Supporting Information

Transition-metal-free phosphorylation of polyfluoroarenes with P(O)H compounds

Bingqian Sun,[a,†] Yu-Ting Liang,[a,†] Meng-Ting Xiang,[a] Jun-Tao Ai,[b] Shuai Wang,[a,c] Hong Zhonga,[c] Jia Yang,[a,c,*] and Hao-Yue Xiang[a,d,*]

[a] College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, P. R. China

[b] Hunan Drug Inspection Center, Changsha, 410001, P. R. China.

[c] Hunan Provincial Key Laboratory of Efficient and Clean Utilization of Manganese Resources, Central South University, Changsha 410083, P. R. China

[d] College of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang 453007, P. R. China

† B. Sun and Y. T. Liang contributed equally.

E-mail: yangjia90@csu.edu.cn; xianghaoyue@csu.edu.cn,

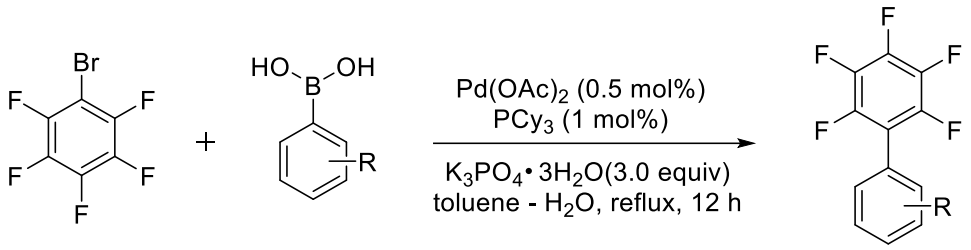
Table of Contents

1. General Information

All reactions were carried out in oven-dried Schlenk tubes under N_2 atmosphere. Dry solvents were obtained by purification according to standard methods or purchased from commercial suppliers. Reagents were used as received unless otherwise noted. All solvents and bases were stored inside a N_2-filled glove box. Column chromatography was performed using Silica Gel 60 (particle size 38–75 μm). The pure products were obtained by means of column chromatography. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR data were acquired on a 400 MHz spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, 162 MHz for ^{31}P NMR spectroscopy and 377 MHz for ^{19}F NMR spectroscopy). Chemical shifts for ^{1}H NMR are referred to internal Me_4Si (0 ppm) and reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Data for ^{31}P NMR were relative to H_3PO_4 (85% solution in D_2O, 0 ppm).

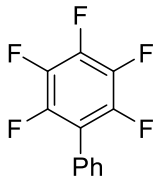
2. Synthesis of the Starting Materials

Polyfluoroarenes **1a**-**1g**, **1h**, **1i** and **1k**, P-H compounds **2a**-**2n** are commercially available. Polyfluoroarenes **1g** and **1j** were known compounds which were synthesized according to the reported method. [1]

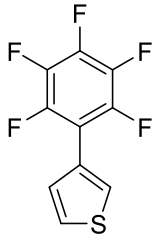


A flask was charged with $Pd(OAc)_2$ (5.60 mg, 0.025 mmol), tricyclohexyl phosphine (14.00 mg, 0.05 mmol), phenylboronic acid or 3-thiopheneboronic acid (6.00 mmol, 1.2 equiv) and potassium phosphate tribasic hydrate (3.18 g, 3.0 equiv) in toluene (20 mL) and H_2O (1 mL). The mixture was stirred for 30 min at room temperature under nitrogen atmosphere. Then bromopentafluorobenzene (0.63 mL, 5.00 mmol) was added to the reaction mixture. After the reaction mixture was stirred for 12 h under reflux. The reaction mixture was then cooled to room temperature. The reaction mixture was quenched with ethyl acetate, the organic layer was separated, dried over Na_2SO_4 and concentrated. The crude material was purified by chromatography on silica gel using hexane to

afford the product.



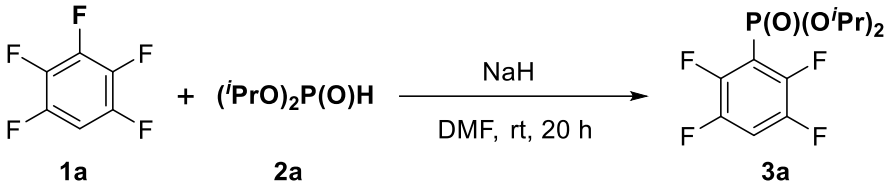
2,3,4,5,6-Pentafluoro-1,1'-biphenyl (**1g**).[1] ^{1}H NMR (400 MHz $CDCl_3$): δ 7.51–7.45 (m, 3H), 7.43–7.41 (m, 2H), ^{19}F NMR (376 MHz $CDCl_3$): δ -143.2–143.3 (m), -155.7–155.8 (m), 162.3–162.5 (m).



3-(Perfluorophenyl)thiophene (**1j**).[1] ^{1}H NMR (400 MHz $CDCl_3$): δ 7.65–7.63 (m, 1H), 7.46–7.44 (m, 1H), 7.37–7.32 (m, 1H),^{19}F NMR (377 MHz $CDCl_3$): δ -141.9–142.0 (m), -156.3–156.4 (m), 162.4–162.5 (m).

3. Experimental Procedures

Typical procedure for C-F phosphorylation of aryl fluorides



Under N_2 atmosphere, 0.1 mmol pentafluorobenzene **1a**, 0.2 mmol diisopropyl phosphite **2a**, 0.1 mmol NaH and 1.0 mL DMF were charged into a 10 mL schlenk tube, and the mixture was stirred at room temperature for 20 h. The reaction mixture was extracted with EtOAc, the organic layer was separated, dried over Na_2SO_4 and concentrated.The residues were passed through a short silica chromatography (particle size 38–75 μm, pether/ethyl acetate as eluent) to afford analytically pure organophosphorus compound **3a**.

Preparation of 3a at 1 mmol scale

Under N_2 atmosphere, 1 mmol pentafluorobenzene **1a**, 1.5 mmol diisopropyl phosphite **2a**, 1 mmol NaH and 5.0 mL DMF were stirred at room temperature for 20 h. The reaction mixture was extracted with ethyl acetate, the organic layer was separated, dried over Na_2SO_4. After removal of the volatile, the crude product was passed through a short silica chromatography (particle size 38–75 μm, pether/ethyl acetate as eluent) to give the analytically pure **3a** in 86% yield.

4. Mechanistic Studies

^{31}P NMR spectra of starting materials, reaction mixture and product 3 in DMF

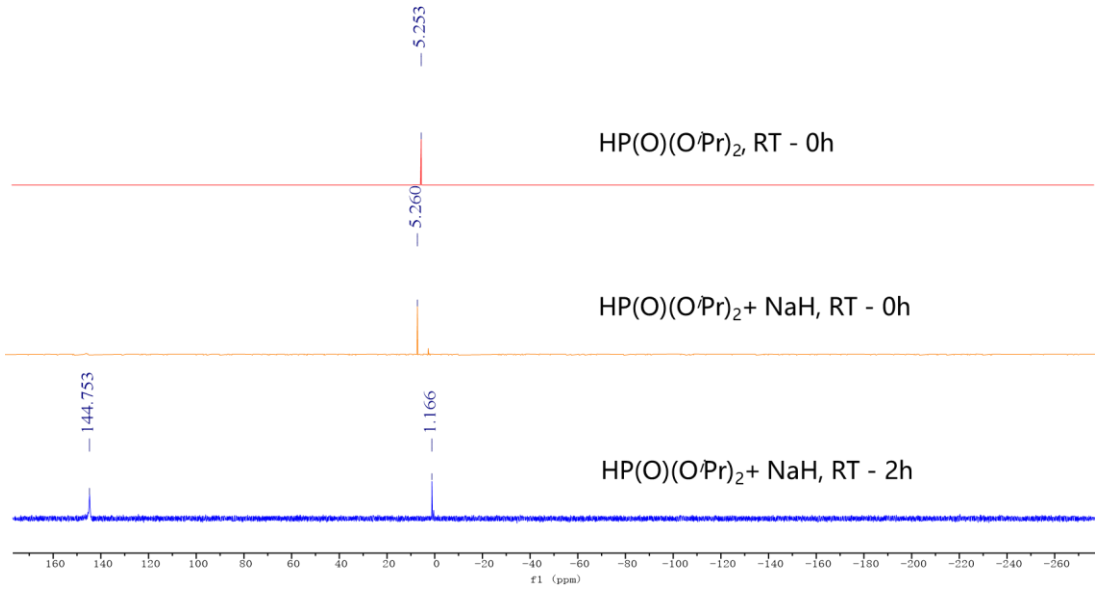


Figure S1. ^{31}P NMR spectra of the control experiments in DMF

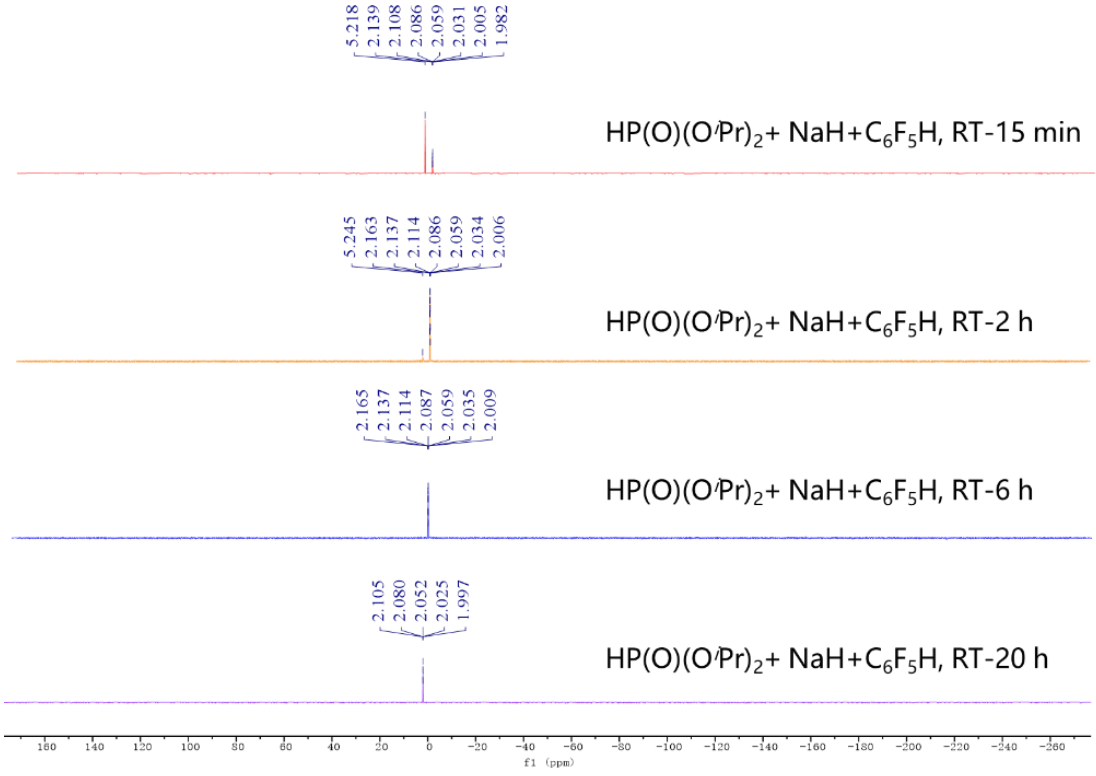


Figure S2. ^{31}P NMR spectra of reaction mixture in DMF

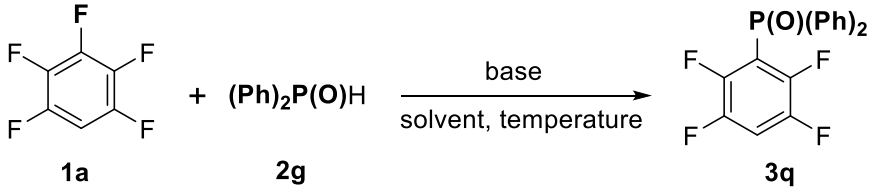
General procedure: The reaction was done in DMF, and the reaction solution was added to the NMR tube in the glove box.

Several control experiments were conducted, and the reactions were monitored by ^{31}P NMR

spectroscopy (Figure S1, S2). As shown in Figure S1, the treatment of diisopropyl phosphite **2a** (0.1 mmol, 5.25 ppm) with NaH (1.0 equiv) caused the formation of sodium phosphinite (144.75 ppm) in DMF at room temperature. [2] The addition of pentafluorobenzene **1a** (0.4 mmol) causes the production of **3a** (2.05 ppm), and the proportion of **3a** increases over time (Figure S2).

5. Reaction Optimization

Table S4 Base-promoted reactions of **1a** with **2g**.

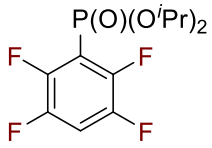


1a **2g** **3q**

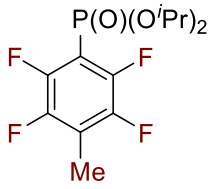
Entry	Base	Solvent	Temp(°C)	Yield (%)[b]
1	NaH	DMF	rt	43
2	KHMDS	DMF	rt	n.d.
3	^{t}BuOK	DMF	rt	n.d.
4	^{t}BuONa	DMF	rt	n.d.
5	Na_3PO_4	DMF	rt	trace
6	Cs_2CO_3	DMF	rt	n.d.
7[c]	NaH	DMF	rt	53
8[c]	NaH	DMA	rt	52
9[c]	NaH	DMSO	rt	41
10[c]	NaH	CH_3CN	rt	22
11[c]	NaH	THF	rt	n.d.
12[c]	NaH	toluene	rt	n.d.
13[c]	NaH	DCM	rt	n.d.
14[d]	NaH	DMF	rt	65
15[e]	NaH	DMF	rt	58
16[d]	NaH	DMF	50	55
17[f]	NaH	DMF	rt	56

[a] Reaction conditions: **1a** (0.2 mmol), **2g** (0.1 mmol), base (2 equiv.), solvent (1.0 mL), N_2, rt, 20 h. [b] GC yield using tridecane as an internal standard. [c] NaH (1.0 equiv). [d] NaH (1.0 equiv), **1a** (0.3mmol). [e] NaH (1.0 equiv), **1a** (0.4mmol). [f] NaH (1.0 equiv), **1a** (0.3mmol), 24 h.

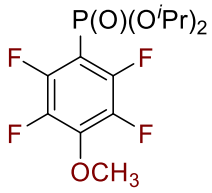
6. Characterization and Analytical Data of Products 3



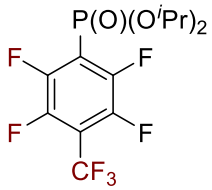
Diisopropyl (2,3,5,6-tetrafluorophenyl) phosphonate (3a). Colorless liquid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.24–7.14 (m, 1H), 4.85–4.76 (m, 2H), 1.36–1.33 (m, 6H), 1.27–1.25 (m, 6H), ^{13}C NMR (100 MHz $CDCl_3$): δ 146.7 (dm, J_{C-F} = 253.7 Hz), 146.0 (dm, J_{C-F} = 249.7 Hz), 111.2 (dt, J_{C-P} = 181.3 Hz, J_{C-F} = 18.6 Hz), 109.9 (td, J_{C-F} = 23.8 Hz, J_{C-P} = 1.8 Hz), 72.8 (d, J_{C-P} = 6.1 Hz), 24.0 (d, J_{C-P} = 4.1 Hz), 23.6 (d, J_{C-P} = 5.3 Hz), ^{31}P NMR (162 MHz $CDCl_3$): δ 2.39–2.22 (m), ^{19}F NMR (377 MHz $CDCl_3$): δ -131.36–-131.49 (m), -137.32–-137.50 (m). HRMS (ESI): Cal. for $C_{12}H_{15}F_4O_3PNa$ ([M+Na]$^+$) : 337.0588. Found: 337.0584.



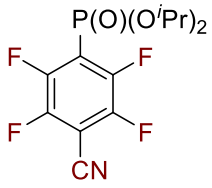
Diisopropyl (2,3,5,6-tetrafluoro-4-methylphenyl) phosphonate (3b). Colorless liquid; ^{1}H NMR (400 MHz $CDCl_3$): δ 4.90–4.85 (m, 2H), 2.33 (s, 3H), 1.44–1.41 (m, 6H), 1.35–1.32 (m, 6H), ^{13}C NMR (100 MHz $CDCl_3$): δ 146.6 (dm, J_{C-F} = 251.6 Hz), 145.1 (dm, J_{C-F} = 240.5 Hz), 121.1 (t, J_{C-F} = 18.8 Hz), 107.4 (dt, J_{C-P} = 183.8 Hz, J_{C-F} = 18.9 Hz), 72.5 (d, J_{C-P} = 6.0 Hz), 24.0 (d, J_{C-P} = 4.1 Hz), 23.6 (d, $_{C-P}$ = 5.1 Hz), 7.9, ^{31}P NMR (162 MHz $CDCl_3$): δ 3.02–2.86 (m), ^{19}F NMR (377 MHz $CDCl_3$): δ -133.02–-133.15 (m), -142.19–-142.32 (m). HRMS (ESI): Cal. for $C_{13}H_{17}F_4O_3PNa$ ([M+Na]$^+$) : 351.0744. Found: 351.0745.



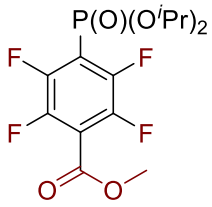
Diisopropyl (2,3,5,6-tetrafluoro-4-methoxyphenyl) phosphonate (3c). Colorless liquid; ^{1}H NMR (400 MHz $CDCl_3$): δ 4.90–4.81 (m, 2H), 4.16 (t, J = 2.0 Hz, 3H), 1.41 (d, J = 6.0 Hz, 6H), 1.32 (d, J = 6.0 Hz, 6H), ^{13}C NMR (100 MHz $CDCl_3$): δ 147.6 (dm, J_{C-F} = 255.2 Hz), 141.7 (t, J_{C-F} = 4.8 Hz), 140.3 (dm, J_{C-F} = 249.7 Hz), 102.5 (dt, J_{C-P} = 186,4 Hz, J_{C-F} = 20.9 Hz), 72.5 (d, J_{C-P} = 6.1 Hz), 61.9 (t, J_{C-P} = 4.2 Hz), 24.1 (d, J_{C-P} = 4.2 Hz), 23.7 (d, J_{C-P} = 5.1 Hz), ^{31}P NMR (162 MHz $CDCl_3$): δ 3.28–3.12 (m), ^{19}F NMR (377 MHz $CDCl_3$): δ -132.38–-132.48 (m), -157.06–-157.19 (m). HRMS (ESI): Cal. for $C_{13}H_{17}F_4O_4PNa$ ([M+Na]$^+$) : 367.0693. Found: 367.0694.



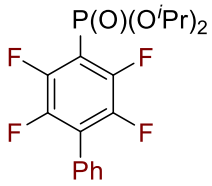
Diisopropyl (2,3,5,6-tetrafluoro-4-(trifluoromethyl) phenyl) phosphonate (3d). Colorless liquid; ^{1}H NMR (400 MHz $CDCl_3$): δ 4.97–4.89 (m, 2H), 1.45 (d, J = 6.4 Hz, 6H), 1.37 (d, J = 6.4 Hz, 6H), ^{13}C NMR (100 MHz $CDCl_3$): δ 146.9 (dm, J_{C-F} = 249.8 Hz), 144.1 (dm, J_{C-F} = 262.5 Hz), 120.4 (q, J_{C-F} = 273.7 Hz), 115.0 (dt, J_{C-P} = 179.0 Hz, J_{C-F} = 19.0 Hz), 113.2–112.6 (m), 73.5 (d, J_{C-P} = 6.2 Hz), 24.0 (d, J_{C-P} = 4.2 Hz), 23.6 (d, J_{C-P} = 5.2 Hz), ^{31}P NMR (162 MHz $CDCl_3$): δ 0.48–0.32 (m), ^{19}F NMR (377 MHz $CDCl_3$): δ -57.0 (t, J_{C-F} = 21.9 Hz), -128.94–-129.06 (m), -138.95–-139.12 (m). HRMS (ESI): Cal. for $C_{13}H_{14}F_7O_3PNa$ ([M+Na]$^+$) : 405.0461. Found: 405.0460.



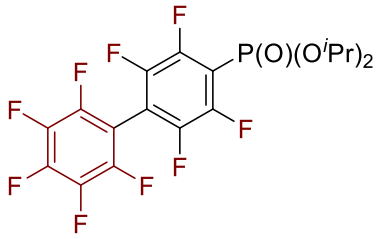
Diisopropyl (4-cyano-2,3,5,6-tetrafluorophenyl) phosphonate (3e). Colorless liquid; ^{1}H NMR (400 MHz $CDCl_3$): δ 4.96–4.88 (m, 2H), 1.44 (d, J = 6.0 Hz, 6H), 1.35 (d, J = 6.0 Hz, 6H), ^{13}C NMR (100 MHz $CDCl_3$): δ 147.1 (dm, J_{C-F} = 261.0 Hz), 146.7 (dm, J_{C-F} = 253.1 Hz), 132.1–131.9 (m), 117.1 (dt, J_{C-P} = 176.8 Hz, J_{C-F} = 19.0 Hz), 106.8 (t, J_{C-F} = 3.8 Hz), 97.7–97.4 (m), 73.9 (d, J_{C-F} = 6.3 Hz), 23.9 (dd, J_{C-P} = 38.0 Hz, J_{C-P} = 4.1 Hz), ^{31}P NMR (162 MHz $CDCl_3$): δ -0.09–-0.25 (m), ^{19}F NMR (377 MHz $CDCl_3$): δ -127.79–-127.91 (m), -130.69–-130.83 (m). HRMS (ESI): Cal. for $C_{13}H_{14}F_4NO_3PNa$ ([M+Na]$^+$) : 362.0540. Found: 362.0528.



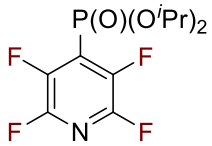
Methyl 4-(diisopropoxyphosphoryl)-2,3,5,6-tetrafluorobenzoate (3f). Colorless liquid; ^{1}H NMR (400 MHz $CDCl_3$): δ 4.94–4.86 (m, 2H), 4.01 (s, 3H), 1.43 (d, J = 6.0 Hz, 6H), 1.35 (d, J = 6.4 Hz, 6H), ^{13}C NMR (100 MHz $CDCl_3$): δ 159.5–159.4 (m), 146.9 (dm, J_{C-F} = 254.4 Hz), 144.3 (dm, J_{C-F} = 258.7 Hz), 116.0 (td, J_{C-F} = 15.4 Hz, J_{C-P} = 2.6 Hz), 113.2 (dt, J_{C-P} = 179.5 Hz, J_{C-F} = 18.8 Hz), 73.2 (d, J_{C-P} = 6.2 Hz), 53.5, 24.0 (d, J_{C-P} = 4.2 Hz), 23.6 (d, J_{C-P} = 5.2 Hz), ^{31}P NMR (162 MHz $CDCl_3$): δ 1.20–1.04 (m), ^{19}F NMR (377 MHz $CDCl_3$): δ -129.95–-130.08 (m), -138.27–-138.40 (m). HRMS (ESI): Cal. for $C_{14}H_{17}F_4O_5PNa$ ([M+Na]$^+$) : 395.0642. Found: 395.0645.



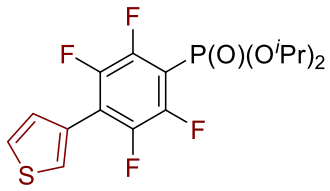
Diisopropyl (2,3,5,6-tetrafluoro-[1,1'-biphenyl]-4-yl) phosphonate (3g). White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.51–7.46 (m, 5H), 4.96–4.88 (m, 2H), 1.45 (d, J = 6.4 Hz, 6H), 1.37 (d, J = 6.4 Hz, 6H), ^{13}C NMR (100 MHz $CDCl_3$): δ 147.2 (dm, J_{C-F} = 253.3 Hz), 143.9 (dm, J_{C-F} = 248.9 Hz), 130.0, 129.7, 128.7, 126.7, 124.8 (t, J_{C-F} = 16.5 Hz), 109.0 (dt, J_{C-P} = 183.4 Hz, J_{C-F} = 18.9 Hz), 72.8 (d, J_{C-P} = 6.1 Hz), 24.1 (d, J_{C-F} = 4.1 Hz), 23.7 (d, J_{C-F} = 5.2 Hz), ^{31}P NMR (162 MHz $CDCl_3$): δ 2.69–2.53 (m), ^{19}F NMR (377 MHz $CDCl_3$): δ -131.65–-131.77 (m), -142.40–-142.60 (m). HRMS (ESI): Cal. for $C_{18}H_{19}F_4O_3PNa$ ([M+Na]$^+$) : 413.0901. Found: 413.0906.



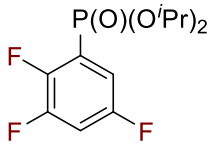
Diisopropyl (perfluoro-[1,1'-biphenyl]-4-yl) phosphonate (3h). White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 4.99–4.91 (m, 2H), 1.46 (d, J = 6.4 Hz, 6H), 1.39 (d, J = 6.4 Hz, 6H), ^{13}C NMR (100 MHz $CDCl_3$): δ 146.9 (dm, J_{C-F} = 250.6 Hz), 144.4 (dm, J_{C-F} = 248.0 Hz), 144.2 (dm, J_{C-F} = 255.3 Hz), 142.7 (dm, J_{C-F} = 257.1 Hz), 137.9 (dm, J_{C-F} = 250.2 Hz), 112.7 (dt, J_{C-P} = 181.2 Hz, J_{C-F} = 18.6 Hz), 110.3–109.9 (m), 102.1–101.7 (m), 73.3 (d, J_{C-F} = 6.2 Hz), 24.1 (d, J_{C-P} = 4.0 Hz), 23.7 (d, J_{C-P} = 5.5 Hz), ^{31}P NMR (162 MHz $CDCl_3$): δ 1.61–1.45 (m), ^{19}F NMR (377 MHz $CDCl_3$): δ -130.05–-130.18 (m), -136.64–-136.79 (m), -136.91–-137.05 (m), -149.32–-149.46 (m), -160.10–-160.27 (m). HRMS (ESI): Cal. for $C_{18}H_{14}F_9O_3PNa$ ([M+Na]$^+$) : 503.0430. Found: 503.0428.



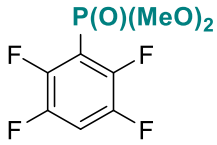
Diisopropyl (perfluoropyridin-4-yl) phosphonate (3i).[3] Colorless liquid; ^{1}H NMR (400 MHz $CDCl_3$): δ 4.98–4.90 (m, 2H), 1.45 (d, J = 7.2 Hz, 6H), 1.37 (d, J = 6.0 Hz, 6H), ^{13}C NMR (100 MHz $CDCl_3$): δ 143.8 (dm, J_{C-F} = 258.3 Hz), 141.7 (dm, J_{C-F} = 264.9 Hz), 124.2 (dt, J_{C-P} = 175.3 Hz, J_{C-F} = 18.0 Hz), 73.9 (d, J_{C-P} = 6.4 Hz), 24.1 (d, J_{C-P} = 4.0 Hz), 23.7 (d, J_{C-P} = 5.3 Hz), ^{31}P NMR (162 MHz $CDCl_3$): δ -0.88–-1.06 (m), ^{19}F NMR (377 MHz $CDCl_3$): δ -89.15–-89.35 (m), -132.63–-132.83 (m).



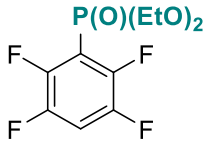
Diisopropyl (2,3,5,6-tetrafluoro-4-(thiophen-3-yl) phenyl) phosphonate (3j). Colorless liquid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.81–7.79 (m, 1H), 7.48–7.44 (m, 2H), 4.93–4.88 (m, 2H), 1.44 (d, J = 6.4 Hz, 6H), 1.36 (d, J = 6.4 Hz, 6H), ^{13}C NMR (100 MHz $CDCl_3$): δ 147.2 (dm, J_{C-F} = 252.8 Hz), 143.8 (dm, J_{C-F} = 249.3 Hz), 128.4 (t, J_{C-F} = 5.2 Hz), 128.2 (t, J_{C-F} = 4.3 Hz),126.2 (t, J_{C-F} = 2.2 Hz), 125.8, 119.6 (t, J_{C-F} = 15.5 Hz), 108.1 (dt, J_{C-P} = 184.1 Hz, J_{C-F} = 19.1 Hz), 72.8 (d, J_{C-P} = 6.1 Hz), 24.1 (d, J_{C-P} = 4.1 Hz), 23.7 (d, J_{C-P} = 5.1 Hz), ^{31}P NMR (162 MHz $CDCl_3$): δ 2.67–2.51 (m), ^{19}F NMR (377 MHz $CDCl_3$): δ -131.86–-131.98 (m), -140.99–-141.12 (m). HRMS (ESI): Cal. for $C_{16}H_{17}F_4O_3PSNa$ ([M+Na]$^+$) : 419.0465. Found: 419.0458.



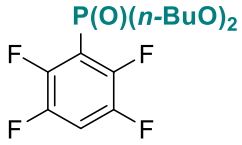
Diisopropyl (2,3,5-trifluorophenyl) phosphonate (3k). Colorless liquid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.42–7.34 (m, 1H), 7.17–7.10 (m, 1H), 4.84–4.76 (m, 2H), 1.41 (d, J = 6.0 Hz, 6H), 1.29 (d, J = 6.0 Hz, 6H), ^{13}C NMR (100 MHz $CDCl_3$): δ 157.2 (dm, J_{C-F} = 247.5 Hz), 150.4 (dm, J_{C-F} = 252.7 Hz), 147.5 (dm, J_{C-F} = 249.6 Hz), 121.3 (ddd, J_{C-P} = 186.2 Hz, J_{C-F} = 17.3 Hz, J_{C-F} = 7.3 Hz), 114.0 (dm, J_{C-F} = 24.5 Hz), 109.6 (ddd, J_{C-F} = 27.2 Hz, J_{C-F} = 20.8 Hz, J_{C-F} = 2.7 Hz), 72.2 (d, J_{C-P} = 5.9 Hz), 23.9 (d, J_{C-P} = 4.1 Hz), 23.6 (d, J_{C-P} = 4.7 Hz), ^{31}P NMR (162 MHz $CDCl_3$): δ 7.47–7.36 (m), ^{19}F NMR (377 MHz $CDCl_3$): δ -113.65–-113.79 (m), -131.44–-131.53 (m), -134.62–-134.72 (m). HRMS (ESI): Cal. for $C_{12}H_{16}F_3O_3PNa$ ([M+Na]$^+$) : 319.0682. Found: 319.0682.



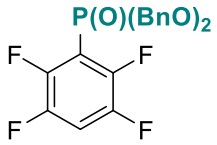
Dibutyl(2,3,5,6-tetrafluorophenyl) phosphine oxide (3l). White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.37–7.29 (m, 1H), 3.93 (d, J = 11.6 Hz, 6H), ^{13}C NMR (100 MHz $CDCl_3$): δ 146.8 (dm, J_{C-F} = 253.1 Hz), 146.1 (dm, J_{C-F} = 245.2 Hz), 110.5 (td, J_{C-F} = 22.3 Hz, J_{C-P} = 2.1 Hz), 108.9 (dt, J_{C-P} = 181.9 Hz, J_{C-F} = 19.1 Hz), 53.6 (d, J_{C-P} = 5.9 Hz), ^{31}P NMR (162 MHz $CDCl_3$): δ 8.02–7.92 (m), ^{19}F NMR (377 MHz $CDCl_3$): δ -131.97–-132.11 (m), -136.70–-136.91 (m). HRMS (ESI): Cal. for $C_8H_7F_4O_3PNa$ ([M+Na]$^+$) : 280.9962. Found: 280.9967.



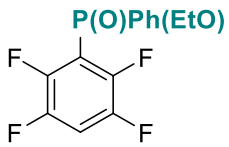
Diethyl (2,3,5,6-tetrafluorophenyl) phosphonate (3m).[4] Colorless liquid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.33–7.24 (m, 1H), 4.35–4.22 (m, 4H), 1.43–1.38 (m, 6H), ^{13}C NMR (100 MHz $CDCl_3$): δ 146.8 (dm, J_{C-F} = 246.1 Hz), 146.0 (dm, J_{C-F} = 254.4 Hz), 110.2 (td, J_{C-F} = 22.3 Hz, J_{C-P} = 2.0 Hz), 110.1 (dt, J_{C-P} = 181.0 Hz, J_{C-F} = 18.9 Hz), 63.5 (d, J_{C-P} = 5.9 Hz), 16.2 (d, J_{C-P} = 6.4 Hz), ^{31}P NMR (162 MHz $CDCl_3$): δ 4.88 (t, J_{P-F} = 9.4 Hz), ^{19}F NMR (377 MHz $CDCl_3$): δ -131.86–-132.01 (m), -137.01–-137.17 (m).



Dibutyl (2,3,5,6-tetrafluorophenyl) phosphonate (3n). Colorless liquid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.30–7.22 (m, 1H), 4.28–4.14 (m, 4H), 1.75–1.68 (m, 4H), 1.48–1.39 (m, 4H), 0.94 (t, J = 7.6 Hz, 6H), ^{13}C NMR (100 MHz $CDCl_3$): δ 146.7 (dm, J_{C-F} = 253.2 Hz), 146.1 (dm, J_{C-F} = 250.4 Hz), 110.1 (td, J_{C-F} = 21.6 Hz, J_{C-P} = 2.2 Hz), 110.0 (dt, J_{C-P} = 180.8 Hz, J_{C-F} = 18.9 Hz), 67.1 (d, J_{C-P} = 6.3 Hz), 32.3 (d, J_{C-P} = 6.6 Hz), 18.59, 13.4 (d, J_{C-P} = 2.1 Hz), ^{31}P NMR (162 MHz $CDCl_3$): δ 5.29–5.14 (m), ^{19}F NMR (377 MHz $CDCl_3$): δ -131.63–-131.79 (m), -136.99–-137.16 (m). HRMS (ESI): Cal. for $C_{14}H_{19}F_4O_3PNa$ ([M+Na]$^+$) : 365.0901. Found: 365.0903.

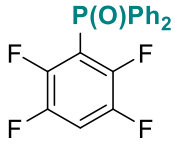


Dibenzyl (2,3,5,6-tetrafluorophenyl) phosphonate (3o). White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.37–7.30 (m, 10H), 7.21–7.16 (m, 1H), 5.24–5.14 (m, 4H), ^{13}C NMR (100 MHz $CDCl_3$): δ 146.6 (dm, J_{C-F} = 254.6 Hz), 146.0 (dm, J_{C-F} = 250.0 Hz), 135.2 (d, J_{C-F} = 6.4 Hz), 128.8, 128.6, 128.2, 110.4 (td, J_{C-F} = 21.9 Hz, J_{C-P} = 2.1 Hz), 109.9 (dt, J_{C-P} = 182.6 Hz, J_{C-P} = 18.5 Hz), 68.9 (d, J_{C-P} = 5.8 Hz), ^{31}P NMR (162 MHz $CDCl_3$): δ 5.87–5.74 (m), ^{19}F NMR (377 MHz $CDCl_3$): δ -131.07–-131.19 (m), -136.83–-137.00 (m). HRMS (ESI): Cal. for $C_{20}H_{15}F_4O_3PNa$ ([M+Na]$^+$) : 433.0588. Found: 433.0579.

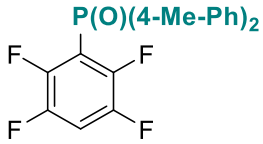


Ethyl phenyl(2,3,5,6-tetrafluorophenyl) phosphinate (3p). Colorless liquid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.85–7.79 (m, 2H), 7.51–7.37 (m, 3H), 7.17–7.09 (m, 1H), 4.28–4.10 (m, 2H), 1.34 (t, J

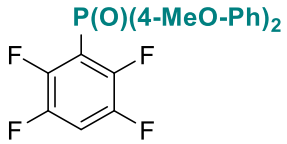
= 6.8 Hz, 3H), ^{13}C NMR (100 MHz $CDCl_3$): δ 146.6 (dm, J_{C-F} = 252.5 Hz), 146.1 (dm, J_{C-F} = 254.5 Hz), 133.1 (d, J_{C-P} = 3.0 Hz), 131.2 (d, J_{C-P} = 10.9 Hz), 131.0 (d, J_{C-P} = 150.7 Hz), 128.7 (d, J_{C-P} = 14.3 Hz), 113.1 (dt, J_{C-P} = 118.0 Hz, J_{C-F} = 18.7 Hz), 110.2 (td, J_{C-F} = 22.3 Hz, J_{C-P} = 1.9 Hz), 62.4 (d, J_{C-P} = 6.2 Hz), 16.2 (d, J_{C-P} = 6.7 Hz), ^{31}P NMR (162 MHz $CDCl_3$): δ 20.93–20.80 (m), ^{19}F NMR (377 MHz $CDCl_3$): δ -131.72–-131.84 (m), -136.76–-136.90 (m). HRMS (ESI): Cal. for $C_{14}H_{11}F_4O_2PNa$ ([M+Na]$^+$) : 341.0325. Found: 341.0328.



Diphenyl(2,3,5,6-tetrafluorophenyl) phosphine oxide (3q). White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.82–7.77 (m, 4H), 7.61–7.57 (m, 2H), 7.53–7.48 (m, 4H), 7.37–7.27 (m, 1H), ^{13}C NMR (100 MHz $CDCl_3$): δ 146.8 (dm, J_{C-F} = 252.3 Hz), 146.3 (dm, J_{C-F} = 256.6 Hz), 132.7 (d, J_{C-P} = 3.0 Hz), 131.6 (d, J_{C-P} = 112.0 Hz), 131.1 (d, J_{C-P} = 10.6 Hz), 128.8 (d, J_{C-P} = 13.1 Hz), 114.0 (dt, J_{C-P} = 85.3 Hz, J_{C-F} = 17.9 Hz), 110.6 (td, J_{C-F} = 22.4 Hz, J_{C-P} = 0.8 Hz), ^{31}P NMR (162 MHz $CDCl_3$): δ 20.9 (t, J_{P-F} = 4.9 Hz), ^{19}F NMR (377 MHz $CDCl_3$): δ -129.06–-129.16 (m), -136.23–-136.39 (m). HRMS (ESI): Cal. for $C_{18}H_{12}F_4OP$ ([M+H]$^+$) : 351.0557. Found: 351.0584.

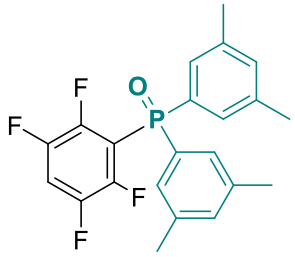


(2,3,5,6-tetrafluorophenyl) di-p-tolylphosphine oxide (3r). White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.67–7.61 (m, 4H), 7.32–7.29 (m, 4H), 7.24–7.22 (m, 1H), 2.42 (s, 6H), ^{13}C NMR (100 MHz $CDCl_3$): δ 146.9 (dm, J_{C-F} = 253.9 Hz), 146.1 (dm, J_{C-F} = 257.9 Hz), 143.3 (d, J_{C-P} = 3.0 Hz), 131.2 (d, J_{C-P} = 11.1 Hz), 129.5 (d, J_{C-P} = 13.5 Hz), 128.6 (d, J_{C-P} = 114.0 Hz), 114.6 (dt, J_{C-P} = 84.2 Hz, J_{C-F} = 17.4 Hz), 110.3 (td, J_{C-F} = 22.0 Hz, J_{C-P} = 1.3 Hz), 21.7 (d, J_{C-P}= 1.5 Hz), ^{31}P NMR (162 MHz $CDCl_3$): δ 21.4 (t, J_{P-F} = 4.9 Hz), ^{19}F NMR (377 MHz $CDCl_3$): δ -128.90–-129.26 (m), -136.54–-136.70 (m). HRMS (ESI): Cal. for $C_{20}H_{15}F_4OPNa$ ([M+Na]$^+$) : 401.0689. Found: 401.0686.

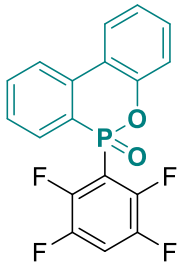


Dis(4-methoxyphenyl) (2,3,5,6-tetrafluorophenyl) phosphine oxide (3s). White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.71–7.64 (m, 4H), 7.31–7.22 (m, 1H), 7.03–6.89 (m, 4H), 3.87–3.84 (m, 6H), ^{13}C NMR (100 MHz $CDCl_3$): δ 163.0 (d, J_{C-P} = 3.1 Hz), 146.8 (dm, J_{C-F} = 251.8 Hz), 146.2 (dm, J_{C-F} = 261.7 Hz), 133.2 (d, J_{C-P} = 12.3 Hz), 123.0 (d, J_{C-P} = 119.6 Hz), 115.2 (t, J_{C-F} = 17.8 Hz), 114.7 (dt, J_{C-P} = 85.3 Hz, J_{C-F} = 17.8 Hz), 110.2 (td, J_{C-F} = 21.9 Hz, J_{C-F} = 1.0 Hz), 55.38, ^{31}P NMR

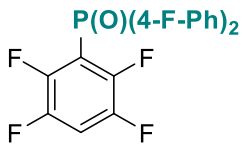
(162 MHz $CDCl_3$): δ 20.9 (t, J_{P-F} = 5.5 Hz), ^{19}F NMR (377 MHz $CDCl_3$): δ -129.52–-129.67 (m), -136.65–-136.80 (m). HRMS (ESI): Cal. for $C_{20}H_{15}F_4O_3PNa$ ([M+Na]$^+$) : 433.0588. Found: 433.0589.



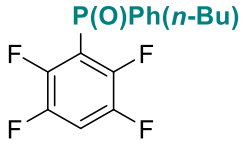
Bis(3,5-dimethylphenyl) (2,3,5,6-tetrafluorophenyl) phosphine oxide (3t). White solid; ^1H NMR (400 MHz $CDCl_3$): δ 7.26 (d, J = 13.6 Hz, 4H), 7.16–7.11 (m, 1H), 7.08–7.06 (m, 2H), 2.21–2.19(m, 12H), ^{13}C NMR (100 MHz $CDCl_3$): δ 146.8 (dm, J_{C-F} = 248.4 Hz), 146.1 (dm, J_{C-F} = 240.7 Hz), 138.5 (d, J_{C-P} = 13.8 Hz), 134.4 (d, J_{C-P} = 3.0 Hz), 131.5 (d, J_{C-P} = 109.9 Hz), 128.6 (d, J_{C-P} = 10.5 Hz), 114.5 (dt, J_{C-P} = 83.8 Hz, J_{C-F} = 17.9 Hz), 110.3 (t, J_{C-F} = 22.4 Hz), 21.2 (d, J_{C-P}= 1.7 Hz), ^{31}P NMR (162 MHz $CDCl_3$): δ 21.6, ^{19}F NMR (377 MHz $CDCl_3$): δ -129.02–-129.15 (m), -136.52–-136.63 (m). HRMS (ESI): Cal. for $C_{22}H_{19}F_4OPNa$ ([M+Na]$^+$) : 429.1002. Found: 429.1006.



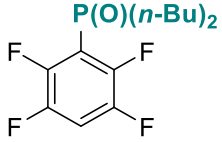
6-(2,3,5,6-tetrafluorophenyl) dibenzo[c,e][1,2]oxaphosphinine 6-oxide (3u). White solid; ^1H NMR (400 MHz $CDCl_3$): δ 8.08–7.92 (m, 3H), 7.76 (t, J = 8.0 Hz, 1H), 7.40 (t, J = 8.4 Hz, 1H), 7.58–7.53 (m, 1H), 7.29–7.25 (m, 2H), 7.23–7.17 (m, 1H), ^{13}C NMR (100 MHz $CDCl_3$): δ 148.6 (d, J_{C-P} = 8.4 Hz), 146.6 (dm, J_{C-F} = 261.2 Hz), 146.1 (dm, J_{C-F} = 247.6 Hz), 136.1 (d, J_{C-P} = 7.6 Hz), 134.4 (d, J_{C-P} = 2.5 Hz), 131.5 (dt, J_{C-P} = 10.6 Hz, J_{C-P} = 2.1 Hz), 131.0, 128.8 (d, J_{C-P} = 14.6 Hz), 125.2, 125.1, 123.9 (d, J_{C-P} = 11.0 Hz), 123.7 (d, J_{C-P} = 138.6 Hz), 121.5 (d, J_{C-P} = 12.0 Hz), 120.6 (d, J_{C-P} = 7.1 Hz), 111.9 (dt, J_{C-P} = 124.6 Hz, J_{C-F} = 19.0 Hz), 110.9 (td, J_{C-F} = 20.8 Hz, J_{C-P} = 2.2 Hz), ^{31}P NMR (162 MHz $CDCl_3$): δ 13.8 (t, J_{P-F} = 6.5 Hz), ^{19}F NMR (377 MHz $CDCl_3$): δ -131.42–-131.53 (m), -136.17–-136.30 (m). HRMS (ESI): Cal. for $C_{18}H_9F_4O_2PNa$ ([M+Na]$^+$) : 387.0169. Found: 387.0186.



Dis(4-fluorophenyl) (2,3,5,6-tetrafluorophenyl) phosphine oxide (3v). Colorless liquid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.72–7.65 (m, 4H), 7.27–7.19 (m, 1H), 7.17–7.11 (m, 4H), ^{13}C NMR (100 MHz $CDCl_3$): δ 165.6 (dd, J_{C-P} = 253.8 Hz, J_{C-P} = 3.5 Hz), 146.8 (dm, J_{C-F} = 244.3 Hz), 146.3 (dm, J_{C-F} = 252.3 Hz), 133.8 (dd, J_{C-P} = 12.2 Hz, J_{C-F} = 8.9 Hz), 127.5 (dd, J_{C-P} = 115.3 Hz, J_{C-P} = 3.9 Hz), 116.4 (dd, J_{C-F} = 21.6 Hz, J_{C-P} = 14.5 Hz), 113.6 (dt, J_{C-F} = 88.1 Hz, J_{C-F} = 17.9 Hz), 110.9 (td, J_{C-P} = 21.4 Hz, J_{C-P} = 1.4 Hz), ^{31}P NMR (162 MHz $CDCl_3$): δ 18.9 (t, J_{P-F} = 5.7 Hz), ^{19}F NMR (377 MHz $CDCl_3$): δ -104.8 (t, J_{C-F} = 21.9 Hz), -129.04–-129.16 (m), -135.86–-136.80 (m). HRMS (ESI): Cal. for $C_{18}H_9F_6OPNa$ ([M+Na]$^+$) : 409.0188. Found: 409.0191.



Butyl(phenyl)(2,3,5,6-tetrafluorophenyl) phosphine oxide (3w). White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.81–7.78 (m, 2H), 7.61–7.49 (m, 3H), 7.30–7.20 (m, 1H), 2.60–2.30 (m, 2H), 1.73–1.26 (m, 4H), 0.94–0.87 (m, 3H), ^{13}C NMR (100 MHz $CDCl_3$): δ 146.6 (dm, J_{C-F} = 250.8 Hz), 146.3 (dm, J_{C-F} = 251.3 Hz), 132.4 (d, J_{C-P} = 2.9 Hz), 132.1 (d, J_{C-P} = 103.8 Hz), 130.2 (d, J_{C-P} = 10.2 Hz), 128.8 (d, J_{C-P} = 12.6 Hz), 114.6 (dt, J_{C-P} = 77.3 Hz, J_{C-F} = 19.7 Hz), 110.0 (td, J_{C-F} = 23.7 Hz, J_{C-P} = 1.4 Hz), 31.4 (dt, J_{C-P} = 74.2 Hz, J_{C-F} = 4.0 Hz), 24.0 (d, J_{C-P} = 16.7 Hz), 23.2 (d, J_{C-P} = 4.3 Hz), 13.5, ^{31}P NMR (162 MHz $CDCl_3$): δ 29.9 (t, J_{P-F} = 4.1 Hz), ^{19}F NMR (377 MHz $CDCl_3$): δ -131.26–-131.40 (m), -136.36–-136.48 (m). HRMS (ESI): Cal. for $C_{16}H_{15}F_4OPNa$ ([M+Na]$^+$) : 353.0689. Found: 353.0693.



Dibutyl(2,3,5,6-tetrafluorophenyl) phosphine oxide (3x). White solid; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.34–7.25 (m, 1H), 2.15–2.07 (m, 4H), 1.73–1.41 (m, 8H), 0.93 (t, J = 7.2 Hz, 6H), ^{13}C NMR (100 MHz $CDCl_3$): δ 146.7 (dm, J_{C-F} = 249.9 Hz), 146.2 (dm, J_{C-F} = 246.9 Hz), 113.0 (dt, J_{C-P} = 68.8 Hz, J_{C-F} = 19.8 Hz), 109.9 (td, J_{C-F} = 22.3 Hz, J_{C-F} = 1.8 Hz), 30.8 (dt, J_{C-P} = 70.7 Hz, J_{C-F} = 2.5 Hz), 23.9 (d, J_{C-P} = 15.7 Hz), 23.5 (d, J_{C-P} = 4.6 Hz), 13.5, ^{31}P NMR (162 MHz $CDCl_3$): δ 42.50–42.36 (m), ^{19}F NMR (377 MHz $CDCl_3$): δ -132.92–-133.05 (m), -136.44–-136.56 (m). HRMS (ESI): Cal. for $C_{14}H_{19}F_4OPNa$ ([M+Na]$^+$) : 333.1002. Found: 333.1001.

7. References

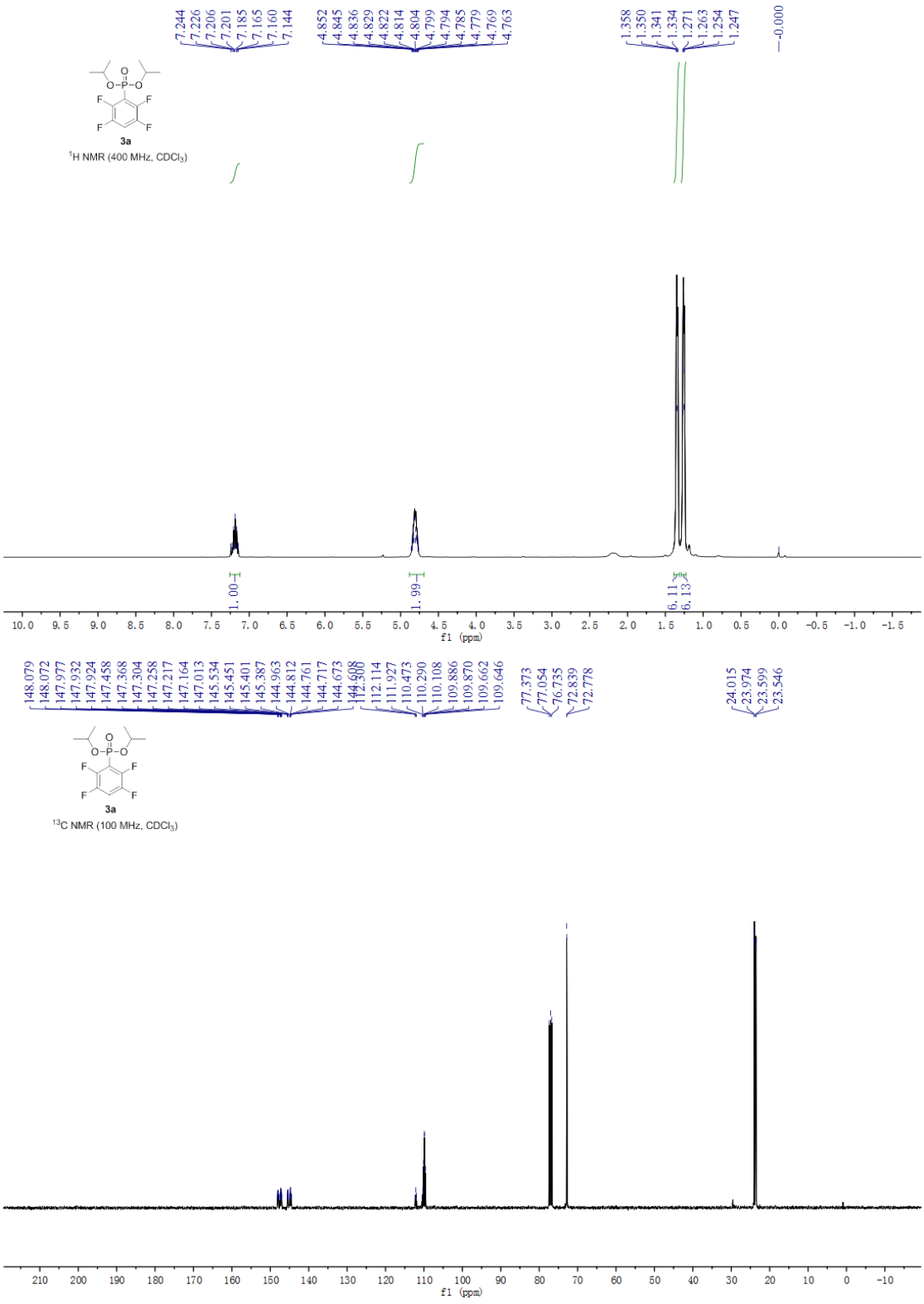
(1) X. Li, B. Fu, Q. Zhang, X. Yuan, Q. Zhang, T. Xiong and Q. Zhang. *Angew. Chem., Int. Ed.*, 2020, **59**, 23056

(2) M. Kalek and J. Stawinski. *Organometallics*, 2008, **27**, 5876

(3) W. Boenigk and G. Hägele. *Chem. Ber.,* 1983, **116**, 2418

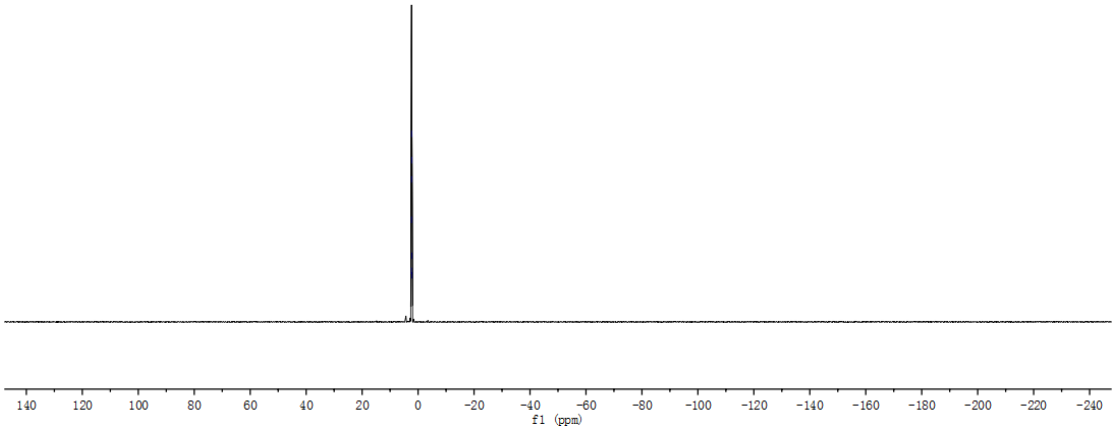
(4) I. Ghosh, J. Khamrai, A. Savateev, N. Shlapakov, M. Antonietti and B. König . *Science,* 2019, **365**, 360

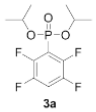
8. Copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{31}P NMR spectra



3a

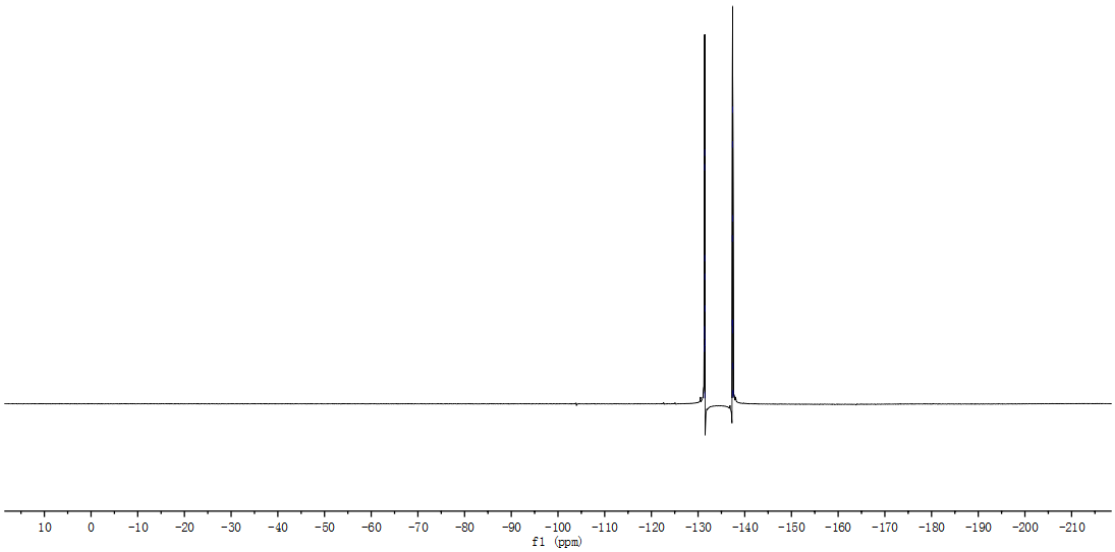
^{31}P NMR (162 MHz, $CDCl_3$)

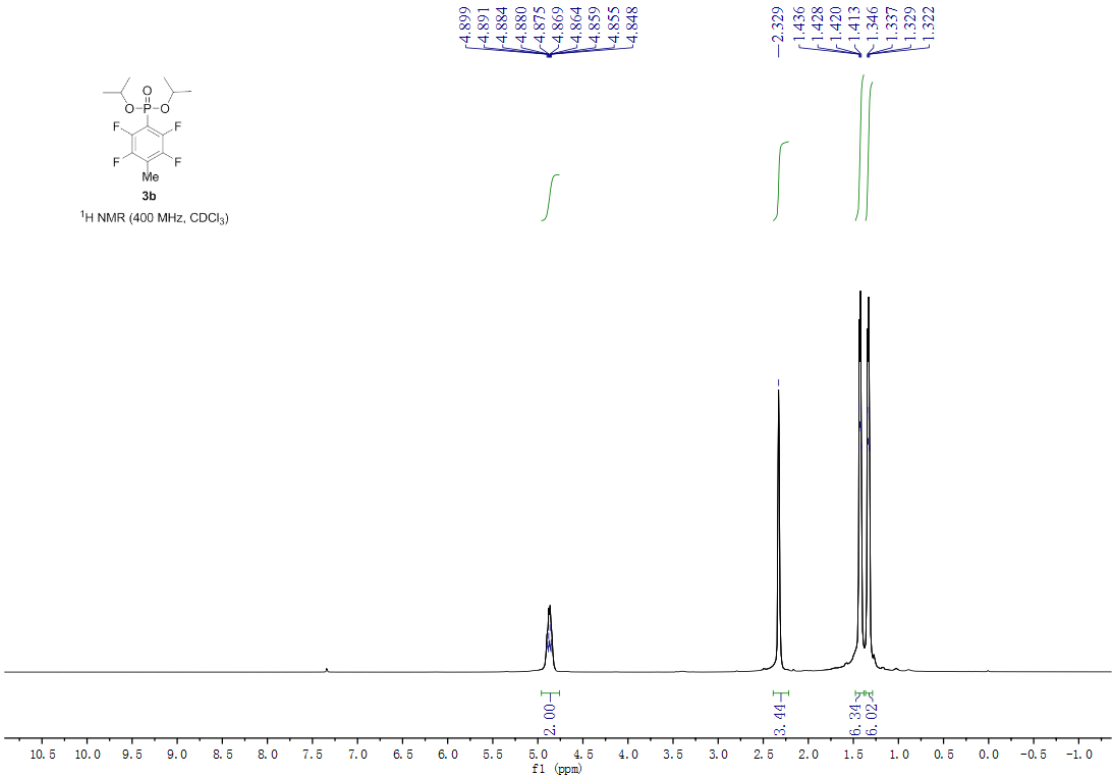


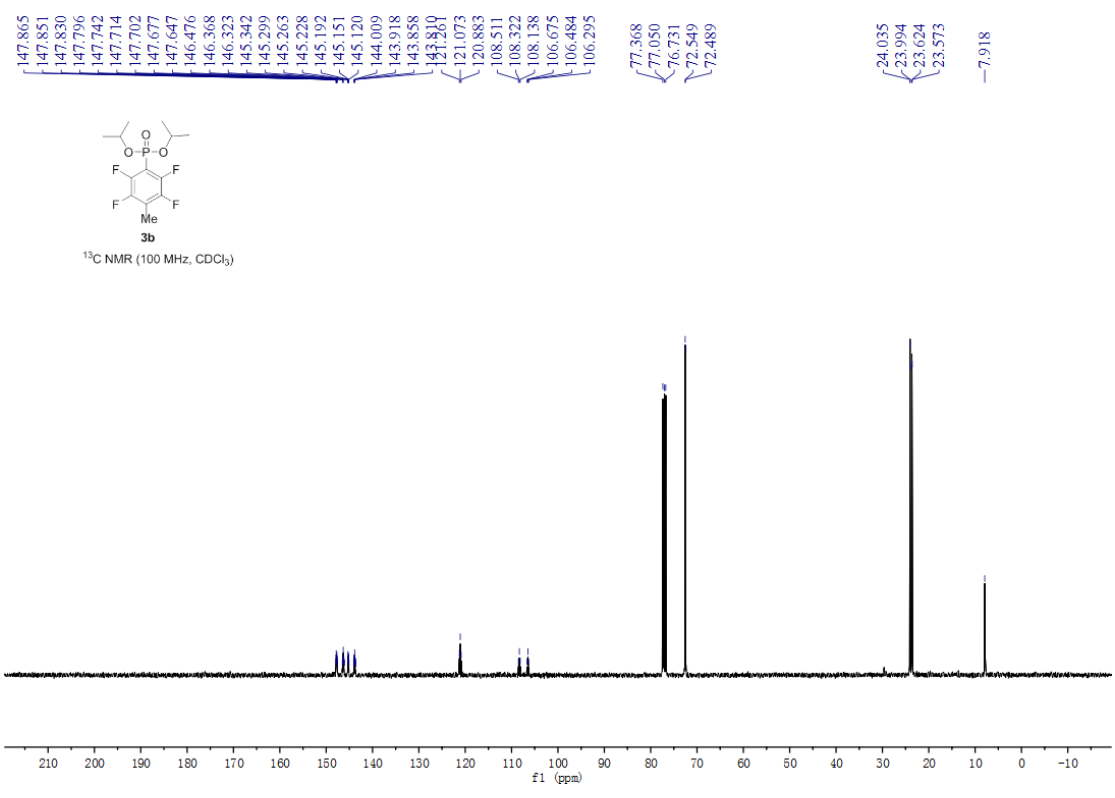


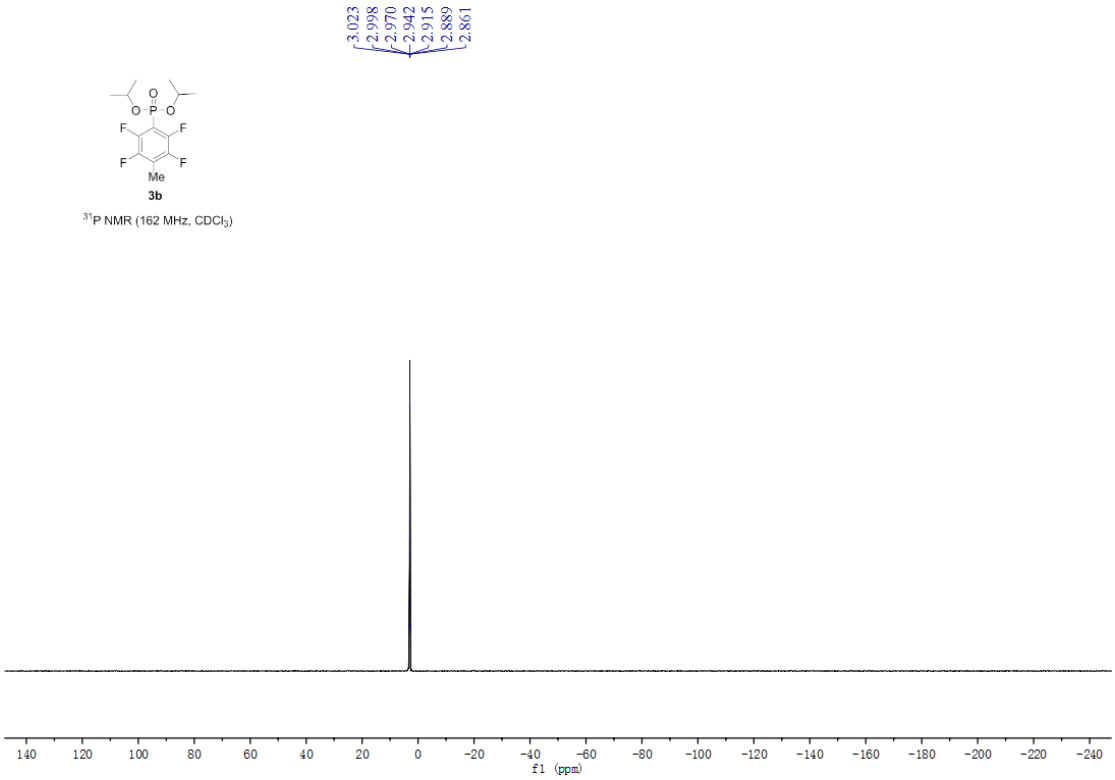
3a

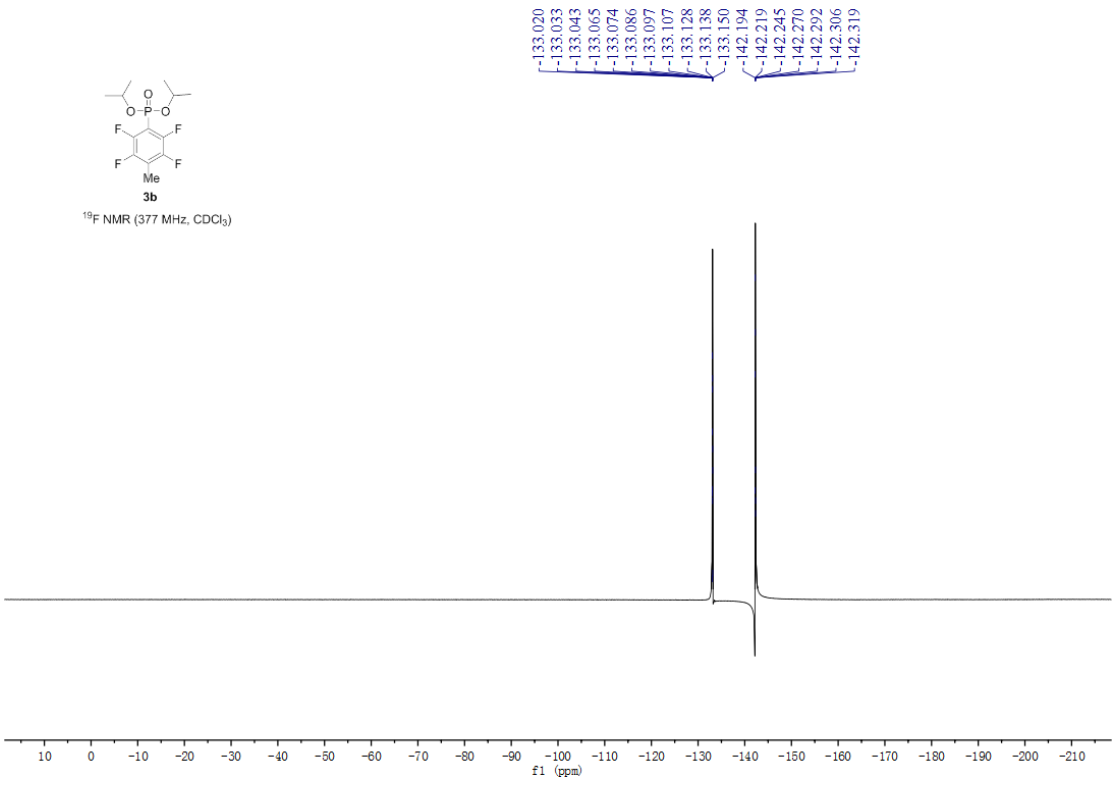
^{19}F NMR (377 MHz, $CDCl_3$)

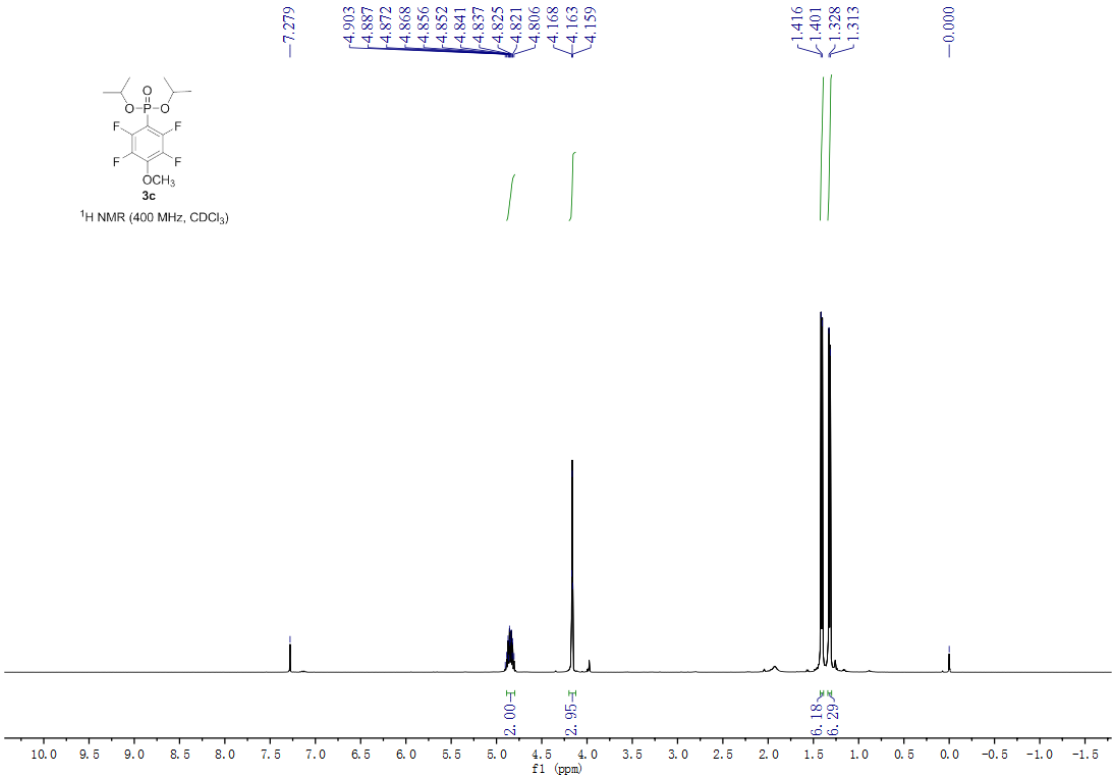


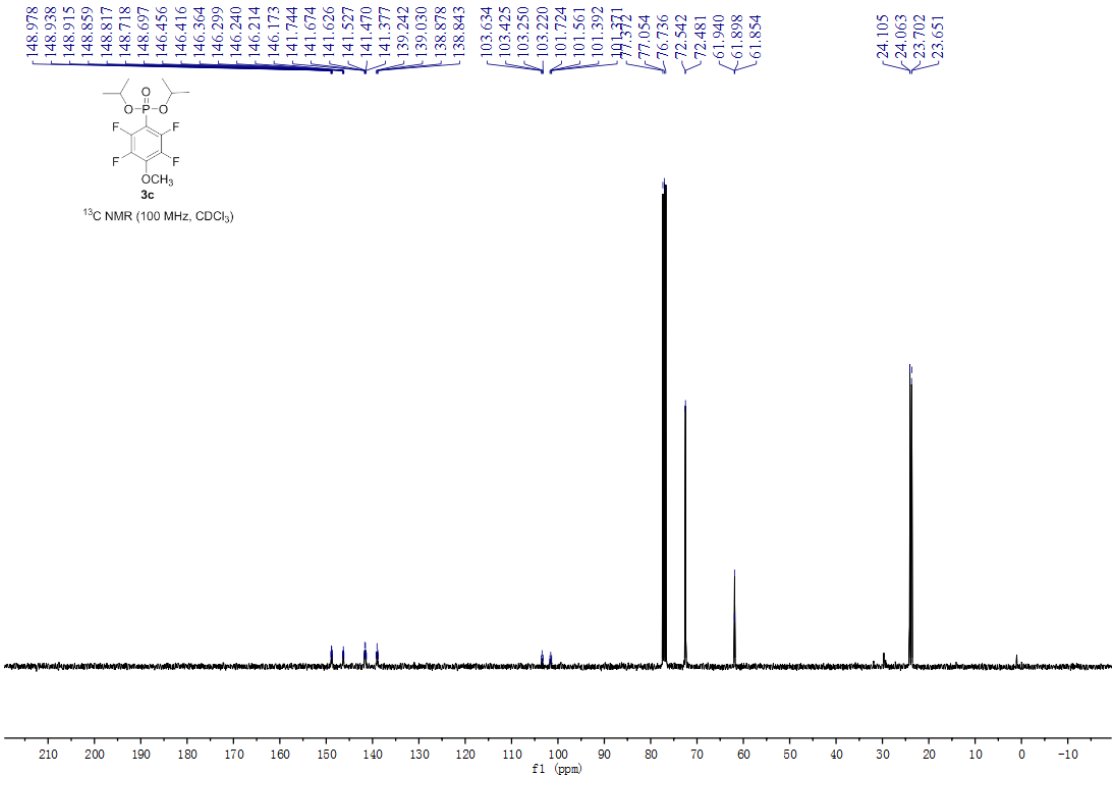

4.899
4.891
4.884
4.880
4.875
4.869
4.864
4.859
4.855
4.848
2.329
1.436
1.428
1.420
1.413
1.346
1.337
1.329
1.322
2.00
3.44
6.31
6.02
f1 (ppm)

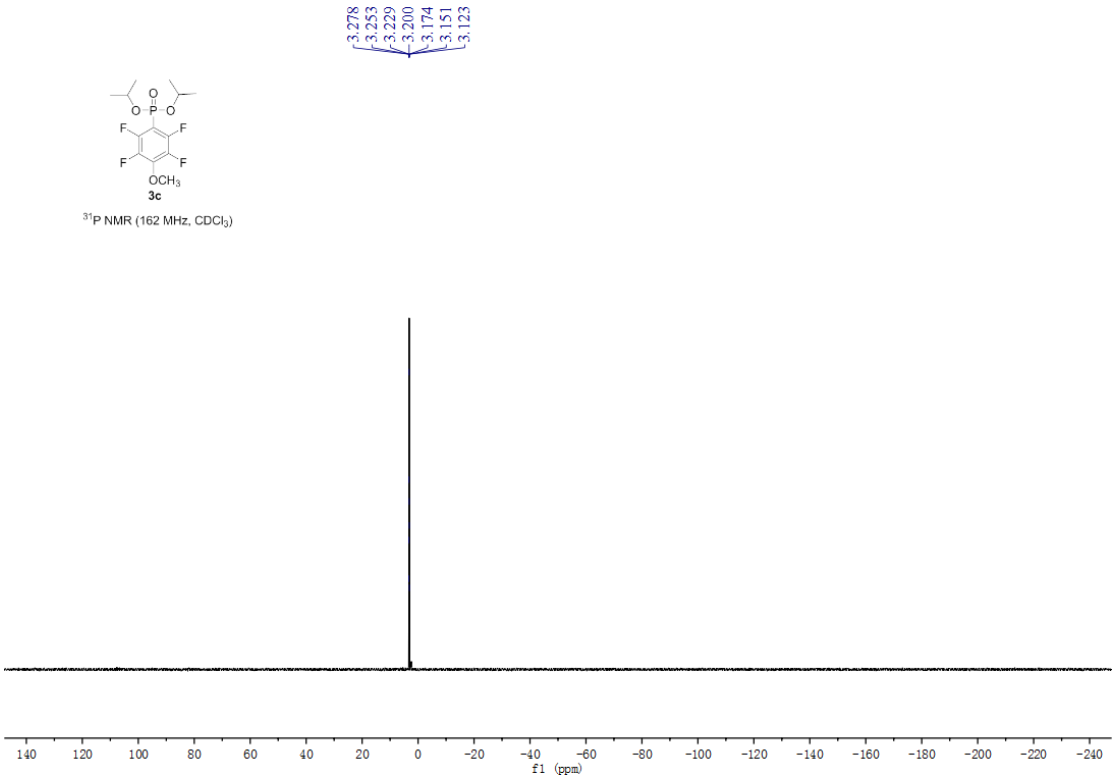

147.865
147.851
147.830
147.796
147.742
147.714
147.702
147.677
147.647
146.476
146.368
146.323
145.342
145.299
145.263
145.228
145.192
145.151
145.120
144.009
143.918
143.858
121.261
121.073
120.883
108.511
108.322
108.138
106.675
106.484
106.295
77.368
77.050
76.731
72.549
72.489
24.035
23.994
23.624
23.573
7.918
f1 (ppm)

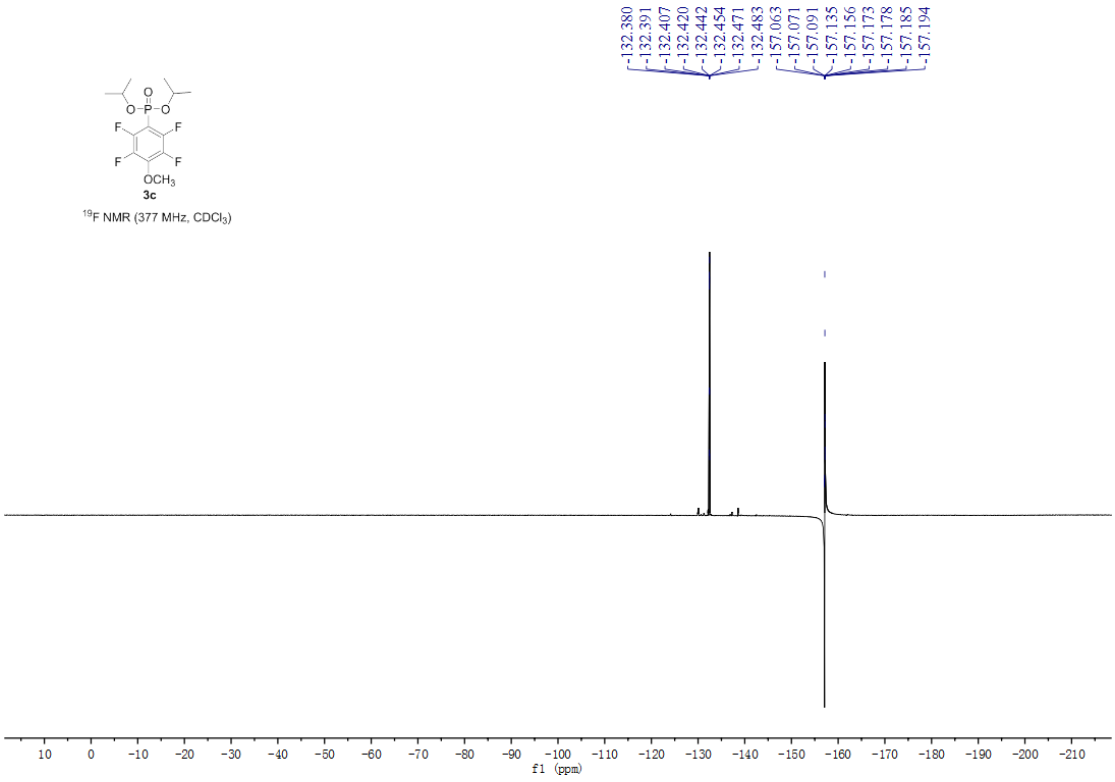

3.023
2.998
2.970
2.942
2.915
2.889
2.861
Me
3b
31P NMR (162 MHz, CDCl3)
f1 (ppm)

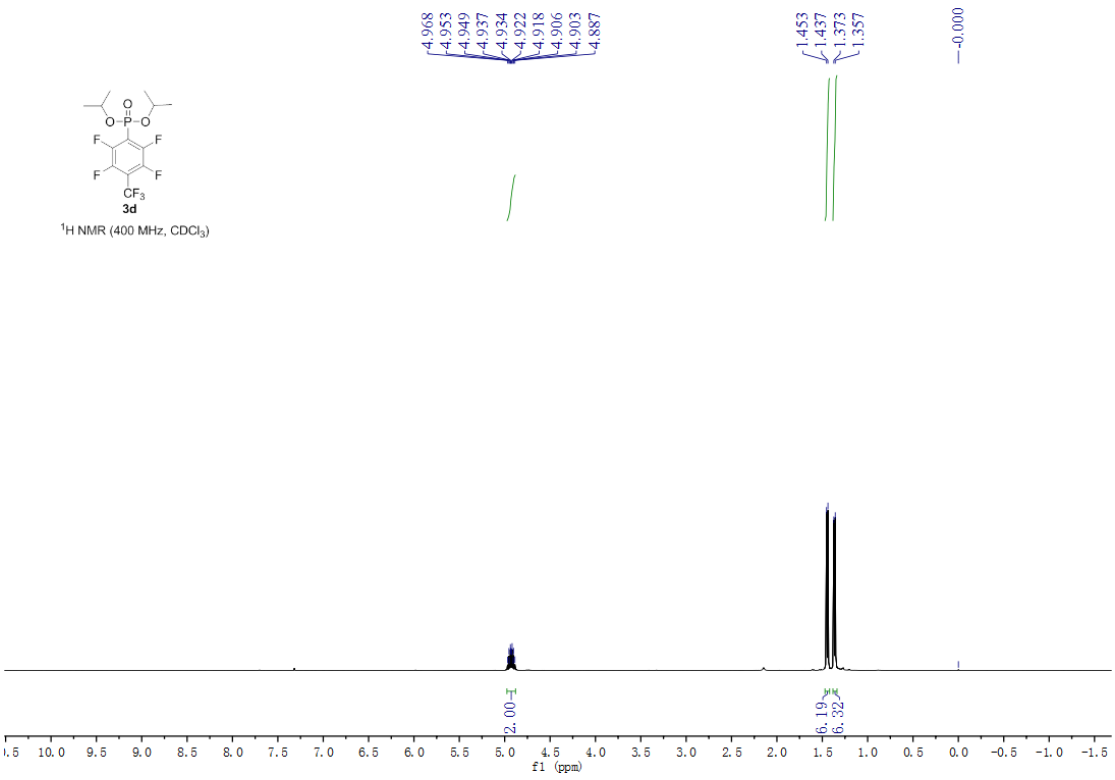

-133.020
-133.033
-133.043
-133.065
-133.074
-133.086
-133.097
-133.107
-133.128
-133.138
-133.150
-142.194
-142.219
-142.245
-142.270
-142.292
-142.306
-142.319
Me
3b
19F NMR (377 MHz, CDCl3)
f1 (ppm)

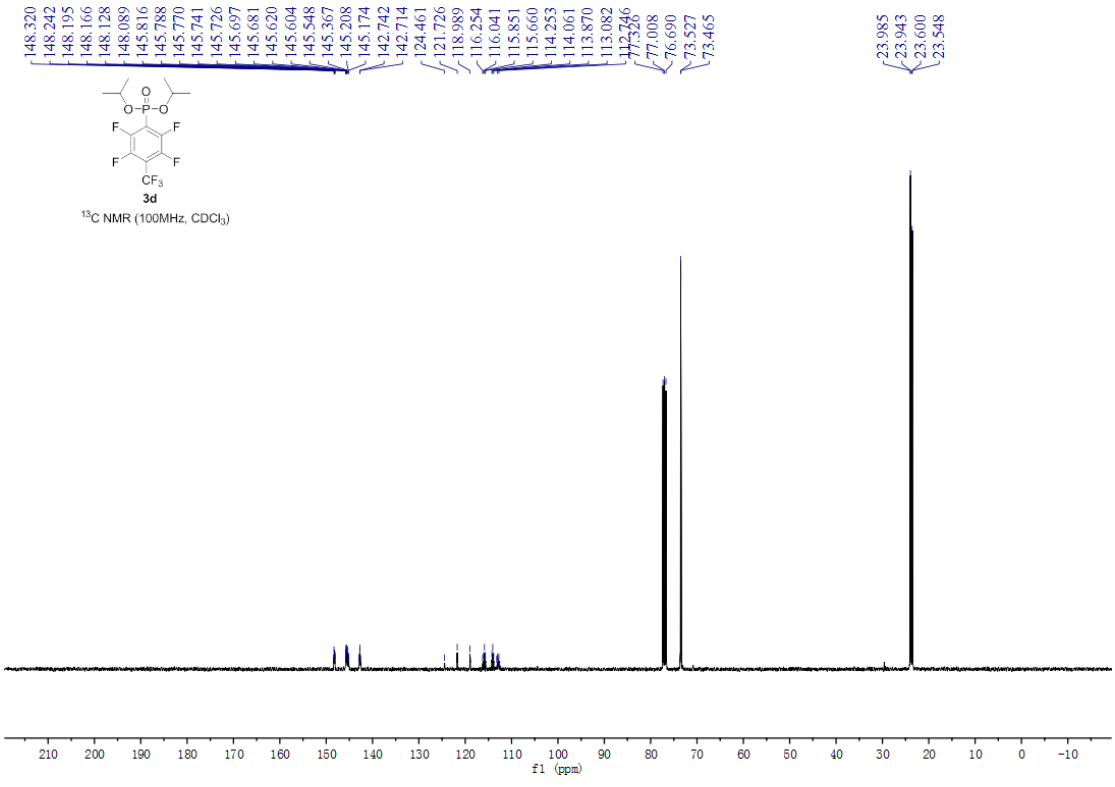

7.279
4.903
4.887
4.872
4.868
4.856
4.852
4.841
4.837
4.825
4.821
4.806
4.168
4.163
4.159
1.416
1.401
1.328
1.313
0.000
3c
1H NMR (400 MHz, CDCl3)
2.00
2.95
6.18
6.29
f1 (ppm)

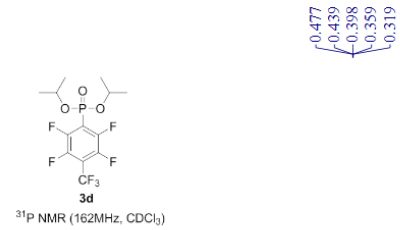

148.978
148.938
148.915
148.859
148.817
148.718
148.697
146.456
146.416
146.364
146.299
146.240
146.214
146.173
141.744
141.674
141.626
141.527
141.470
141.377
139.242
139.030
138.878
138.843
103.634
103.425
103.250
103.220
101.724
101.561
101.392
101.371
77.372
77.054
76.736
72.542
72.481
61.940
61.898
61.854
24.105
24.063
23.702
23.651
3c
13C NMR (100 MHz, CDCl3)
f1 (ppm)


3.278
3.253
3.229
3.200
3.174
3.151
3.123
OCH3
3c
31P NMR (162 MHz, CDCl3)
f1 (ppm)


-132.380
-132.391
-132.407
-132.420
-132.442
-132.454
-132.471
-132.483
-157.063
-157.071
-157.091
-157.135
-157.156
-157.173
-157.178
-157.185
-157.194
OCH3
3c
19F NMR (377 MHz, CDCl3)
f1 (ppm)

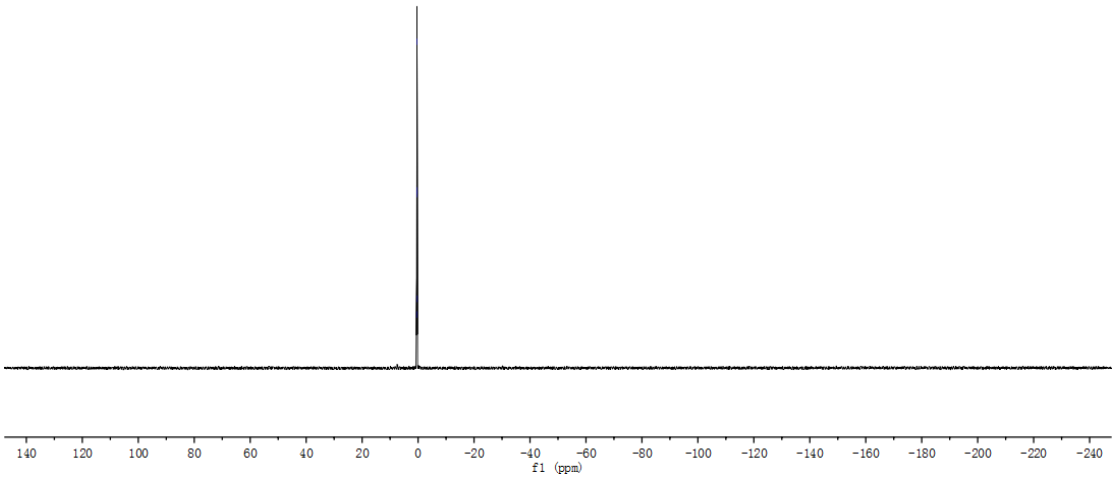

4.968
4.953
4.949
4.937
4.934
4.922
4.918
4.906
4.903
4.887
1.453
1.437
1.373
1.357
0.000
3d
1H NMR (400 MHz, CDCl3)
2.00
6.19
6.32
f1 (ppm)

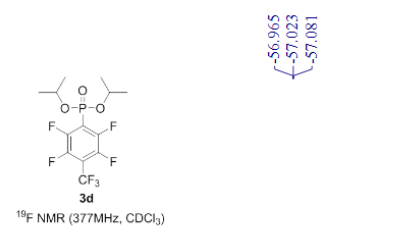

148.320
148.242
148.195
148.166
148.128
148.089
145.816
145.788
145.770
145.741
145.726
145.697
145.681
145.620
145.604
145.548
145.367
145.208
145.174
142.742
142.714
124.461
121.726
118.989
116.254
116.041
115.851
115.660
114.253
114.061
113.870
113.082
112.746
77.326
77.008
76.690
73.527
73.465
23.985
23.943
23.600
23.548
3d
13C NMR (100MHz, CDCl3)
f1 (ppm)



3d

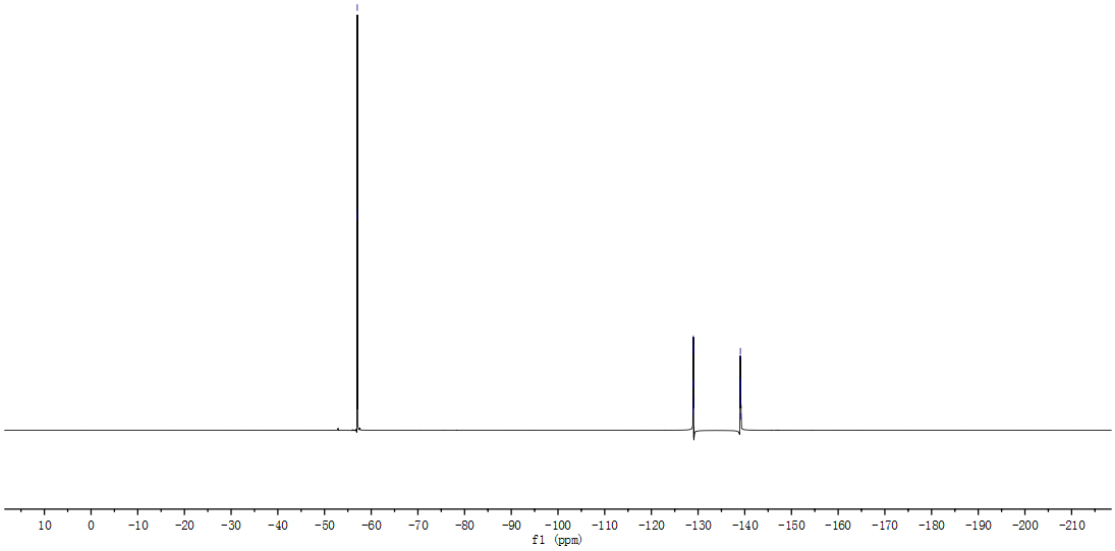
^{31}P NMR (162MHz, $CDCl_3$)

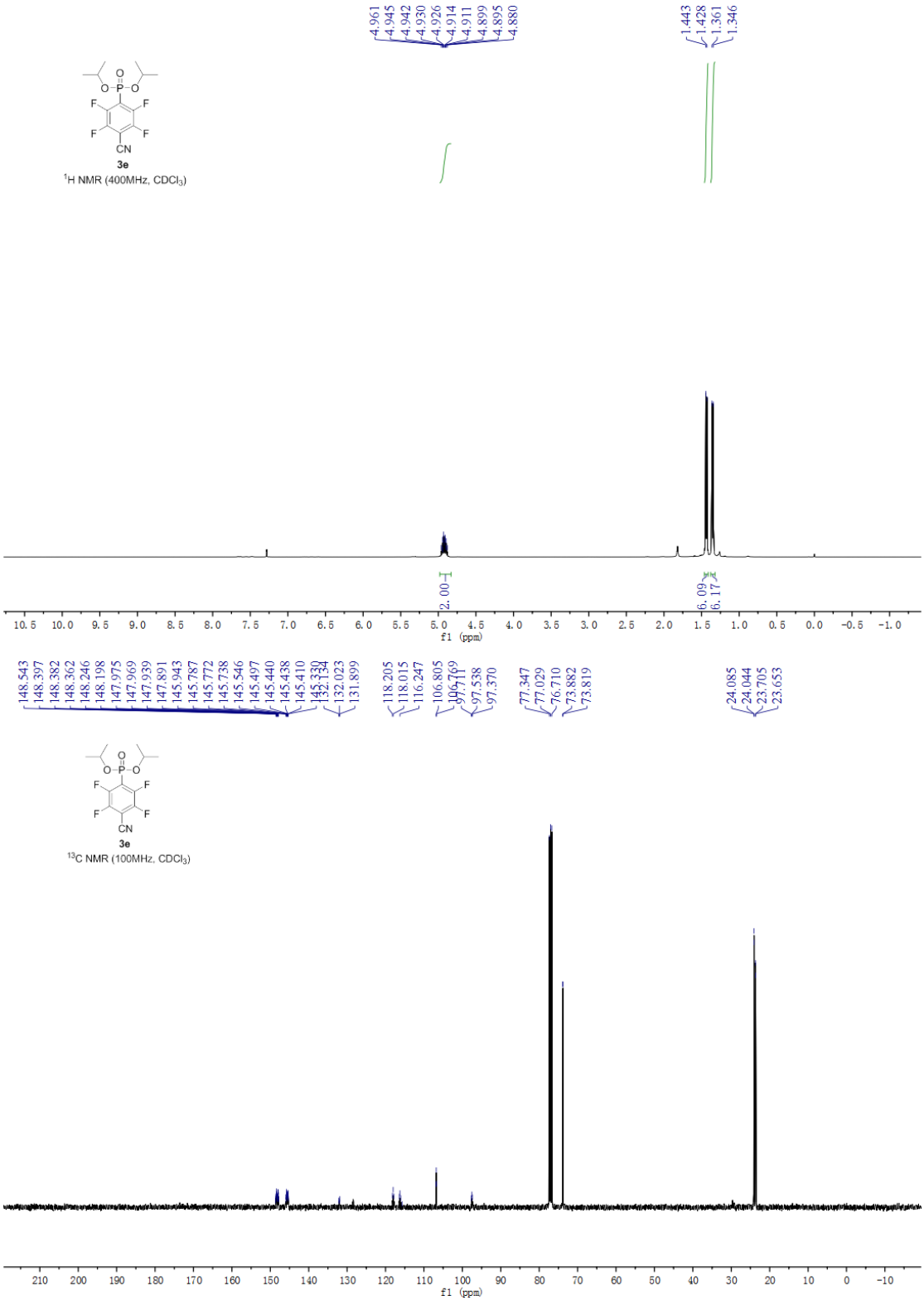


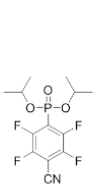


3d

^{19}F NMR (377MHz, $CDCl_3$)

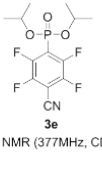



4.961
4.945
4.942
4.930
4.926
4.914
4.911
4.899
4.895
4.880
1.443
1.428
1.361
1.346
3e
1H NMR (400MHz, CDCl3)
2.00
6.09
6.17
f1 (ppm)
148.543
148.397
148.382
148.362
148.246
148.198
147.975
147.969
147.939
147.891
145.943
145.787
145.772
145.738
145.546
145.497
145.440
145.438
145.410
132.023
131.899
118.205
118.015
116.247
106.805
106.769
97.538
97.370
77.347
77.029
76.710
73.882
73.819
24.085
24.044
23.705
23.653
3e
13C NMR (100MHz, CDCl3)
f1 (ppm)



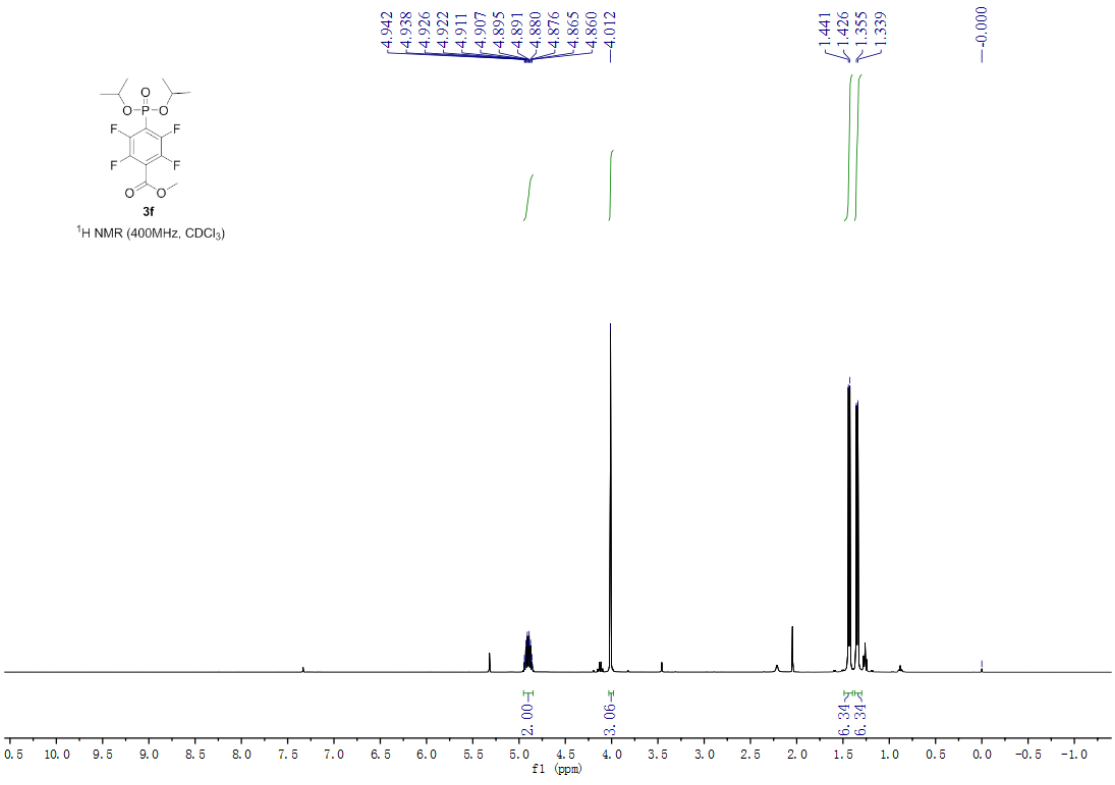
3e

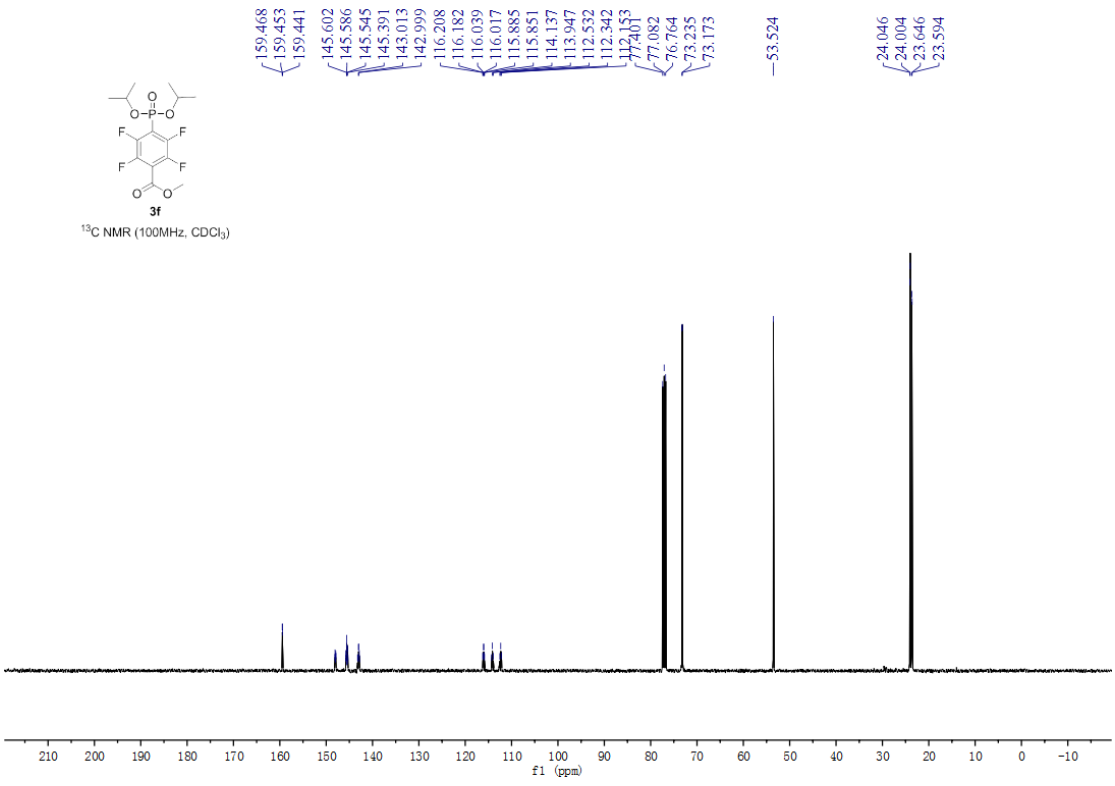
^{31}P NMR (162MHz, $CDCl_3$)

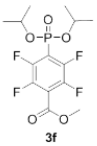


3e

^{19}F NMR (377MHz, $CDCl_3$)

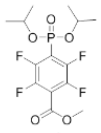

4.942
4.938
4.926
4.922
4.911
4.907
4.895
4.891
4.880
4.876
4.865
4.860
4.012
1.441
1.426
1.355
1.339
0.000
3f
^{1}H NMR (400MHz, CDCl$_3$)
2.00
3.06
6.34
6.34
f1 (ppm)


159.468
159.453
159.441
145.602
145.586
145.545
145.391
143.013
142.999
116.208
116.182
116.039
116.017
115.885
115.851
114.137
113.947
112.532
112.342
77.401
77.082
76.764
73.235
73.173
53.524
24.046
24.004
23.646
23.594
3f
^{13}C NMR (100MHz, CDCl$_3$)
f1 (ppm)



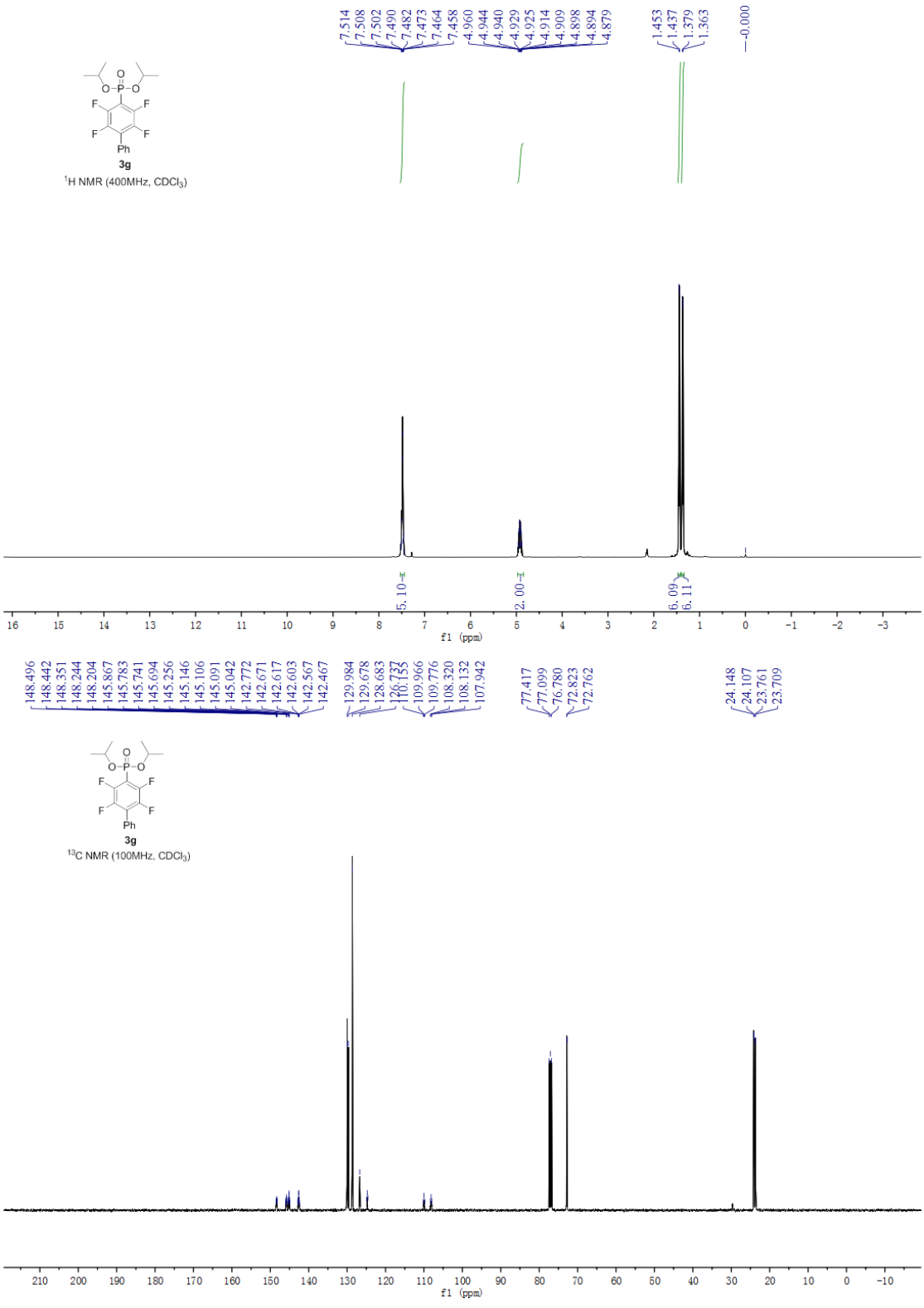
3f

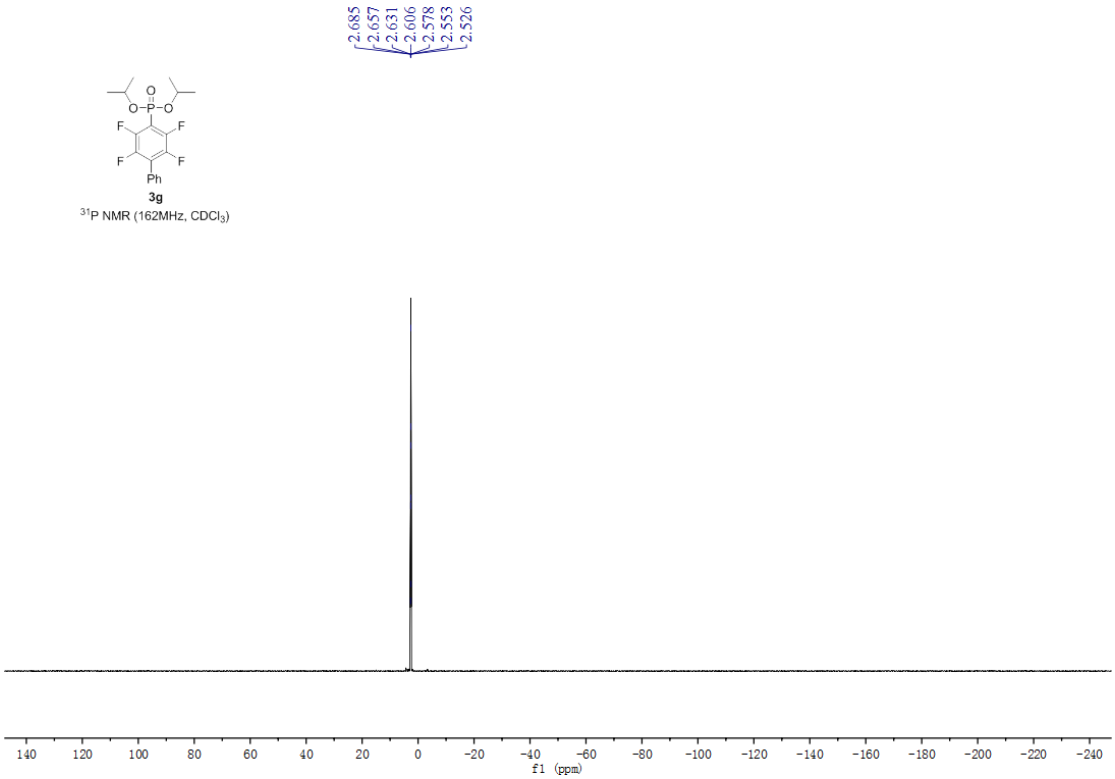
^{31}P NMR (162MHz, $CDCl_3$)

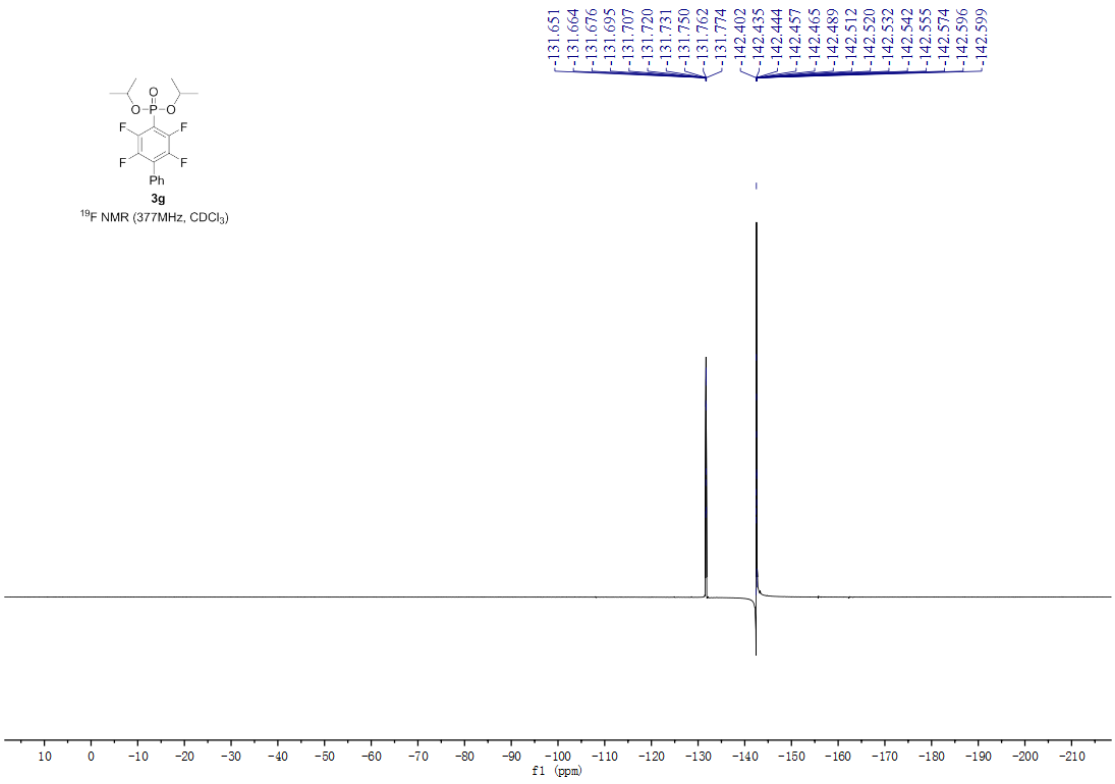


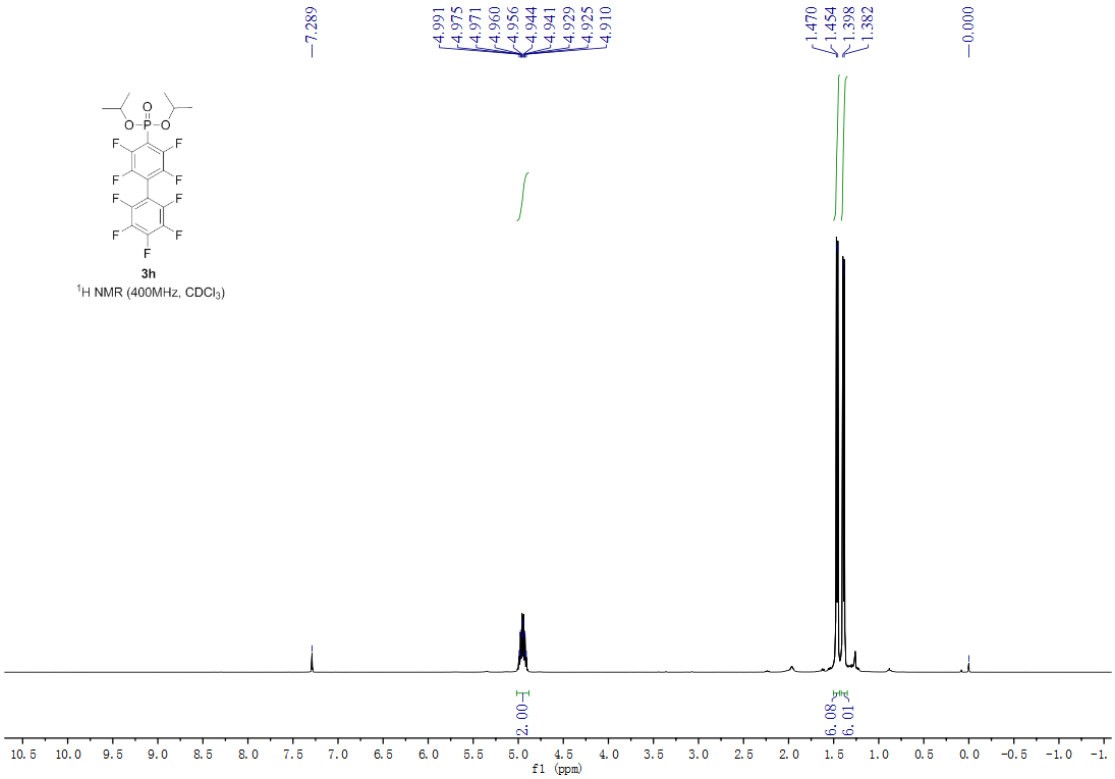
3f

^{19}F NMR (377MHz, $CDCl_3$)


7.514
7.508
7.502
7.490
7.482
7.473
7.464
7.458
4.960
4.944
4.940
4.929
4.925
4.914
4.909
4.898
4.894
4.879
1.453
1.437
1.379
1.363
0.000
3g
1H NMR (400MHz, CDCl3)
5.10
2.00
6.09
6.11
f1 (ppm)
148.496
148.442
148.351
148.244
148.204
145.867
145.783
145.741
145.694
145.256
145.146
145.106
145.091
145.042
142.772
142.671
142.617
142.603
142.567
142.467
129.984
129.678
128.683
126.737
110.155
109.966
109.776
108.320
108.132
107.942
77.417
77.099
76.780
72.823
72.762
24.148
24.107
23.761
23.709
3g
13C NMR (100MHz, CDCl3)
f1 (ppm)

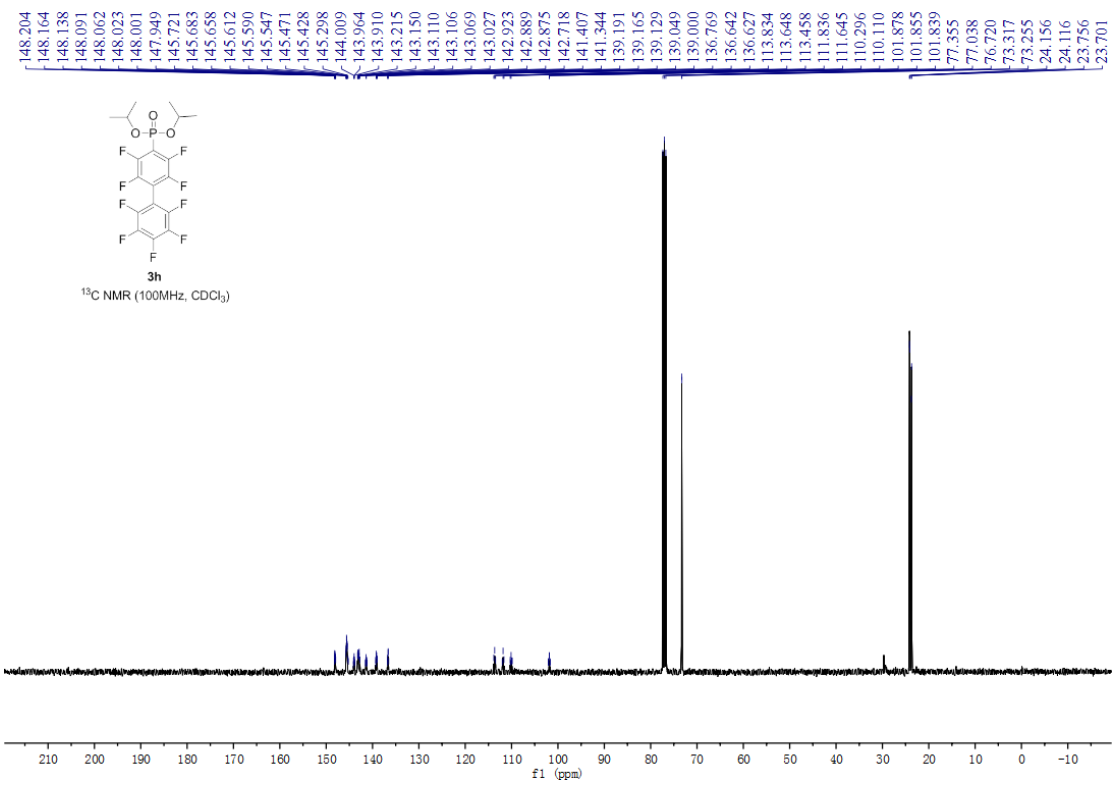

2.685
2.657
2.631
2.606
2.578
2.553
2.526
Ph
3g
31P NMR (162MHz, CDCl3)
f1 (ppm)


-131.651
-131.664
-131.676
-131.695
-131.707
-131.720
-131.731
-131.750
-131.762
-131.774
-142.402
-142.435
-142.444
-142.457
-142.465
-142.489
-142.512
-142.520
-142.532
-142.542
-142.555
-142.574
-142.596
-142.599
Ph
3g
19F NMR (377MHz, CDCl3)
f1 (ppm)



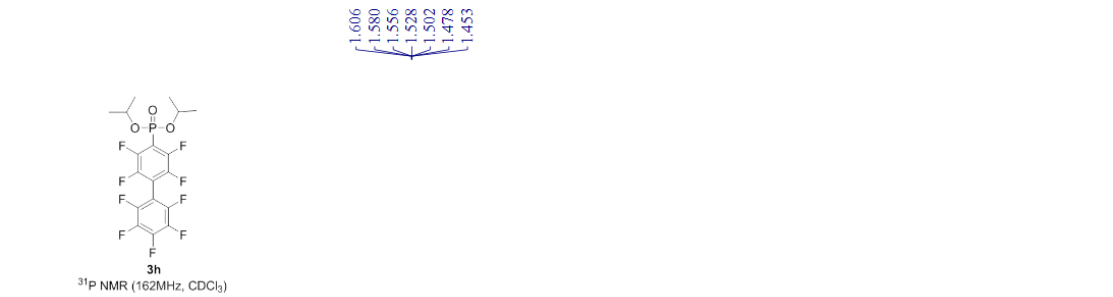
3h

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



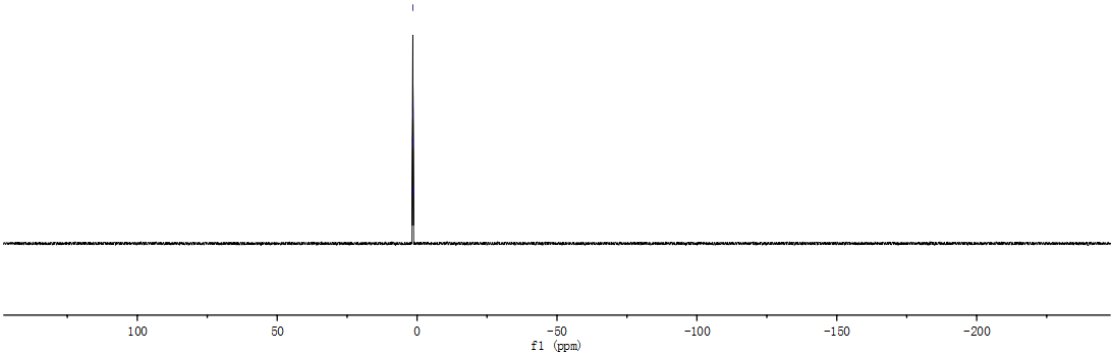
3h

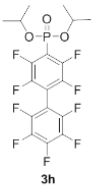
^{13}C NMR (100MHz, $CDCl_3$)



3h

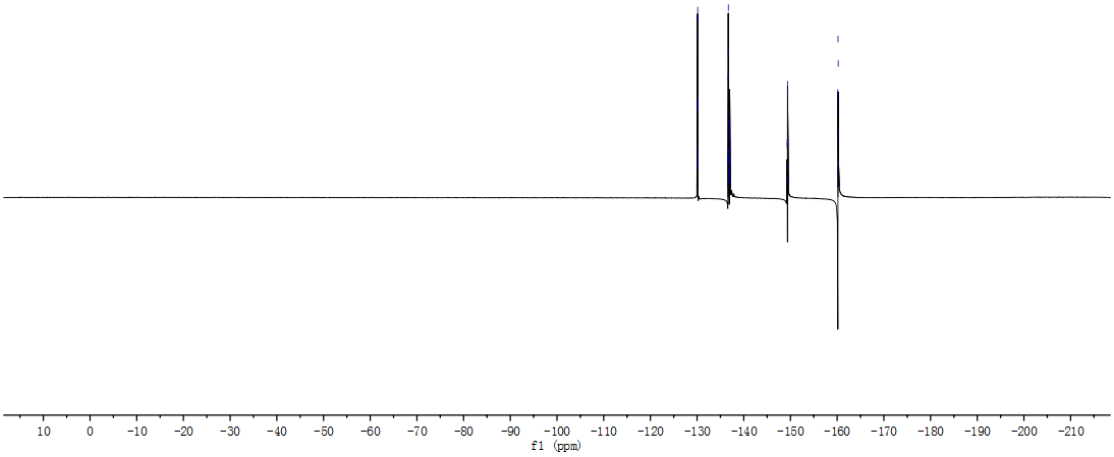
^{31}P NMR (162MHz, $CDCl_3$)

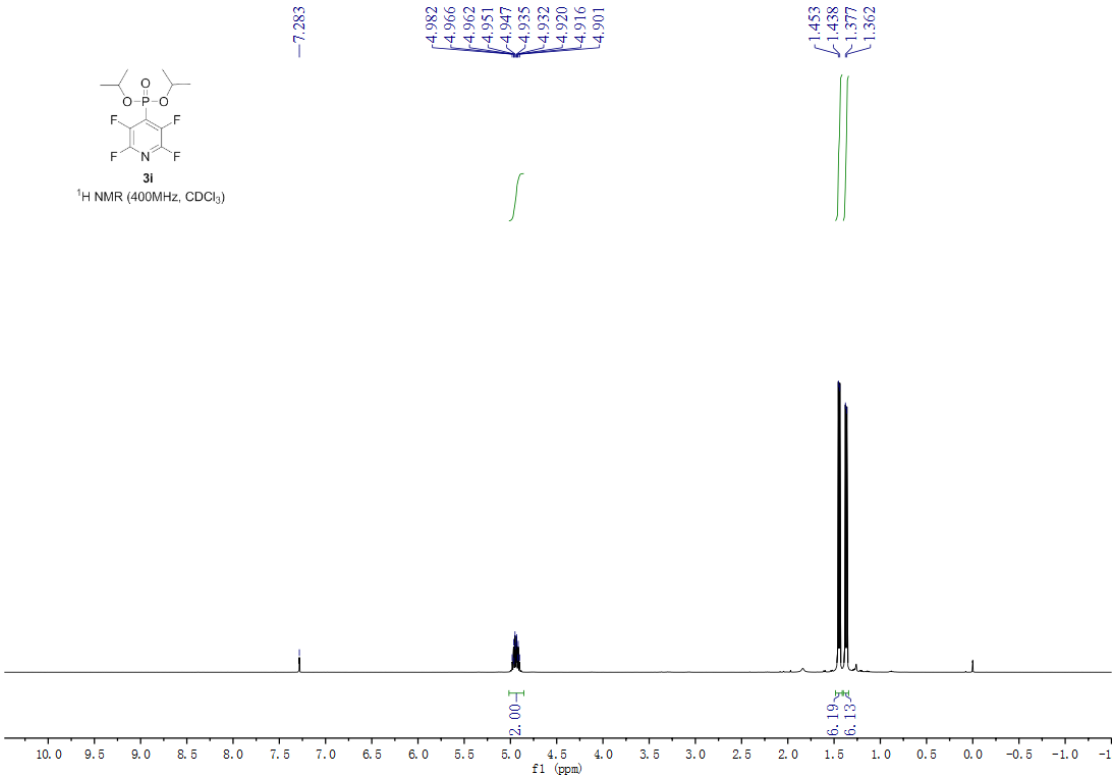


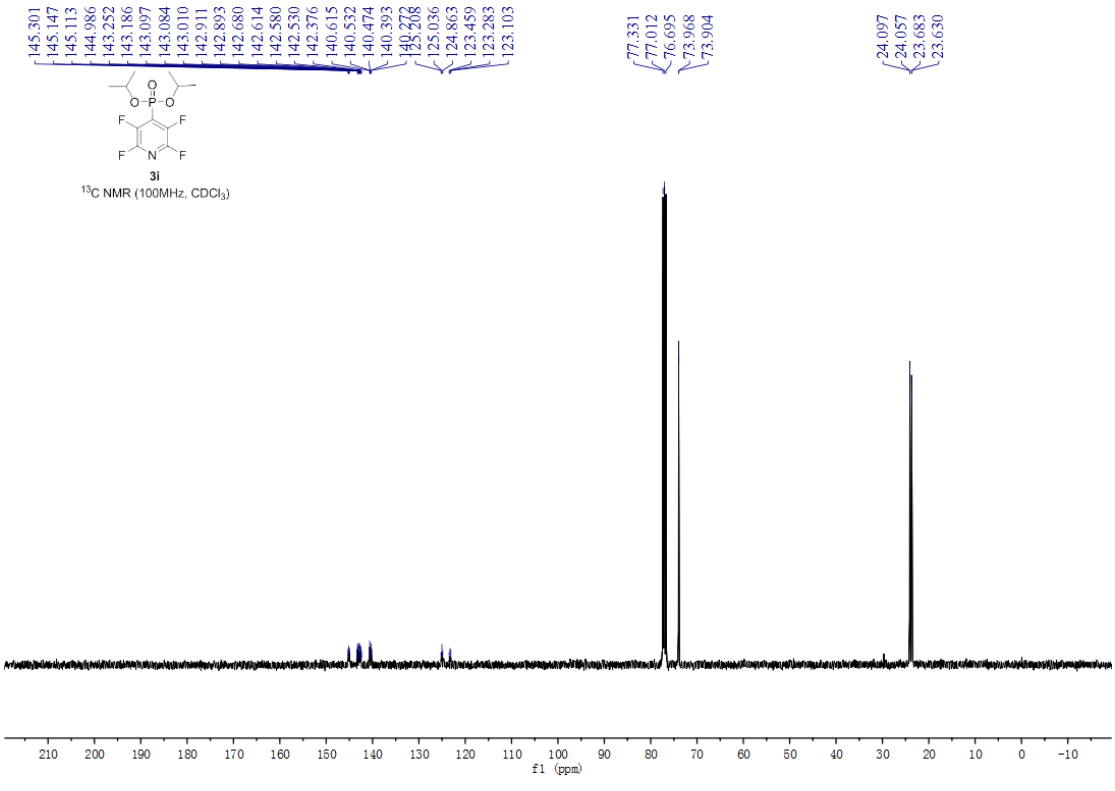


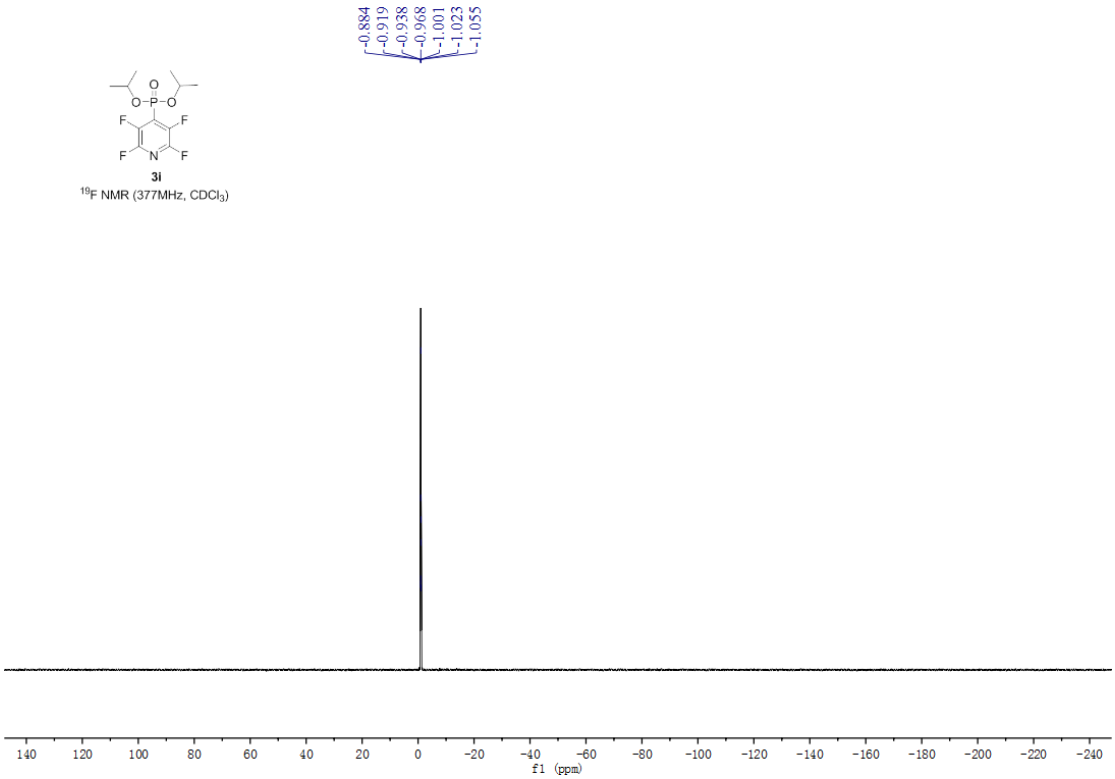
3h

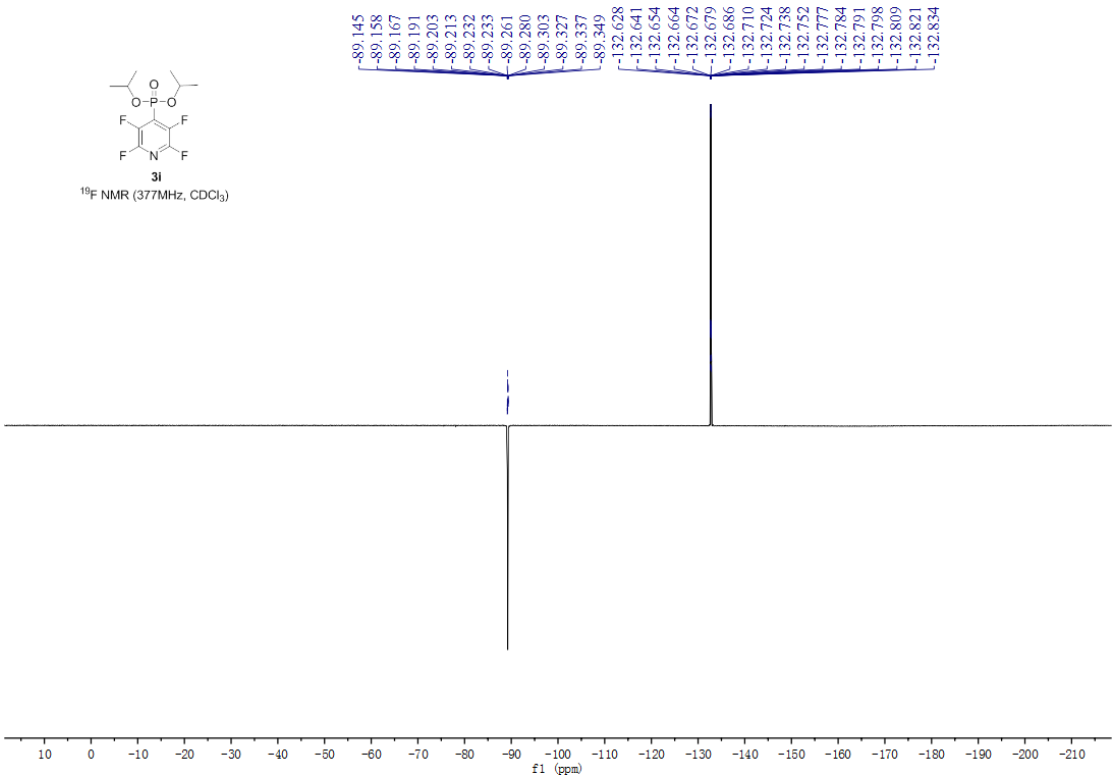
^{19}F NMR (377MHz, $CDCl_3$)

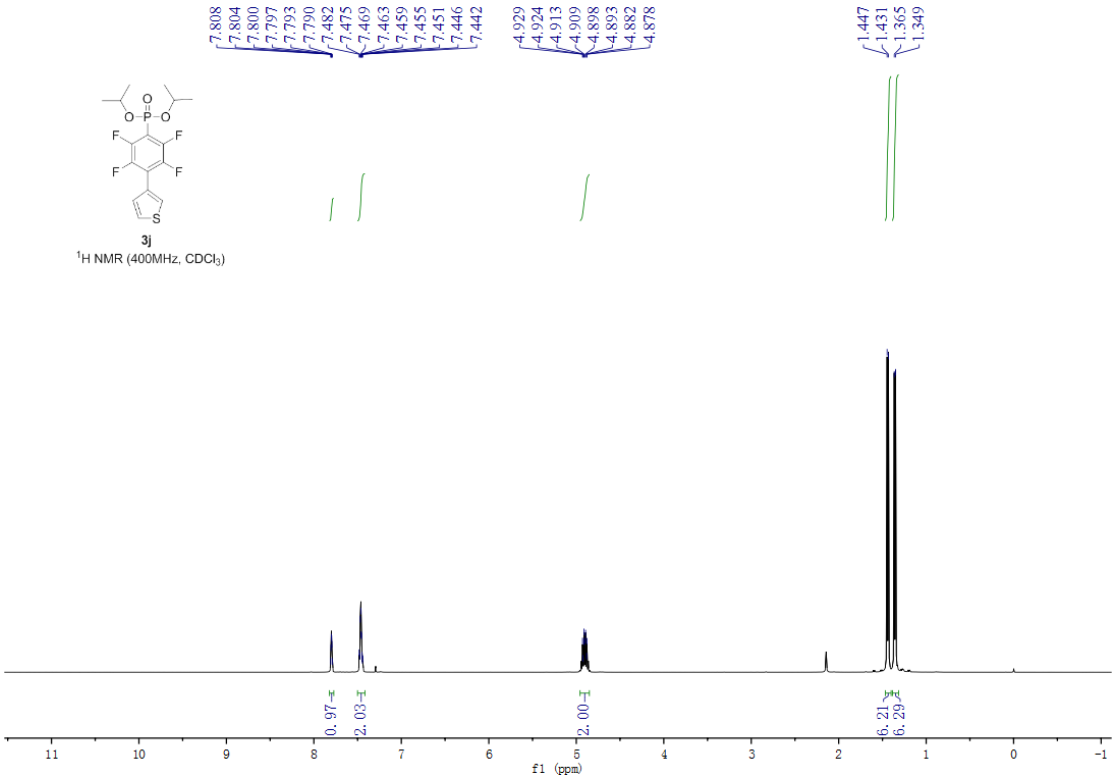



7.283
4.982
4.966
4.962
4.951
4.947
4.935
4.932
4.920
4.916
4.901
1.453
1.438
1.377
1.362
3i
1H NMR (400MHz, CDCl3)
2.00
6.19
6.13
f1 (ppm)


145.301
145.147
145.113
144.986
143.252
143.186
143.097
143.084
143.010
142.911
142.893
142.680
142.614
142.580
142.530
142.376
140.615
140.532
140.474
140.393
140.272
125.208
125.036
124.863
123.459
123.283
123.103
77.331
77.012
76.695
73.968
73.904
24.097
24.057
23.683
23.630
3i
13C NMR (100MHz, CDCl3)
f1 (ppm)

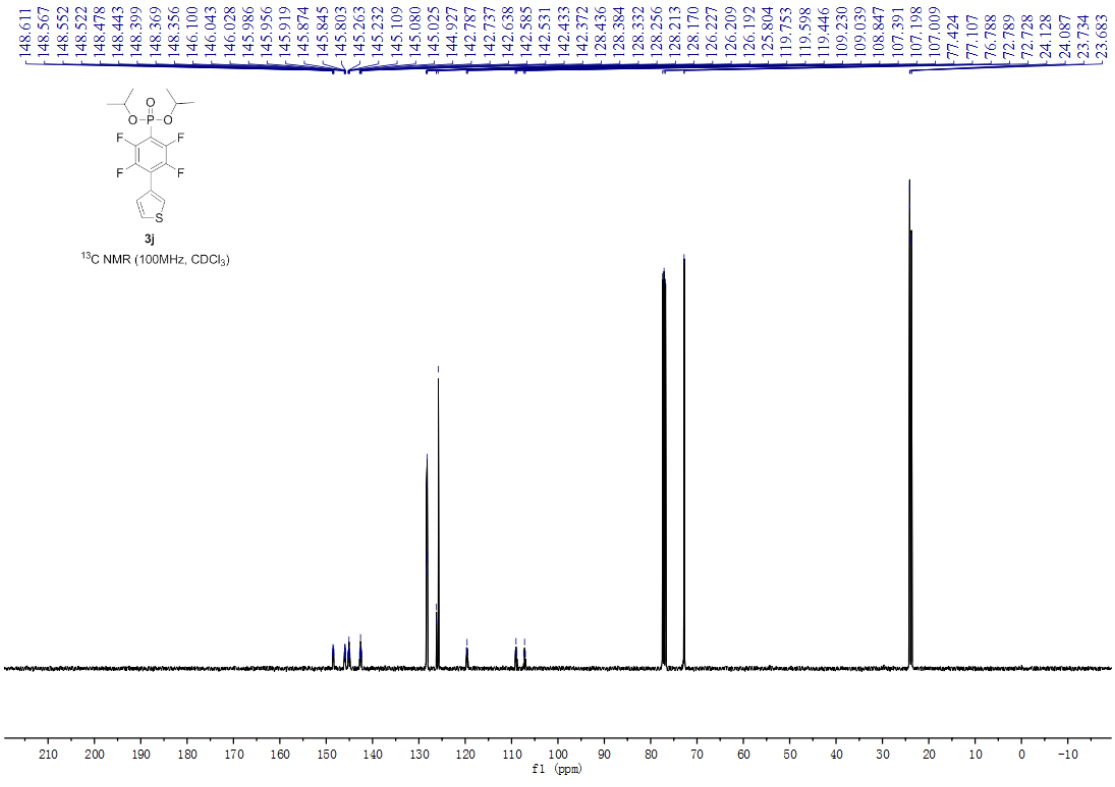

-0.884
-0.919
-0.938
-0.968
-1.001
-1.023
-1.055
3i
19F NMR (377MHz, CDCl3)
f1 (ppm)


-89.145
-89.158
-89.167
-89.191
-89.203
-89.213
-89.232
-89.233
-89.261
-89.280
-89.303
-89.327
-89.337
-89.349
-132.628
-132.641
-132.654
-132.664
-132.672
-132.679
-132.686
-132.710
-132.724
-132.738
-132.752
-132.777
-132.784
-132.791
-132.798
-132.809
-132.821
-132.834
3i
19F NMR (377MHz, CDCl3)
f1 (ppm)



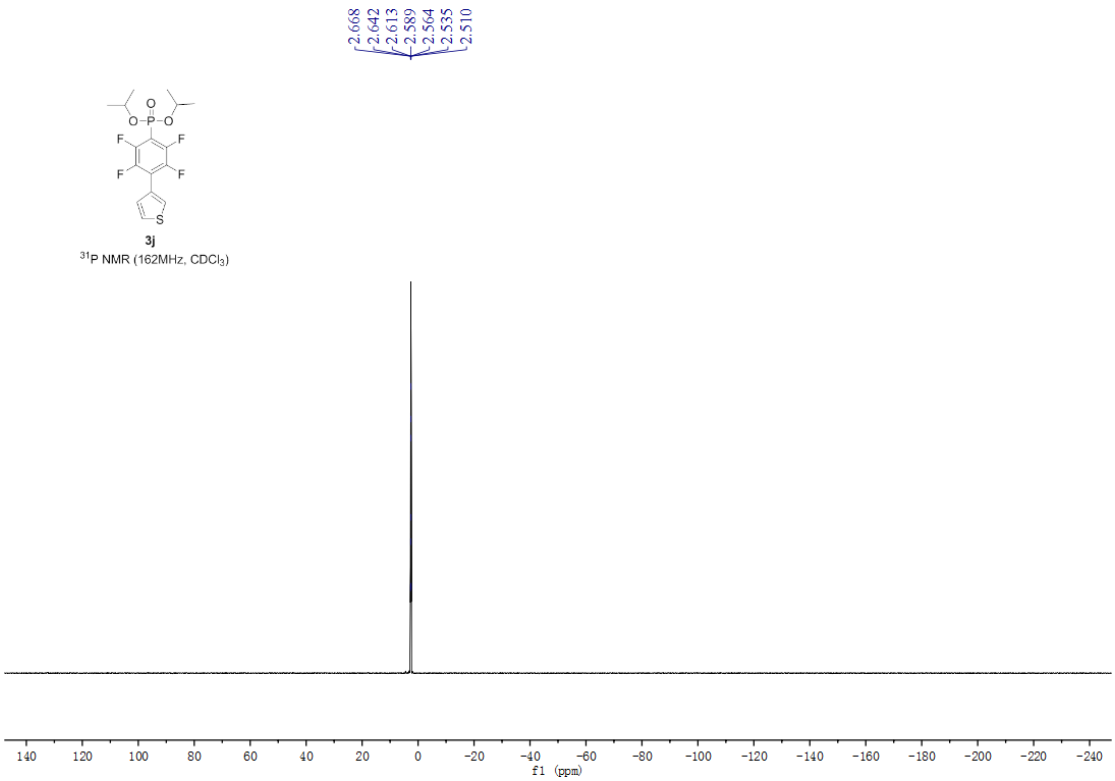
3j

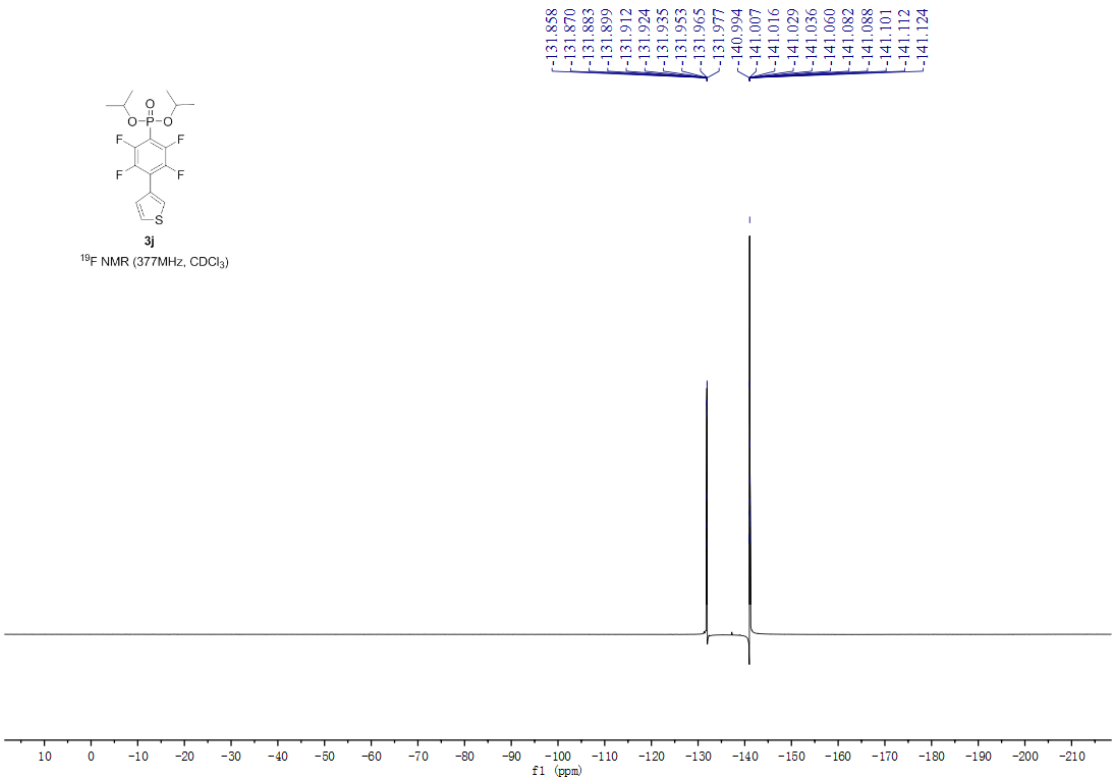
^{1}H NMR (400MHz, $CDCl_3$)

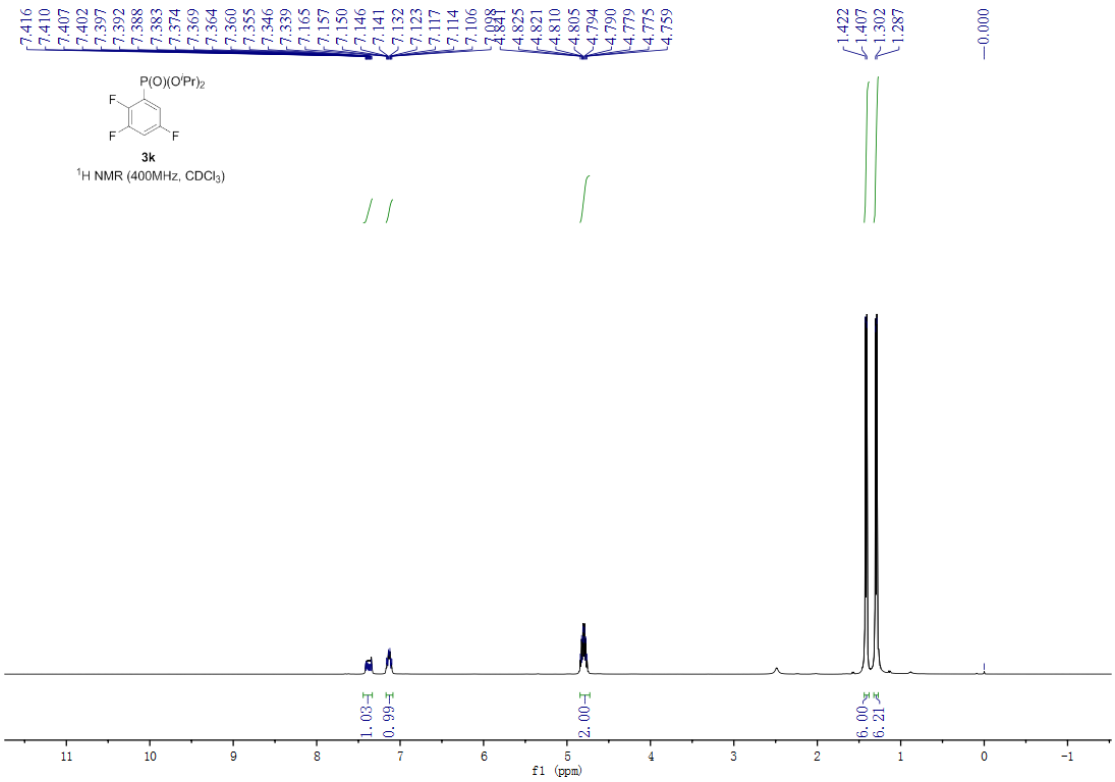


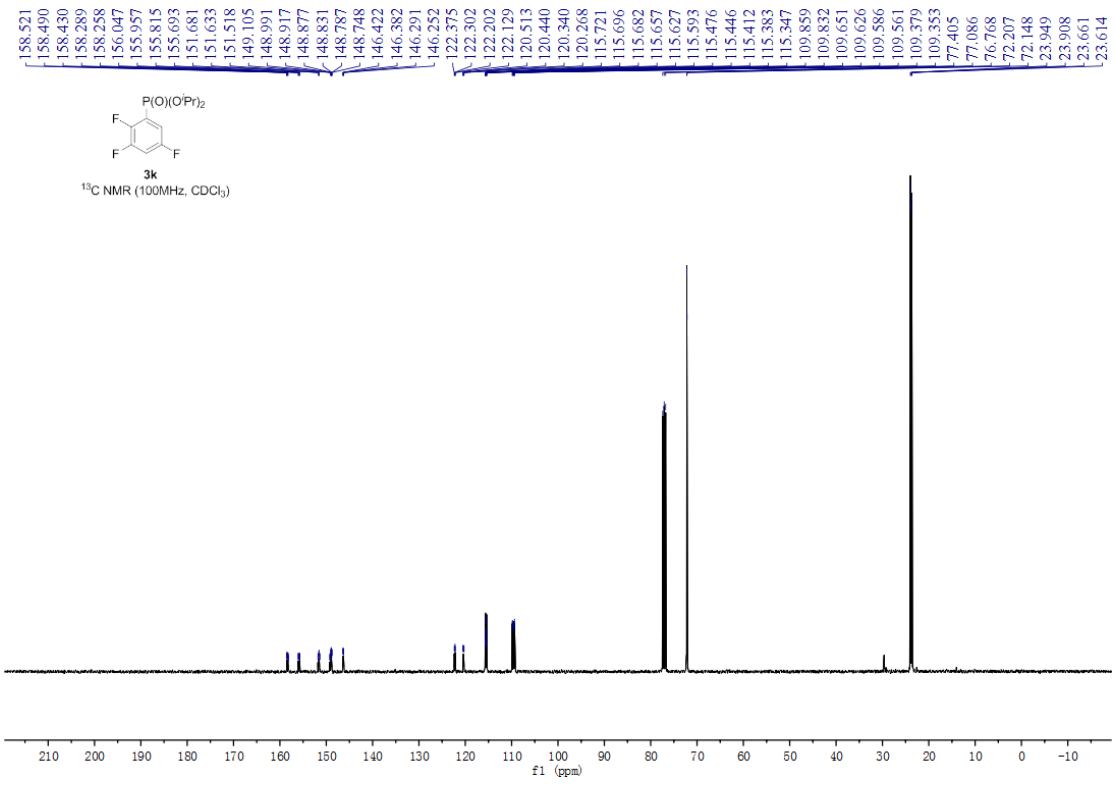
3j

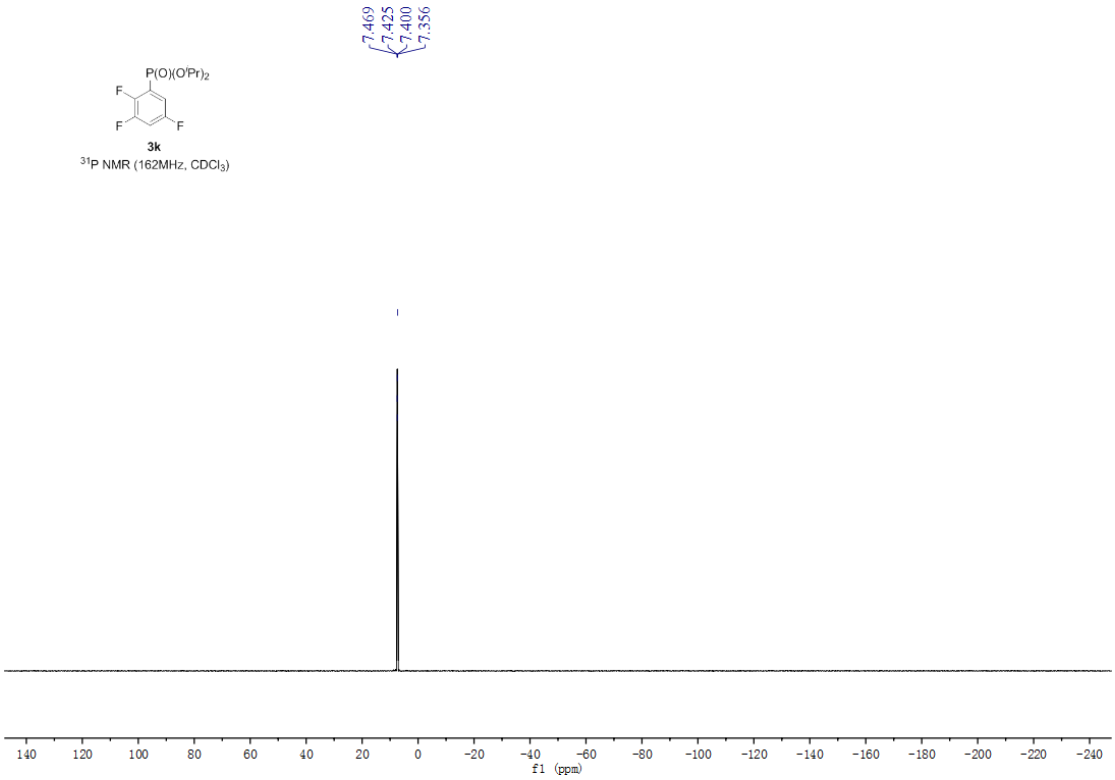
^{13}C NMR (100MHz, $CDCl_3$)

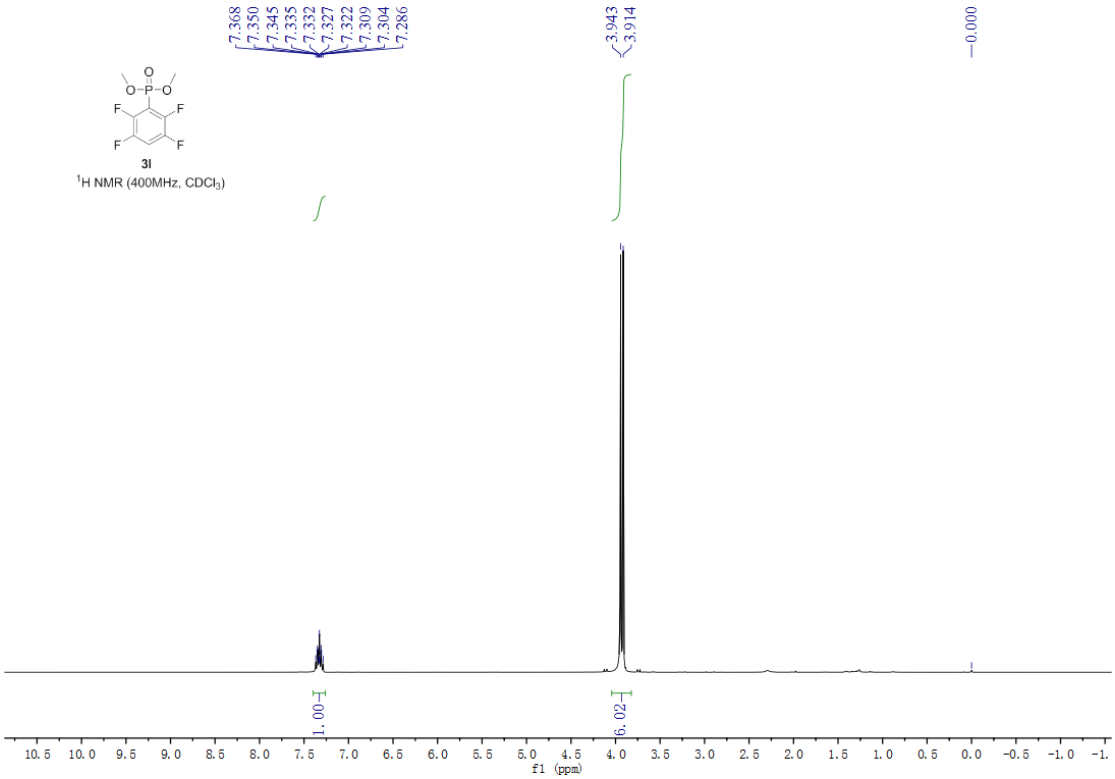

2.668
2.642
2.613
2.589
2.564
2.535
2.510
3j
31P NMR (162MHz, CDCl3)
f1 (ppm)

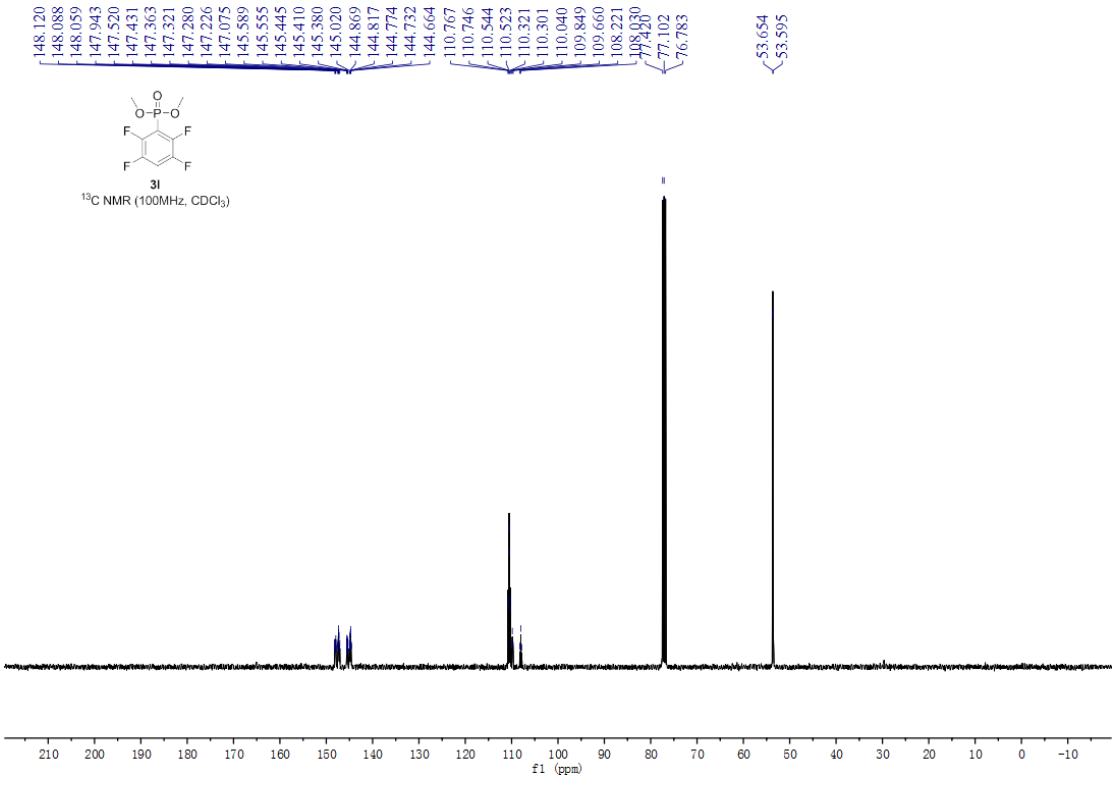

-131.858
-131.870
-131.883
-131.899
-131.912
-131.924
-131.935
-131.953
-131.965
-131.977
-140.994
-141.007
-141.016
-141.029
-141.036
-141.060
-141.082
-141.088
-141.101
-141.112
-141.124
3j
19F NMR (377MHz, CDCl3)
f1 (ppm)

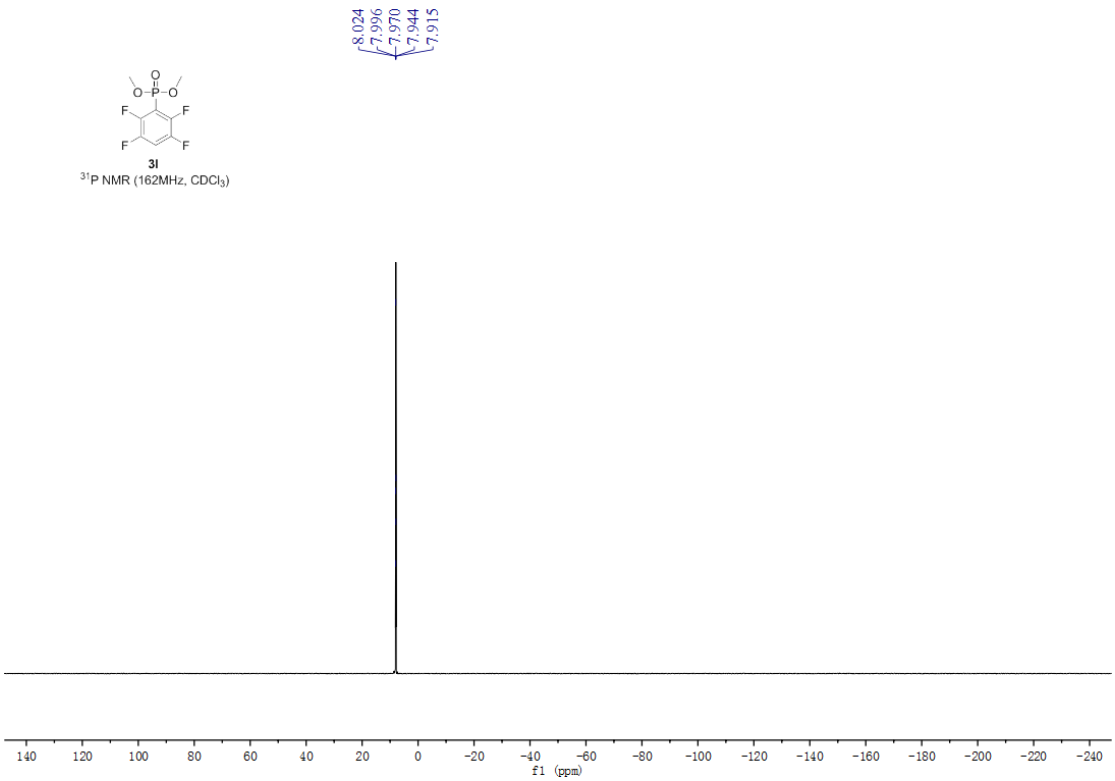

7.416
7.410
7.407
7.402
7.397
7.392
7.388
7.383
7.374
7.369
7.364
7.360
7.355
7.346
7.339
7.165
7.157
7.150
7.146
7.141
7.132
7.123
7.117
7.114
7.106
7.098
4.841
4.825
4.821
4.810
4.805
4.794
4.790
4.779
4.775
4.759
1.422
1.407
1.302
1.287
0.000
P(O)(OiPr)2
F
F
F
3k
1H NMR (400MHz, CDCl3)
1.03
0.99
2.00
6.00
6.21
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

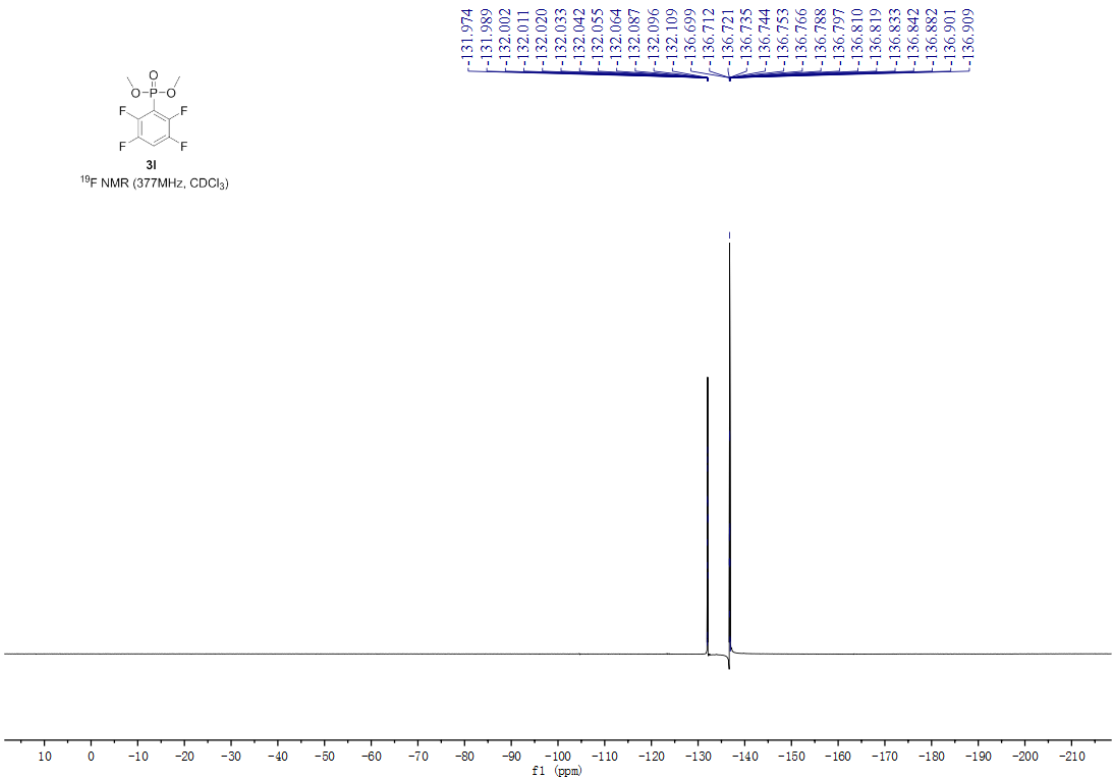

158.521
158.490
158.430
158.289
158.258
156.047
155.957
155.815
155.693
151.681
151.633
151.518
149.105
148.991
148.917
148.877
148.831
148.787
148.748
146.422
146.382
146.291
146.252
122.375
122.302
122.202
122.129
120.513
120.440
120.340
120.268
115.721
115.696
115.682
115.657
115.627
115.593
115.476
115.446
115.412
115.383
115.347
109.859
109.832
109.651
109.626
109.586
109.561
109.379
109.353
77.405
77.086
76.768
72.207
72.148
23.949
23.908
23.661
23.614
P(O)(OiPr)2
F
F
F
3k
13C NMR (100MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

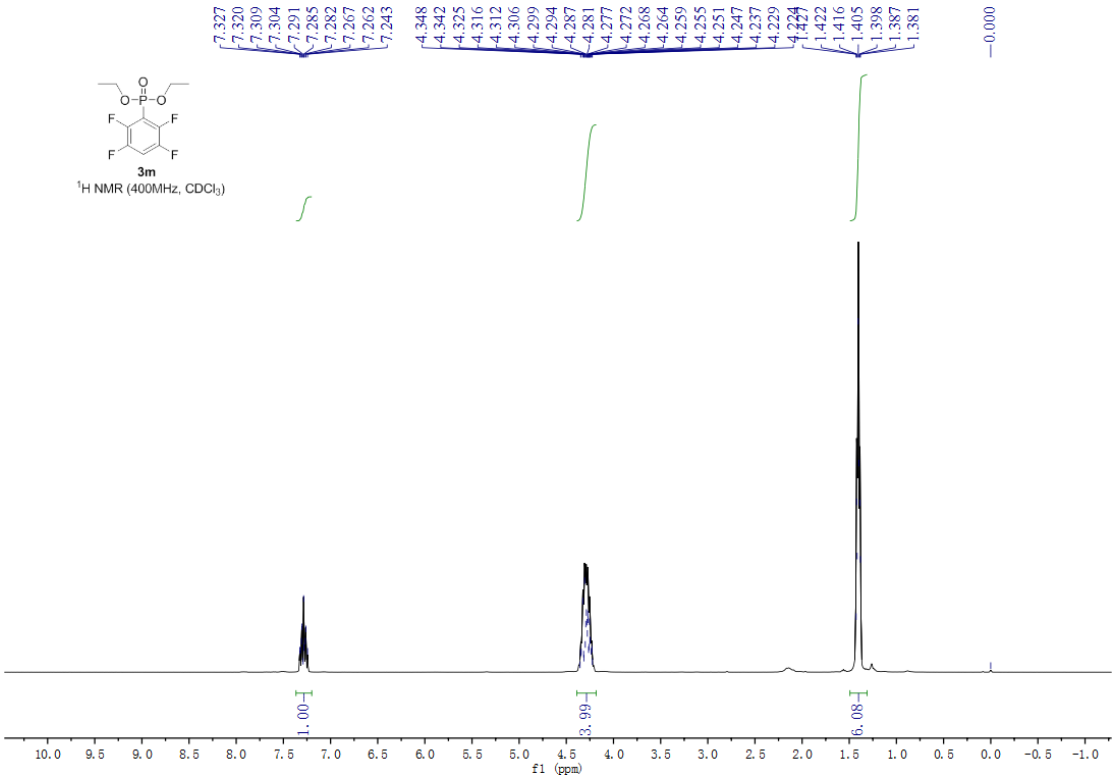

7.469
7.425
7.400
7.356
P(O)(OiPr)2
F
F
F
3k
31P NMR (162MHz, CDCl3)
f1 (ppm)
-113.651
-113.661
-113.679
-113.691
-113.699
-113.710
-113.724
-113.735
-113.743
-113.754
-113.773
-113.784
-113.785
-131.436
-131.447
-131.466
-131.477
-131.494
-131.505
-131.523
-131.534
-134.620
-134.662
-134.665
-134.678
-134.690
-134.723
P(O)(OiPr)2
F
F
F
3k
19F NMR (377MHz, CDCl3)
f1 (ppm)

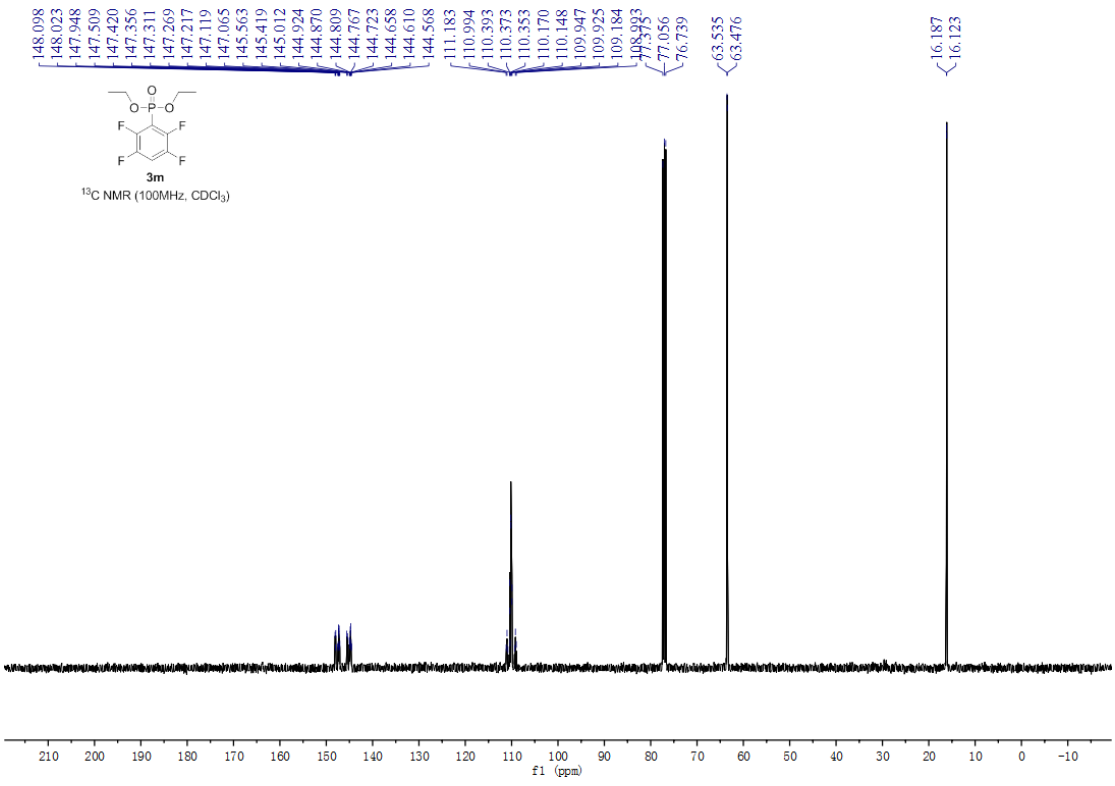

7.368
7.350
7.345
7.335
7.332
7.327
7.322
7.309
7.304
7.286
3.943
3.914
0.000
3l
1H NMR (400MHz, CDCl3)
1.00
6.02
f1 (ppm)

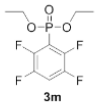

148.120
148.088
148.059
147.943
147.520
147.431
147.363
147.321
147.280
147.226
147.075
145.589
145.555
145.445
145.410
145.380
145.020
144.869
144.817
144.774
144.732
144.664
110.767
110.746
110.544
110.523
110.321
110.301
110.040
109.849
109.660
108.221
77.420
77.102
76.783
53.654
53.595
3l
13C NMR (100MHz, CDCl3)
f1 (ppm)


8.024
7.996
7.970
7.944
7.915
3l
31P NMR (162MHz, CDCl3)
f1 (ppm)


-131.974
-131.989
-132.002
-132.011
-132.020
-132.033
-132.042
-132.055
-132.064
-132.087
-132.096
-132.109
-136.699
-136.712
-136.721
-136.735
-136.744
-136.753
-136.766
-136.788
-136.797
-136.810
-136.819
-136.833
-136.842
-136.882
-136.901
-136.909
3l
19F NMR (377MHz, CDCl3)
f1 (ppm)


7.327
7.320
7.309
7.304
7.291
7.285
7.282
7.267
7.262
7.243
4.348
4.342
4.325
4.316
4.312
4.306
4.299
4.294
4.287
4.281
4.277
4.272
4.268
4.264
4.259
4.255
4.251
4.247
4.237
4.229
4.224
1.422
1.416
1.405
1.398
1.387
1.381
0.000
3m
1H NMR (400MHz, CDCl3)
1.00
3.99
6.08
f1 (ppm)


148.098
148.023
147.948
147.509
147.420
147.356
147.311
147.269
147.217
147.119
147.065
145.563
145.419
145.012
144.924
144.870
144.809
144.767
144.723
144.658
144.610
144.568
111.183
110.994
110.393
110.373
110.353
110.170
110.148
109.947
109.925
109.184
77.375
77.056
76.739
63.535
63.476
16.187
16.123
3m
13C NMR (100MHz, CDCl3)
f1 (ppm)

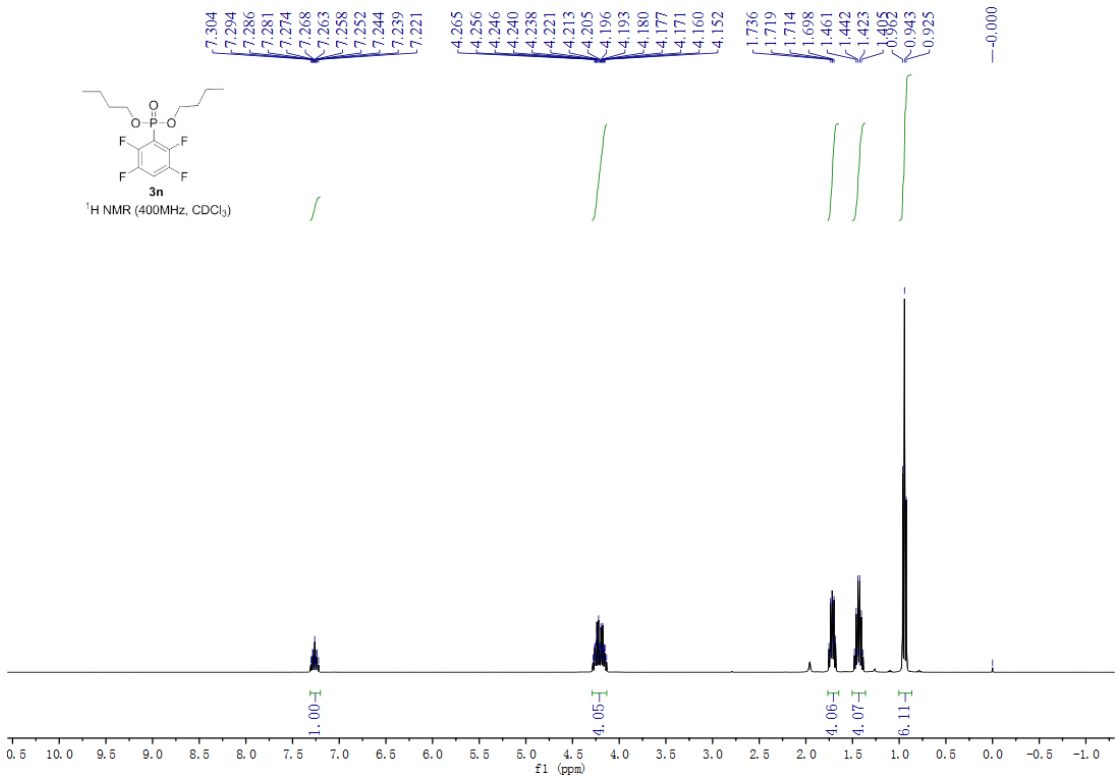


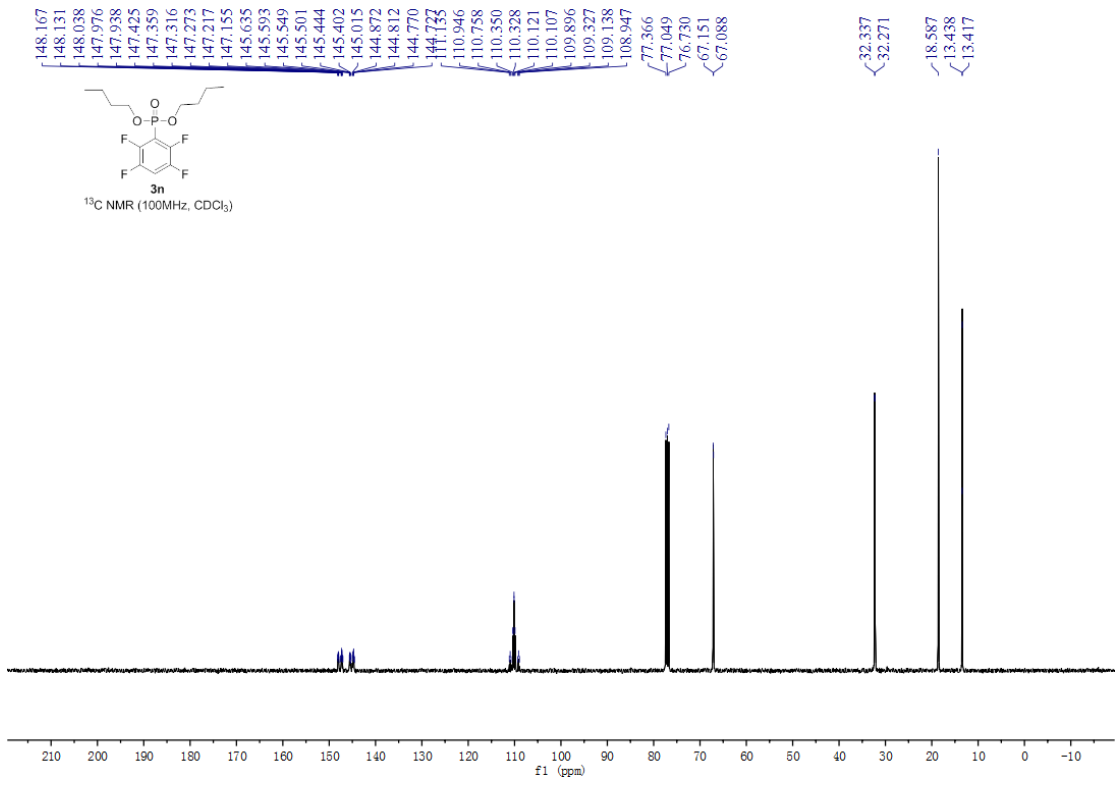
3m

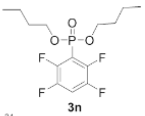
^{31}P NMR (162MHz, $CDCl_3$)

3m

^{19}F NMR (377MHz, $CDCl_3$)

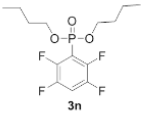

7.304
7.294
7.286
7.281
7.274
7.268
7.263
7.258
7.252
7.244
7.239
7.221
4.265
4.256
4.246
4.240
4.238
4.221
4.213
4.205
4.196
4.193
4.180
4.177
4.171
4.160
4.152
1.736
1.719
1.714
1.698
1.461
1.442
1.423
1.405
0.962
0.943
0.925
-0.000
3n
^{1}H NMR (400MHz, CDCl$_3$)
1.00
4.05
4.06
4.07
6.11
f1 (ppm)


148.167
148.131
148.038
147.976
147.938
147.425
147.359
147.316
147.273
147.217
147.155
145.635
145.593
145.549
145.501
145.444
145.402
145.015
144.872
144.812
144.770
144.727
111.135
110.946
110.758
110.350
110.328
110.121
110.107
109.896
109.327
109.138
108.947
77.366
77.049
76.730
67.151
67.088
32.337
32.271
18.587
13.438
13.417
3n
^{13}C NMR (100MHz, CDCl$_3$)
f1 (ppm)



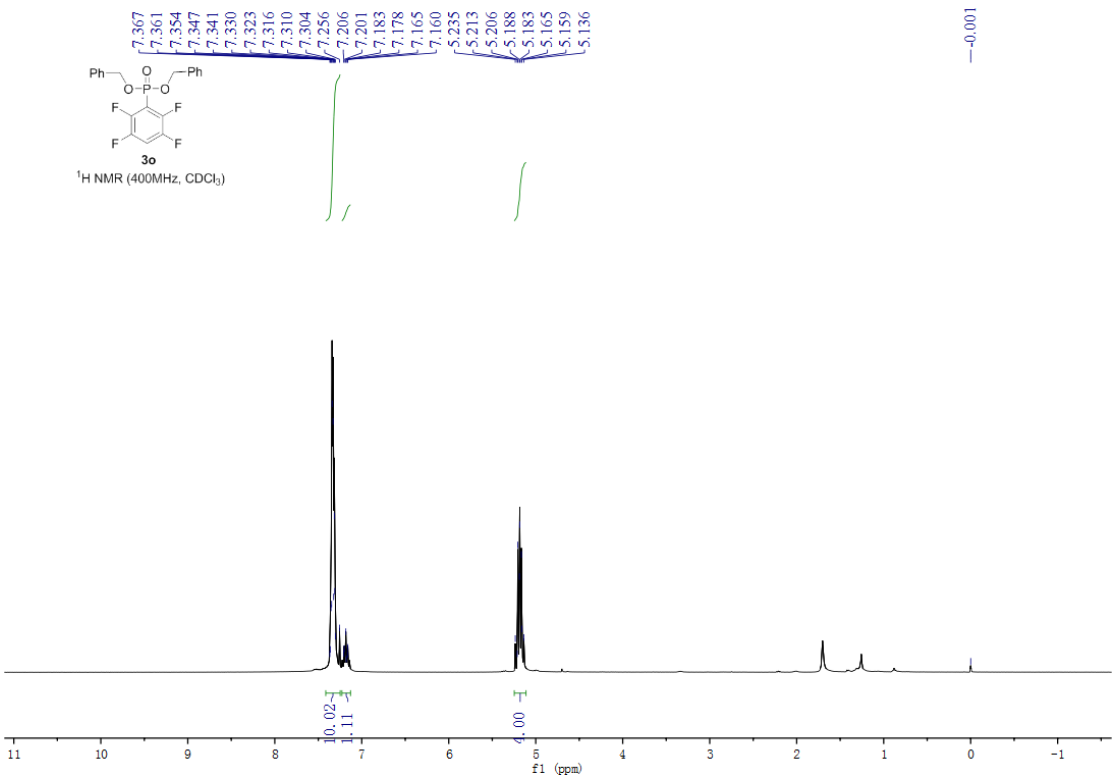
3n

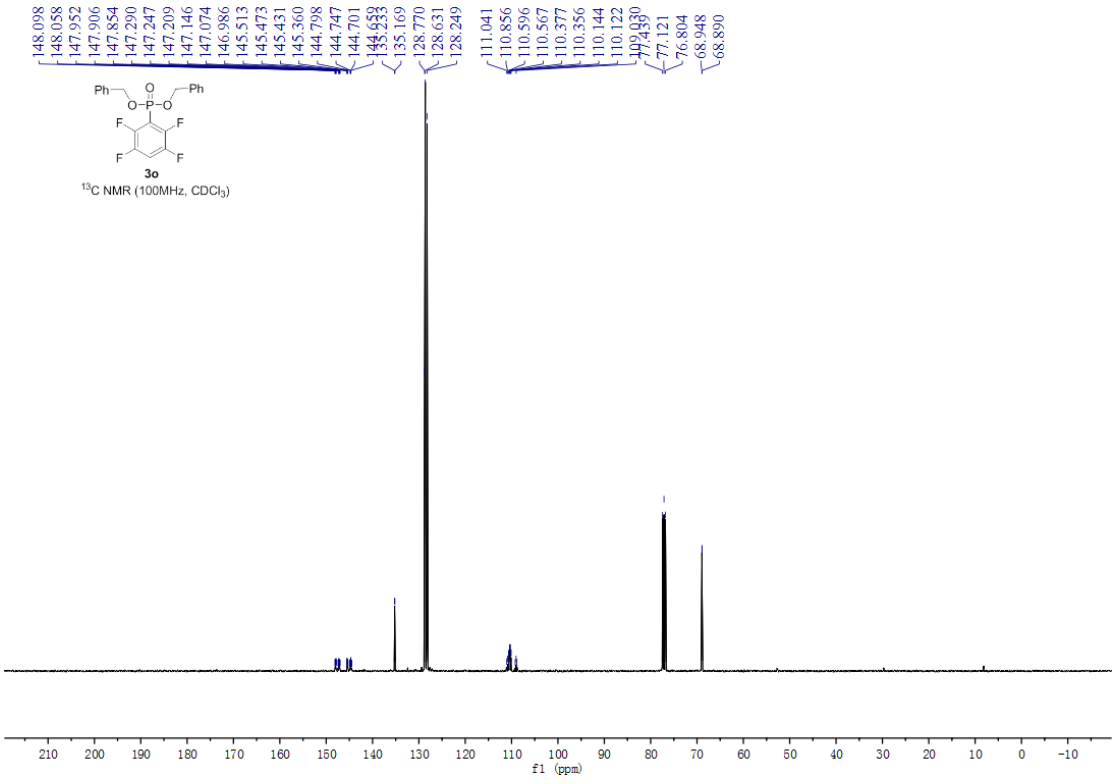
^{31}P NMR (162MHz, $CDCl_3$)

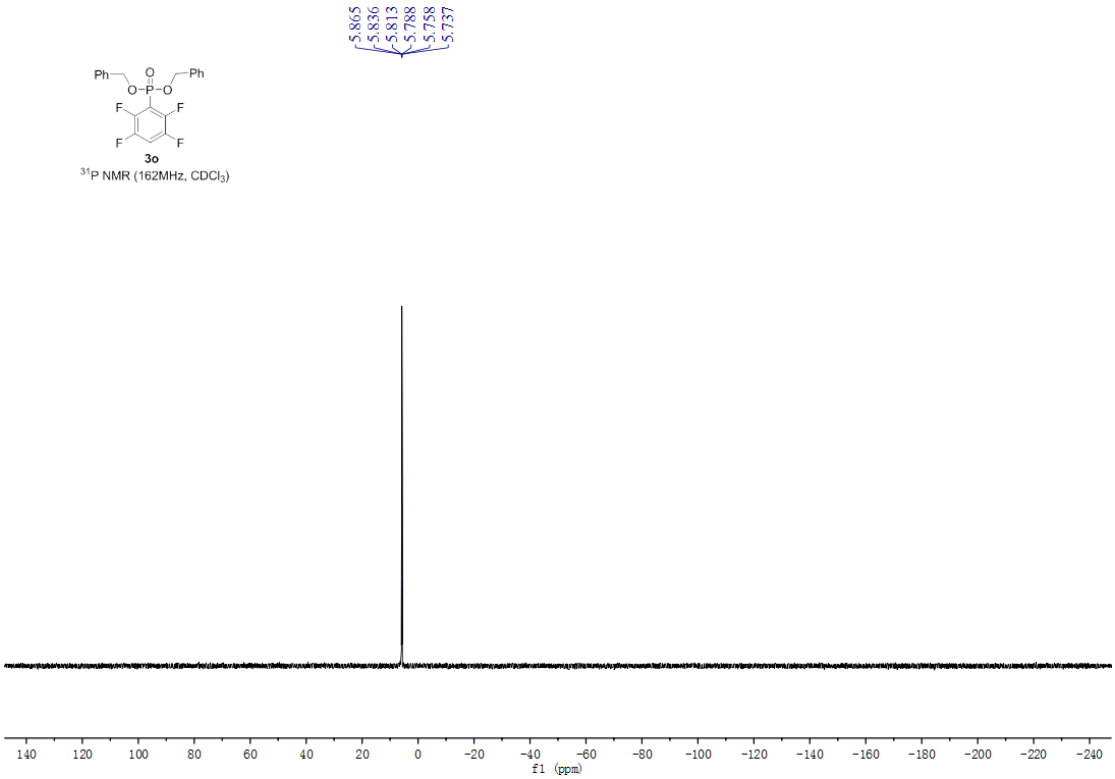


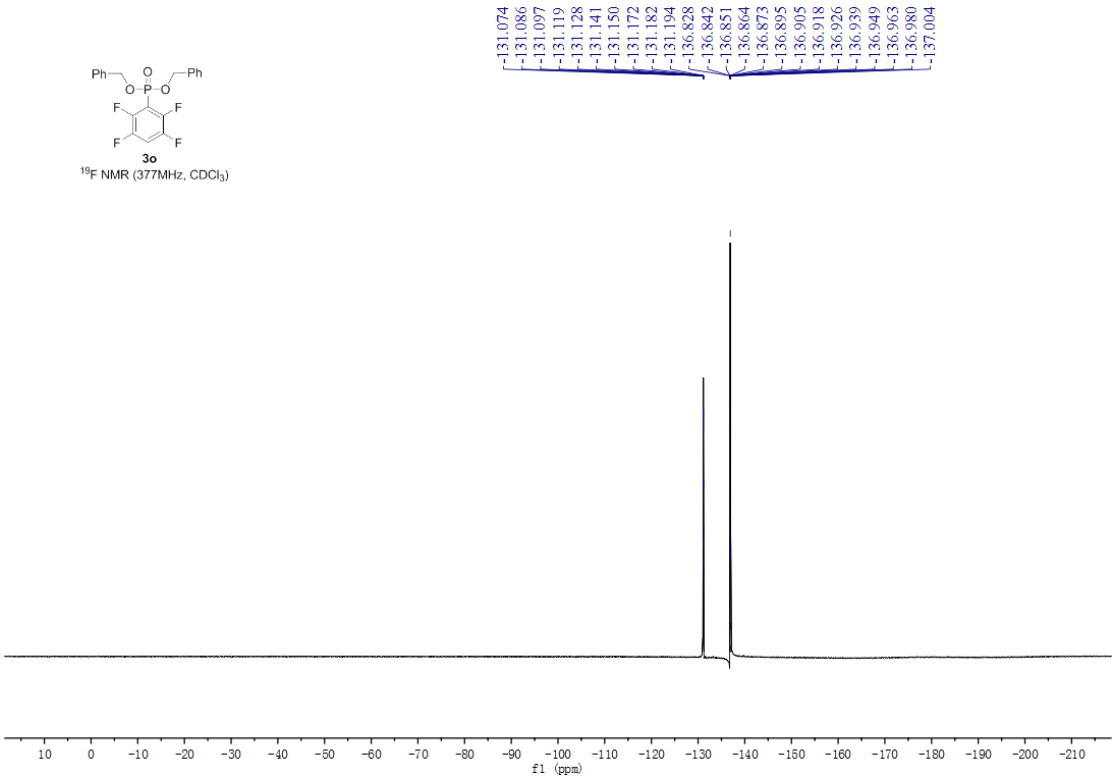
3n

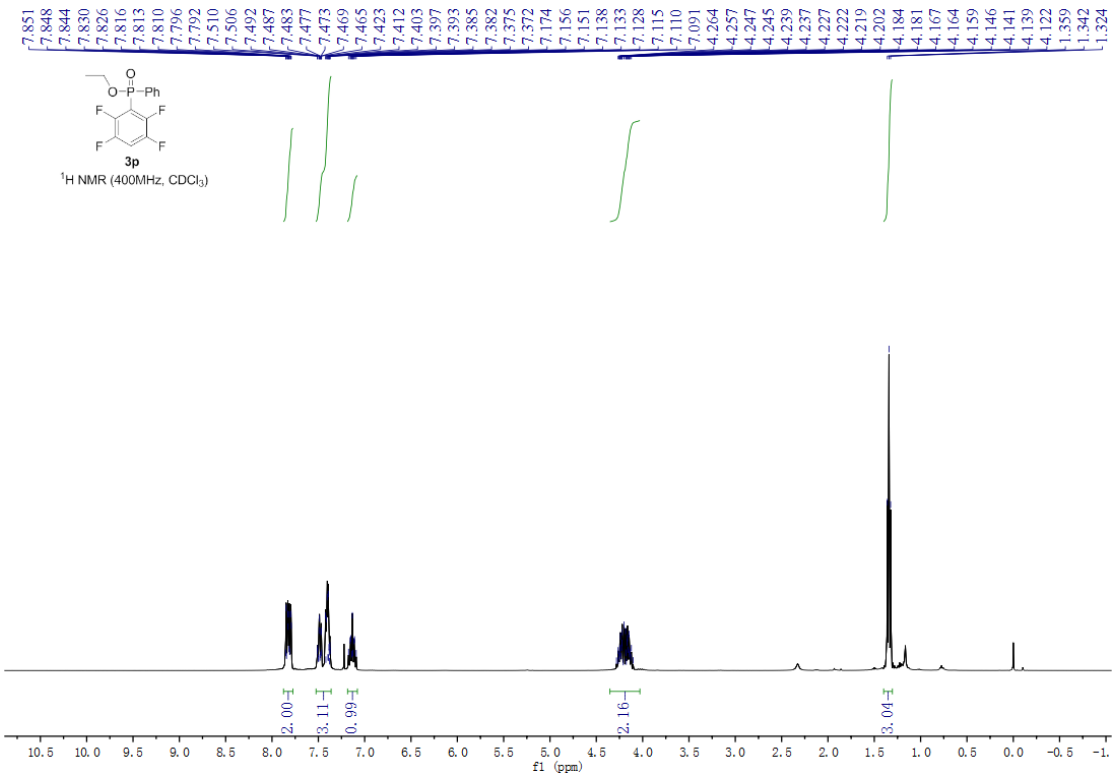
^{19}F NMR (377MHz, $CDCl_3$)

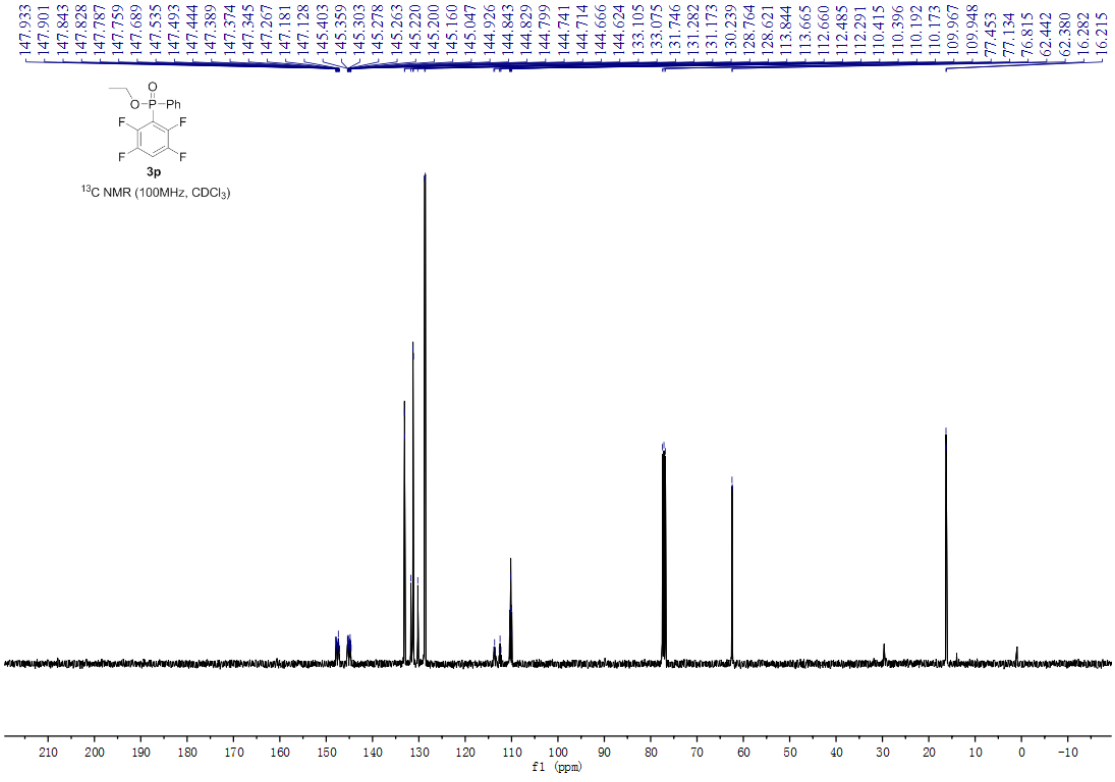

7.367
7.361
7.354
7.347
7.341
7.330
7.323
7.316
7.310
7.304
7.256
7.206
7.201
7.183
7.178
7.165
7.160
5.235
5.213
5.206
5.188
5.183
5.165
5.159
5.136
-0.001
Ph
O
Ph
O-P-O
F
F
F
F
3o
1H NMR (400MHz, CDCl3)
10.02
1.11
4.00
f1 (ppm)

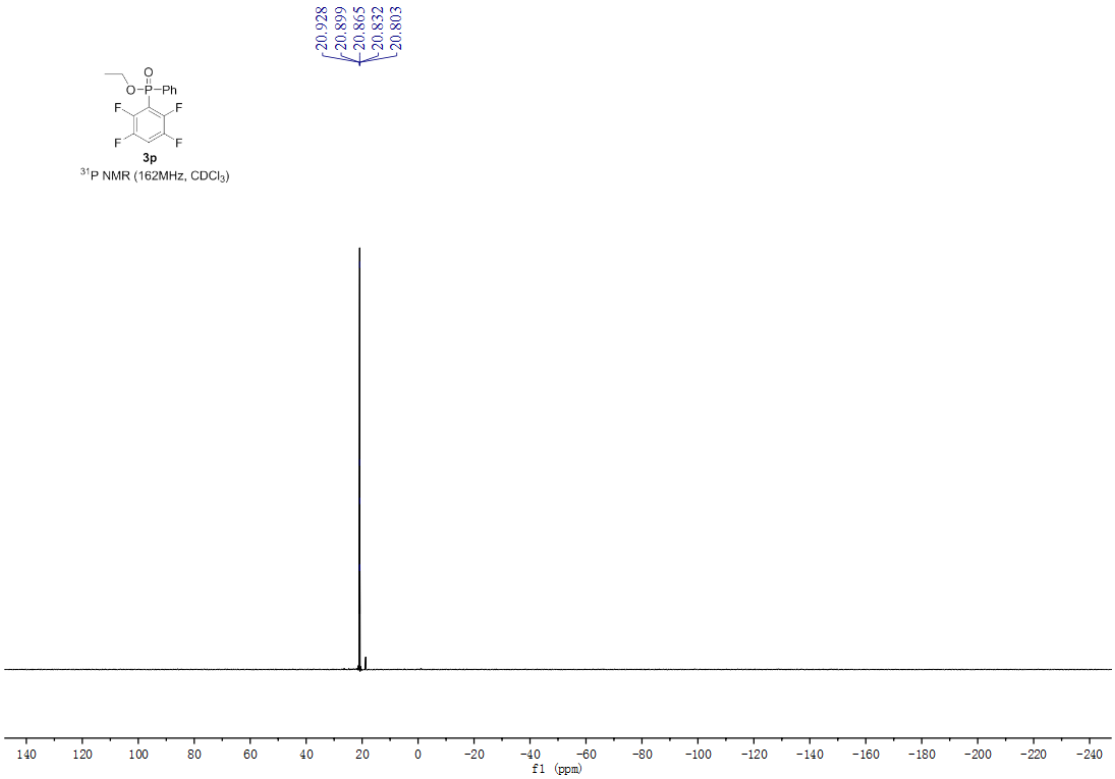

148.098
148.058
147.952
147.906
147.854
147.290
147.247
147.209
147.146
147.074
146.986
145.513
145.473
145.431
145.360
144.798
144.747
144.701
135.233
135.169
128.770
128.631
128.249
111.041
110.856
110.596
110.567
110.377
110.356
110.144
110.122
77.439
77.121
76.804
68.948
68.890
Ph
O
Ph
O-P-O
F
F
F
F
3o
13C NMR (100MHz, CDCl3)
f1 (ppm)

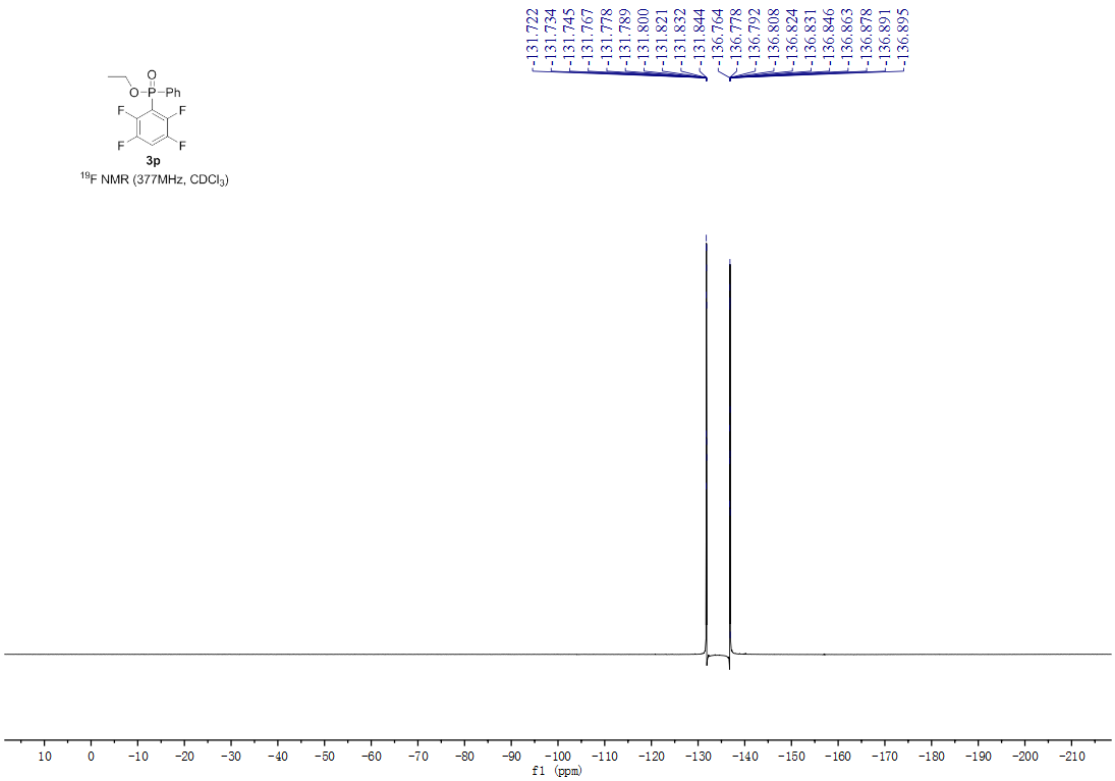

5.865
5.836
5.813
5.788
5.758
5.737
Ph
Ph
O
O
P
O
F
F
F
F
3o
31P NMR (162MHz, CDCl3)
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

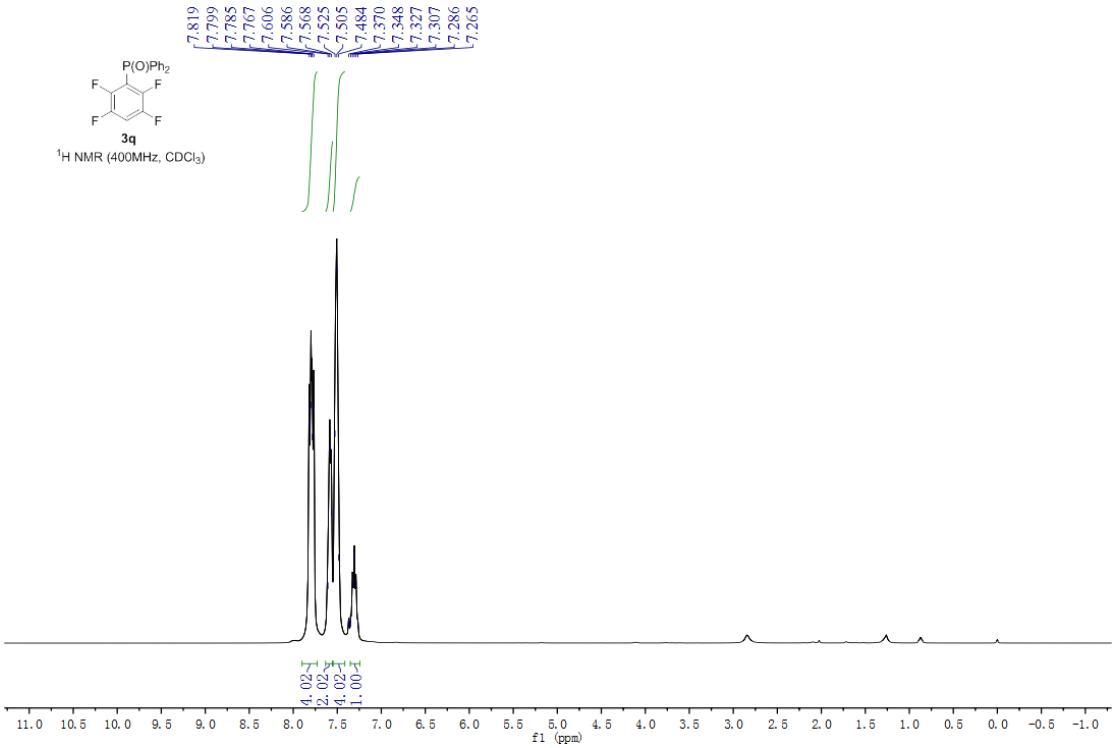

-131.074
-131.086
-131.097
-131.119
-131.128
-131.141
-131.150
-131.172
-131.182
-131.194
-136.828
-136.842
-136.851
-136.864
-136.873
-136.895
-136.905
-136.918
-136.926
-136.939
-136.949
-136.963
-136.980
-137.004
Ph
Ph
O
O
P
O
F
F
F
F
3o
19F NMR (377MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

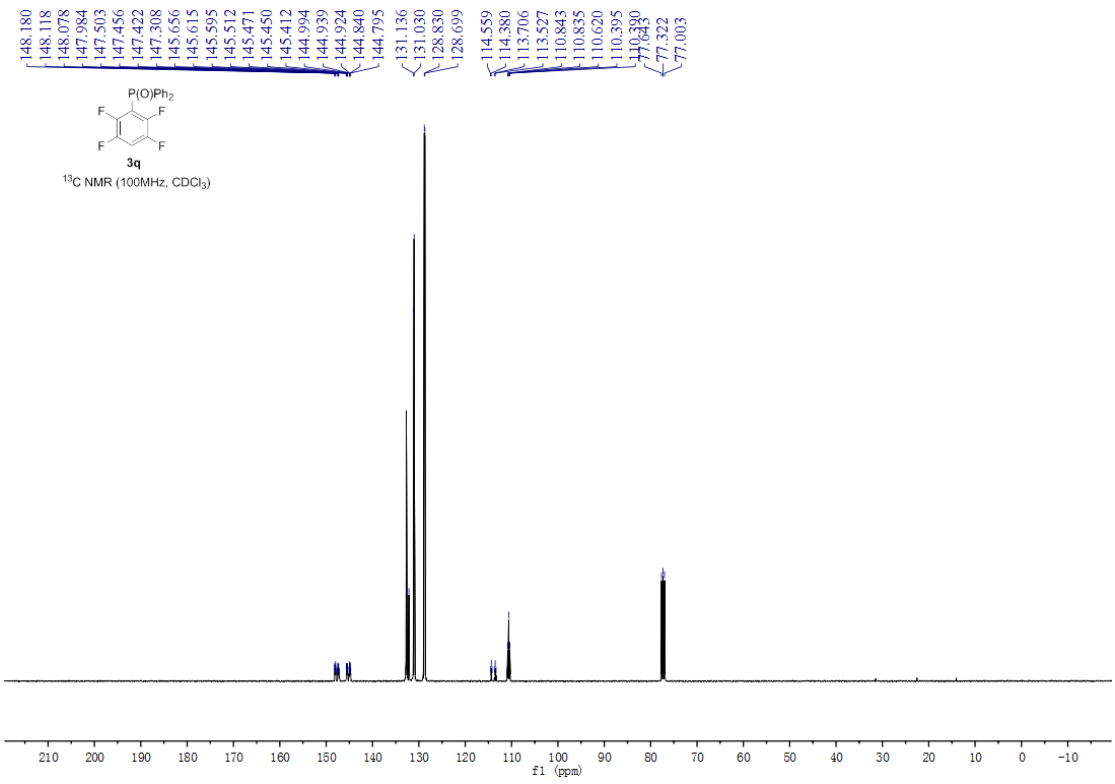

7.851
7.848
7.844
7.830
7.826
7.816
7.813
7.810
7.796
7.792
7.510
7.506
7.492
7.487
7.483
7.477
7.473
7.469
7.465
7.423
7.412
7.403
7.397
7.393
7.385
7.382
7.375
7.372
7.174
7.156
7.151
7.138
7.133
7.128
7.115
7.110
7.091
4.264
4.257
4.247
4.245
4.239
4.237
4.227
4.222
4.219
4.202
4.184
4.181
4.167
4.164
4.159
4.146
4.141
4.139
4.122
1.359
1.342
1.324
O
O-P-Ph
F
F
F
F
3p
1H NMR (400MHz, CDCl3)
2.00
3.11
0.99
2.16
3.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

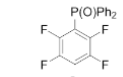

147.933
147.901
147.843
147.828
147.787
147.759
147.689
147.535
147.493
147.444
147.389
147.374
147.345
147.267
147.181
147.128
145.403
145.359
145.303
145.278
145.263
145.220
145.200
145.160
145.047
144.926
144.843
144.829
144.799
144.741
144.714
144.666
144.624
133.105
133.075
131.746
131.282
131.173
130.239
128.764
128.621
113.844
113.665
112.660
112.485
112.291
110.415
110.396
110.192
110.173
109.967
109.948
77.453
77.134
76.815
62.442
62.380
16.282
16.215
O
O-P-Ph
F
F
F
F
3p
13C NMR (100MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


20.928
20.899
20.865
20.832
20.803
3p
31P NMR (162MHz, CDCl3)
f1 (ppm)


-131.722
-131.734
-131.745
-131.767
-131.778
-131.789
-131.800
-131.821
-131.832
-131.844
-136.764
-136.778
-136.792
-136.808
-136.824
-136.831
-136.846
-136.863
-136.878
-136.891
-136.895
3p
19F NMR (377MHz, CDCl3)
f1 (ppm)

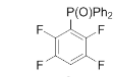

7.819
7.799
7.785
7.767
7.606
7.586
7.568
7.525
7.505
7.484
7.370
7.348
7.327
7.307
7.286
7.265
P(O)Ph2
F
F
F
F
3q
1H NMR (400MHz, CDCl3)
4.02
2.02
4.02
1.00
f1 (ppm)


148.180
148.118
148.078
147.984
147.503
147.456
147.422
147.308
145.656
145.615
145.595
145.512
145.471
145.450
145.412
144.994
144.939
144.924
144.840
144.795
131.136
131.030
128.830
128.699
114.559
114.380
113.706
113.527
110.843
110.835
110.620
110.395
77.322
77.003
P(O)Ph2
F
F
F
F
3q
13C NMR (100MHz, CDCl3)
f1 (ppm)



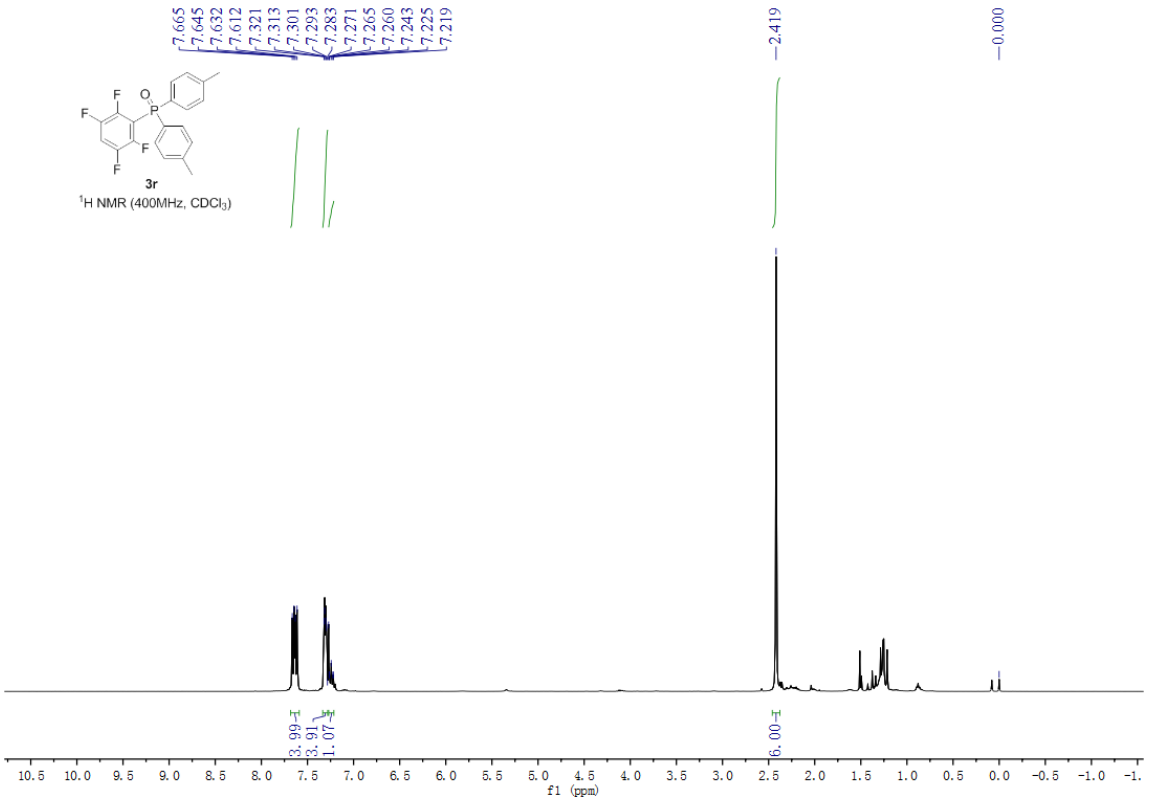
3q

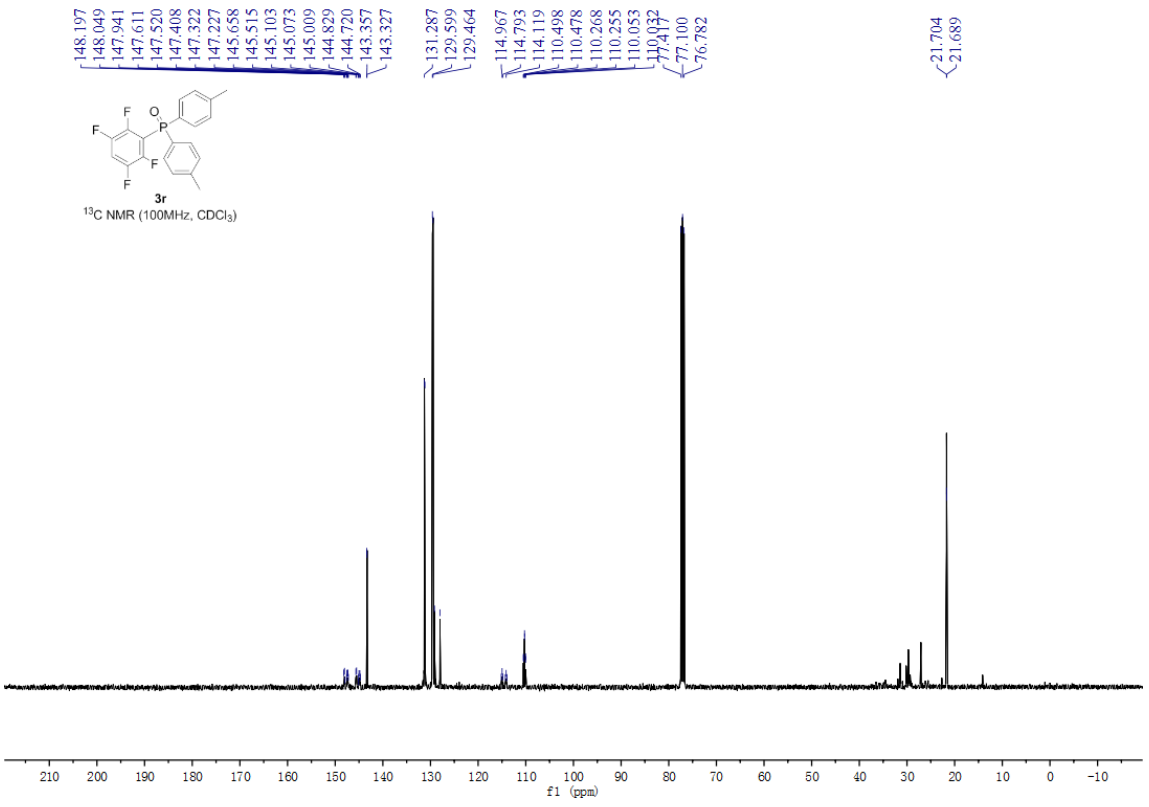
^{31}P NMR (162MHz, $CDCl_3$)

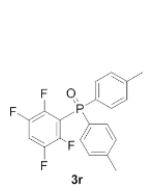


3q

^{19}F NMR (377MHz, $CDCl_3$)


7.665
7.645
7.632
7.612
7.321
7.313
7.301
7.293
7.283
7.271
7.265
7.260
7.243
7.225
7.219
2.419
0.000
3r
1H NMR (400MHz, CDCl3)
3.99
3.91
1.07
6.00
f1 (ppm)

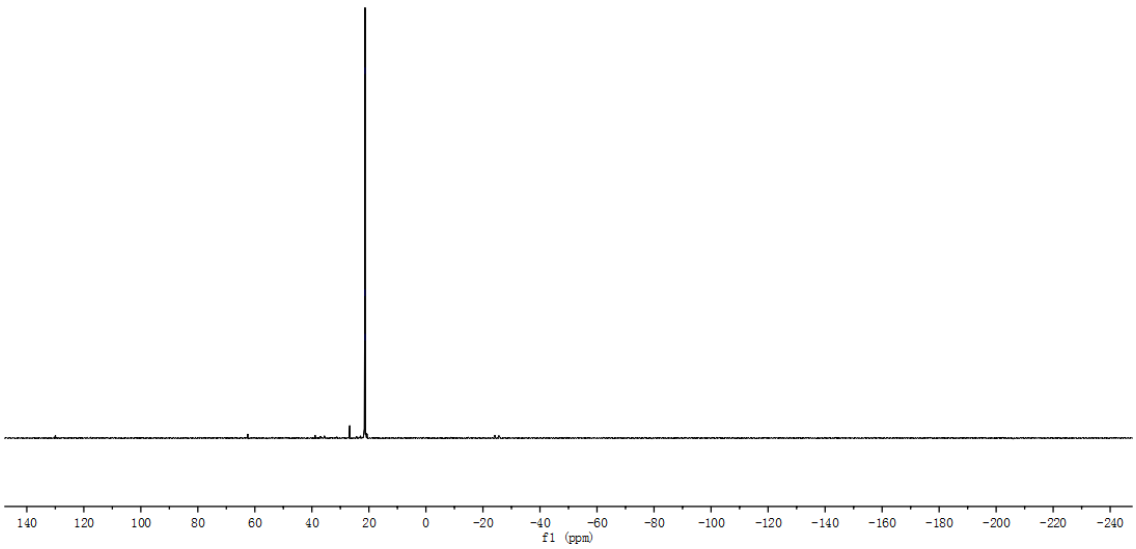

148.197
148.049
147.941
147.611
147.520
147.408
147.322
147.227
145.658
145.515
145.103
145.073
145.009
144.829
144.720
143.357
143.327
131.287
129.599
129.464
114.967
114.793
114.119
110.498
110.478
110.268
110.255
110.053
110.032
77.417
77.100
76.782
21.704
21.689
3r
13C NMR (100MHz, CDCl3)
f1 (ppm)



3r

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

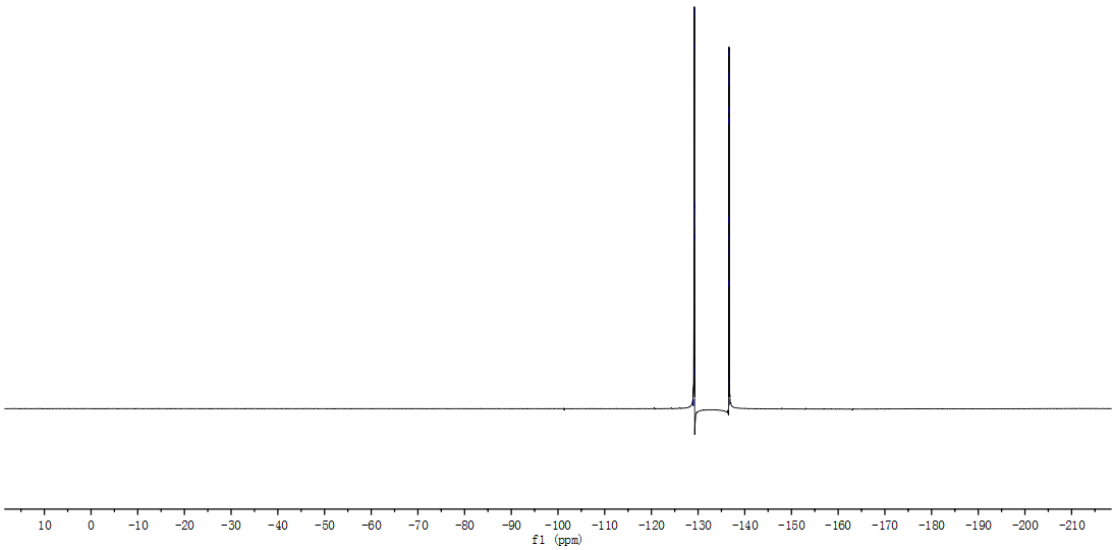
21.381
21.351
21.326

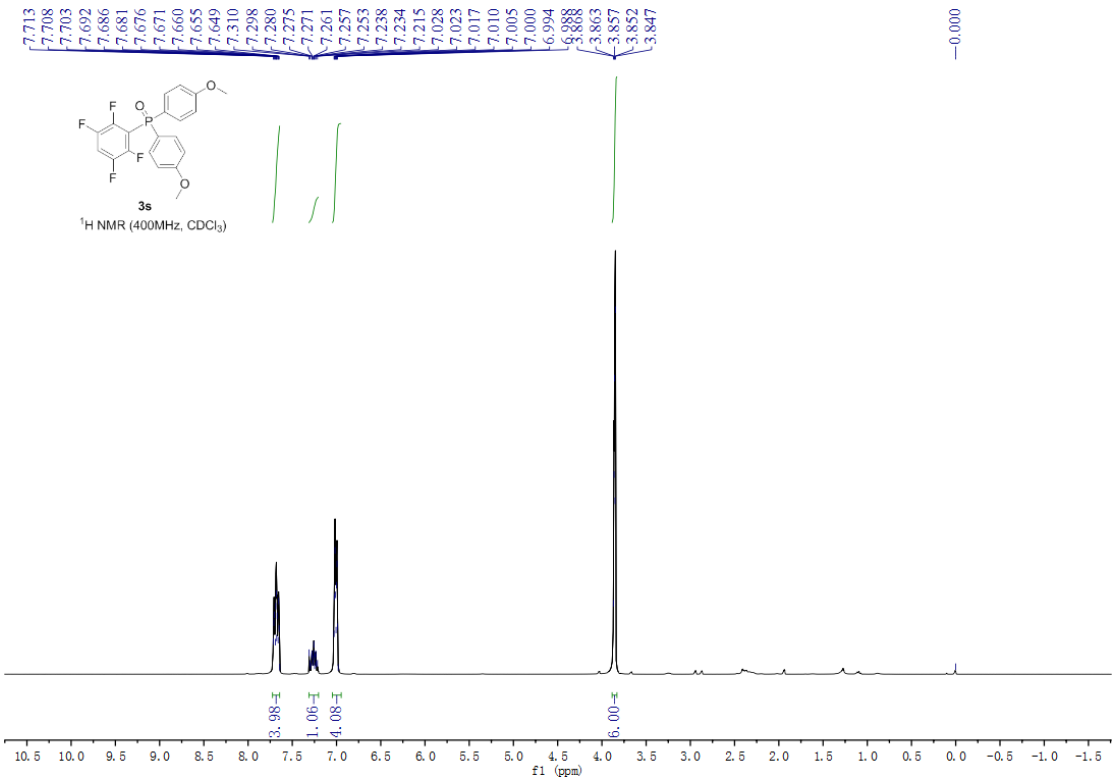


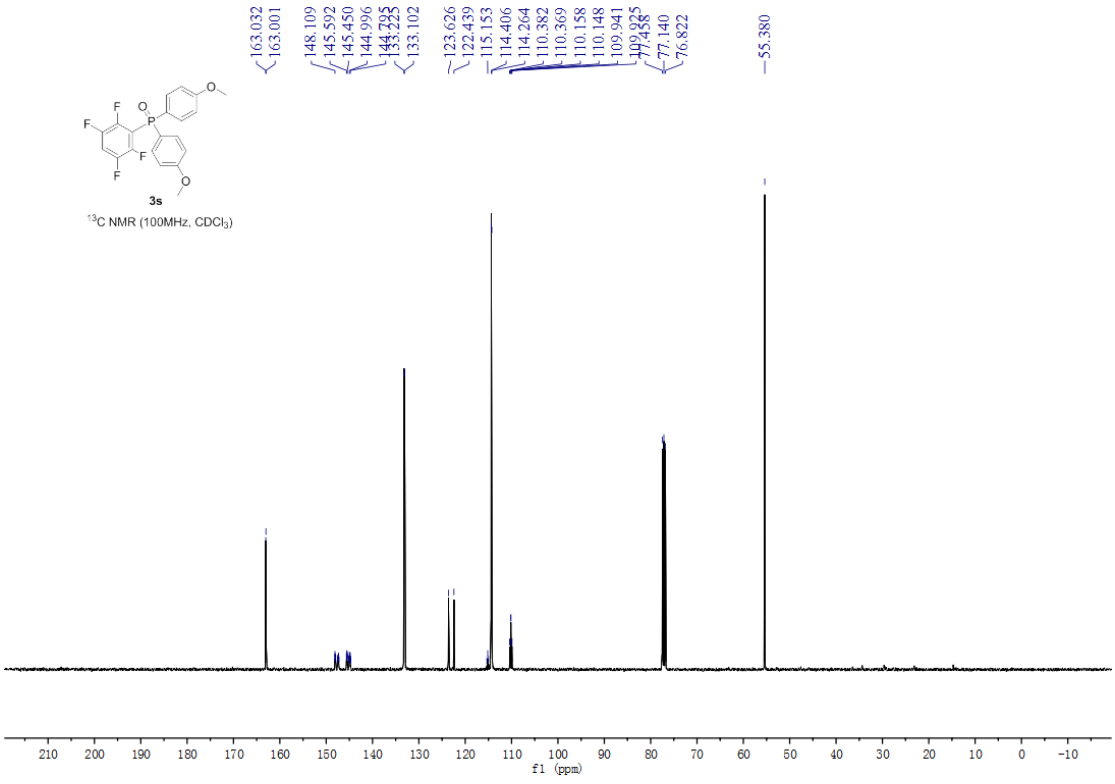
3r

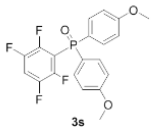
^{19}F NMR (377MHz, $CDCl_3$)

-128.896
-128.906
-128.933
-128.944
-128.956
-128.967
-129.001
-129.119
-129.147
-129.158
-129.191
-129.215
-129.247
-129.257
-136.539
-136.551
-136.562
-136.582
-136.594
-136.605
-136.618
-136.638
-136.650
-136.661
-136.681
-136.703



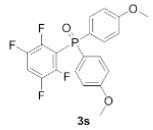

7.713
7.708
7.703
7.692
7.686
7.681
7.676
7.671
7.660
7.655
7.649
7.310
7.298
7.280
7.275
7.271
7.261
7.257
7.253
7.238
7.234
7.215
7.028
7.023
7.017
7.010
7.005
7.000
6.994
3.863
3.857
3.852
3.847
0.000
3s
1H NMR (400MHz, CDCl3)
3.98
1.06
4.08
6.00
f1 (ppm)


163.032
163.001
148.109
145.592
145.450
144.996
133.225
133.102
123.626
122.439
115.153
114.406
114.264
110.382
110.369
110.158
110.148
109.941
77.458
77.140
76.822
55.380
3s
13C NMR (100MHz, CDCl3)
f1 (ppm)



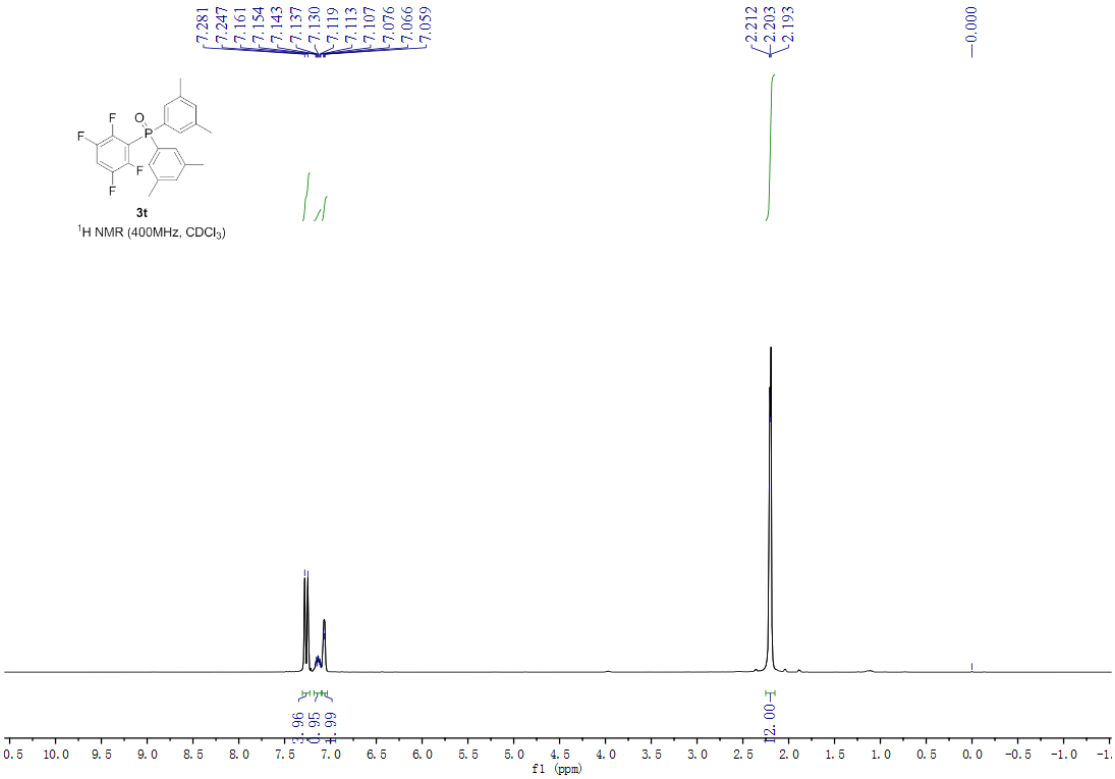
3s

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



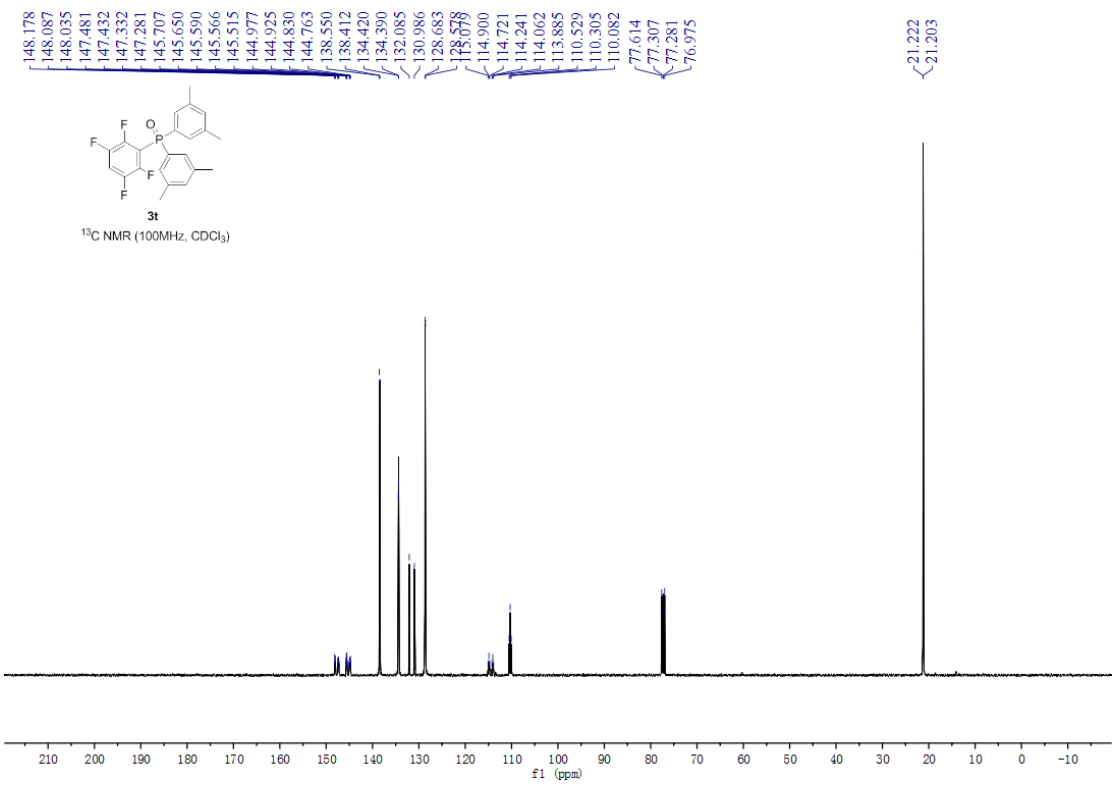
3s

^{19}F NMR (377MHz, $CDCl_3$)



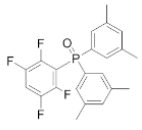
3t

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



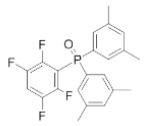
3t

^{13}C NMR (100MHz, $CDCl_3$)



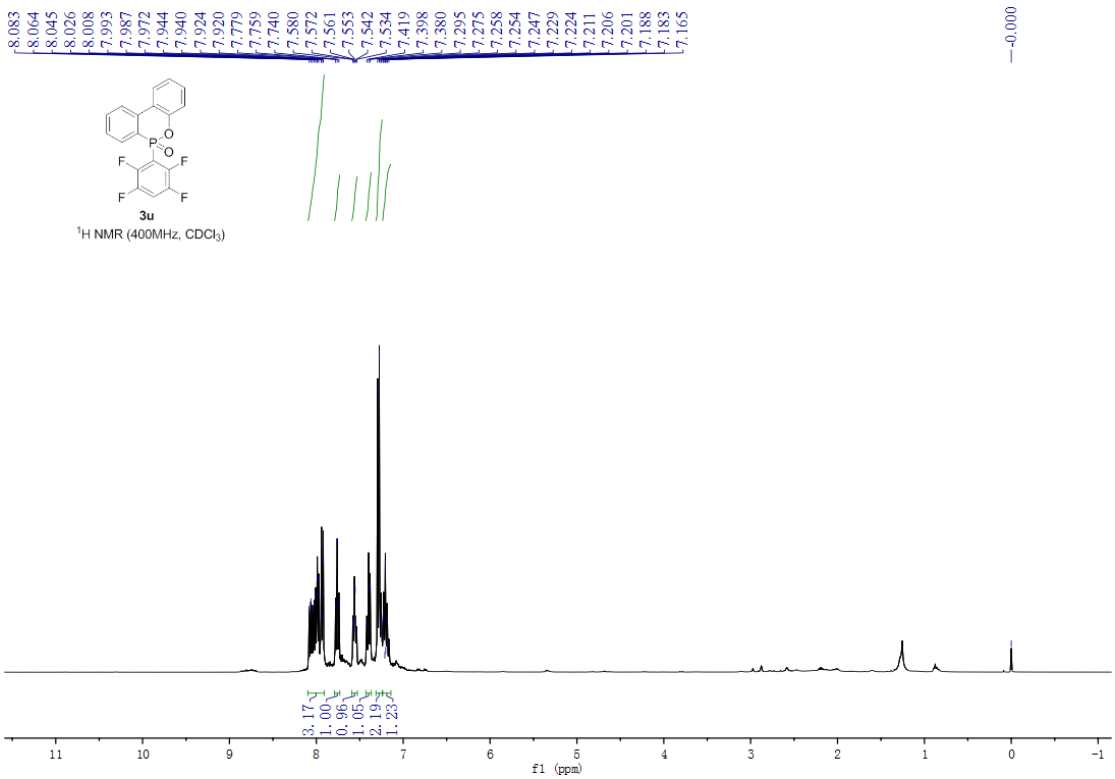
3t

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



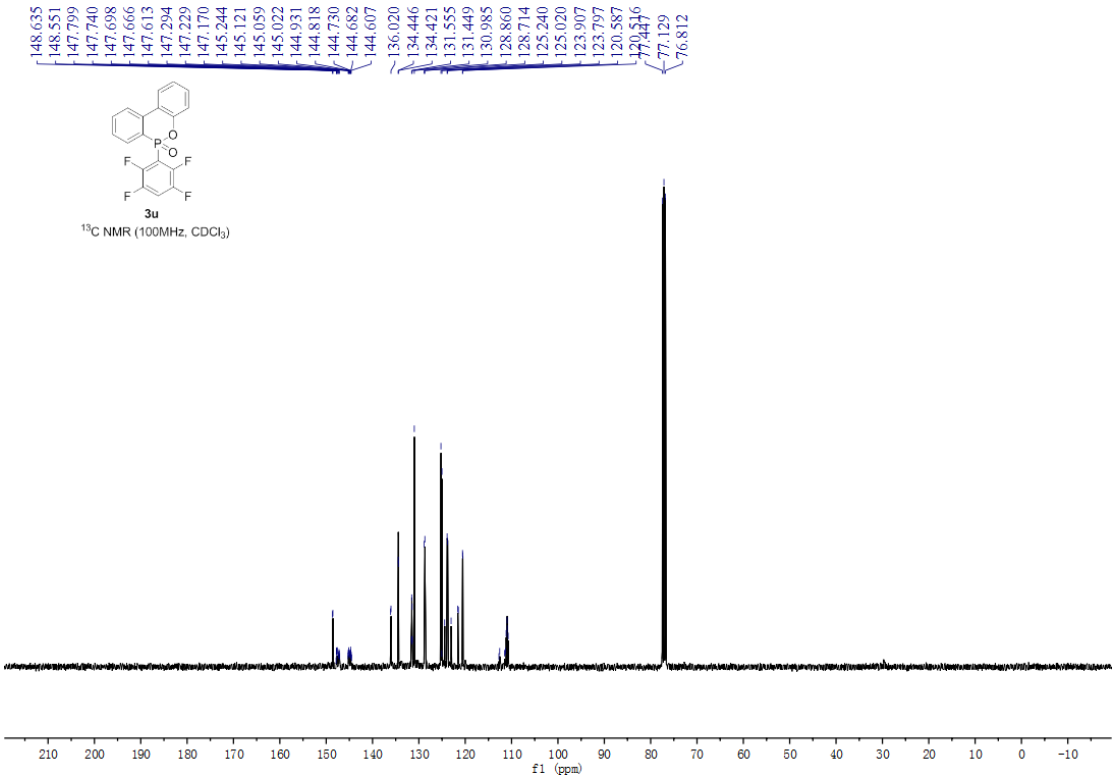
3t

^{19}F NMR (377MHz, $CDCl_3$)



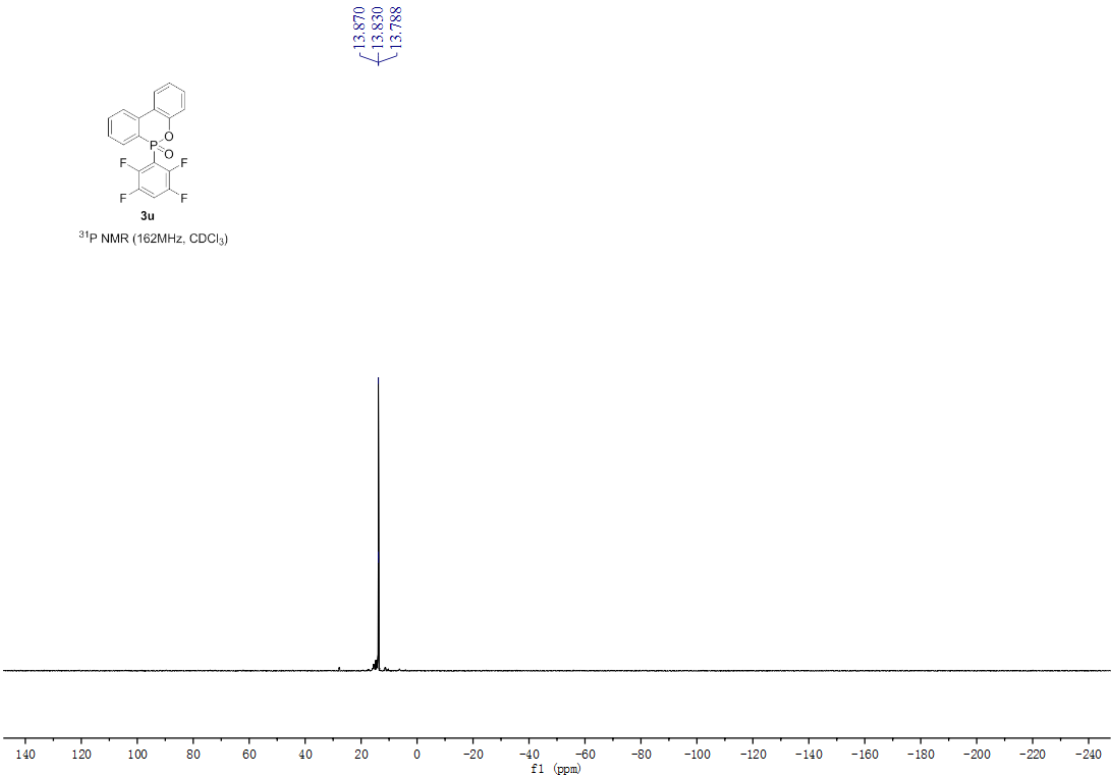
3u

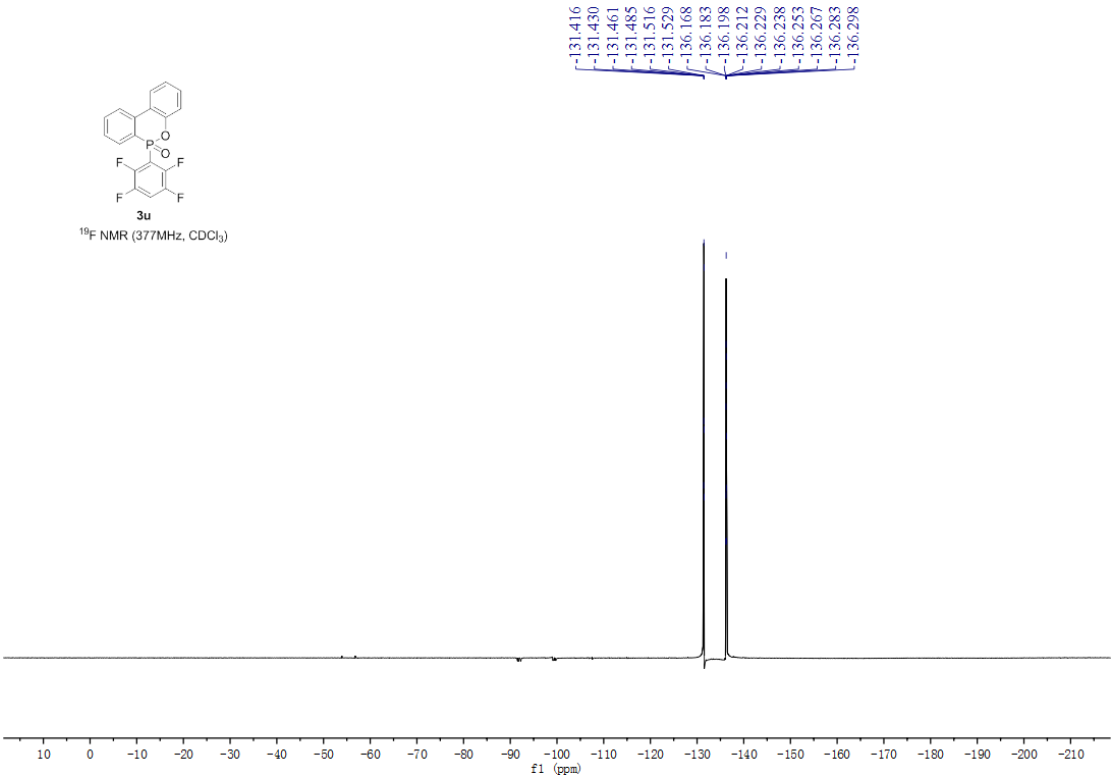
^{1}H NMR (400MHz, $CDCl_3$)



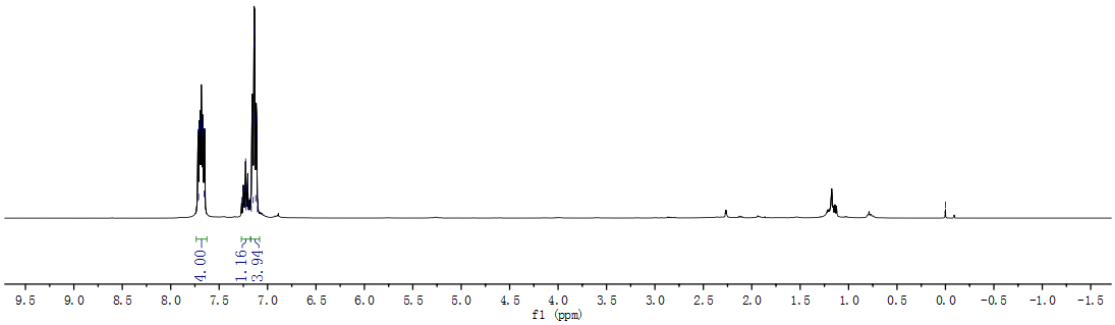
3u

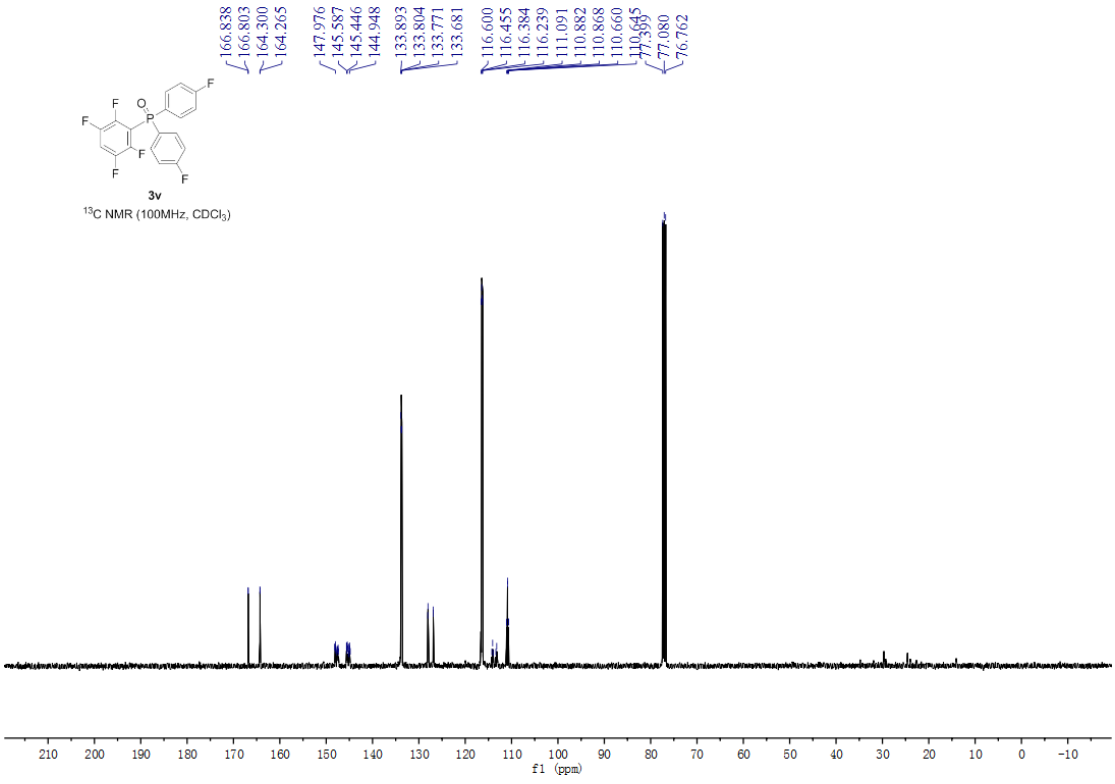
^{13}C NMR (100MHz, $CDCl_3$)

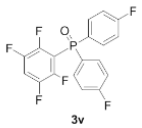

13.870
13.830
13.788
3u
31P NMR (162MHz, CDCl3)
f1 (ppm)


-131.416
-131.430
-131.461
-131.485
-131.516
-131.529
-136.168
-136.183
-136.198
-136.212
-136.229
-136.238
-136.253
-136.267
-136.283
-136.298
3u
19F NMR (377MHz, CDCl3)
f1 (ppm)


7.718
7.712
7.704
7.696
7.686
7.682
7.672
7.665
7.656
7.651
7.268
7.250
7.245
7.232
7.227
7.221
7.208
7.204
7.186
7.168
7.161
7.155
7.149
7.139
7.133
7.123
7.118
7.112
7.105
0.000
3v
1H NMR (400MHz, CDCl3)

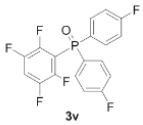

4.00
1.16
3.94
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


166.838
166.803
164.300
164.265
147.976
145.587
145.446
144.948
133.893
133.804
133.771
133.681
116.600
116.455
116.384
116.239
111.091
110.882
110.868
110.660
110.645
77.399
77.080
76.762
3v
13C NMR (100MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



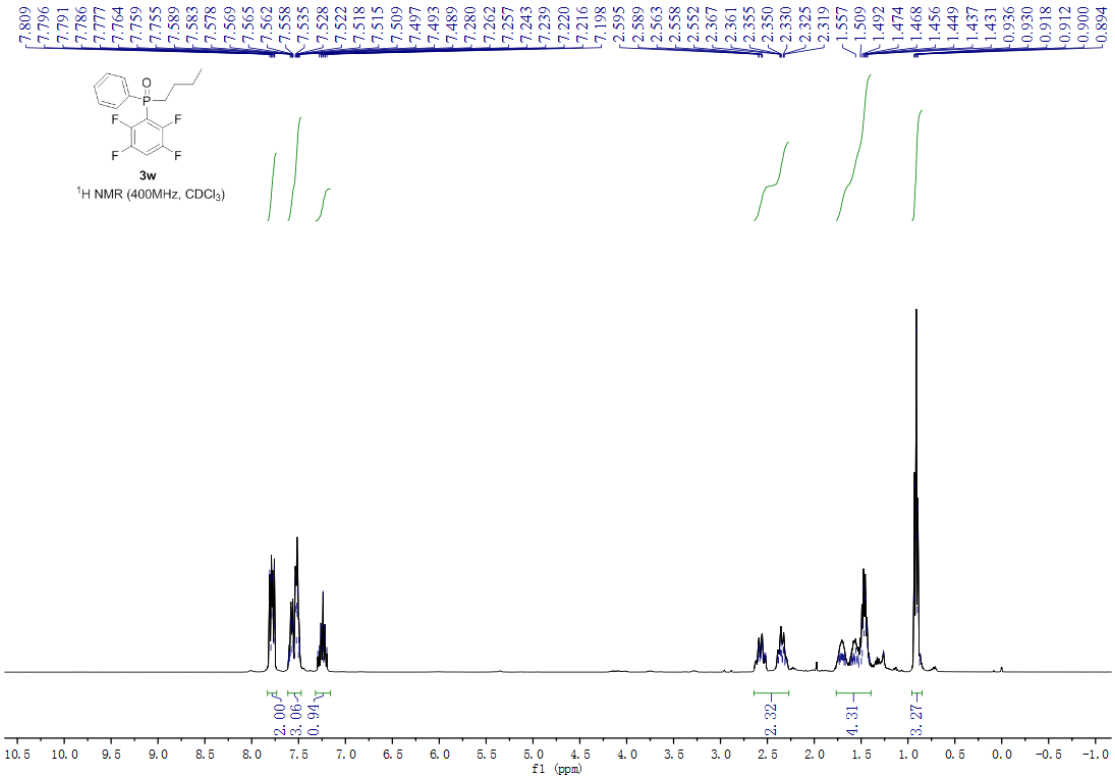
3v

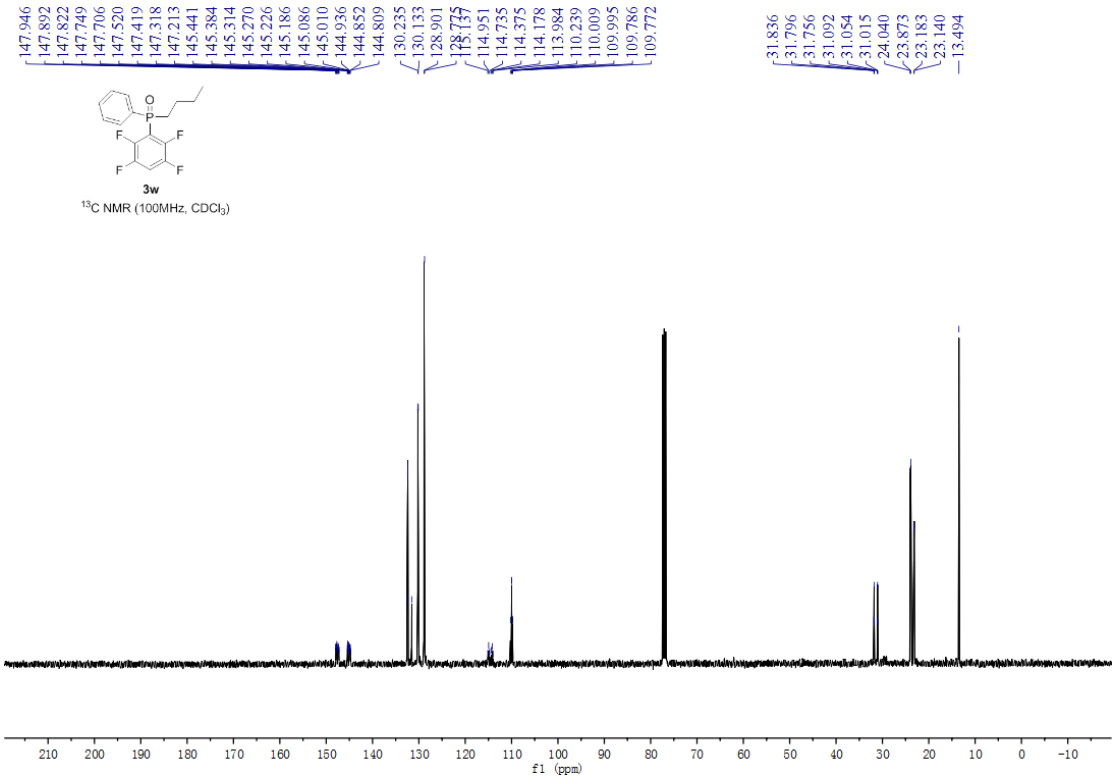
^{31}P NMR (162MHz, $CDCl_3$)

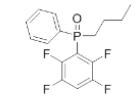


3v

^{19}F NMR (377MHz, $CDCl_3$)

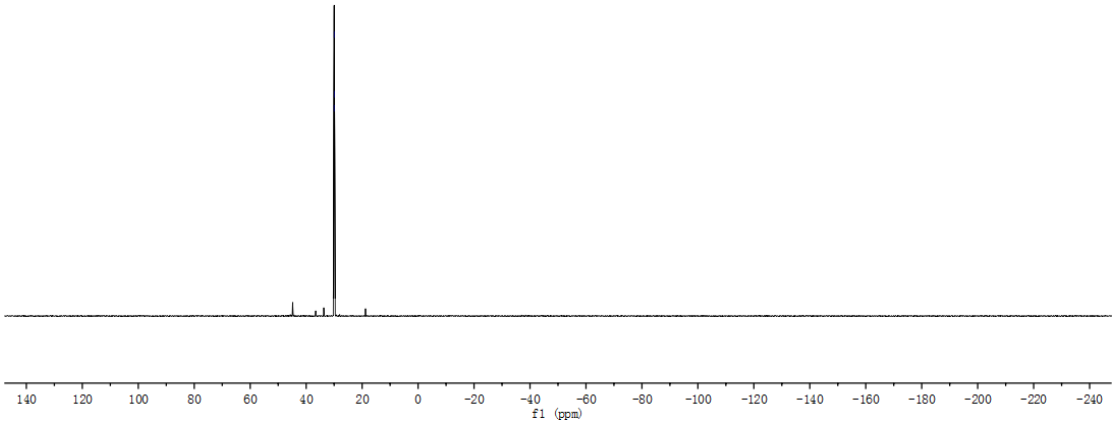

7.809
7.796
7.791
7.786
7.777
7.764
7.759
7.755
7.589
7.583
7.578
7.569
7.565
7.562
7.558
7.535
7.528
7.522
7.518
7.515
7.509
7.497
7.493
7.489
7.280
7.262
7.257
7.243
7.239
7.220
7.216
7.198
2.595
2.589
2.563
2.558
2.552
2.367
2.361
2.355
2.350
2.330
2.325
2.319
1.557
1.509
1.492
1.474
1.468
1.456
1.449
1.437
1.431
0.936
0.930
0.918
0.912
0.900
0.894
3w
1H NMR (400MHz, CDCl3)
2.00
3.06
0.94
2.32
4.31
3.27
f1 (ppm)

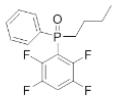

147.946
147.892
147.822
147.749
147.706
147.520
147.419
147.318
147.213
145.441
145.384
145.314
145.270
145.226
145.186
145.086
145.010
144.936
144.852
144.809
130.235
130.133
128.901
114.951
114.735
114.375
114.178
113.984
110.239
110.009
109.995
109.786
109.772
31.836
31.796
31.756
31.092
31.054
31.015
24.040
23.873
23.183
23.140
13.494
3w
13C NMR (100MHz, CDCl3)
f1 (ppm)



3w

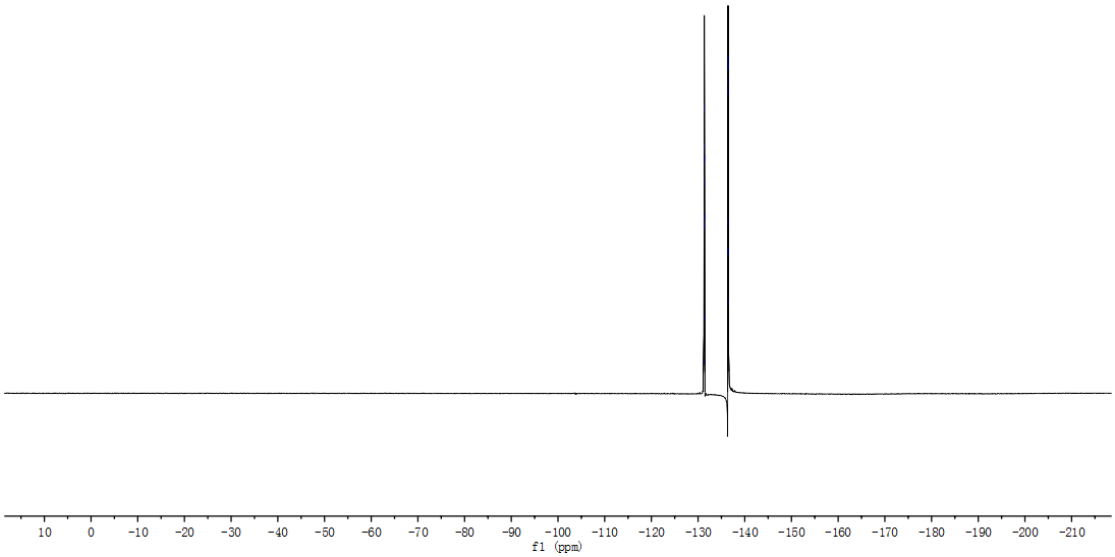
^{31}P NMR (162MHz, $CDCl_3$)

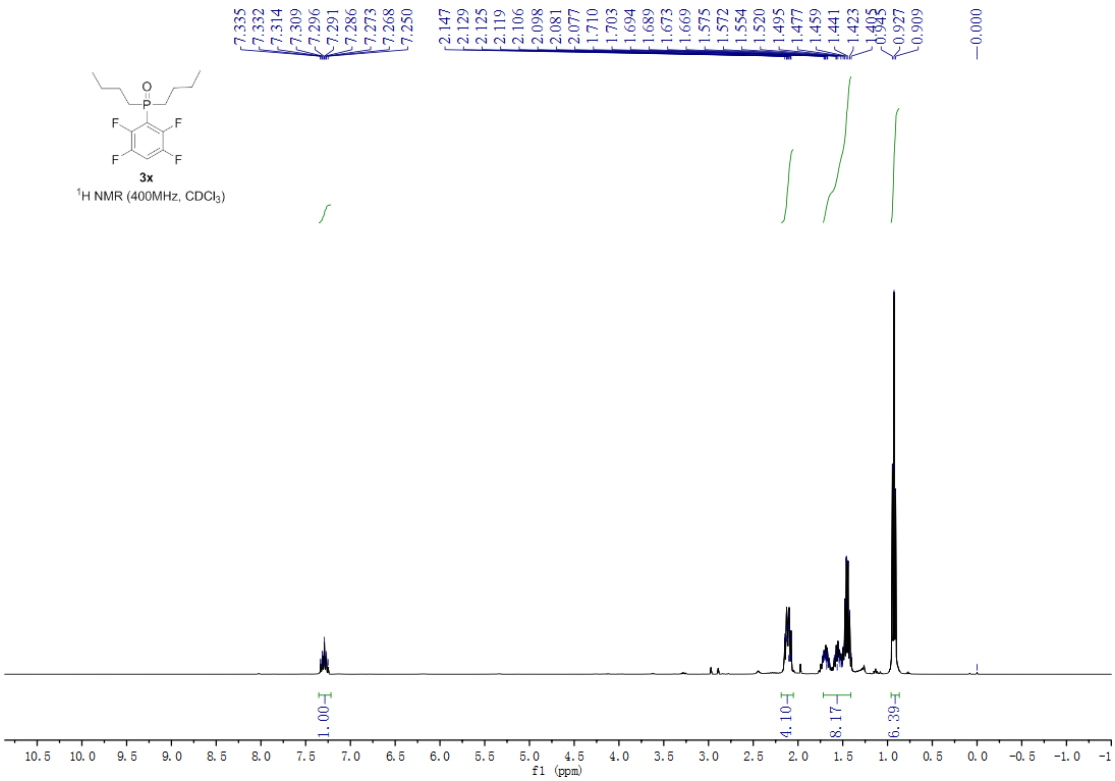


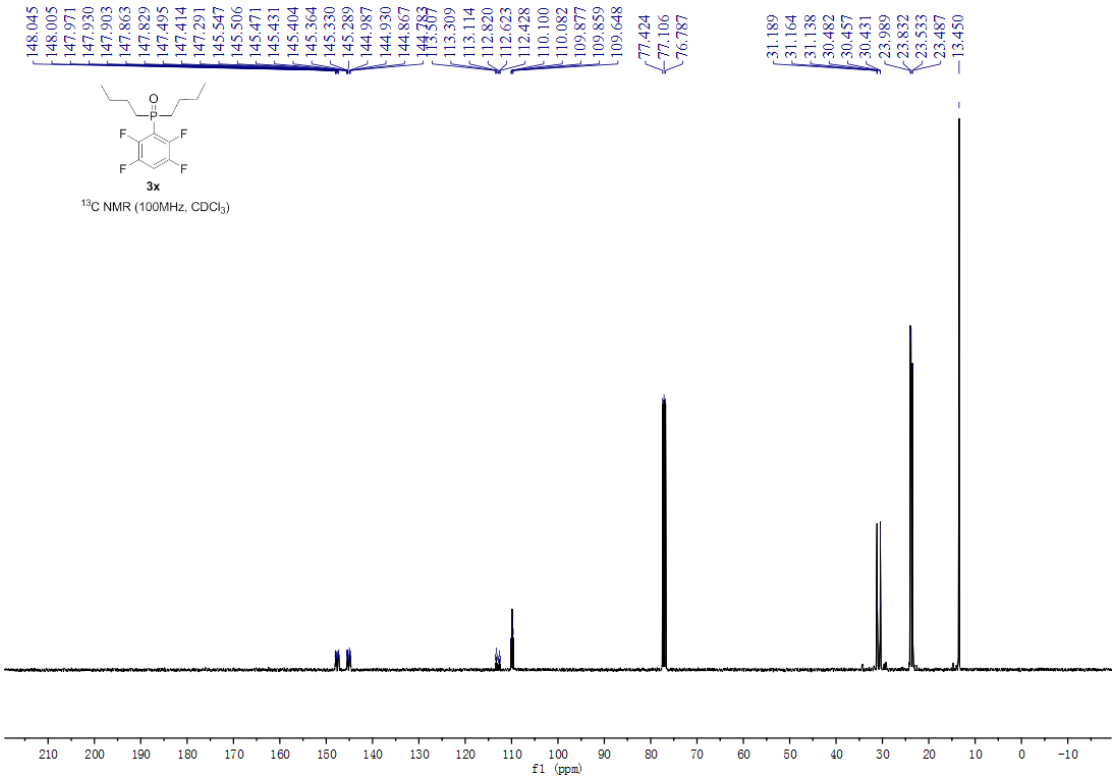


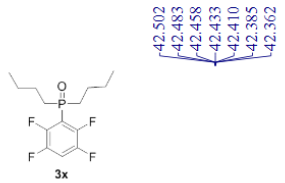
3w

^{19}F NMR (377MHz, $CDCl_3$)



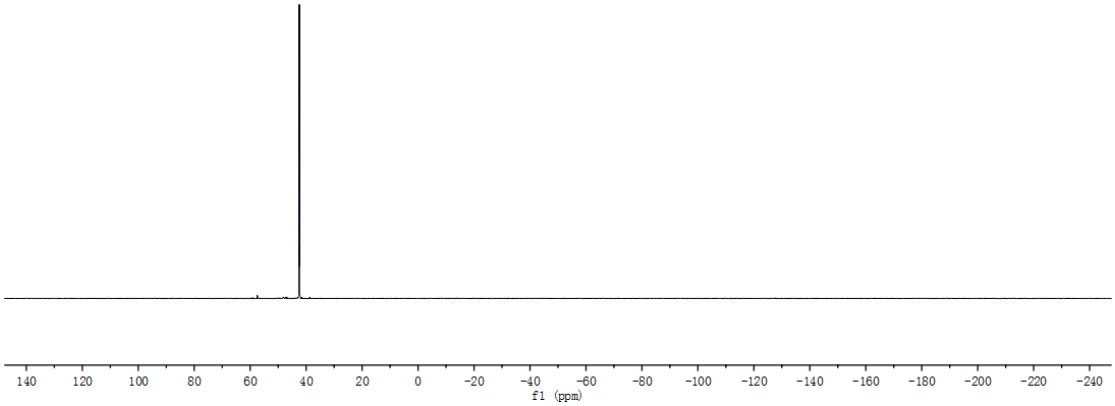

7.335
7.332
7.314
7.309
7.296
7.291
7.286
7.273
7.268
7.250
2.147
2.129
2.125
2.119
2.106
2.098
2.081
2.077
1.710
1.703
1.694
1.689
1.673
1.669
1.575
1.572
1.554
1.520
1.495
1.477
1.459
1.441
1.423
0.927
0.909
0.000
3x
1H NMR (400MHz, CDCl3)
1.00
4.10
8.17
6.39
f1 (ppm)

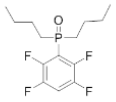

148.045
148.005
147.971
147.930
147.903
147.863
147.829
147.495
147.414
147.291
145.547
145.506
145.471
145.431
145.404
145.364
145.330
145.289
144.987
144.930
144.867
113.309
113.114
112.820
112.623
112.428
110.100
110.082
109.877
109.859
109.648
77.424
77.106
76.787
31.189
31.164
31.138
30.482
30.457
30.431
23.989
23.832
23.533
23.487
13.450
3x
13C NMR (100MHz, CDCl3)
f1 (ppm)



3x

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





3x

^{19}F NMR (377MHz, $CDCl_3$)