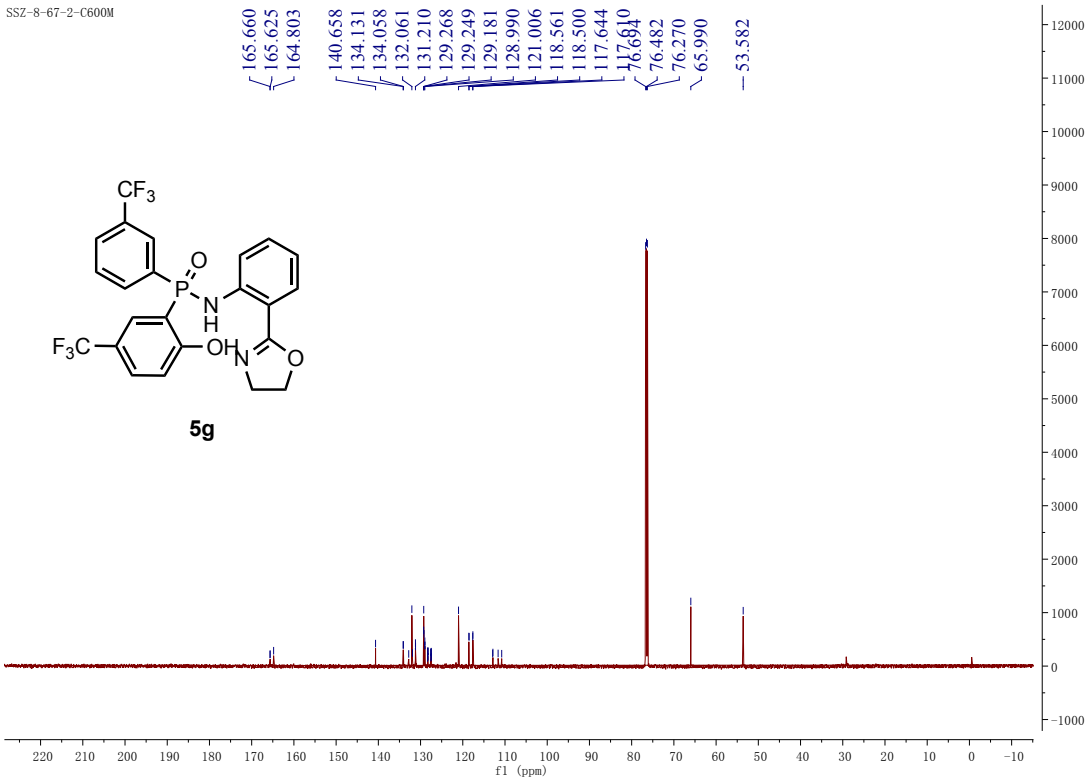
5f

^{1}H NMR for Compound 5g



5g

^{13}C NMR for Compound 5g



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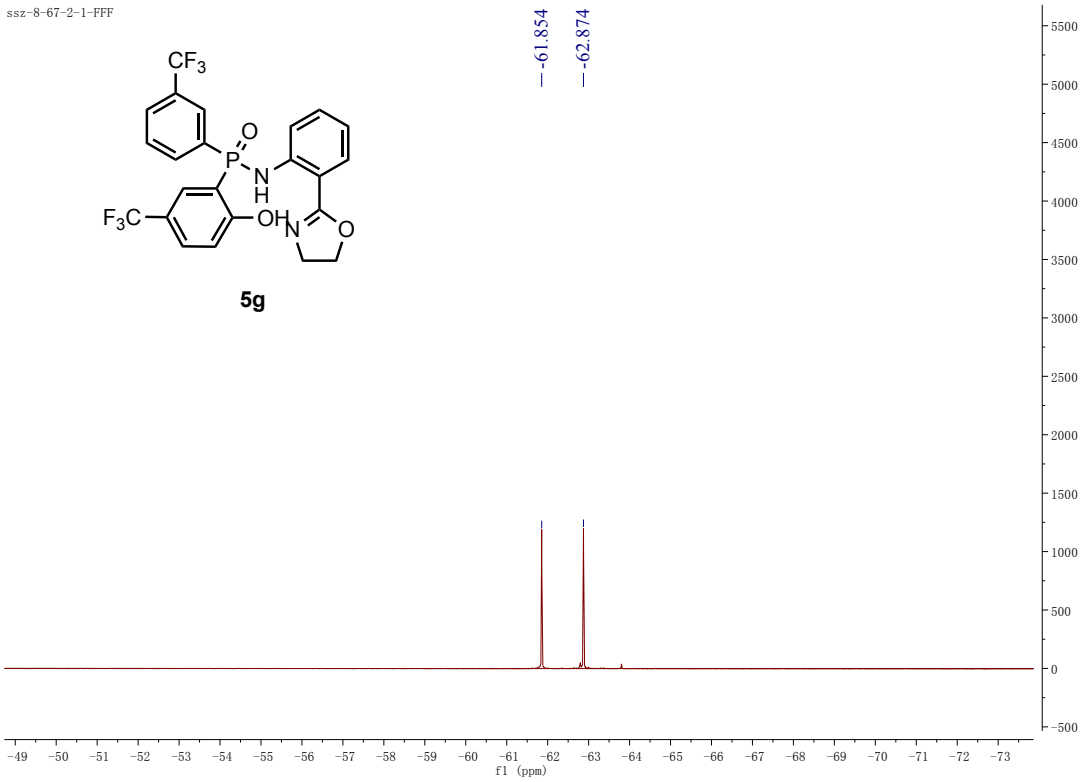

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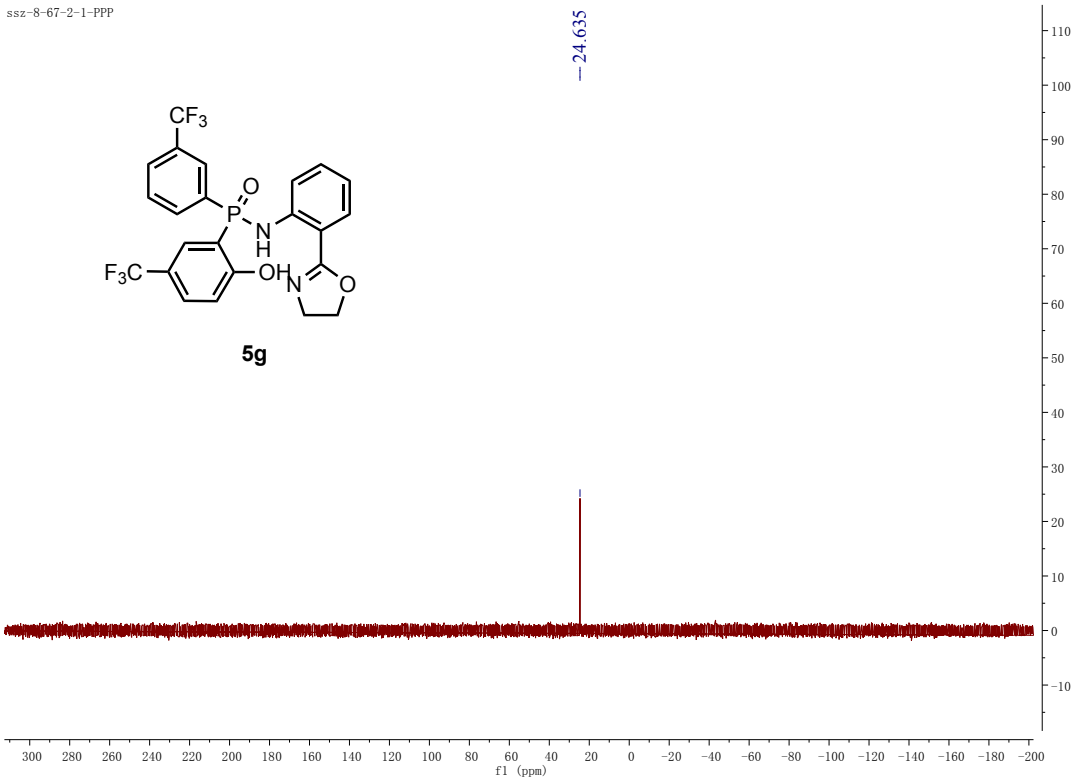
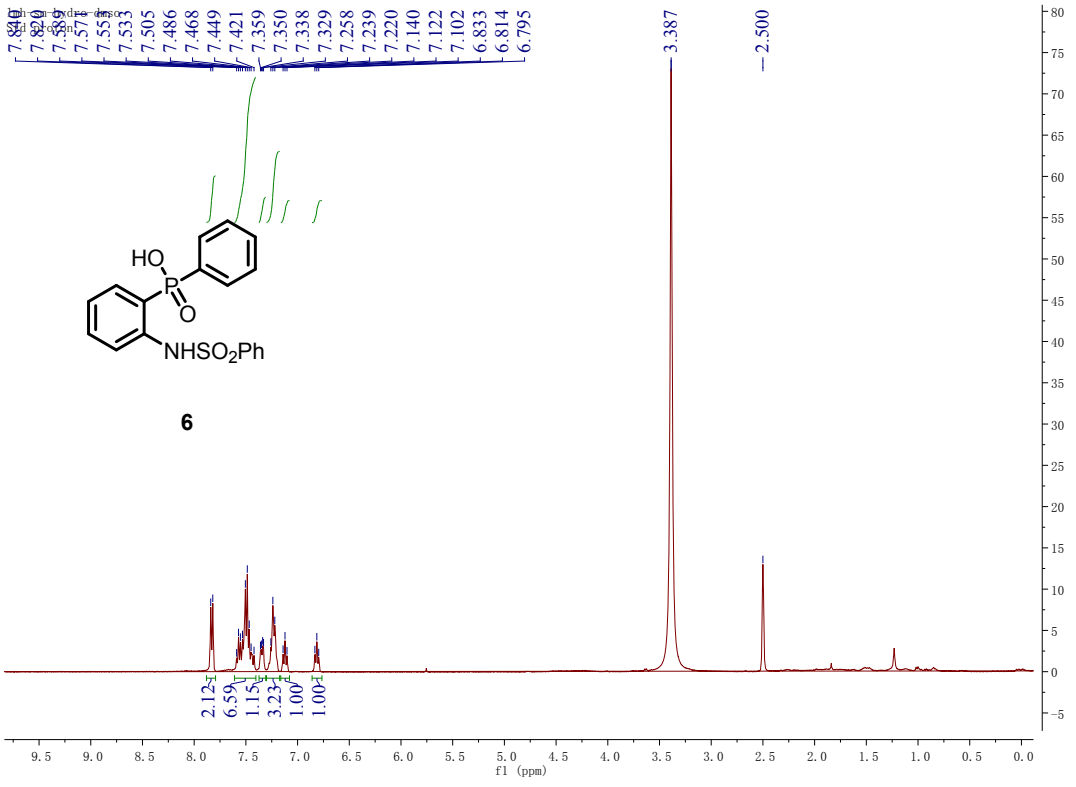
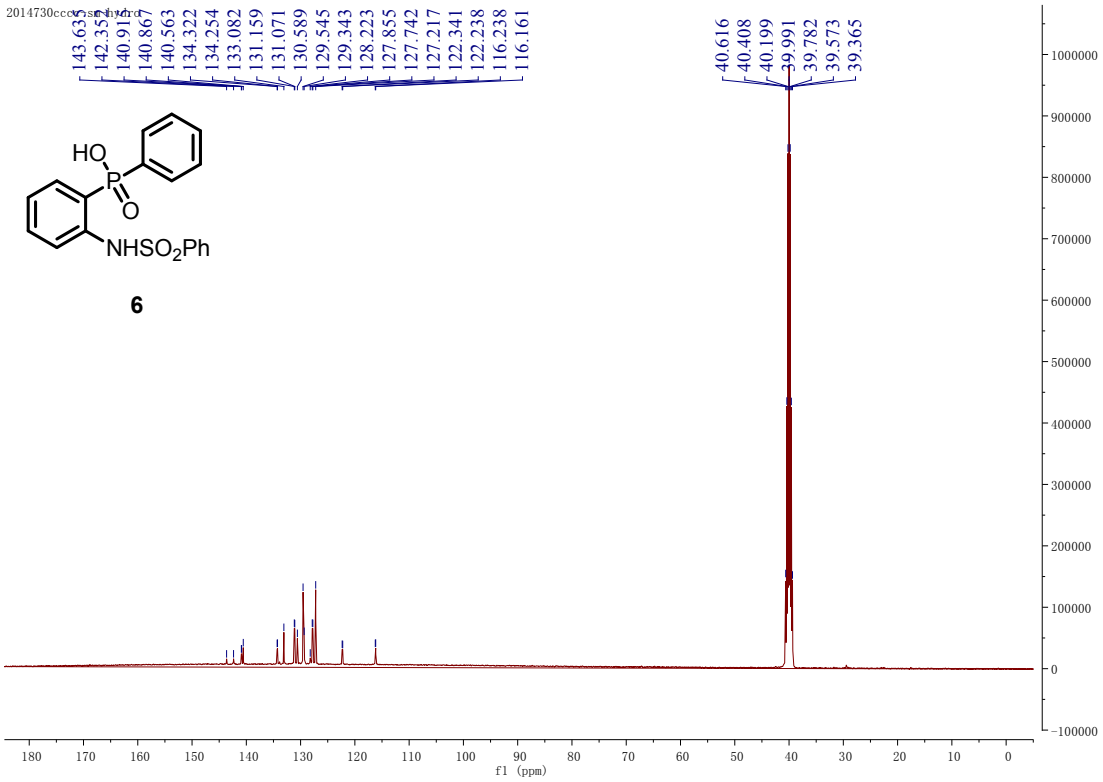


^{1}H NMR for Compound 6



^{13}C NMR for Compound 6



^{31}P NMR for Compound 6