

Supplementary Information

Palladium-Catalyzed Synthesis of Aryl Phosphonates Using Sodium Hypophosphite

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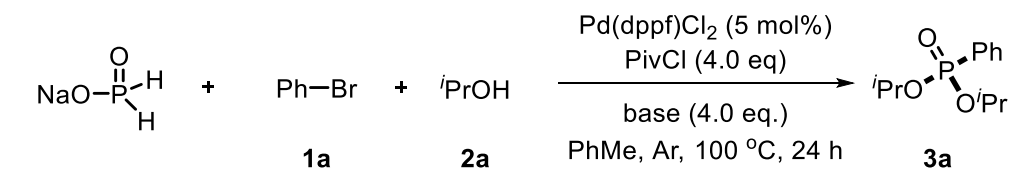
I. General information and experimental section

General Information

^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, ^{31}P NMR and ^{19}F NMR spectra were recorded at room temperature using a Avance-400 instruments (^1H NMR at 400 MHz, $^{13}\text{C}\{^1\text{H}\}$ NMR at 101 MHz, ^{31}P NMR at 162 MHz and $^{19}\text{F}\{^1\text{H}\}$ NMR at 376 MHz), NMR spectra of all products were reported in ppm with reference to solvent signals [^1H NMR: $\text{CD}(\text{H})\text{Cl}_3$ (7.26 ppm), ^{13}C NMR: $\text{CD}(\text{H})\text{Cl}_3$ (77.00 ppm)]. Signal patterns are indicated as s, singlet; d, doublet; dd, doublets of doublet; t, triplet, and m, multiplet. The mass spectrometry was performed in the positive electrospray ionization (ESI+) mode. Reactions were monitored by thin-layer chromatography Column chromatography (petroleum ether/ethyl acetate) was performed on silica gel (200-300 mesh). Analytical grade solvents and commercially available reagents were purchased from commercial sources and used directly without further purification unless otherwise stated.

II. Optimization of the reaction conditions

Table S1. Effect of bases on the reaction.^{a,b}

		
entry	base	Yield (%) ^b
1	Na_2CO_3	93
2	NaHCO_3	45
3	NaOAc	n.r.
4	Cs_2CO_3	24
5	DABCO	38
6	DBU	51
7	Et_3N	46

^aReaction conditions: bromobenzene (0.2 mmol), NaH_2PO_2 (0.4 mmol), base (0.8 mmol), $i\text{PrOH}$ (1.6 mmol), PivCl (0.8 mmol), $\text{Pd}(\text{dppf})\text{Cl}_2$ (5 mol%), PhMe (2.0 mL), under Ar, 100 °C, 24 h.

^bIsolated yield.

Table S2. Effect of Na₂CO₃ equivalents on the reaction.^{a,b}

$\text{NaO}-\overset{\text{O}}{\parallel}{\text{P}}(\text{H})_2 + \text{Ph}-\text{Br} + \text{}^i\text{PrOH} \xrightarrow[\text{PhMe, Ar, 100 }^\circ\text{C, 24 h}]{\text{Pd(dppf)Cl}_2 (5 \text{ mol}\%), \text{PivCl (4.0 eq.)}} \text{}^i\text{PrO}-\overset{\text{O}}{\parallel}{\text{P}}(\text{Ph})(\text{O}^i\text{Pr})$			
$\text{Na}_2\text{CO}_3 (X \text{ eq.})$			
entry	1a	2a	3a
entry	Na ₂ CO ₃ (X eq.)		Yield (%) ^b
1	1.0		n.r.
2	2.0		trace
3	3.0		44
4	4.0		93
5	5.0		90
6	6.0		77

^aReaction conditions: bromobenzene (0.2 mmol), NaH₂PO₂ (0.4 mmol), Na₂CO₃ (X eq.), ⁱPrOH (1.6 mmol), PivCl (0.8 mmol), Pd(dppf)Cl₂ (5 mol%), PhMe (2.0 mL), under Ar, 100 °C, 24 h. ^bIsolated yield.

Table S3. Effect of additive PivCl equivalents on the reaction.^{a,b}

$\text{NaO}-\overset{\text{O}}{\parallel}{\text{P}}(\text{H})_2 + \text{Ph}-\text{Br} + \text{}^i\text{PrOH} \xrightarrow[\text{PhMe, Ar, 100 }^\circ\text{C, 24 h}]{\text{Pd(dppf)Cl}_2 (5 \text{ mol}\%), \text{PivCl (Y eq.)}} \text{}^i\text{PrO}-\overset{\text{O}}{\parallel}{\text{P}}(\text{Ph})(\text{O}^i\text{Pr})$			
$\text{Na}_2\text{CO}_3 (4.0 \text{ eq.})$			
entry	1a	2a	3a
entry	PivCl (Y eq.)		Yield (%) ^b
1	1.0		n.r.
2	2.0		trace
3	3.0		45
4	4.0		93
5	5.0		93
6	6.0		89

^aReaction conditions: bromobenzene (0.2 mmol), NaH₂PO₂ (0.4 mmol), Na₂CO₃ (0.8 mmol), ⁱPrOH (1.6 mmol), PivCl (Y eq.), Pd(dppf)Cl₂ (5 mol%), PhMe (2.0 mL), under Ar, 100 °C, 24 h. ^bIsolated yield.

Table S4. Effect of catalyst Pd(dppf)Cl₂ equivalents on the reaction.^{a,b}

$\text{NaO}-\overset{\text{O}}{\parallel}{\text{P}}-\text{H} + \text{Ph}-\text{Br} + \text{}^i\text{PrOH} \xrightarrow[\text{Na}_2\text{CO}_3 (4.0 \text{ eq.})]{\text{Pd(dppf)Cl}_2 (Z \text{ mol}\%) \text{ PivCl (4.0 eq.)}} \text{}^i\text{PrO}-\overset{\text{O}}{\parallel}{\text{P}}(\text{Ph})-\text{O}^i\text{Pr}$			
$\text{1a} \qquad \qquad \text{2a} \qquad \qquad \text{PhMe, Ar, 100 }^\circ\text{C, 24 h} \qquad \qquad \text{3a}$			
entry	Pd(dppf)Cl ₂ (Z mol%)		Yield (%) ^b
1	1		74
2	2.5		87
3	3		89
4	5		93
5	10		90

^aReaction conditions: bromobenzene (0.2 mmol), NaH₂PO₂ (0.4 mmol), Na₂CO₃ (0.8 mmol), ⁱPrOH (1.6 mmol), PivCl (0.8 mmol), Pd(dppf)Cl₂ (Z mol%), PhMe (2.0 mL), under Ar, 100 °C, 24 h. ^bIsolated yield.

Table S5. Effect of ligand on the reaction.^{a,b}

$\text{NaO}-\overset{\text{O}}{\parallel}{\text{P}}-\text{H} + \text{Ph}-\text{Br} + \text{}^i\text{PrOH} \xrightarrow[\text{Na}_2\text{CO}_3 (4.0 \text{ eq.})]{\text{PdCl}_2 (5 \text{ mol}\%) \text{ L (mol\%) PivCl (4.0 eq.)}} \text{}^i\text{PrO}-\overset{\text{O}}{\parallel}{\text{P}}(\text{Ph})-\text{O}^i\text{Pr}$			
$\text{1a} \qquad \qquad \text{2a} \qquad \qquad \text{PhMe, Ar, 100 }^\circ\text{C, 24 h} \qquad \qquad \text{3a}$			
entry	L (mol%)		Yield (%) ^b
1	PPh ₃ (10 mol%)		12
2	Dppf (5 mol%)		93
3	Dppp (5 mol%)		trace
4	BINAP (5 mol%)		66
5	DPEphos (5 mol%)		34
6	Xantphos (5 mol%)		n.r.

^aReaction conditions: bromobenzene (0.2 mmol), NaH₂PO₂ (0.4 mmol), Na₂CO₃ (0.8 mmol), ⁱPrOH (1.6 mmol), PivCl (Y eq.), PdCl₂ (5 mol%), L (5-10 mol%), PhMe (2.0 mL), under Ar, 100 °C, 24 h. ^bIsolated yield.

Table S6. Effect of temperature on the reaction.^{a,b}

$\text{NaO}-\overset{\text{O}}{\parallel}{\text{P}}-\text{H} + \text{Ph}-\text{Br} + \text{}^i\text{PrOH} \xrightarrow[\text{Na}_2\text{CO}_3 (4.0 \text{ eq.})]{\text{Pd(dppf)Cl}_2 (5 \text{ mol}\%), \text{PivCl} (4.0 \text{ eq.})} \text{}^i\text{PrO}-\overset{\text{O}}{\parallel}{\text{P}}(\text{Ph})-\text{O}^i\text{Pr}$			
$\text{1a} \qquad \qquad \text{2a} \qquad \qquad \qquad \text{3a}$			
entry	T (°C)	Yield (%) ^b	
1	rt	n.r.	
2	40	trace	
3	60	48	
4	80	69	
5	100	93	
6	120	90	

^aReaction conditions: bromobenzene (0.2 mmol), NaH₂PO₂ (0.4 mmol), Na₂CO₃ (0.8 mmol), ⁱPrOH (1.6 mmol), PivCl (0.8 mmol), Pd(dppf)Cl₂ (5 mol%), PhMe (2.0 mL), under Ar, 24 h. ^bIsolated yield.

Table S7. Effect of solvents on the reaction.^{a,b}

$\text{NaO}-\overset{\text{O}}{\parallel}{\text{P}}-\text{H} + \text{Ph}-\text{Br} + \text{}^i\text{PrOH} \xrightarrow[\text{Na}_2\text{CO}_3 (4.0 \text{ eq.})]{\text{Pd(dppf)Cl}_2 (5 \text{ mol}\%), \text{PivCl} (4.0 \text{ eq.})} \text{}^i\text{PrO}-\overset{\text{O}}{\parallel}{\text{P}}(\text{Ph})-\text{O}^i\text{Pr}$			
$\text{1a} \qquad \qquad \text{2a} \qquad \qquad \qquad \text{3a}$			
entry	Sol.	Yield (%) ^b	
1	PhMe	93	
2	1,4-dioxane	60	
3	THF	48	
4	EtOAc	38	
5	DCE	n.r.	
6	MeCN	31	

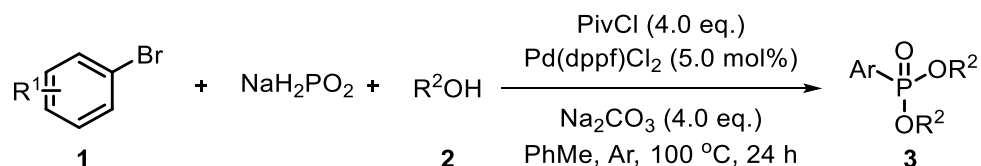
^aReaction conditions: bromobenzene (0.2 mmol), NaH₂PO₂ (0.4 mmol), Na₂CO₃ (0.8 mmol), ⁱPrOH (1.6 mmol), PivCl (0.8 mmol), Pd(dppf)Cl₂ (5 mol%), solvent (2.0 mL), under Ar, 100 °C, 24 h. ^bIsolated yield.

Table S8. Effect of catalysts on the reaction.^{a,b}

entry	Catalyst (5 mol%)	Yield (%) ^b
1	PdCl ₂	93
2	Pd(OAc) ₂	81
3	Pd(acac) ₂	69
4	Pd ₂ (dba) ₃	trace
5	NiCl ₂	n.r.
6	CoCl ₂	n.r.

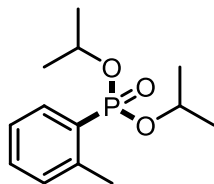
^aReaction conditions: bromobenzene (0.2 mmol), NaH₂PO₂ (0.4 mmol), Na₂CO₃ (0.8 mmol), *i*PrOH (1.6 mmol), PivCl (0.8 mmol), catalyst (5 mol%), dppf (5 mol%), PhMe (2.0 mL), under Ar, 100 °C, 24 h. ^bIsolated yield.

III. Experimental procedure for the synthesis of product

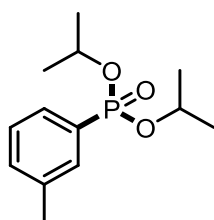


Under an inert gas atmosphere, sodium hypophosphite solid (0.4 mmol, 2.0 equiv), sodium carbonate (0.8 mmol, 4.0 equiv), and Pd(dppf)Cl₂ (0.01 mmol, 5.0 mol%) were weighed into a dried reaction tube containing 2 mL of anhydrous toluene. Subsequently, the aryl halide (0.2 mmol, 1.0 equiv), the alcohol compound (1.6 mmol, 8.0 equiv), and the activator pivaloyl chloride (PivCl, 0.8 mmol, 4.0 equiv) were added to the reaction mixture via a microsyringe. The mixture was heated in an oil bath at 100 °C for 24 hours until thin-layer chromatography (TLC) analysis confirmed complete consumption of the aryl halide starting material. After completion, the reaction was removed from heating and allowed to cool gradually to ambient temperature. Silica gel was directly added to the reaction mixture, followed by concentration under reduced

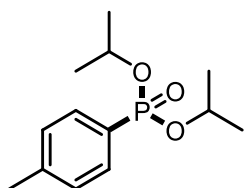
= 3.1 Hz), 131.69 (d, $J = 9.8$ Hz), 129.91 (d, $J = 188.6$ Hz), 128.28 (d, $J = 15.0$ Hz), 70.69 (d, $J = 5.5$ Hz), 24.04 (d, $J = 4.0$ Hz), 23.80 (d, $J = 4.8$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 16.61 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{20}\text{O}_3\text{P}^+$ 243.1145, found 243.1145.



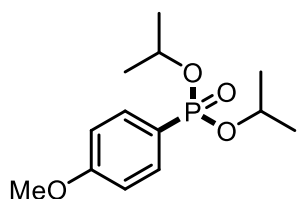
diisopropyl o-tolylphosphonate (3b): Compound **3b** was isolated in 61% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.94 (dd, $J = 14.7, 7.6$ Hz, 1H), 7.40 (t, $J = 7.5$ Hz, 1H), 7.31 – 7.12 (m, 2H), 4.81 – 4.50 (m, 2H), 2.57 (d, $J = 1.2$ Hz, 3H), 1.37 (d, $J = 6.2$ Hz, 7H), 1.23 (d, $J = 6.2$ Hz, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 141.63 (d, $J = 9.9$ Hz), 133.85 (d, $J = 10.5$ Hz), 132.15 (d, $J = 3.0$ Hz), 131.09 (d, $J = 14.8$ Hz), 128.34 (d, $J = 184.8$ Hz), 125.26 (d, $J = 15.0$ Hz), 70.59 (d, $J = 5.7$ Hz), 24.10 (d, $J = 4.1$ Hz), 23.78 (d, $J = 4.7$ Hz), 21.28 (d, $J = 3.5$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 17.19 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{22}\text{O}_3\text{P}^+$ 257.1301, found 257.1301.



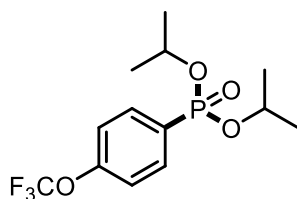
diisopropyl m-tolylphosphonate (3c): Compound **3c** was isolated in 84% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.72 – 7.54 (m, 2H), 7.33 (t, $J = 3.9$ Hz, 2H), 4.68 (dq, $J = 12.5, 6.2$ Hz, 2H), 2.39 (s, 3H), 1.37 (d, $J = 6.2$ Hz, 6H), 1.23 (d, $J = 6.2$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 138.05 (d, $J = 15.0$ Hz), 132.84 (d, $J = 3.2$ Hz), 132.29 (d, $J = 10.0$ Hz), 130.64 (s), 128.75 (d, $J = 9.6$ Hz), 128.22 (d, $J = 15.7$ Hz), 70.61 (d, $J = 5.5$ Hz), 24.07 (d, $J = 3.9$ Hz), 23.84 (d, $J = 4.9$ Hz), 21.32 (s). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 17.15 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{22}\text{O}_3\text{P}^+$ 257.1301, found 257.1303.



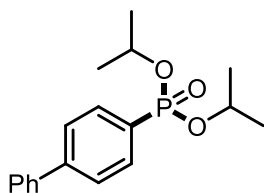
diisopropyl p-tolylphosphonate (3d): Compound **3d** was isolated in 90% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.69 (dd, $J = 12.9, 7.6$ Hz, 2H), 7.25 (t, $J = 6.7$ Hz, 2H), 4.65 (dq, $J = 12.3, 6.0$ Hz, 2H), 2.38 (s, 3H), 1.35 (d, $J = 5.4$ Hz, 6H), 1.20 (d, $J = 5.6$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 142.50 (d, $J = 3.1$ Hz), 131.78 (d, $J = 10.2$ Hz), 129.02 (d, $J = 15.4$ Hz), 126.67 (d, $J = 190.8$ Hz), 70.50 (d, $J = 5.4$ Hz), 24.06 (d, $J = 3.9$ Hz), 23.82 (d, $J = 4.8$ Hz), 21.60 (s). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 17.33 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{22}\text{O}_3\text{P}^+$ 257.1301, found 257.1306. **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{22}\text{O}_3\text{P}^+$ 257.1301, found 257.1306.



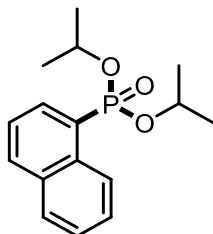
diisopropyl (4-methoxyphenyl)phosphonate (3e): Compound **3e** was isolated in 96% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.75 (dd, $J = 12.7, 8.6$ Hz, 2H), 6.95 (dd, $J = 8.6, 3.1$ Hz, 2H), 4.78 – 4.49 (m, 2H), 3.85 (s, 3H), 1.36 (d, $J = 6.2$ Hz, 6H), 1.21 (d, $J = 6.2$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 162.58 (d, $J = 3.4$ Hz), 133.70 (d, $J = 11.3$ Hz), 121.26 (d, $J = 195.3$ Hz), 113.81 (d, $J = 16.0$ Hz), 70.41 (d, $J = 5.4$ Hz), 55.27 (s), 24.07 (d, $J = 3.9$ Hz), 23.83 (d, $J = 4.9$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 17.47 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{22}\text{O}_4\text{P}^+$ 273.1250, found 273.1250.



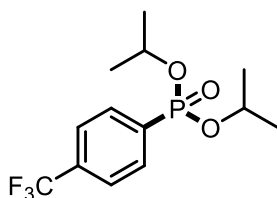
diisopropyl (4-(trifluoromethoxy)phenyl)phosphonate (3f): Compound **3f** was isolated in 91% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 (dd, $J = 12.7, 8.5$ Hz, 2H), 7.23 (d, $J = 5.3$ Hz, 2H), 4.66 (dq, $J = 12.6, 6.3$ Hz, 2H), 1.33 (d, $J = 6.1$ Hz, 6H), 1.19 (d, $J = 6.3$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) 151.98 (s), 133.71 (d, $J = 10.9$ Hz), 129.73 (s), 127.82 (s), 120.29 (d, $J = 15.8$ Hz), 120.28 (q, $J = 259.57$ Hz), 71.09 (d, $J = 5.6$ Hz), 23.92 (dd, $J = 20.2, 4.4$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 14.81 (s). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -57.68 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{19}\text{F}_3\text{O}_4\text{P}^+$ 319.1458, found 319.1457.



diisopropyl [1,1'-biphenyl]-4-ylphosphonate (3g): Compound **3g** was isolated in 92% yield; flash column chromatography eluent: PE /EA (2:1, v/v); **¹H NMR** (400 MHz, CDCl₃) δ 7.68 (dd, *J* = 12.9, 8.1 Hz, 2H), 7.46 (dd, *J* = 7.7, 3.5 Hz, 2H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 2H), 7.17 (d, *J* = 7.2 Hz, 1H), 4.51 (dd, *J* = 13.4, 6.4 Hz, 2H), 1.18 (d, *J* = 6.1 Hz, 6H), 1.03 (t, *J* = 9.5 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 144.81 (d, *J* = 3.2 Hz), 140.04 (s), 132.25 (d, *J* = 10.2 Hz), 128.91 (s), 128.56 (d, *J* = 191.9 Hz), 128.08 (s), 127.25 (s), 127.00 (d, *J* = 15.3 Hz), 70.75 (d, *J* = 5.5 Hz), 24.11 (d, *J* = 3.9 Hz), 23.90 (d, *J* = 4.8 Hz). **³¹P NMR** (162 MHz, CDCl₃) δ 16.76 (s). **HRMS (ESI):** [M+H]⁺ calcd for C₁₈H₂₄O₃P⁺ 319.1458, found 319.1455.

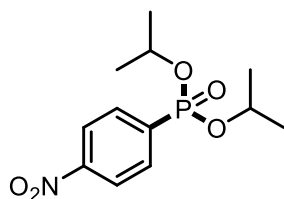


diisopropyl naphthalen-1-ylphosphonate (3h): Compound **3h** was isolated in 49% yield; flash column chromatography eluent: PE /EA (2:1, v/v); **¹H NMR** (400 MHz, CDCl₃) δ 8.52 (d, *J* = 8.5 Hz, 1H), 8.28 (ddd, *J* = 16.4, 7.0, 1.3 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.64 – 7.48 (m, 3H), 4.73 (ddt, *J* = 12.4, 8.0, 6.2 Hz, 2H), 1.41 (d, *J* = 6.2 Hz, 6H), 1.15 (d, *J* = 6.2 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 134.53 (d, *J* = 9.3 Hz), 133.62 (d, *J* = 12.6 Hz), 133.36 (d, *J* = 3.4 Hz), 132.70 (d, *J* = 10.6 Hz), 128.69 (d, *J* = 1.8 Hz), 127.08 (d, *J* = 2.8 Hz), 126.22 (s), 125.21 (s), 124.51 (d, *J* = 16.6 Hz), 70.96 (d, *J* = 5.3 Hz), 24.18 (d, *J* = 3.8 Hz), 23.78 (d, *J* = 4.9 Hz). **³¹P NMR** (162 MHz, CDCl₃) δ 16.73 (s). **HRMS (ESI):** [M+H]⁺ calcd for C₁₆H₂₂O₃P⁺ 293.1301, found 293.1303.

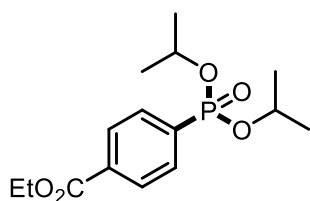


diisopropyl (4-(trifluoromethyl)phenyl)phosphonate (3i): Compound **3i** was isolated in 92% yield; flash column chromatography eluent: PE /EA (2:1, v/v); flash

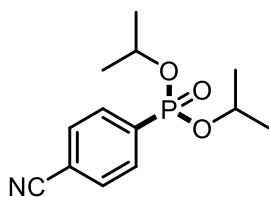
column chromatography eluent: PE /EA (2:1, v/v); **¹H NMR** (400 MHz, CDCl₃) δ 7.87 (dd, *J* = 12.9, 8.1 Hz, 2H), 7.64 (dd, *J* = 7.9, 3.0 Hz, 2H), 4.66 (dq, *J* = 12.5, 6.2 Hz, 2H), 1.31 (d, *J* = 6.2 Hz, 6H), 1.16 (d, *J* = 6.3 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 135.34 (s), 133.71 (dd, *J* = 39.3, 6.7 Hz), 132.12 (d, *J* = 10.1 Hz), 125.23 (d, *J* = 3.8 Hz), 125.08 (d, *J* = 3.7 Hz), 71.33 (d, *J* = 5.7 Hz), 24.02 (d, *J* = 4.1 Hz), 23.81 (d, *J* = 4.8 Hz). **³¹P NMR** (162 MHz, CDCl₃) δ 14.04 (s). **HRMS (ESI):** [M+H]⁺ calcd for C₁₃H₁₉F₃O₃P⁺ 311.1018, found 311.1013.



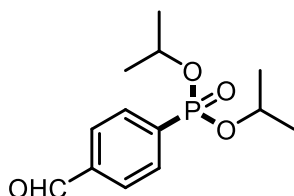
diisopropyl (4-nitrophenyl)phosphonate (3j): Compound **3j** was isolated in 88% yield; flash column chromatography eluent: PE /EA (2:1, v/v); **¹H NMR** (400 MHz, CDCl₃) δ 8.22 (dd, *J* = 8.7, 3.2 Hz, 2H), 7.93 (dd, *J* = 12.6, 8.7 Hz, 2H), 4.69 (qd, *J* = 12.4, 6.2 Hz, 2H), 1.33 (d, *J* = 6.2 Hz, 6H), 1.18 (d, *J* = 6.2 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 150.09 (s), 137.42 (d, *J* = 187.8 Hz), 132.85 (d, *J* = 10.5 Hz), 123.25 (d, *J* = 15.3 Hz), 71.75 (d, *J* = 5.8 Hz), 24.05 (d, *J* = 4.1 Hz), 23.86 (d, *J* = 4.8 Hz). **³¹P NMR** (162 MHz, CDCl₃) δ 12.67 (s). **HRMS (ESI):** [M+H]⁺ calcd for C₁₂H₁₉NO₅P⁺ 288.0995, found 288.0995.



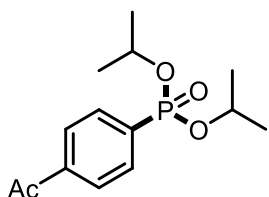
ethyl 4-(diisopropoxyphosphoryl)benzoate (3k): Compound **3k** was isolated in 87% yield; flash column chromatography eluent: PE /EA (2:1, v/v); **¹H NMR** (400 MHz, CDCl₃) δ 8.14 – 7.96 (m, 2H), 7.82 (dd, *J* = 12.9, 8.0 Hz, 2H), 4.64 (dq, *J* = 12.5, 6.3 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.32 (dd, *J* = 14.1, 6.6 Hz, 9H), 1.15 (d, *J* = 6.2 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 165.81 (s), 134.70 (d, *J* = 187.1 Hz), 133.59 (d, *J* = 3.2 Hz), 131.68 (d, *J* = 10.0 Hz), 129.24 (d, *J* = 15.0 Hz), 71.16 (d, *J* = 5.6 Hz), 61.37 (s), 24.03 (d, *J* = 4.0 Hz), 23.79 (d, *J* = 4.8 Hz), 14.25 (s). **³¹P NMR** (162 MHz, CDCl₃) δ 14.83 (s). **HRMS (ESI):** [M+H]⁺ calcd for C₁₅H₂₄O₅P⁺ 315.1356, found 315.1356.



diisopropyl (4-cyanophenyl)phosphonate (3l): Compound **3l** was isolated in 88% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.93 (dd, $J = 13.0, 8.1$ Hz, 2H), 7.75 (dd, $J = 8.1, 3.5$ Hz, 2H), 4.74 (dq, $J = 12.5, 6.2$ Hz, 2H), 1.39 (d, $J = 6.2$ Hz, 6H), 1.24 (d, $J = 6.2$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 135.50 (d, $J = 188.4$ Hz), 132.17 (d, $J = 9.8$ Hz), 131.88 (d, $J = 14.9$ Hz), 117.94 (s), 115.68 (d, $J = 3.6$ Hz), 71.59 (d, $J = 5.8$ Hz), 24.02 (d, $J = 4.1$ Hz), 23.83 (d, $J = 4.8$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 13.08 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_3\text{P}^+$ 268.1097, found 268.1097.

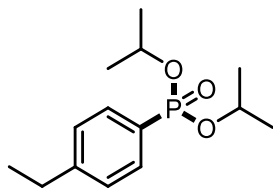


diisopropyl (4-formylphenyl)phosphonate (3m): Compound **3m** was isolated in 94% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.02 (s, 1H), 8.08 – 7.71 (m, 4H), 4.67 (qd, $J = 12.4, 6.2$ Hz, 2H), 1.32 (d, $J = 6.2$ Hz, 6H), 1.17 (d, $J = 6.2$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 191.72 (s), 138.54 (d, $J = 3.0$ Hz), 136.52 (d, $J = 186.5$ Hz), 132.30 (d, $J = 9.9$ Hz), 129.27 (d, $J = 15.1$ Hz), 71.38 (d, $J = 5.7$ Hz), 24.06 (d, $J = 4.1$ Hz), 23.84 (d, $J = 4.8$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 14.11 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{20}\text{O}_4\text{P}^+$ 271.1094, found 271.1094.

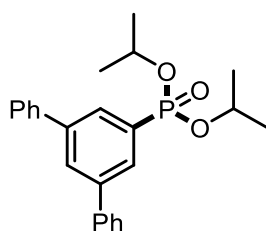


diisopropyl (4-acetylphenyl)phosphonate (3n): Compound **3n** was isolated in 89% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.94 (dd, $J = 8.0, 3.8$ Hz, 2H), 7.85 (dd, $J = 12.8, 8.0$ Hz, 2H), 4.65 (dq, $J = 12.6, 6.3$ Hz, 2H), 2.57 (s, 3H), 1.31 (d, $J = 6.2$ Hz, 6H), 1.16 (d, $J = 6.2$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 197.60 (s), 139.59 (d, $J = 3.2$ Hz), 134.99 (d, $J = 187.2$ Hz), 131.99 (d, $J = 10.0$ Hz), 127.94 (d, $J = 15.0$ Hz), 71.24 (d, $J = 5.7$ Hz), 26.80 (s), 24.05

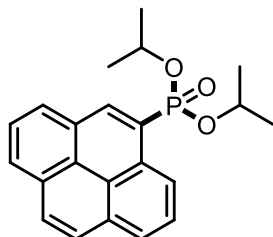
(d, $J = 4.0$ Hz), 23.83 (d, $J = 4.8$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 14.60 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{22}\text{O}_4\text{P}^+$ 285.1250, found 285.1256.



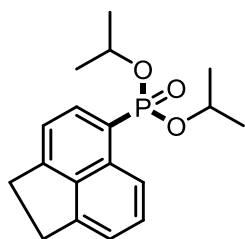
diisopropyl (4-ethylphenyl)phosphonate (3o): Compound **3o** was isolated in 87% yield; flash column chromatography eluent: PE /EA (2:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 7.65 (dd, $J = 13.1, 7.9$ Hz, 2H), 7.20 (dd, $J = 7.8, 3.7$ Hz, 2H), 4.60 (dq, $J = 12.6, 6.3$ Hz, 2H), 2.61 (q, $J = 7.6$ Hz, 2H), 1.29 (d, $J = 6.2$ Hz, 6H), 1.18 (d, $J = 7.6$ Hz, 3H), 1.15 (d, $J = 6.1$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.68 (d, $J = 3.1$ Hz), 131.86 (d, $J = 10.3$ Hz), 127.86 (d, $J = 15.3$ Hz), 125.90 (s), 70.52 (d, $J = 5.5$ Hz), 28.92 (s), 24.08 (d, $J = 3.9$ Hz), 23.84 (d, $J = 4.9$ Hz), 15.14 (s). ^{31}P NMR (162 MHz, CDCl_3) δ 17.36 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{24}\text{O}_3\text{P}^+$ 271.1458, found 271.1461.



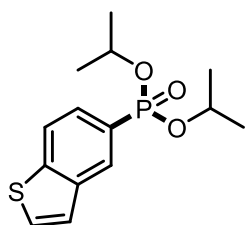
diisopropyl [1,1':3',1''-terphenyl]-5'-ylphosphonate (3p): Compound **3p** was isolated in 89% yield; flash column chromatography eluent: PE /EA (2:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 1.7$ Hz, 1H), 7.93 (d, $J = 1.7$ Hz, 1H), 7.88 (d, $J = 0.9$ Hz, 1H), 7.63 – 7.55 (m, 4H), 7.40 (t, $J = 7.5$ Hz, 4H), 7.31 (t, $J = 7.3$ Hz, 2H), 4.89 – 4.46 (m, 2H), 1.34 (d, $J = 6.2$ Hz, 6H), 1.21 (d, $J = 6.2$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.99 (d, $J = 15.5$ Hz), 140.16 (d, $J = 1.2$ Hz), 131.20 (d, $J = 187.9$ Hz), 129.68 (d, $J = 3.2$ Hz), 129.24 (d, $J = 10.3$ Hz), 128.97 (s), 127.94 (s), 127.33 (s), 71.01 (d, $J = 5.6$ Hz), 24.09 (dd, $J = 16.1, 4.4$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 16.54 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{28}\text{O}_3\text{P}^+$ 395.1771, found 395.1776.



diisopropyl pyren-4-ylphosphonate (3q): Compound **3q** was isolated in 31% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.78 (d, $J = 9.3$ Hz, 1H), 8.64 (dd, $J = 14.4, 7.9$ Hz, 1H), 8.16 (ddd, $J = 20.4, 16.2, 8.5$ Hz, 5H), 8.01 (dd, $J = 15.4, 8.0$ Hz, 2H), 4.81 – 4.62 (m, 2H), 1.38 (d, $J = 6.1$ Hz, 6H), 1.07 (d, $J = 6.2$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 134.46 (s), 132.70 (d, $J = 10.7$ Hz), 132.03 (d, $J = 9.5$ Hz), 131.03 (s), 130.43 (s), 129.63 (s), 128.72 (s), 127.27 (s), 126.30 (d, $J = 10.6$ Hz), 126.17 (s), 124.77 (d, $J = 14.1$ Hz), 124.25 (s), 123.97 (d, $J = 15.6$ Hz), 121.68 (s), 71.11 (d, $J = 5.1$ Hz), 24.24 (d, $J = 3.7$ Hz), 23.82 (d, $J = 4.9$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 17.40 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{24}\text{O}_3\text{P}^+$ 367.1458, found 367.1451.

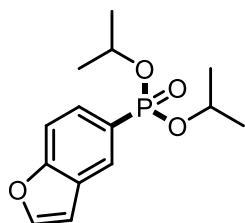


diisopropyl (1,2-dihydroacenaphthylen-5-yl)phosphonate (3r): Compound **3r** was isolated in 66% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.19 (dd, $J = 16.0, 7.1$ Hz, 1H), 8.11 (d, $J = 8.4$ Hz, 1H), 7.54 (dd, $J = 8.3, 7.0$ Hz, 1H), 7.33 (dd, $J = 11.5, 4.5$ Hz, 2H), 4.68 (ddt, $J = 12.4, 8.0, 6.2$ Hz, 2H), 3.41 (s, 4H), 1.40 (d, $J = 6.2$ Hz, 6H), 1.12 (d, $J = 6.2$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 152.22 (d, $J = 3.4$ Hz), 146.37 (d, $J = 2.1$ Hz), 139.22 (d, $J = 13.8$ Hz), 136.40 (d, $J = 11.4$ Hz), 131.18 (d, $J = 10.7$ Hz), 129.00 (s), 122.42 (d, $J = 3.0$ Hz), 121.91 (s), 120.04 (d, $J = 5.3$ Hz), 118.41 (d, $J = 16.8$ Hz), 70.59 (d, $J = 5.2$ Hz), 30.35 (d, $J = 15.6$ Hz), 24.22 (d, $J = 3.8$ Hz), 23.82 (d, $J = 5.0$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 17.49 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{24}\text{O}_3\text{P}^+$ 319.1458, found 319.1457.

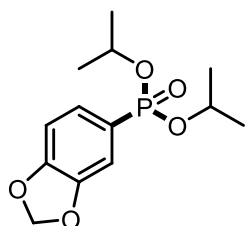


diisopropyl benzo[b]thiophen-5-ylphosphonate (3s): Compound **3s** was isolated in 74% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.34 (d, $J = 14.5$ Hz, 1H), 7.94 (dd, $J = 8.3, 3.4$ Hz, 1H), 7.71 (ddd, $J = 8.3, 3.4, 1.5$ Hz, 1H), 7.54 (dd, $J = 8.3, 7.0$ Hz, 1H), 7.33 (dd, $J = 11.5, 4.5$ Hz, 2H), 4.68 (ddt, $J = 12.4, 8.0, 6.2$ Hz, 2H), 3.41 (s, 4H), 1.40 (d, $J = 6.2$ Hz, 6H), 1.12 (d, $J = 6.2$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 152.22 (d, $J = 3.4$ Hz), 146.37 (d, $J = 2.1$ Hz), 139.22 (d, $J = 13.8$ Hz), 136.40 (d, $J = 11.4$ Hz), 131.18 (d, $J = 10.7$ Hz), 129.00 (s), 122.42 (d, $J = 3.0$ Hz), 121.91 (s), 120.04 (d, $J = 5.3$ Hz), 118.41 (d, $J = 16.8$ Hz), 70.59 (d, $J = 5.2$ Hz), 30.35 (d, $J = 15.6$ Hz), 24.22 (d, $J = 3.8$ Hz), 23.82 (d, $J = 5.0$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 17.49 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{24}\text{O}_3\text{P}^+$ 319.1458, found 319.1457.

= 11.9, 8.3, 1.0 Hz, 1H), 7.51 (d, $J = 5.4$ Hz, 1H), 7.40 (d, $J = 5.5$ Hz, 1H), 4.81 – 4.30 (m, 2H), 1.38 (d, $J = 6.2$ Hz, 7H), 1.21 (t, $J = 4.5$ Hz, 7H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.34 (d, $J = 3.2$ Hz), 139.09 (d, $J = 17.1$ Hz), 128.09 (d, $J = 10.9$ Hz), 127.57 (s), 126.26 (d, $J = 11.0$ Hz), 125.60 (d, $J = 190.9$ Hz), 124.17 (d, $J = 1.3$ Hz), 122.59 (d, $J = 15.9$ Hz), 70.73 (d, $J = 5.4$ Hz), 24.11 (d, $J = 3.9$ Hz), 23.88 (d, $J = 4.9$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 17.56 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{20}\text{O}_3\text{P}^+$ 299.0856, found 299.0856.

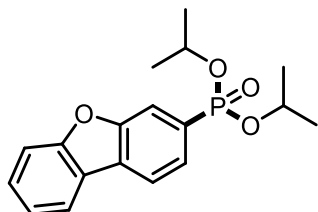


diisopropyl benzofuran-5-ylphosphonate (3t): Compound **3t** was isolated in 80% yield; flash column chromatography eluent: PE /EA (2:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 8.15 (dd, $J = 13.8, 0.7$ Hz, 1H), 7.74 (ddd, $J = 12.4, 8.5, 1.4$ Hz, 1H), 7.69 (d, $J = 2.2$ Hz, 1H), 7.57 (dd, $J = 8.5, 3.0$ Hz, 1H), 6.95 – 6.74 (m, 1H), 4.85 – 4.56 (m, 2H), 1.39 (d, $J = 6.2$ Hz, 6H), 1.22 (d, $J = 6.2$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.88 (d, $J = 3.3$ Hz), 146.04 (s), 127.67 (d, $J = 11.8$ Hz), 127.41 (d, $J = 18.6$ Hz), 126.17 (d, $J = 11.5$ Hz), 124.20 (d, $J = 190.7$ Hz), 111.60 (d, $J = 16.5$ Hz), 106.85 (d, $J = 1.4$ Hz), 70.63 (d, $J = 5.4$ Hz), 24.10 (d, $J = 3.9$ Hz), 23.87 (d, $J = 4.9$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 17.72 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{20}\text{O}_4\text{P}^+$ 283.1094, found 283.1093.

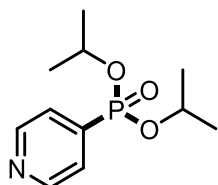


diisopropyl benzo[d][1,3]dioxol-5-ylphosphonate (3u): Compound **3u** was isolated in 86% yield; flash column chromatography eluent: PE /EA (2:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 7.38 (ddd, $J = 14.0, 7.9, 1.4$ Hz, 1H), 7.20 (dd, $J = 12.9, 1.3$ Hz, 1H), 6.86 (dd, $J = 7.9, 3.6$ Hz, 1H), 6.01 (s, 2H), 4.80 – 4.48 (m, 2H), 1.36 (d, $J = 6.2$ Hz, 6H), 1.22 (d, $J = 6.2$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.88 (d, $J = 3.4$ Hz), 147.67 (d, $J = 22.5$ Hz), 127.31 (d, $J = 11.1$ Hz), 123.01 (d, $J = 194.0$ Hz), 111.25 (d, $J = 12.1$ Hz), 108.41 (d, $J = 18.6$ Hz), 101.50 (s), 70.64 (d, $J = 5.5$ Hz), 24.06 (d, $J = 4.0$

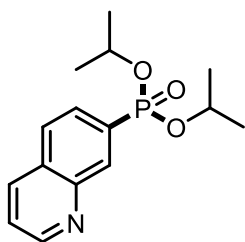
Hz), 23.83 (d, $J = 4.9$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 16.72 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{20}\text{O}_5\text{P}^+$ 287.1043, found 287.1043.



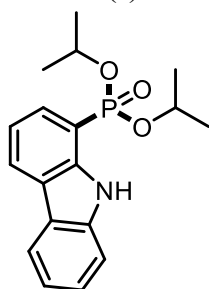
diisopropyl dibenzo[b,d]furan-3-ylphosphonate (3v): Compound **3v** was isolated in 86% yield; flash column chromatography eluent: PE /EA (2:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 8.10 – 8.01 (m, 2H), 7.98 (d, $J = 7.7$ Hz, 1H), 7.82 (dd, $J = 12.6, 7.9$ Hz, 1H), 7.60 (d, $J = 8.3$ Hz, 1H), 7.56 – 7.46 (m, 1H), 7.37 (td, $J = 7.8, 1.0$ Hz, 1H), 4.92 – 4.55 (m, 2H), 1.41 (d, $J = 6.2$ Hz, 6H), 1.25 (d, $J = 6.2$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.99 (s), 155.42 (d, $J = 22.2$ Hz), 129.50 (s), 128.45 (s), 128.17 – 126.88 (m), 125.96 (d, $J = 10.3$ Hz), 123.33 (s), 123.12 (s), 121.26 (s), 120.69 (d, $J = 17.5$ Hz), 115.32 (d, $J = 11.2$ Hz), 111.97 (s), 70.98 (d, $J = 5.5$ Hz), 24.11 (d, $J = 4.0$ Hz), 23.86 (d, $J = 4.8$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 16.48 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{22}\text{O}_4\text{P}^+$ 333.1250, found 333.1253.



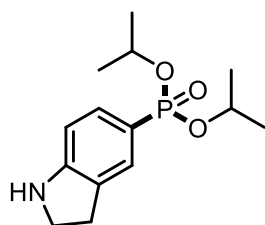
diisopropyl pyridin-4-ylphosphonate (3w): Compound **3w** was isolated in 94% yield; flash column chromatography eluent: PE /EA (1:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 8.74 (t, $J = 4.6$ Hz, 2H), 7.65 (dd, $J = 13.4, 5.4$ Hz, 2H), 4.73 (dq, $J = 12.5, 6.2$ Hz, 2H), 1.38 (d, $J = 6.2$ Hz, 6H), 1.24 (d, $J = 6.2$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 149.95 (d, $J = 12.3$ Hz), 139.02 (d, $J = 186.5$ Hz), 125.22 (d, $J = 8.1$ Hz), 71.65 (d, $J = 5.8$ Hz), 24.03 (d, $J = 4.1$ Hz), 23.82 (d, $J = 4.8$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 12.36 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{19}\text{NO}_3\text{P}^+$ 244.1097, found 244.1105.



diisopropyl quinolin-7-ylphosphonate (3x): Compound **3x** was isolated in 48% yield; flash column chromatography eluent: PE /EA (1:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.89 (dd, $J = 5.7, 3.8$ Hz, 1H), 8.66 – 8.39 (m, 1H), 8.19 – 8.01 (m, 1H), 7.81 (dd, $J = 9.2, 5.6$ Hz, 2H), 7.38 (dt, $J = 7.7, 4.6$ Hz, 1H), 4.94 – 4.45 (m, 2H), 1.30 (dd, $J = 8.6, 3.8$ Hz, 6H), 1.16 (dd, $J = 8.6, 3.8$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 151.32 (s), 147.24 (d, $J = 19.1$ Hz), 135.85 (s), 134.40 (d, $J = 9.3$ Hz), 131.32 (d, $J = 188.1$ Hz), 129.93 (d, $J = 2.7$ Hz), 128.14 (d, $J = 15.2$ Hz), 127.53 (d, $J = 9.9$ Hz), 122.74 (s), 71.08 (d, $J = 5.7$ Hz), 24.02 (d, $J = 4.0$ Hz), 23.83 (d, $J = 4.8$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 15.07 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{21}\text{NO}_3\text{P}^+$ 294.1254, found 294.1255.

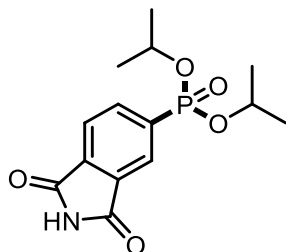


diisopropyl (9H-carbazol-1-yl)phosphonate (3y): Compound **3y** was isolated in 63% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.05 (s, 1H), 8.24 (d, $J = 7.7$ Hz, 1H), 8.09 (d, $J = 7.8$ Hz, 1H), 7.67 (dd, $J = 14.2, 7.4$ Hz, 1H), 7.47 (ddd, $J = 11.9, 9.2, 4.6$ Hz, 2H), 7.35 – 7.14 (m, 2H), 4.86 – 4.53 (m, 2H), 1.41 (d, $J = 6.2$ Hz, 6H), 1.19 (d, $J = 6.2$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 141.92 (d, $J = 7.7$ Hz), 139.68 (s), 128.93 (d, $J = 6.8$ Hz), 126.58 (s), 124.51 (d, $J = 3.1$ Hz), 123.79 (d, $J = 11.5$ Hz), 122.42 (s), 120.40 (s), 119.65 (s), 118.67 (d, $J = 13.7$ Hz), 71.14 (d, $J = 4.9$ Hz), 24.15 (d, $J = 3.8$ Hz), 23.76 (d, $J = 5.1$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 17.53 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2\text{P}^+$ 311.0944, found 311.0944.

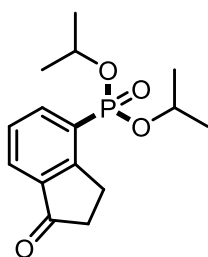


diisopropyl indolin-5-ylphosphonate (3z): Compound **3z** was isolated in 51% yield; flash column chromatography eluent: PE /EA (1:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.28 (dd, $J = 8.1, 3.3$ Hz, 1H), 7.65 (d, $J = 12.7$ Hz, 2H), 4.64 (tt, $J = 7.3, 3.6$ Hz, 2H), 4.28 (t, $J = 8.2$ Hz, 2H), 3.18 (t, $J = 8.2$ Hz, 2H), 1.38 (d, $J = 1.0$ Hz, 14H), 1.21 (d, $J = 6.2$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 177.14 (s), 148.13 (d, $J = 3.4$ Hz), 131.86

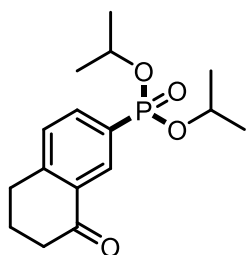
(d, $J = 10.8$ Hz), 130.96 (d, $J = 16.4$ Hz), 127.79 (d, $J = 11.1$ Hz), 124.16 (d, $J = 191.9$ Hz), 117.84 (d, $J = 15.6$ Hz), 70.52 (d, $J = 5.4$ Hz), 49.68 (s), 40.38 (s), 27.60 (s), 24.06 (d, $J = 3.9$ Hz), 23.84 (d, $J = 4.8$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 17.36 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{23}\text{NO}_3\text{P}^+$ 332.1410, found 332.1410.



diisopropyl (1,3-dioxoisindolin-5-yl)phosphonate (3A): Compound **3A** was isolated in 90% yield; flash column chromatography eluent: PE /EA (2:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 9.07 (s, 1H), 8.20 (t, $J = 10.6$ Hz, 2H), 7.88 (d, $J = 5.1$ Hz, 1H), 4.73 (d, $J = 5.7$ Hz, 2H), 1.34 (d, $J = 5.2$ Hz, 6H), 1.19 (d, $J = 5.1$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.62 (s), 137.70 (d, $J = 11.3$ Hz), 137.32 (d, $J = 189.9$ Hz), 135.45 (s), 132.59 (d, $J = 16.1$ Hz), 126.56 (d, $J = 10.3$ Hz), 123.41 (d, $J = 15.4$ Hz), 72.01 (d, $J = 5.9$ Hz), 24.04 (d, $J = 4.1$ Hz), 23.90 (d, $J = 4.6$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 12.68 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_5\text{P}^+$ 312.0995, found 312.0999.

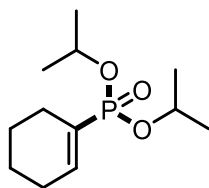


diisopropyl (1-oxo-2,3-dihydro-1H-inden-4-yl)phosphonate (3B): Compound **3B** was isolated in 86% yield; flash column chromatography eluent: PE /EA (2:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 8.05 (dd, $J = 13.8, 7.3$ Hz, 1H), 7.84 (d, $J = 7.6$ Hz, 1H), 7.52 – 7.37 (m, 1H), 4.71 (dq, $J = 12.5, 6.2$ Hz, 2H), 3.40 – 3.21 (m, 2H), 2.79 – 2.50 (m, 2H), 1.33 (d, $J = 6.2$ Hz, 6H), 1.18 (d, $J = 6.2$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 206.30 (s), 157.80 (d, $J = 9.9$ Hz), 138.68 (d, $J = 11.0$ Hz), 137.62 (d, $J = 12.5$ Hz), 129.32 (s), 127.45 (d, $J = 3.4$ Hz), 127.25 (d, $J = 13.9$ Hz), 71.17 (d, $J = 5.9$ Hz), 36.00 (s), 26.28 (d, $J = 2.1$ Hz), 24.10 (d, $J = 4.1$ Hz), 23.88 (d, $J = 4.6$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 13.93 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{22}\text{O}_4\text{P}^+$ 297.1250, found 297.1254.

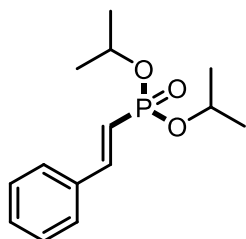


diisopropyl (8-oxo-5,6,7,8-tetrahydronaphthalen-2-yl)phosphonate (3C):

Compound **3C** was isolated in 92% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.35 (dd, $J = 13.9, 1.0$ Hz, 1H), 7.84 (ddd, $J = 12.5, 7.8, 1.5$ Hz, 1H), 7.38 – 7.20 (m, 1H), 4.69 – 4.51 (m, 2H), 2.92 (t, $J = 6.0$ Hz, 2H), 2.65 – 2.53 (m, 2H), 2.13 – 2.01 (m, 2H), 1.28 (d, $J = 6.2$ Hz, 6H), 1.14 (d, $J = 6.2$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 197.26 (s), 148.22 (d, $J = 2.9$ Hz), 136.02 (d, $J = 10.8$ Hz), 132.43 (d, $J = 14.2$ Hz), 130.76 (d, $J = 10.6$ Hz), 129.05 (d, $J = 14.4$ Hz), 128.83 (d, $J = 192.9$ Hz), 70.96 (d, $J = 5.7$ Hz), 39.03 (s), 29.79 (s), 24.03 (d, $J = 4.0$ Hz), 23.86 (d, $J = 4.8$ Hz), 22.83 (s). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 15.35 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{24}\text{O}_4\text{P}^+$ 311.1407, found 311.1409.

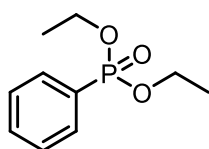


diisopropyl cyclohex-1-en-1-ylphosphonate (3D): Compound **3D** was isolated in 87% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.87 – 6.57 (m, 1H), 4.56 (tt, $J = 13.9, 6.2$ Hz, 2H), 2.09 (s, 4H), 1.56 (d, $J = 4.7$ Hz, 4H), 1.26 (d, $J = 6.2$ Hz, 6H), 1.21 (d, $J = 6.2$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 142.46 (d, $J = 9.3$ Hz), 128.78 (d, $J = 181.9$ Hz), 69.89 (d, $J = 5.7$ Hz), 25.94 (d, $J = 18.2$ Hz), 24.29 (d, $J = 8.9$ Hz), 24.09 (d, $J = 3.9$ Hz), 23.87 (d, $J = 4.7$ Hz), 21.99 (d, $J = 10.0$ Hz), 21.43 (d, $J = 1.4$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 18.12 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{24}\text{O}_3\text{P}^+$ 247.1458, found 247.1458.

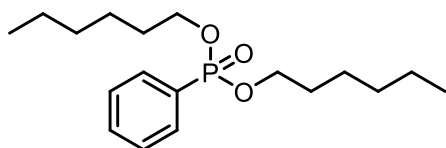


diisopropyl (E)-styrylphosphonate (3E): Compound **3E** was isolated in 58% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3)

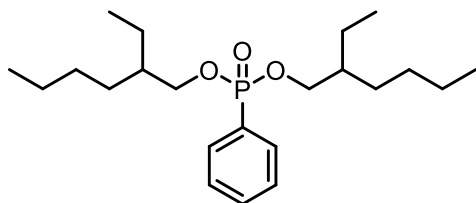
δ 7.57 – 7.43 (m, 3H), 7.42 – 7.33 (m, 3H), 6.28 (t, J = 17.4 Hz, 1H), 4.72 (dq, J = 12.5, 6.2 Hz, 2H), 1.37 (d, J = 6.2 Hz, 6H), 1.32 (d, J = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.80 (d, J = 6.7 Hz), 135.01 (d, J = 23.3 Hz), 130.06 (s), 128.23 (d, J = 118.6 Hz), 115.57 (d, J = 191.9 Hz), 70.46 (d, J = 5.6 Hz), 24.10 (d, J = 4.1 Hz), 24.01 (d, J = 4.7 Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 17.32 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{22}\text{O}_3\text{P}^+$ 269.1301, found 269.1298.



diethyl phenylphosphonate (4a): Compound **4a** was isolated in 93% yield; flash column chromatography eluent: PE /EA (2:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 7.82 – 7.64 (m, 2H), 7.54 – 7.44 (m, 1H), 7.39 (td, J = 7.4, 4.3 Hz, 2H), 4.18 – 3.89 (m, 4H), 1.25 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 131.35 (d, J = 3.0 Hz), 130.75 (d, J = 9.9 Hz), 127.45 (d, J = 15.0 Hz), 127.39 (d, J = 188.9 Hz), 61.09 (d, J = 5.4 Hz), 15.31 (d, J = 6.5 Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 18.81 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{16}\text{O}_3\text{P}^+$ 215.0832, found 215.0839.

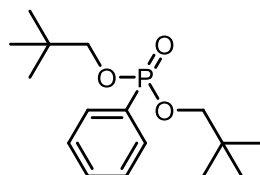


dihexyl phenylphosphonate (4b): Compound **4b** was isolated in 90% yield; flash column chromatography eluent: PE /EA (2:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 7.73 (dd, J = 13.2, 7.9 Hz, 2H), 7.48 (dd, J = 10.1, 4.5 Hz, 1H), 7.39 (dd, J = 6.9, 3.7 Hz, 2H), 4.15 – 3.78 (m, 4H), 1.79 – 1.47 (m, 4H), 1.22 (dt, J = 19.3, 11.3 Hz, 12H), 0.79 (t, J = 6.3 Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 132.30 (d, J = 2.9 Hz), 131.76 (d, J = 9.8 Hz), 128.41 (d, J = 15.0 Hz), 128.351 (d, J = 188.9 Hz), 66.13 (d, J = 5.7 Hz), 31.28 (s), 30.37 (d, J = 6.5 Hz), 25.16 (s), 22.49 (s), 13.94 (s). ^{31}P NMR (162 MHz, CDCl_3) δ 18.78 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{32}\text{O}_3\text{P}^+$ 327.2084, found 327.2080.

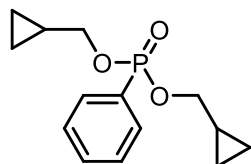


bis(2-ethylhexyl) phenylphosphonate (4c): Compound **4c** was isolated in 86% yield; flash column chromatography eluent: PE /EA (2:1, v/v); ^1H NMR (400 MHz, Chloroform-

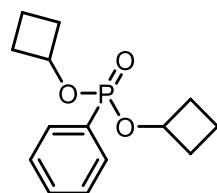
δ 7.80 (dd, $J = 13.3, 7.4$ Hz, 2H), 7.55 (t, $J = 7.5$ Hz, 1H), 7.46 (td, $J = 7.3, 4.0$ Hz, 2H), 4.05 – 3.95 (m, 2H), 3.90 (ddd, $J = 13.2, 10.4, 5.8$ Hz, 2H), 1.56 (p, $J = 6.0$ Hz, 2H), 1.41 – 1.13 (m, 16H), 0.86 (dt, $J = 7.6, 3.8$ Hz, 12H). ^{13}C NMR (101 MHz, Chloroform- d) δ 132.24 (d, $J = 3.0$ Hz), 131.76 (d, $J = 9.7$ Hz), 128.33 (d, $J = 188.9$ Hz), 128.37 (d, $J = 15.0$ Hz), 68.00 (dd, $J = 6.1, 1.8$ Hz), 40.14 (dd, $J = 6.9, 2.2$ Hz), 29.93, 28.82 (d, $J = 4.9$ Hz), 23.31, 22.94, 14.00, 10.88 (d, $J = 1.7$ Hz). ^{31}P NMR (162 MHz, Chloroform- d) δ 18.71. **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{40}\text{O}_3\text{P}^+$ 383.2710, found 383.2706.



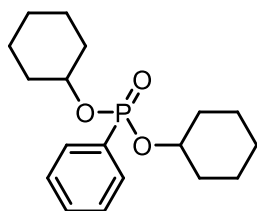
dineopentyl phenylphosphonate (4d): Compound **4d** was isolated in 87% yield; flash column chromatography eluent: PE /EA (2:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 7.88 – 7.77 (m, 2H), 7.61 – 7.51 (m, 1H), 7.51 – 7.42 (m, 2H), 4.00 – 3.41 (m, 4H), 0.94 (d, $J = 2.0$ Hz, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 132.27 (d, $J = 3.0$ Hz), 131.76 (d, $J = 9.6$ Hz), 128.38 (d, $J = 15.0$ Hz), 128.10 (d, $J = 189.9$ Hz), 75.19 (d, $J = 6.4$ Hz), 32.14 (d, $J = 7.3$ Hz), 26.08 (s). ^{31}P NMR (162 MHz, CDCl_3) δ 18.43 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{28}\text{O}_3\text{P}^+$ 299.1771, found 299.1769.



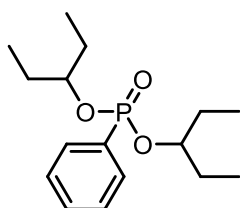
bis(cyclopropylmethyl) phenylphosphonate (4e): Compound **4e** was isolated in 81% yield; flash column chromatography eluent: PE /EA (2:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 7.85 (dd, $J = 13.2, 7.6$ Hz, 2H), 7.55 (d, $J = 7.4$ Hz, 1H), 7.52 – 7.38 (m, 2H), 4.27 – 3.40 (m, 4H), 1.22 – 1.09 (m, 2H), 0.74 – 0.38 (m, 4H), 0.28 (dt, $J = 14.2, 10.1$ Hz, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 132.27 (d, $J = 3.0$ Hz), 131.85 (d, $J = 9.9$ Hz), 128.37 (d, $J = 15.0$ Hz), 128.68 (d, $J = 188.9$ Hz), 70.94 (d, $J = 5.4$ Hz), 11.37 (d, $J = 7.0$ Hz), 3.43 (d, $J = 13.9$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 18.77 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{20}\text{O}_3\text{P}^+$ 267.1145, found 267.1144.



dicyclobutyl phenylphosphonate (4f): Compound **4f** was isolated in 84% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.79 (dd, $J = 13.3, 7.0$ Hz, 2H), 7.61 – 7.50 (m, 1H), 7.45 (dt, $J = 11.5, 5.8$ Hz, 2H), 4.74 (dt, $J = 14.5, 7.1$ Hz, 2H), 2.39 – 2.08 (m, 8H), 1.72 (dd, $J = 19.8, 10.0$ Hz, 2H), 1.58 – 1.37 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 132.27 (d, $J = 3.0$ Hz), 131.68 (d, $J = 10.0$ Hz), 129.04 (d, $J = 186.9$ Hz), 128.35 (d, $J = 15.0$ Hz), 69.77 (d, $J = 7.2$ Hz), 32.07 (d, $J = 4.7$ Hz), 31.82 (d, $J = 5.1$ Hz), 12.66 (s). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 15.48 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{20}\text{O}_3\text{P}^+$ 267.1145, found 267.1143.

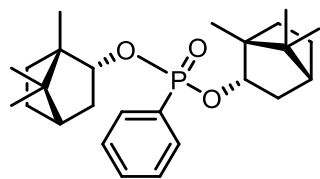


dicyclohexyl phenylphosphonate (4g): Compound **4g** was isolated in 89% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.75 (dd, $J = 13.3, 7.1$ Hz, 2H), 7.44 (t, $J = 6.9$ Hz, 1H), 7.36 (dt, $J = 11.4, 5.8$ Hz, 2H), 4.47 – 4.00 (m, 2H), 2.02 – 1.80 (m, 2H), 1.77 – 1.49 (m, 8H), 1.39 (dd, $J = 13.2, 6.7$ Hz, 4H), 1.22 (ddt, $J = 27.3, 19.7, 6.1$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 131.93 (d, $J = 3.0$ Hz), 131.63 (d, $J = 9.8$ Hz), 130.31 (d, $J = 189.4$ Hz), 128.22 (d, $J = 15.0$ Hz), 75.53 (d, $J = 5.9$ Hz), 33.64 (dd, $J = 24.1, 3.9$ Hz), 25.17 (s), 23.61 (d, $J = 7.6$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 16.60 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{28}\text{O}_3\text{P}^+$ 323.1771, found 323.1771.

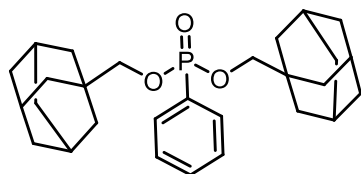


di(pentan-3-yl) phenylphosphonate (4h): Compound **4h** was isolated in 87% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.91 – 7.76 (m, 2H), 7.52 (dd, $J = 10.9, 3.9$ Hz, 1H), 7.44 (td, $J = 7.5, 4.5$ Hz, 2H), 4.36 (dp, $J = 8.1, 5.9$ Hz, 2H), 1.82 – 1.61 (m, 4H), 1.63 – 1.47 (m, 4H), 0.97 (t, $J = 7.4$ Hz, 6H), 0.77 (t, $J = 7.4$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 131.87 (d, $J = 3.0$ Hz), 131.70 (d, $J = 9.6$ Hz), 130.37 (d, $J = 190.9$ Hz), 128.16 (d, $J = 15.0$ Hz), 80.04 (d, $J = 6.3$ Hz), 27.46 (d, $J = 3.7$ Hz), 27.16 (d, $J = 4.4$ Hz), 9.19 (d, $J = 10.1$ Hz). $^{31}\text{P NMR}$

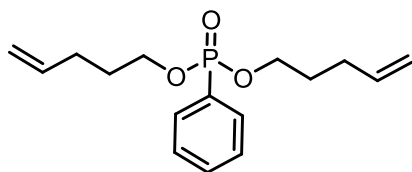
(162 MHz, CDCl₃) δ 18.76 (s). **HRMS (ESI):** [M+H]⁺ calcd for C₁₈H₂₈O₃P⁺ 299.1771, found 299.1773.



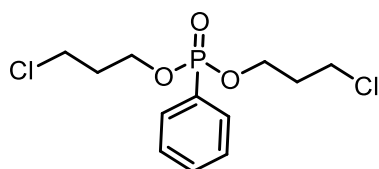
(1R,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl ((1S,2R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl) phenylphosphonate (4i): Compound **4i** was isolated in 63% yield; flash column chromatography eluent: PE /EA (2:1, v/v); **¹H NMR** (400 MHz, CDCl₃) δ 7.82 (dd, J = 13.2, 7.2 Hz, 2H), 7.52 (t, J = 7.0 Hz, 1H), 7.45 (dd, J = 11.4, 7.2 Hz, 2H), 4.59 (dd, J = 42.1, 34.8 Hz, 2H), 2.41 – 2.26 (m, 1H), 2.17 (ddd, J = 17.8, 9.2, 4.6 Hz, 1H), 2.07 – 1.87 (m, 2H), 1.70 (ddd, J = 13.1, 8.5, 4.1 Hz, 3H), 1.61 (d, J = 3.7 Hz, 1H), 1.40 – 1.15 (m, 6H), 1.14 – 0.98 (m, 2H), 0.93 (s, 3H), 0.85 (d, J = 8.0 Hz, 12H), 0.73 (d, J = 8.6 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 131.95 (s), 131.71 (dd, J = 9.5, 3.5 Hz), 128.30 (d, J = 2.9 Hz), 128.15 (d, J = 2.9 Hz), 84.51 – 79.95 (m), 50.20 – 49.04 (m), 47.55 (dd, J = 11.6, 4.7 Hz), 44.92 (d, J = 1.9 Hz), 37.36 (d, J = 85.4 Hz), 28.76 – 27.38 (m), 26.96 – 25.89 (m), 19.10 (dd, J = 59.2, 56.7 Hz), 13.34 (d, J = 21.1 Hz). **³¹P NMR** (162 MHz, CDCl₃) δ 18.06 (t, J = 83.4 Hz). **HRMS (ESI):** [M+H]⁺ calcd for C₂₆H₄₀O₃P⁺ 431.2710, found 431.2710.



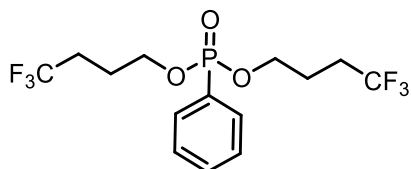
bis(adamantan-1-ylmethyl) phenylphosphonate (4j): Compound **4j** was isolated in 83% yield; flash column chromatography eluent: PE /EA (2:1, v/v); **¹H NMR** (400 MHz, CDCl₃) δ 7.81 (dd, J = 13.2, 7.9 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.51 – 7.42 (m, 2H), 3.60 (ddd, J = 32.9, 9.5, 5.2 Hz, 4H), 1.98 (s, 6H), 1.71 (d, J = 12.1 Hz, 6H), 1.63 (d, J = 12.1 Hz, 6H), 1.54 (s, 12H). **¹³C NMR** (101 MHz, CDCl₃) δ 132.21 (d, J = 3.0 Hz), 131.82 (d, J = 9.6 Hz), 128.37 (d, J = 14.9 Hz), 128.18 (d, J = 189.9 Hz), 75.49 (d, J = 6.4 Hz), 38.91 (s), 36.94 (s), 33.91 (d, J = 7.2 Hz), 27.99 (s). **³¹P NMR** (162 MHz, CDCl₃) δ 18.84 (s). **HRMS (ESI):** [M+H]⁺ calcd for C₂₈H₄₀O₃P⁺ 455.2710, found 455.2705.



di(pent-4-en-1-yl) phenylphosphonate (4k): Compound **4k** was isolated in 91% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 (dd, $J = 13.1, 7.3$ Hz, 2H), 7.56 (t, $J = 6.8$ Hz, 1H), 7.47 (d, $J = 3.9$ Hz, 2H), 5.77 (ddt, $J = 13.3, 10.1, 6.6$ Hz, 1H), 5.63 – 5.29 (m, 1H), 4.99 (t, $J = 14.0$ Hz, 2H), 4.20 – 3.85 (m, 4H), 2.51 – 2.28 (m, 1H), 2.14 (dd, $J = 14.2, 7.0$ Hz, 2H), 1.85 – 1.72 (m, 2H), 1.71 – 1.54 (m, 2H), 1.29 (dd, $J = 20.3, 6.2$ Hz, 2H), 0.88 (t, $J = 6.8$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 137.26 (s), 132.42 (s), 131.77 (d, $J = 9.8$ Hz), 128.47 (dd, $J = 15.0, 2.4$ Hz), 125.28 (d, $J = 109.9$ Hz), 115.40 (s), 65.38 (d, $J = 5.6$ Hz), 29.60 (d, $J = 2.1$ Hz), 27.61 (s). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 18.96 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{24}\text{O}_3\text{P}^+$ 295.1458, found 295.1454.

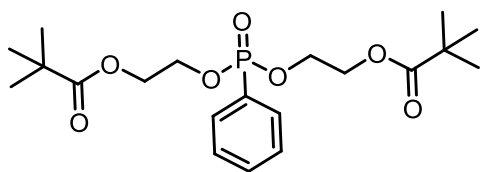


bis(3-chloropropyl) phenylphosphonate (4l): Compound **4l** was isolated in 88% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.73 (dd, $J = 13.1, 7.4$ Hz, 2H), 7.50 (d, $J = 7.4$ Hz, 1H), 7.42 (dt, $J = 11.6, 6.0$ Hz, 2H), 4.31 – 3.88 (m, 4H), 3.57 (t, $J = 6.1$ Hz, 4H), 2.05 (dd, $J = 7.5, 3.7$ Hz, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 132.79 (d, $J = 2.9$ Hz), 131.75 (d, $J = 9.9$ Hz), 128.66 (d, $J = 15.1$ Hz), 127.32 (d, $J = 188.4$ Hz), 62.67 (d, $J = 5.3$ Hz), 40.73 (s), 33.15 (d, $J = 6.7$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 19.38 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{18}\text{Cl}_2\text{O}_3\text{P}^+$ 311.0365, found 311.0366.



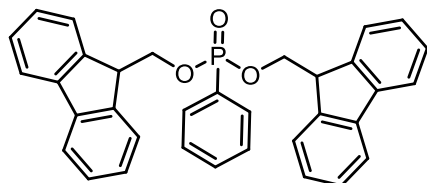
bis(4,4,4-trifluorobutyl) phenylphosphonate (4m): Compound **4m** was isolated in 57% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.88 – 7.74 (m, 2H), 7.62 (td, $J = 7.5, 1.3$ Hz, 1H), 7.51 (td, $J = 7.5, 4.4$ Hz, 2H), 4.27 – 3.96 (m, 4H), 2.35 – 2.10 (m, 4H), 2.05 – 1.85 (m, 4H). $^{13}\text{C NMR}$ (101

MHz, CDCl₃) δ 132.96 (d, *J* = 3.1 Hz), 131.73 (d, *J* = 10.0 Hz), 128.75 (d, *J* = 15.1 Hz), 64.32 (d, *J* = 5.2 Hz), 30.29 (q, *J* = 29.4 Hz), 23.27 (dd, *J* = 6.7, 3.2 Hz). ³¹P NMR (162 MHz, CDCl₃) δ 19.66 (s). ¹⁹F NMR (376 MHz, CDCl₃) δ -66.29 (s). **HRMS (ESI):** [M+H]⁺ calcd for C₁₄H₁₈F₆O₃P⁺ 379.0892, found 379.0889.

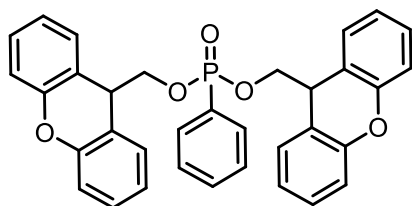


((phenylphosphoryl)bis(oxy))bis(ethane-2,1-diyl) bis(2,2-dimethylpropanoate)

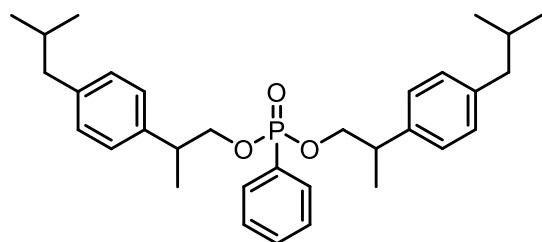
(4n): Compound **4n** was isolated in 80% yield; flash column chromatography eluent: PE /EA (2:1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 7.81 (dd, *J* = 13.5, 7.2 Hz, 2H), 7.58 (dd, *J* = 10.7, 4.0 Hz, 1H), 7.48 (dd, *J* = 11.7, 7.4 Hz, 2H), 4.38 – 4.06 (m, 8H), 1.18 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 178.19 (s), 132.82 (d, *J* = 3.0 Hz), 131.78 (d, *J* = 10.1 Hz), 128.59 (d, *J* = 15.3 Hz), 127.23 (d, *J* = 190.4 Hz), 63.77 (d, *J* = 5.4 Hz), 62.97 (d, *J* = 7.3 Hz), 38.71 (s), 27.08 (s). ³¹P NMR (162 MHz, CDCl₃) δ 19.60 (s). **HRMS (ESI):** [M+Na]⁺ calcd for C₂₀H₃₂O₇P⁺ 415.1880., found 415.1878.



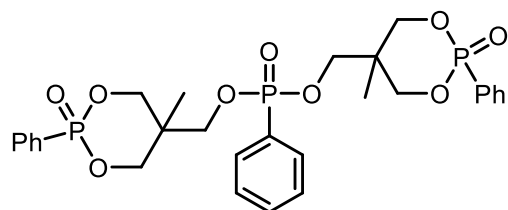
bis((9H-fluoren-9-yl)methyl) phenylphosphonate (4o): Compound **4o** was isolated in 85% yield; flash column chromatography eluent: PE /EA (2:1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 7.57 (dd, *J* = 17.4, 8.4 Hz, 6H), 7.39 (dd, *J* = 13.1, 8.2 Hz, 5H), 7.32 – 7.17 (m, 6H), 7.12 (td, *J* = 7.0, 4.1 Hz, 4H), 4.22 (dt, *J* = 12.7, 6.5 Hz, 2H), 4.16 – 4.07 (m, 2H), 4.02 (t, *J* = 6.5 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 143.34 (d, *J* = 1.5 Hz), 141.42 (d, *J* = 3.0 Hz), 132.65 (d, *J* = 2.9 Hz), 131.79 (d, *J* = 10.0 Hz), 128.62 (d, *J* = 15.2 Hz), 127.86 (d, *J* = 1.8 Hz), 127.12 (d, *J* = 2.5 Hz), 125.19 (d, *J* = 10.6 Hz), 120.03 (d, *J* = 4.3 Hz), 67.66 (d, *J* = 5.9 Hz), 48.14 (d, *J* = 7.3 Hz). ³¹P NMR (162 MHz, CDCl₃) δ 18.94 (s). **HRMS (ESI):** [M+H]⁺ calcd for C₃₄H₂₈O₃P⁺ 515.1771, found 515.1776.



bis((9H-xanthen-9-yl)methyl) phenylphosphonate (4p): Compound **4p** was isolated in 78% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.47 – 7.37 (m, 1H), 7.35 – 7.13 (m, 10H), 7.12 – 6.92 (m, 10H), 4.11 (t, $J = 6.1$ Hz, 2H), 4.01 – 3.75 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 152.22 (d, $J = 1.6$ Hz), 132.44 (d, $J = 3.1$ Hz), 131.63 (d, $J = 10.0$ Hz), 129.50 (d, $J = 10.3$ Hz), 128.53 (d, $J = 1.0$ Hz), 128.41 (d, $J = 15.2$ Hz), 126.75 (d, $J = 188.7$ Hz), 123.23 (d, $J = 4.1$ Hz), 120.81 (d, $J = 7.8$ Hz), 116.51 (d, $J = 1.4$ Hz), 70.51 (d, $J = 6.2$ Hz), 39.90 (d, $J = 7.5$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 18.67 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{34}\text{H}_{28}\text{O}_5\text{P}^+$ 547.1669, found 547.1662.

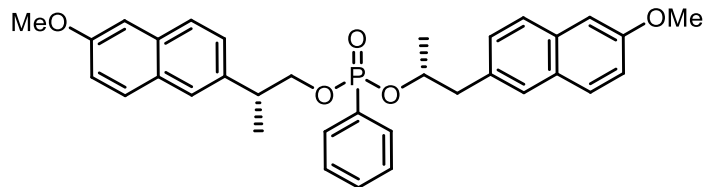


bis(2-(4-isobutylphenyl)propyl) phenylphosphonate (4q): Compound **4q** was isolated in 84% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.66 – 7.52 (m, 2H), 7.52 – 7.43 (m, 1H), 7.42 – 7.30 (m, 2H), 7.14 – 6.98 (m, 8H), 4.21 – 3.81 (m, 4H), 3.13 – 2.95 (m, 2H), 2.43 (d, $J = 7.1$ Hz, 4H), 1.83 (dp, $J = 13.4, 6.7$ Hz, 2H), 1.26 (t, $J = 6.2$ Hz, 6H), 0.89 (d, $J = 6.6$ Hz, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 140.07 (s), 139.85 (d, $J = 3.6$ Hz), 132.30 (s), 131.77 (d, $J = 9.9$ Hz), 129.18 (s), 128.35 (d, $J = 15.1$ Hz), 127.17 (s), 70.84 (dt, $J = 9.7, 6.4$ Hz), 45.07 (s), 41.59 – 38.21 (m), 30.27 (s), 22.44 (s), 18.47 – 16.16 (m). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 18.51 (t, $J = 25.0$ Hz). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{44}\text{O}_3\text{P}^+$ 507.3023, found 507.3023.

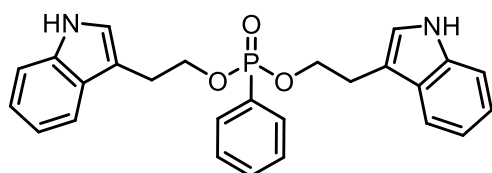


bis((5-methyl-2-oxido-2-phenyl-1,3,2-dioxaphosphinan-5-yl)methyl) phenylphosphonate (4r): Compound **4r** was isolated in 79% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.80 – 7.56 (m, 1H), 7.46 (dd, $J = 13.8, 9.4$ Hz, 1H), 7.41 – 7.24 (m, 1H), 4.31 (dt, $J = 32.5, 14.7$ Hz, 1H), 4.23 – 4.05 (m, 1H), 4.06 – 3.89 (m, 1H), 1.24 – 0.26 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ

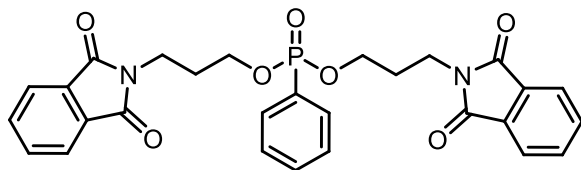
133.25 (d, $J = 21.8$ Hz), 131.77 (d, $J = 10.3$ Hz), 129.31 – 128.13 (m), 126.28 (s), 124.35 (s), 69.66 (dd, $J = 12.3, 5.9$ Hz), 66.67 (s), 36.90 (d, $J = 5.0$ Hz), 16.79 (d, $J = 68.6$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 20.30 (s), 17.36 (s). **HRMS (ESI):** $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{28}\text{H}_{33}\text{NaO}_9\text{P}_3^+$ 629.1230., found 629.1233.



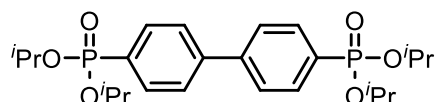
(R)-1-(6-methoxynaphthalen-2-yl)propan-2-yl ((R)-2-(6-methoxynaphthalen-2-yl)propyl) phenylphosphonate (4s): Compound **4s** was isolated in 86% yield; flash column chromatography eluent: PE /EA (2:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 7.59 (td, $J = 8.6, 2.5$ Hz, 4H), 7.55 – 7.43 (m, 4H), 7.39 (t, $J = 7.2$ Hz, 1H), 7.27 – 7.14 (m, 4H), 7.14 – 7.07 (m, 2H), 7.06 (s, 2H), 4.26 – 3.95 (m, 4H), 3.85 (s, 6H), 3.14 (td, $J = 13.7, 6.9$ Hz, 2H), 1.28 (dd, $J = 16.7, 7.0$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.47 (s), 137.84 (d, $J = 2.8$ Hz), 133.58 (s), 132.31 (d, $J = 2.9$ Hz), 131.71 (d, $J = 9.9$ Hz), 129.20 (s), 128.98 (s), 128.33 (d, $J = 15.1$ Hz), 127.79 (d, $J = 189.9$ Hz), 126.99 (d, $J = 2.0$ Hz), 126.37 (d, $J = 2.9$ Hz), 125.85 (d, $J = 7.7$ Hz), 118.88 (d, $J = 2.9$ Hz), 105.57 (s), 70.71 (d, $J = 5.1$ Hz), 55.31 (s), 40.32 (dd, $J = 6.8, 1.9$ Hz), 17.73 (d, $J = 9.2$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 18.59 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{34}\text{H}_{36}\text{O}_5\text{P}^+$ 555.2295, found 555.2287.



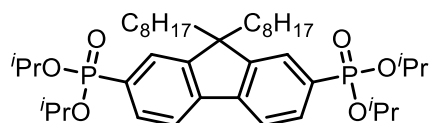
bis(2-(1H-indol-3-yl)ethyl) phenylphosphonate (4t): Compound **4t** was isolated in 44% yield; flash column chromatography eluent: PE /EA (1:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 8.35 (s, 2H), 7.80 – 7.61 (m, 2H), 7.50 (dd, $J = 12.4, 8.3$ Hz, 3H), 7.35 (td, $J = 7.6, 4.3$ Hz, 2H), 7.29 (d, $J = 8.1$ Hz, 2H), 7.14 (t, $J = 7.2$ Hz, 2H), 7.05 (dd, $J = 11.0, 3.9$ Hz, 2H), 6.85 (d, $J = 1.1$ Hz, 2H), 4.38 – 4.10 (m, 4H), 3.07 (t, $J = 7.1$ Hz, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 136.18 (s), 132.49 (d, $J = 3.0$ Hz), 131.76 (d, $J = 9.9$ Hz), 128.51 (d, $J = 15.1$ Hz), 127.36 (s), 122.60 (s), 121.92 (s), 119.29 (s), 118.59 (s), 111.29 (s), 111.03 (s), 66.09 (d, $J = 5.9$ Hz), 26.58 (d, $J = 6.7$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 19.13 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_3\text{P}^+$ 445.1676, found 445.1676.



bis(3-(1,3-dioxoisindolin-2-yl)propyl) phenylphosphonate (4u): Compound **4u** was isolated in 90% yield; flash column chromatography eluent: PE /EA (2:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.87 – 7.74 (m, 6H), 7.69 (dd, $J = 5.2, 3.1$ Hz, 4H), 7.53 (t, $J = 7.4$ Hz, 1H), 7.44 (dd, $J = 12.1, 6.9$ Hz, 2H), 4.26 – 3.99 (m, 4H), 3.91 – 3.65 (m, 4H), 2.18 – 1.94 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.15 (s), 133.91 (s), 132.52 (d, $J = 3.0$ Hz), 132.04 (s), 131.77 (d, $J = 10.0$ Hz), 128.49 (d, $J = 15.2$ Hz), 126.56 (s), 123.20 (s), 63.56 (d, $J = 5.6$ Hz), 34.81 (s), 29.38 (d, $J = 6.6$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 19.24 (s). **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{26}\text{N}_2\text{O}_7\text{P}^+$ 533.1472, found 533.1462.

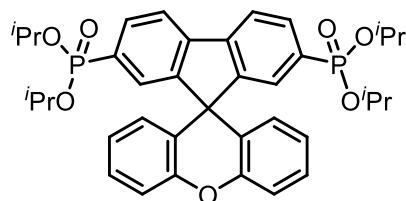


tetraisopropyl [1,1'-biphenyl]-4,4'-diylbis(phosphonate) (5a): Compound **5a** was isolated in 93% yield; flash column chromatography eluent: PE /EA (1:2, v/v); $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.83 (dd, $J = 13.0, 8.0$ Hz, 4H), 7.61 (dd, $J = 8.2, 3.7$ Hz, 4H), 4.64 (dp, $J = 7.8, 6.1$ Hz, 4H), 1.31 (d, $J = 6.2$ Hz, 12H), 1.17 (d, $J = 6.2$ Hz, 12H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 143.55 (d, $J = 3.4$ Hz), 132.30 (d, $J = 10.1$ Hz), 129.55 (d, $J = 190.1$ Hz), 127.11 (d, $J = 15.3$ Hz), 70.79 (d, $J = 5.5$ Hz), 24.05 (d, $J = 4.0$ Hz), 23.84 (d, $J = 4.8$ Hz). $^{31}\text{P NMR}$ (162 MHz, Chloroform-*d*) δ 16.28. **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{37}\text{O}_6\text{P}_2^+$ 483.2060, found 483.2058.



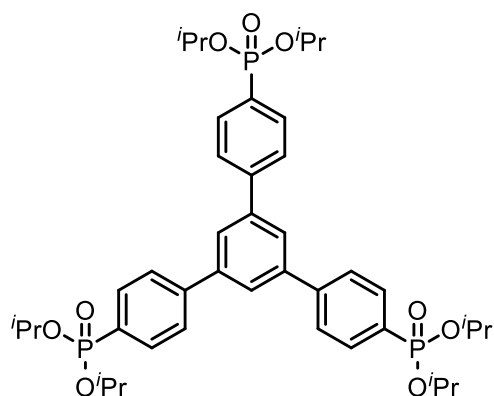
tetraisopropyl (9,9-dioctyl-9H-fluorene-2,7-diyl)bis(phosphonate) (5b): Compound **5b** was isolated in 61% yield; flash column chromatography eluent: PE /EA (1:2, v/v); $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.17 – 7.51 (m, 6H), 5.12 – 4.29 (m, 4H), 2.78 – 1.68 (m, 4H), 1.39 (d, $J = 6.2$ Hz, 12H), 1.29 – 1.15 (m, 18H), 1.04 (dddd, $J = 41.3, 14.7, 11.6, 5.3$ Hz, 18H), 0.80 (t, $J = 7.1$ Hz, 6H), 0.62 – 0.40 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 151.25 (d, $J = 15.3$ Hz), 143.71 (d, $J = 2.2$ Hz), 130.93 (d, $J = 10.7$ Hz), 129.31 (d, $J = 186.6$ Hz), 126.34 (d, $J = 10.6$ Hz), 120.35 (d, $J = 16.2$ Hz),

70.76 (d, $J = 5.4$ Hz), 55.70, 40.10, 31.70, 29.85, 29.21 (d, $J = 16.0$ Hz), 24.10 (d, $J = 4.2$ Hz), 23.83, 23.73 (d, $J = 4.6$ Hz), 22.52, 14.03. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 17.20. **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{41}\text{H}_{69}\text{O}_6\text{P}_2^+$ 719.4564, found 719.4563.



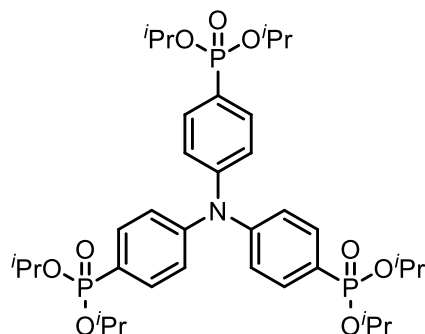
tetraisopropyl spiro[fluorene-9,9'-xanthene]-2,7-diylbis(phosphonate) (5c):

Compound **5c** was isolated in 56% yield; flash column chromatography eluent: PE /EA (1:2, v/v); ^1H NMR (400 MHz, Chloroform-*d*) δ 8.14 – 7.79 (m, 4H), 7.61 (d, $J = 13.3$ Hz, 2H), 7.20 (dt, $J = 15.3, 8.1$ Hz, 4H), 6.72 (t, $J = 7.4$ Hz, 2H), 6.29 (dd, $J = 7.9, 1.7$ Hz, 2H), 4.96 – 4.33 (m, 4H), 1.27 (dd, $J = 6.3, 1.8$ Hz, 12H), 1.05 (dd, $J = 6.3, 1.7$ Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.71 (d, $J = 15.8$ Hz), 151.24, 142.14 (d, $J = 3.1$ Hz), 131.88 (d, $J = 10.6$ Hz), 129.97, 129.41 (d, $J = 10.8$ Hz), 128.55, 127.55, 123.20, 122.81, 120.59 (d, $J = 16.1$ Hz), 117.16, 70.87 (d, $J = 5.4$ Hz), 54.37, 23.98 (d, $J = 4.0$ Hz), 23.53 (d, $J = 4.8$ Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 16.10. **HRMS (ESI):** $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{37}\text{H}_{43}\text{O}_7\text{P}_2^+$ 661.2479, found 661.2473.

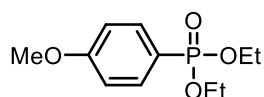


bis(propan-2-yl) {4-[3,5-bis(4-{oxo[bis(prop-2-yloxidanyl)]-λ5-phosphanyl}-phenyl)phenyl]phenyl}phosphonate (5d): Compound **5d** was isolated in 68% yield; flash column chromatography eluent: PE /EA (1:4, v/v); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.95 (dd, $J = 13.0, 7.9$ Hz, 6H), 7.85 (s, 3H), 7.79 (dd, $J = 8.1, 3.7$ Hz, 6H), 4.75 (ddtd, $J = 12.4, 7.4, 6.1, 1.2$ Hz, 6H), 1.41 (dd, $J = 6.3, 1.3$ Hz, 18H), 1.28 (d, $J = 6.3$ Hz, 18H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.17 (d, $J = 3.2$ Hz), 141.66, 132.41 (d, $J = 10.2$ Hz), 129.33 (d, $J = 190.1$ Hz), 127.21 (d, $J = 15.2$ Hz), 126.01, 70.84 (d, $J = 5.6$ Hz), 24.10 (d, $J = 4.0$ Hz), 23.90 (d, $J = 4.9$ Hz). ^{31}P NMR (162 MHz,

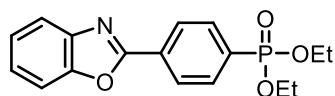
Chloroform-*d*) δ 16.33. **HRMS (ESI):** $[M+H]^+$ calcd for $C_{42}H_{58}O_9P_3^+$ 799.3288, found 799.3287.



hexaisopropyl (nitrilotris(benzene-4,1-diyl))tris(phosphonate) (5e): Compound **5e** was isolated in 62% yield; flash column chromatography eluent: PE /EA (1:4, v/v); **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.71 (ddd, $J = 11.6, 8.4, 2.5$ Hz, 6H), 7.13 (dt, $J = 8.8, 2.9$ Hz, 6H), 4.73 (qt, $J = 6.4, 2.0$ Hz, 6H), 1.39 (dd, $J = 6.5, 2.7$ Hz, 18H), 1.28 (dd, $J = 6.4, 2.6$ Hz, 18H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 149.58 (d, $J = 3.4$ Hz), 133.20 (d, $J = 10.9$ Hz), 125.77, 123.78 (d, $J = 15.6$ Hz), 70.74 (d, $J = 5.8$ Hz), 24.06 (d, $J = 4.0$ Hz), 23.91 (d, $J = 4.9$ Hz). **³¹P NMR** (162 MHz, Chloroform-*d*) δ 16.39. **HRMS (ESI):** $[M+H]^+$ calcd for $C_{36}H_{55}NO_9P_3^+$ 738.3084, found 738.3076.



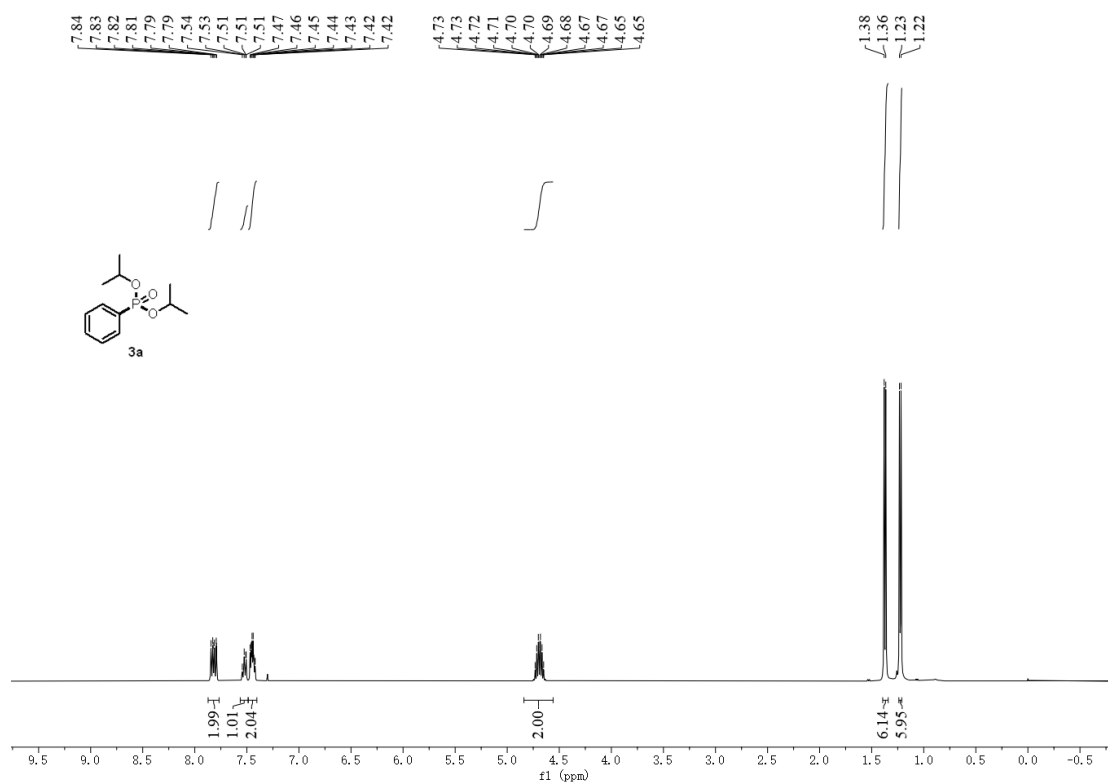
diethyl (4-methoxyphenyl)phosphonate (6): Compound **6** was isolated in 89% yield; flash column chromatography eluent: PE /EA (1:4, v/v); **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.75 (dd, $J = 12.7, 8.4$ Hz, 2H), 6.97 (dd, $J = 8.7, 3.2$ Hz, 2H), 4.41 – 3.92 (m, 4H), 3.85 (s, 3H), 1.31 (t, $J = 7.0$ Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 162.84 (d, $J = 3.3$ Hz), 133.78 (d, $J = 11.4$ Hz), 119.54 (d, $J = 194.8$ Hz), 114.00 (d, $J = 16.0$ Hz), 61.91 (d, $J = 5.2$ Hz), 55.33, 16.33 (d, $J = 6.6$ Hz). **³¹P NMR** (162 MHz, Chloroform-*d*) δ 19.74. **HRMS (ESI):** $[M+H]^+$ calcd for $C_{11}H_{18}O_4P^+$ 245.0937, found 245.0933.



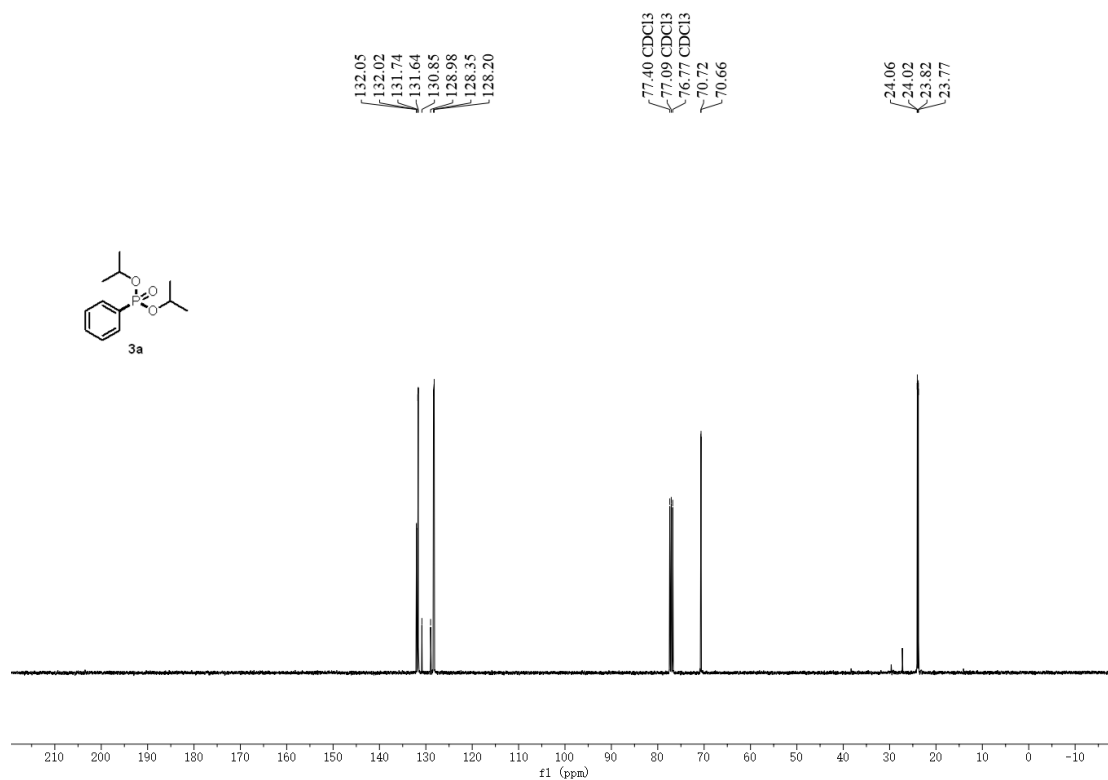
diethyl (4-(benzo[d]oxazol-2-yl)phenyl)phosphonate (7): Compound **7** was isolated in 76% yield; flash column chromatography eluent: PE /EA (1:2, v/v); **¹H NMR** (400 MHz, Chloroform-*d*) δ 8.18 (dd, $J = 8.2, 3.7$ Hz, 2H), 8.09 (d, $J = 8.2$ Hz, 1H), 8.00 – 7.82 (m, 3H), 7.57 – 7.46 (m, 1H), 7.45 – 7.35 (m, 1H), 4.87 – 3.60 (m, 4H), 1.35 (t, $J = 7.1$ Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 166.43, 154.02, 137.01 (d, $J = 3.3$ Hz), 135.17, 132.43 (d, $J = 10.2$ Hz), 130.90 (d, $J = 188.2$ Hz), 127.36 (d, $J = 15.2$ Hz), 126.58, 125.71, 123.56, 121.72, 62.34 (d, $J = 5.5$ Hz), 16.35 (d, $J = 6.3$ Hz). **³¹P NMR** (162 MHz, Chloroform-*d*) δ 17.46. **HRMS (ESI):** [M+H]⁺ calcd for C₁₇H₁₉NO₄P⁺ 332.1046, found 332.1040.

VI. NMR spectra of the products

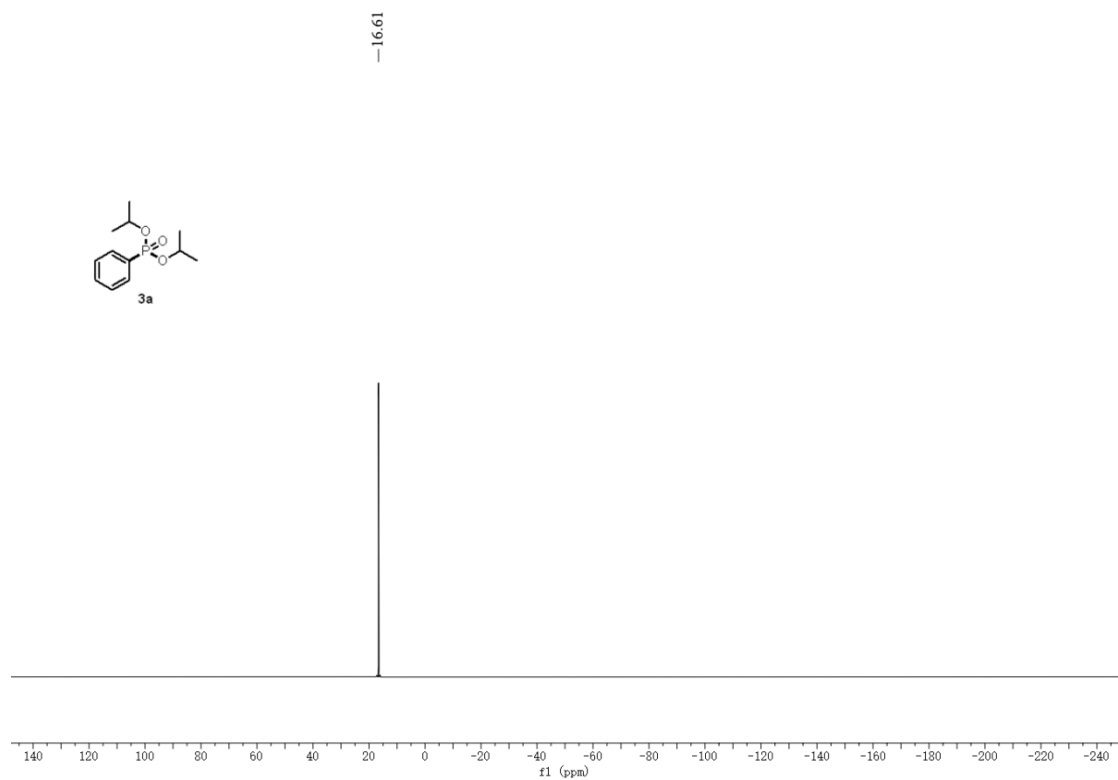
^1H NMR (400 MHz, CDCl_3) spectrum for 3a



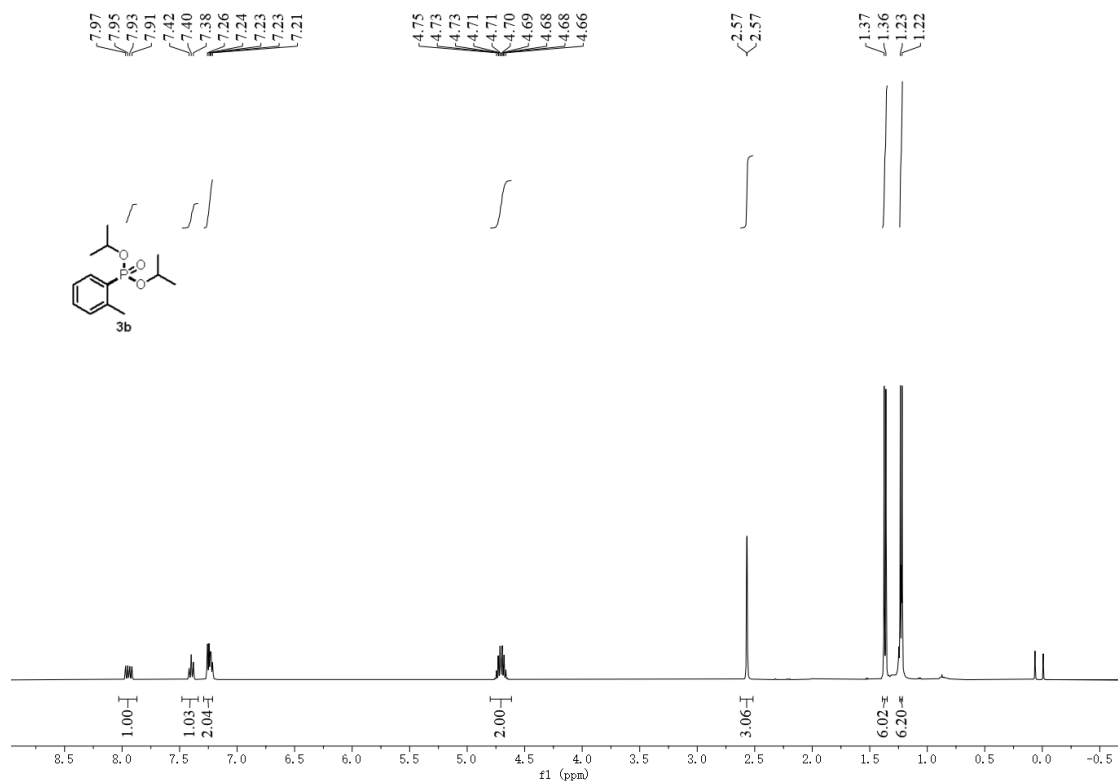
^{13}C NMR (101 MHz, CDCl_3) spectrum for 3a



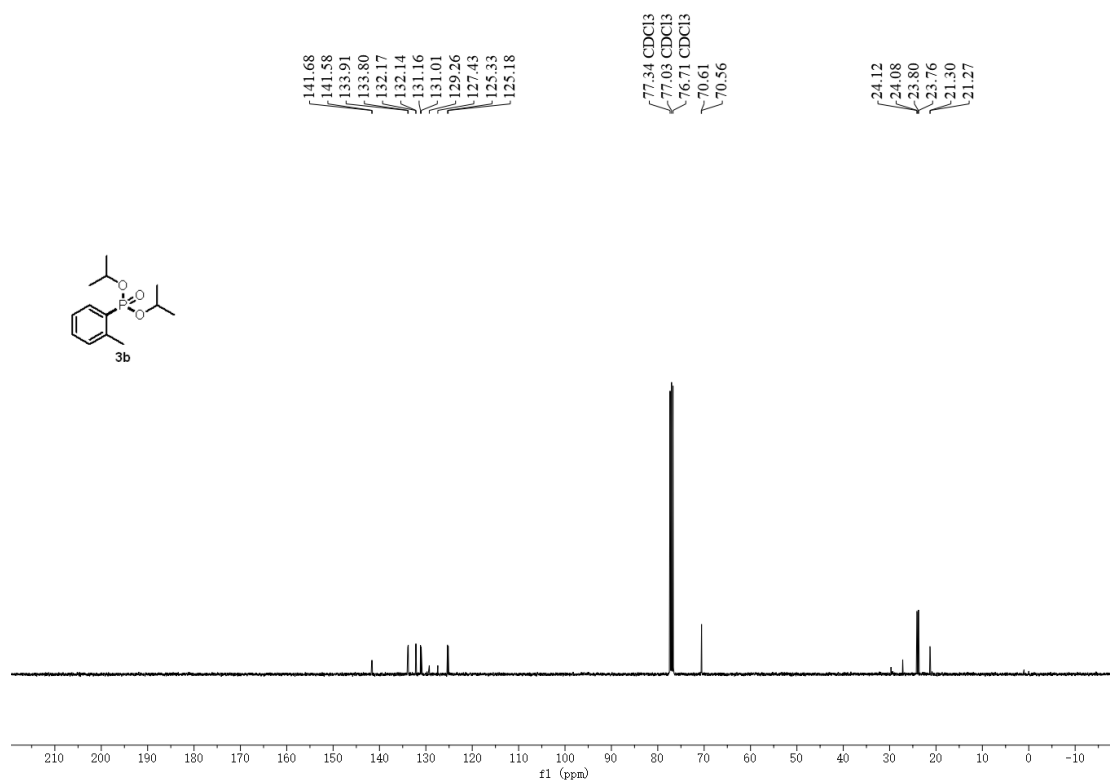
^{31}P NMR (121 MHz, CDCl_3) spectrum for 3a



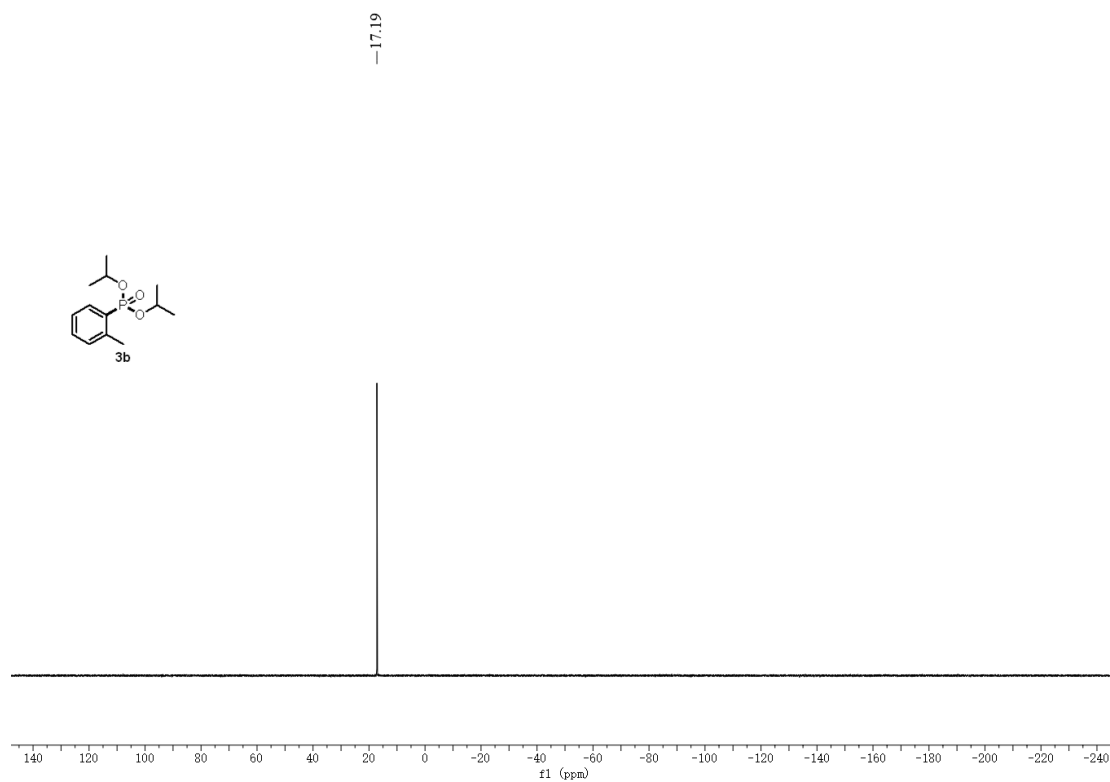
^1H NMR (400 MHz, CDCl_3) spectrum for 3b



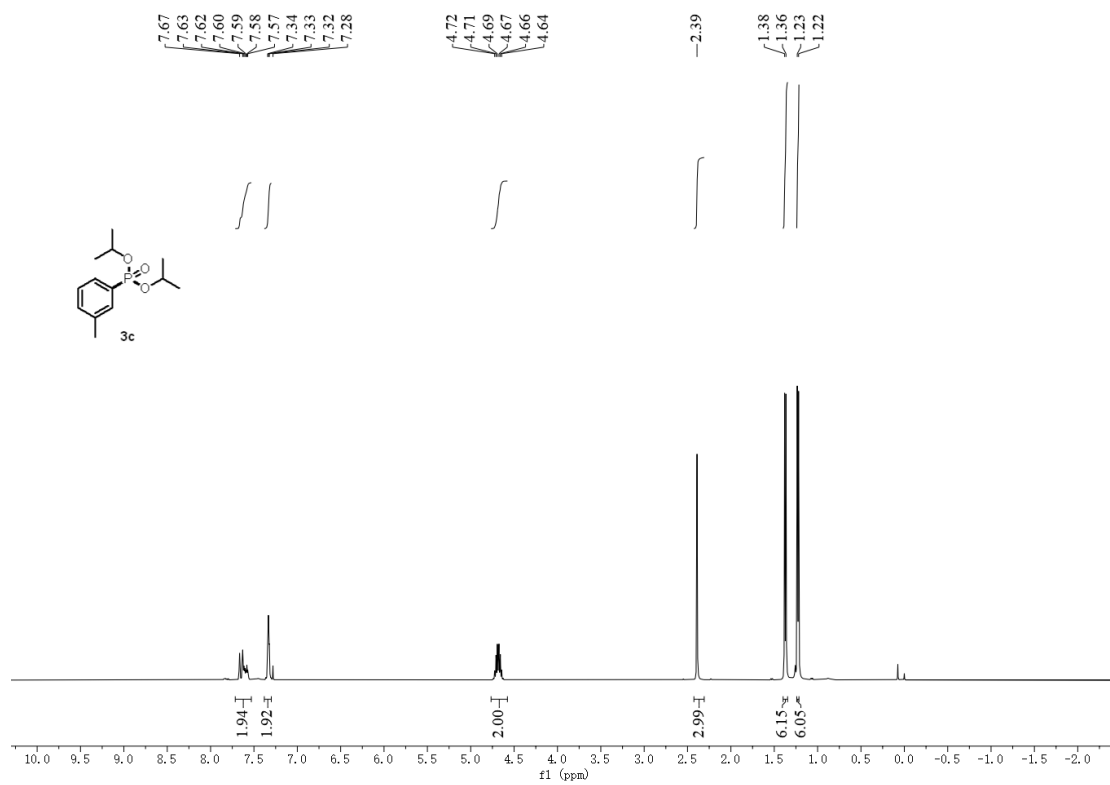
¹³C NMR (101 MHz, CDCl₃) spectrum for 3b



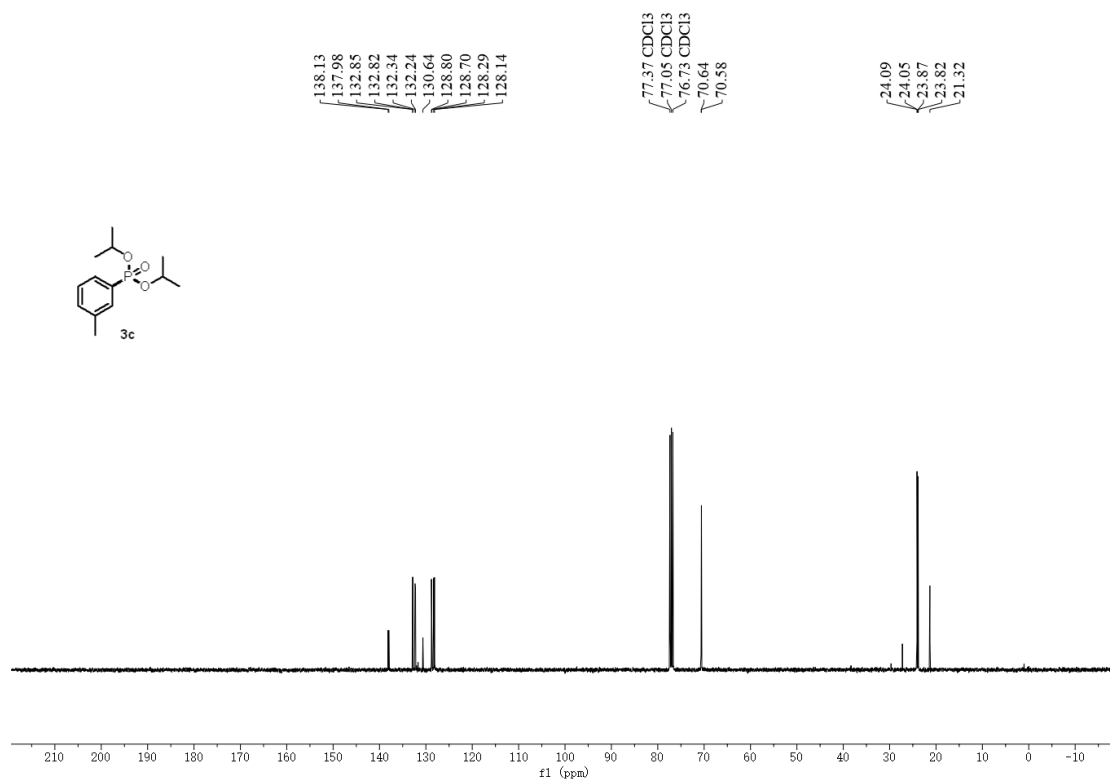
³¹P NMR (121 MHz, CDCl₃) spectrum for 3b



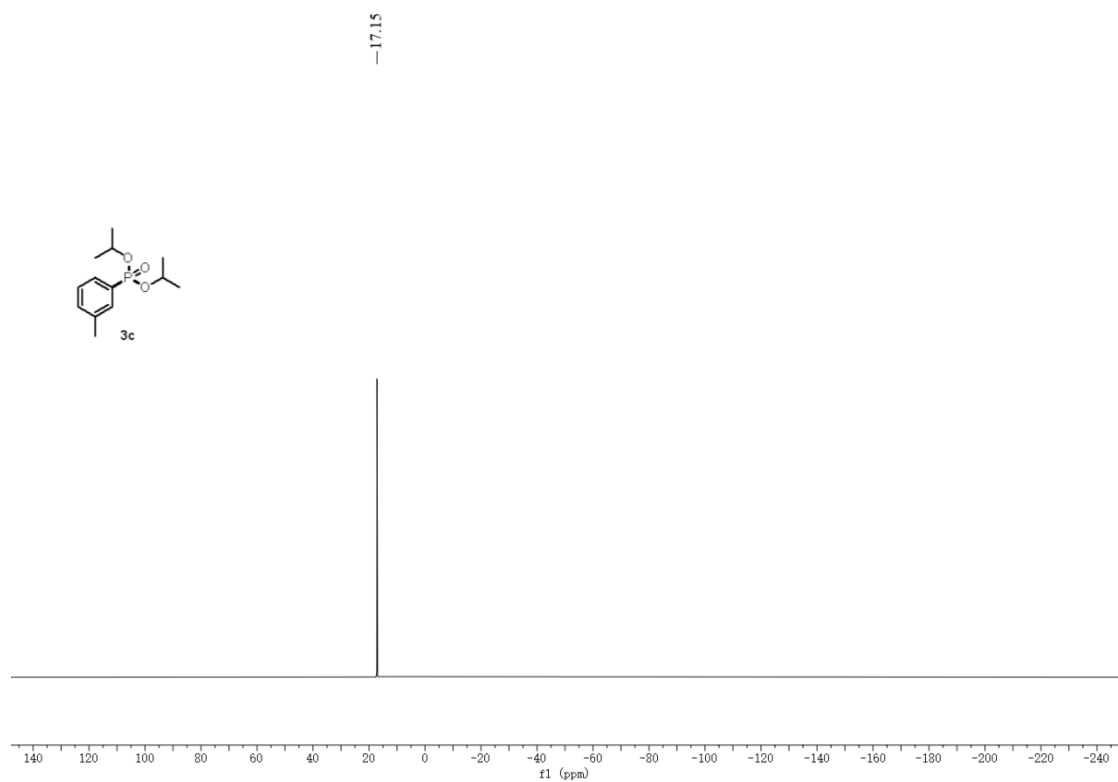
^1H NMR (400 MHz, CDCl_3) spectrum for **3c**



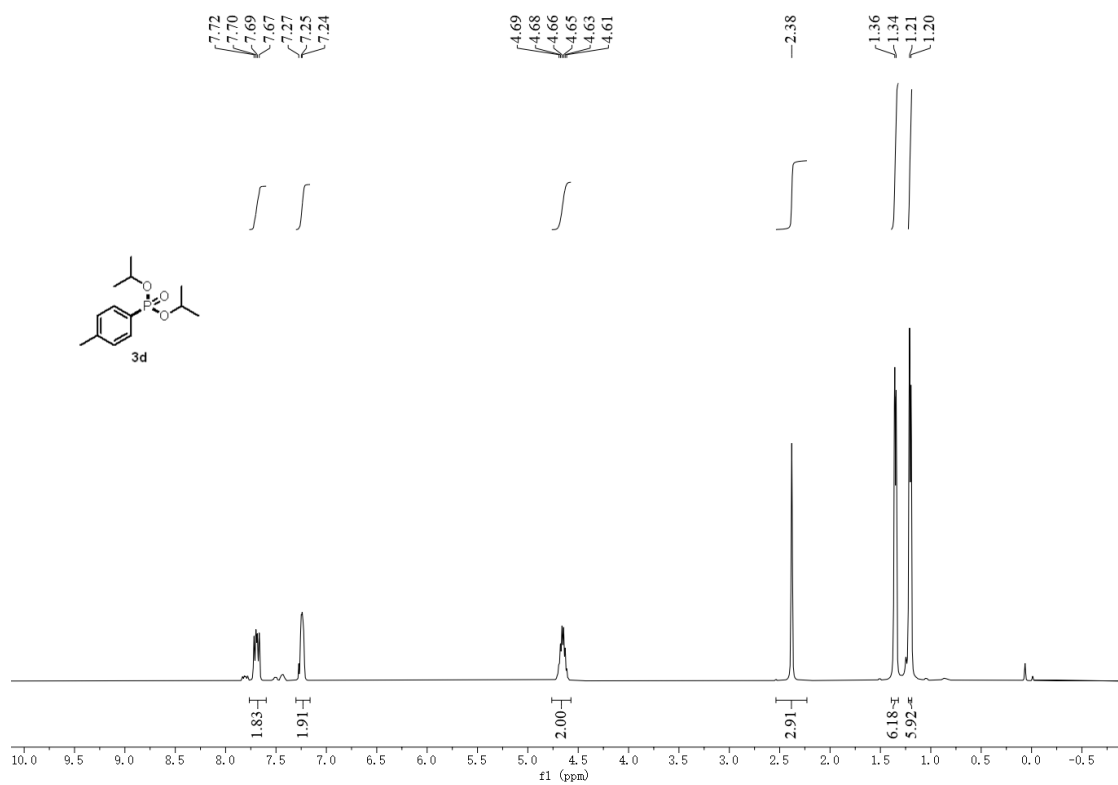
^{13}C NMR (101 MHz, CDCl_3) spectrum for **3s**



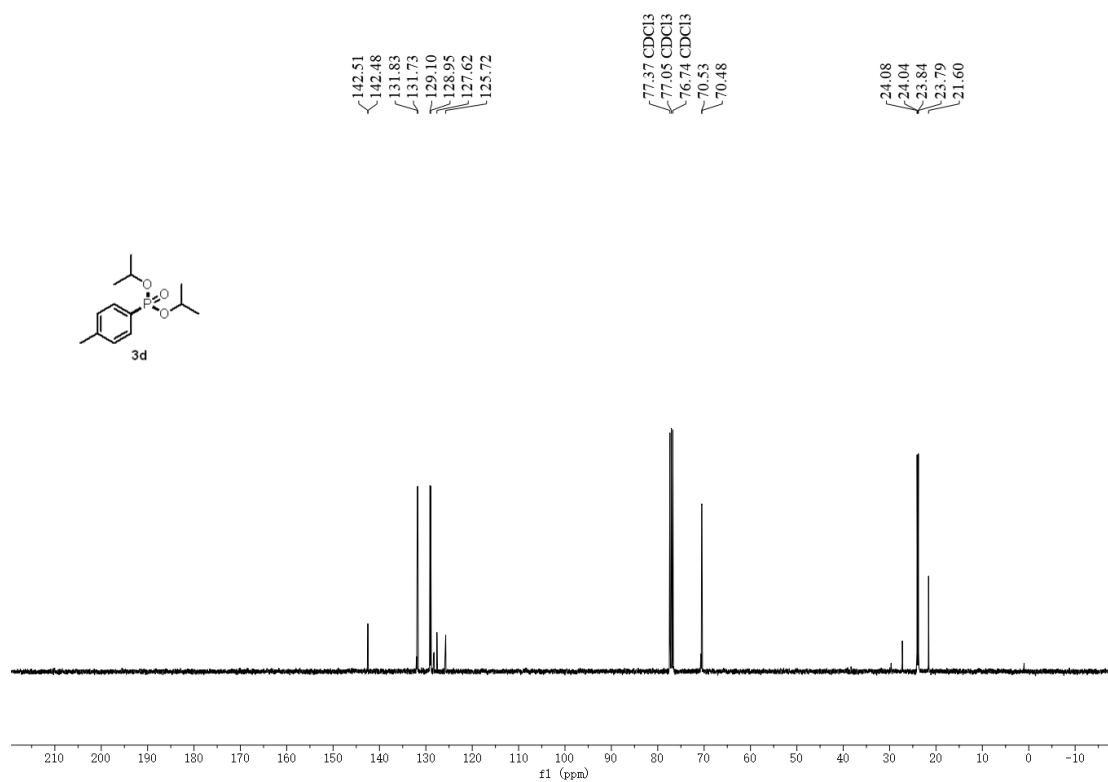
^{31}P NMR (121 MHz, CDCl_3) spectrum for 3c



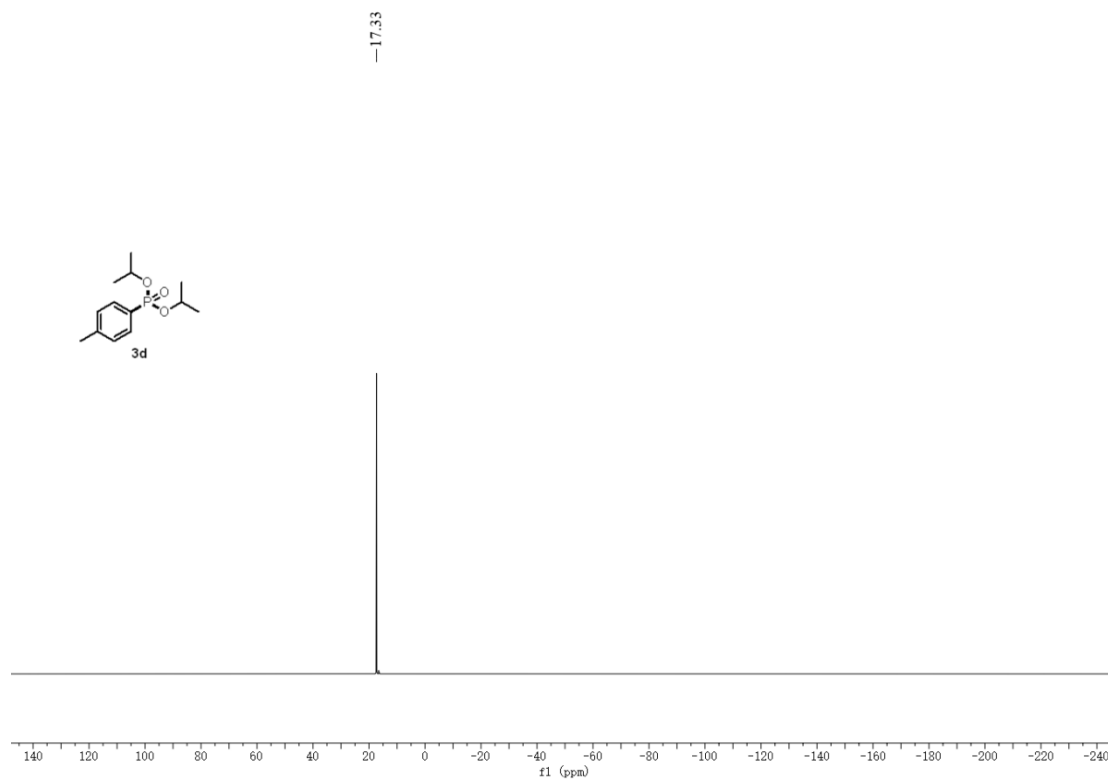
^1H NMR (400 MHz, CDCl_3) spectrum for 3d



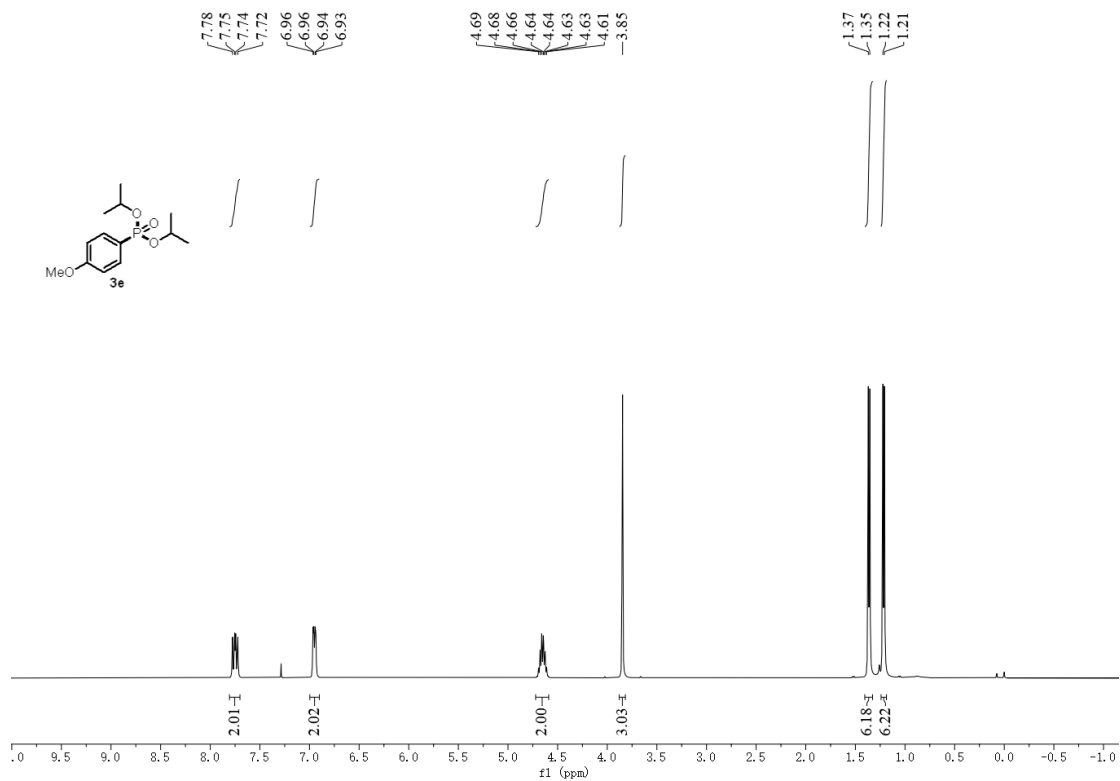
¹³C NMR (101 MHz, CDCl₃) spectrum for 3d



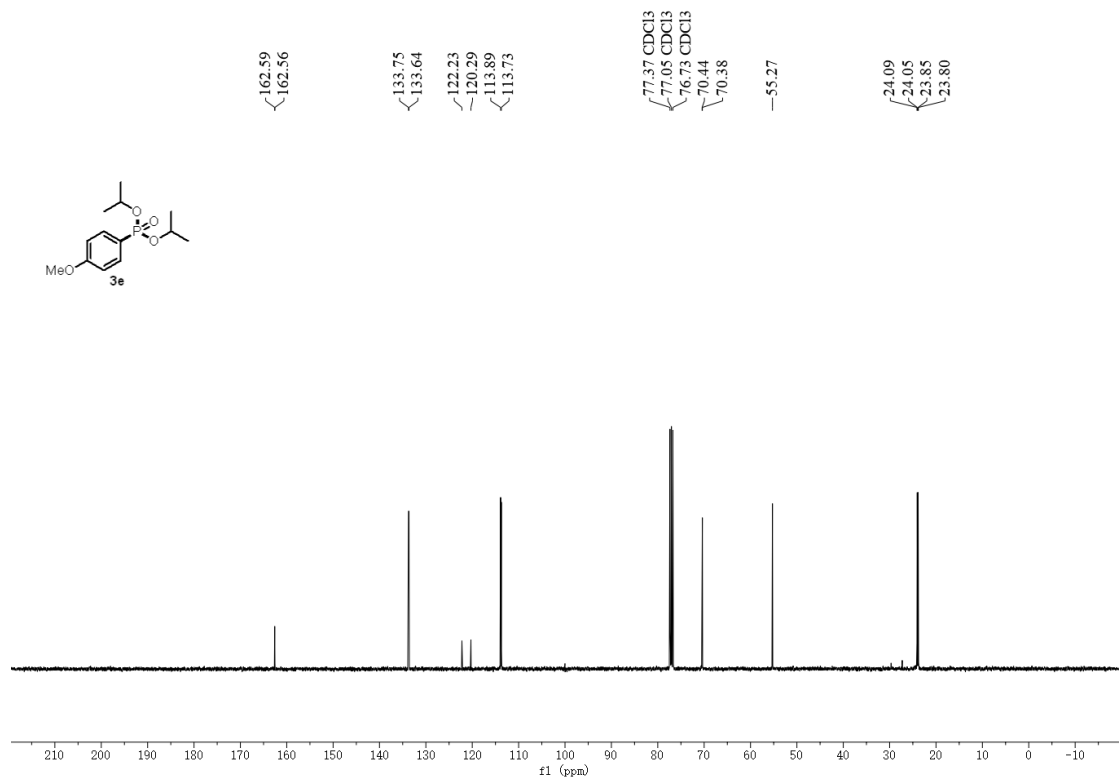
³¹P NMR (121 MHz, CDCl₃) spectrum for 3d



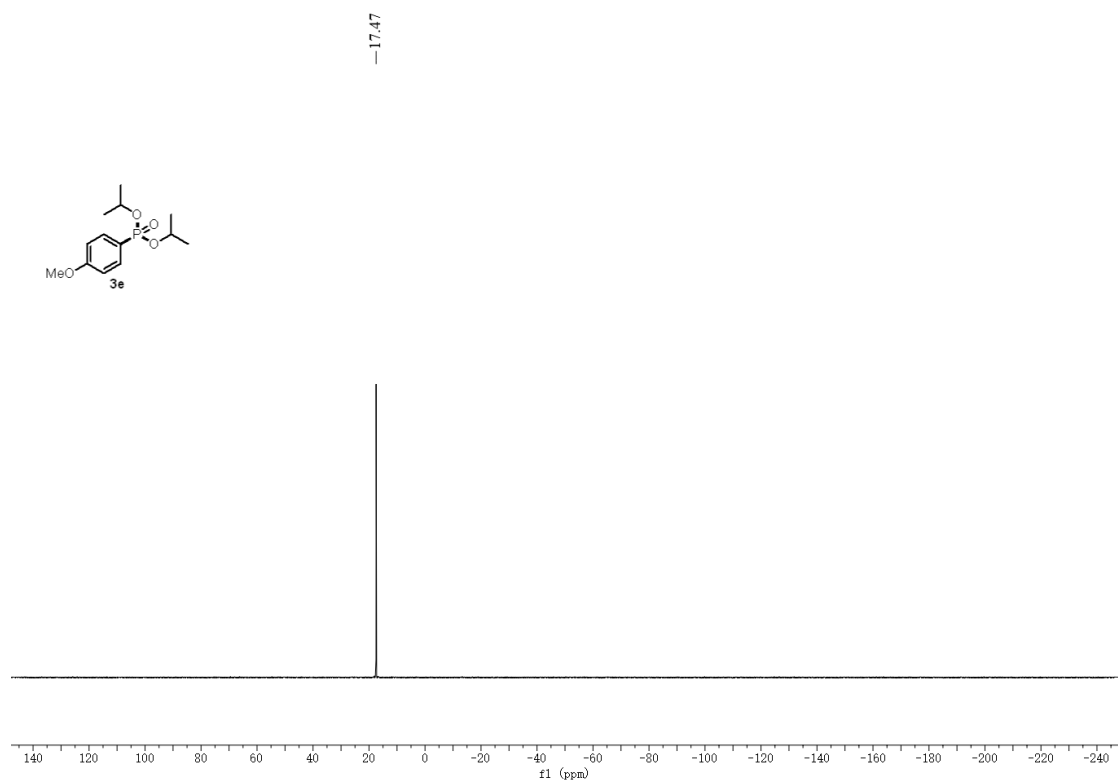
¹H NMR (400 MHz, CDCl₃) spectrum for 3e



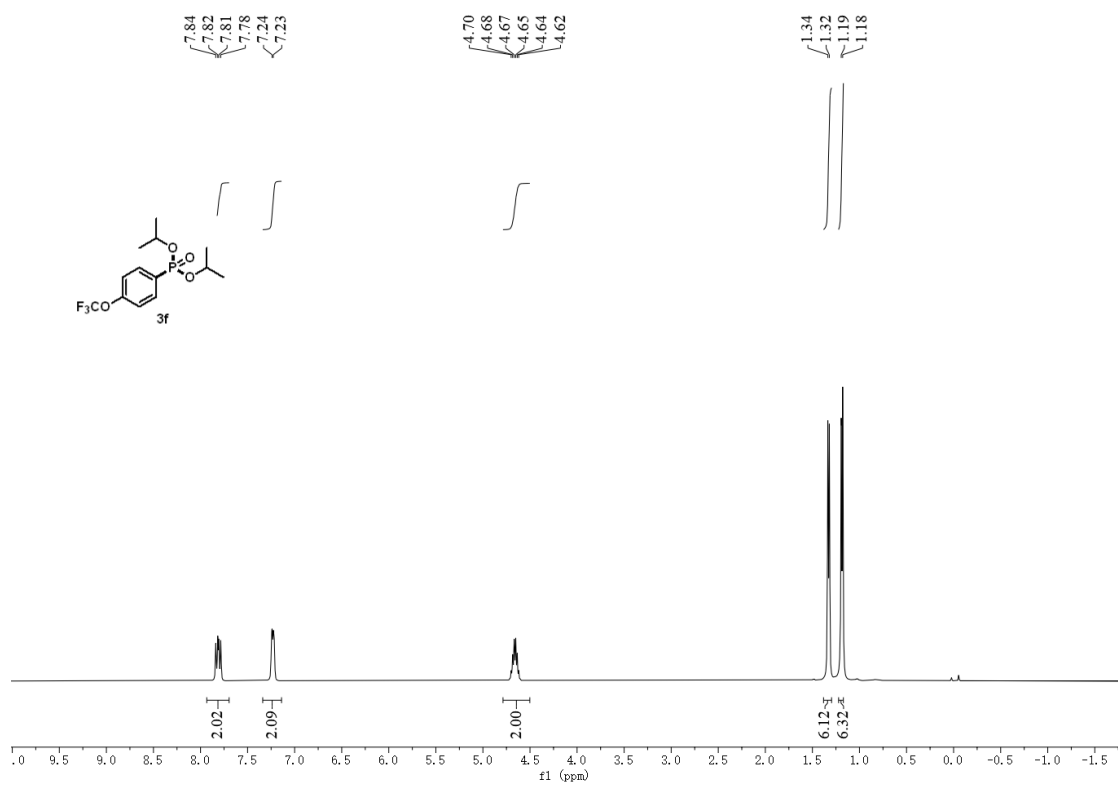
¹³C NMR (101 MHz, CDCl₃) spectrum for 3e



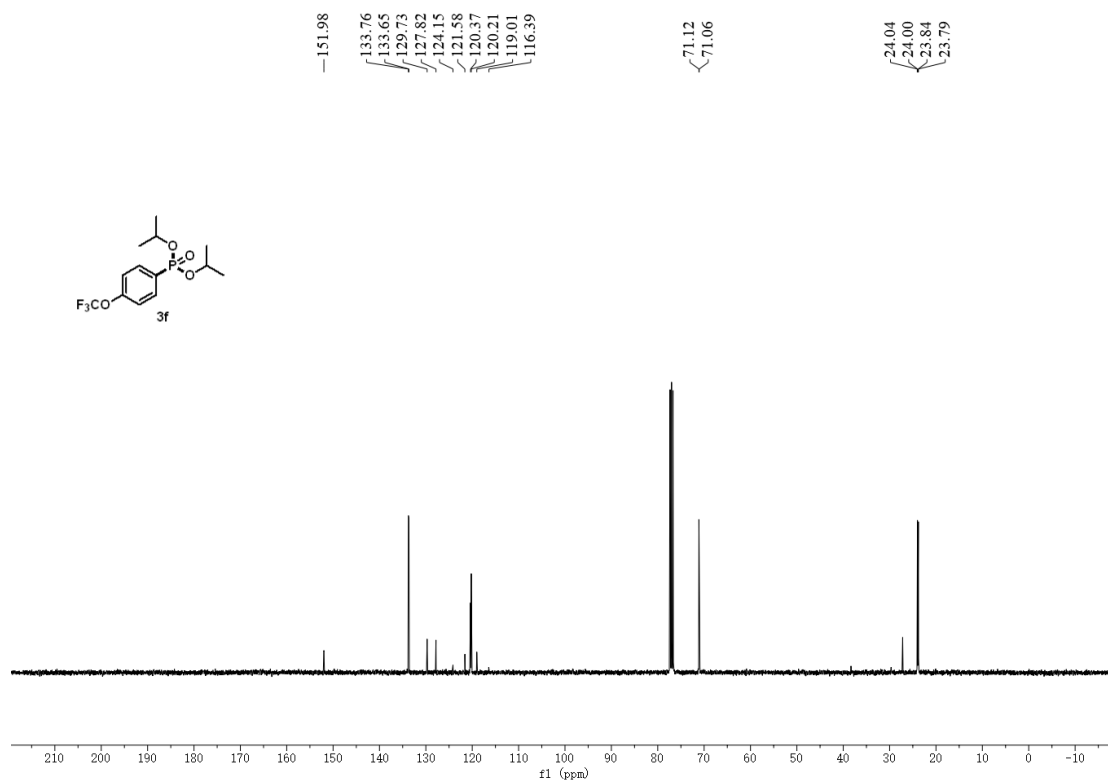
³¹P NMR (121 MHz, CDCl₃) spectrum for 3e



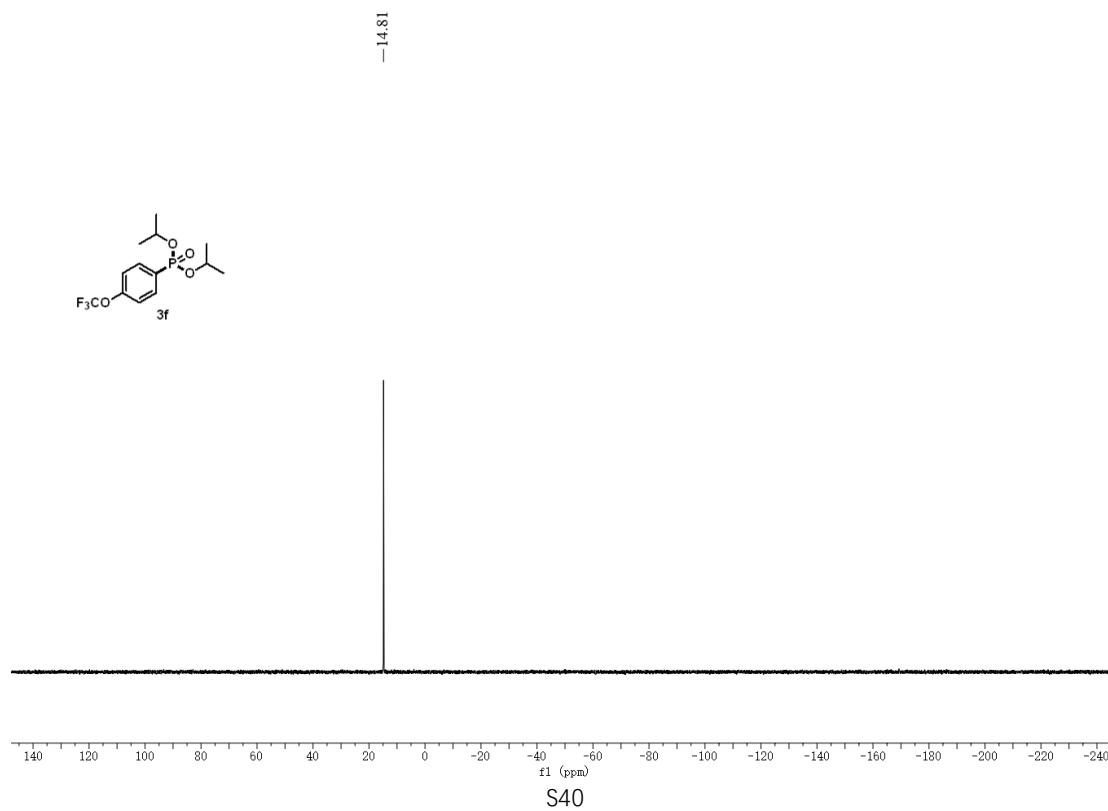
¹H NMR (400 MHz, CDCl₃) spectrum for 3f



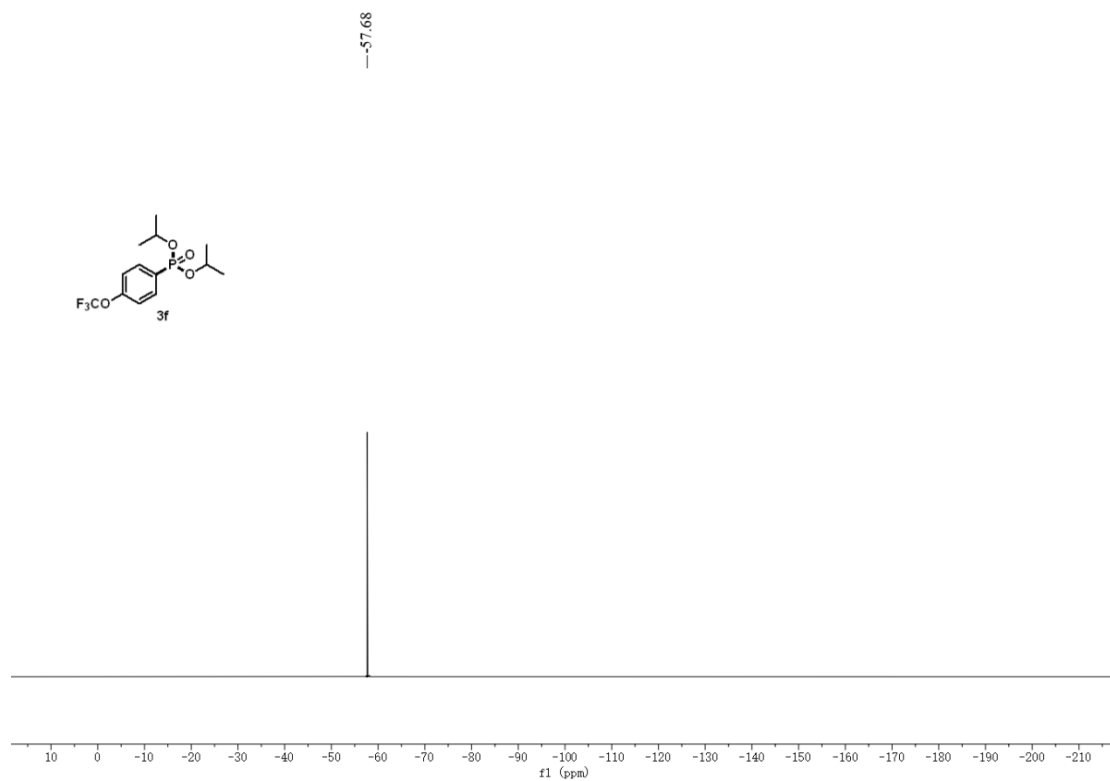
¹³C NMR (101 MHz, CDCl₃) spectrum for 3f



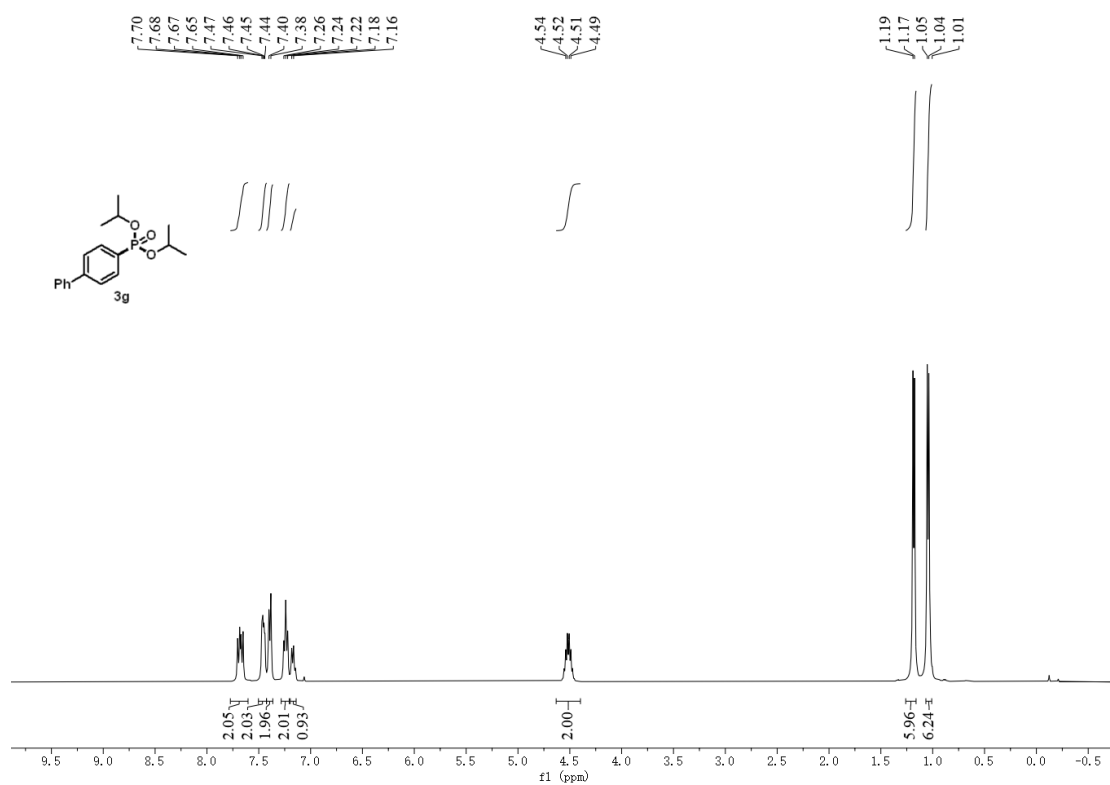
³¹P NMR (121 MHz, CDCl₃) spectrum for 3f



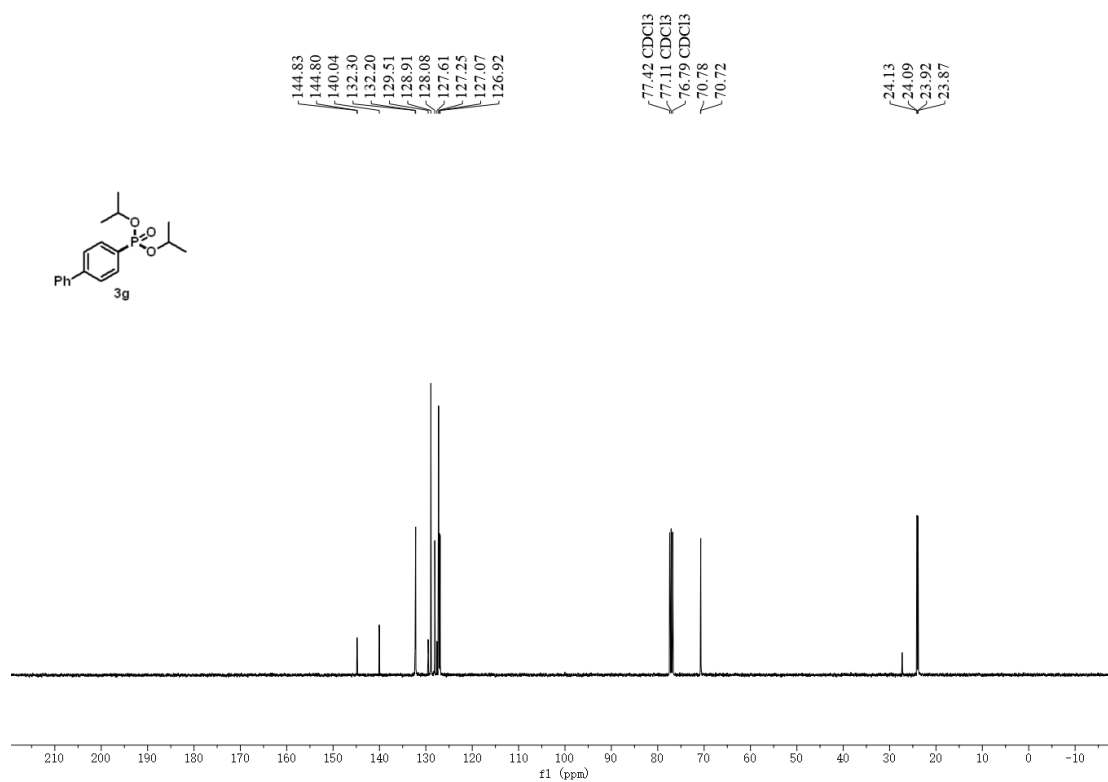
^{19}F NMR (282 MHz, CDCl_3) spectrum for 3f



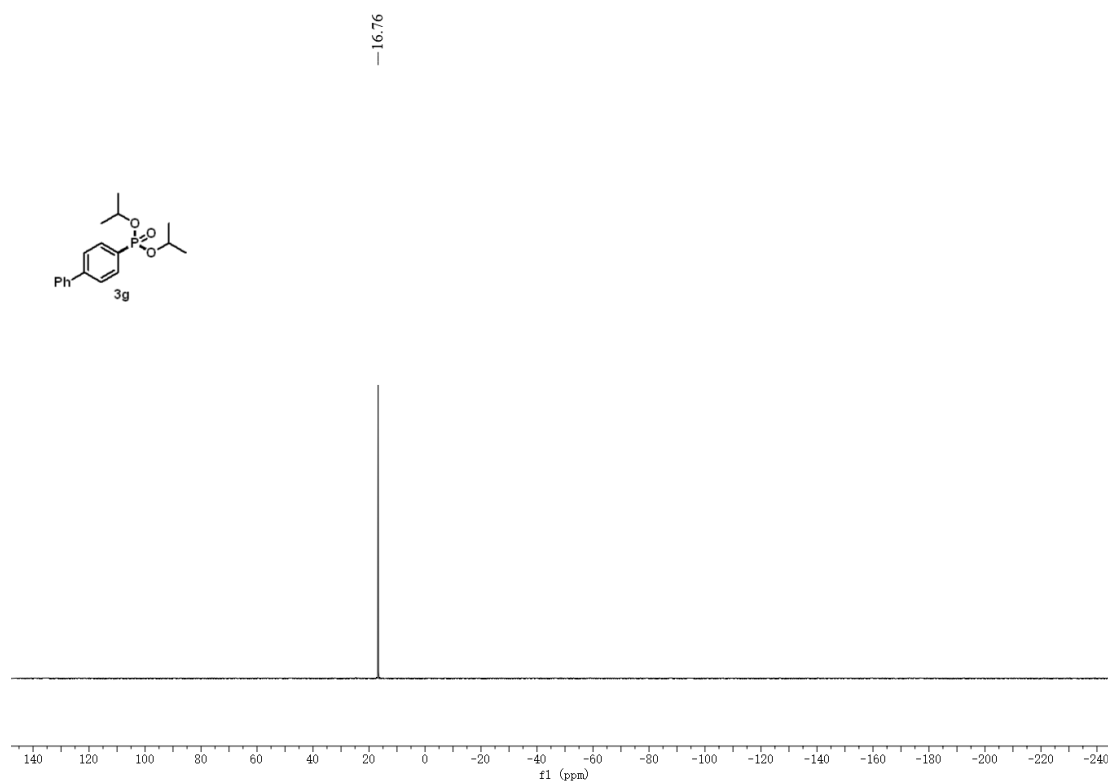
^1H NMR (400 MHz, CDCl_3) spectrum for 3g



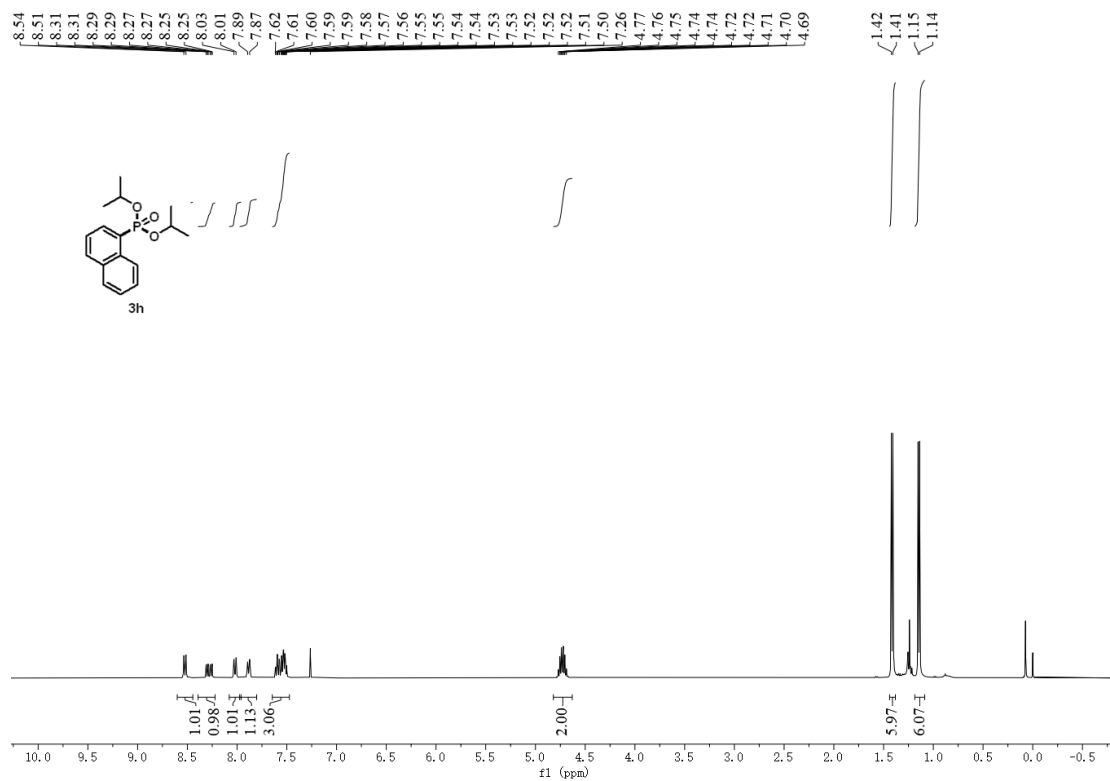
^{13}C NMR (101 MHz, CDCl_3) spectrum for 3g



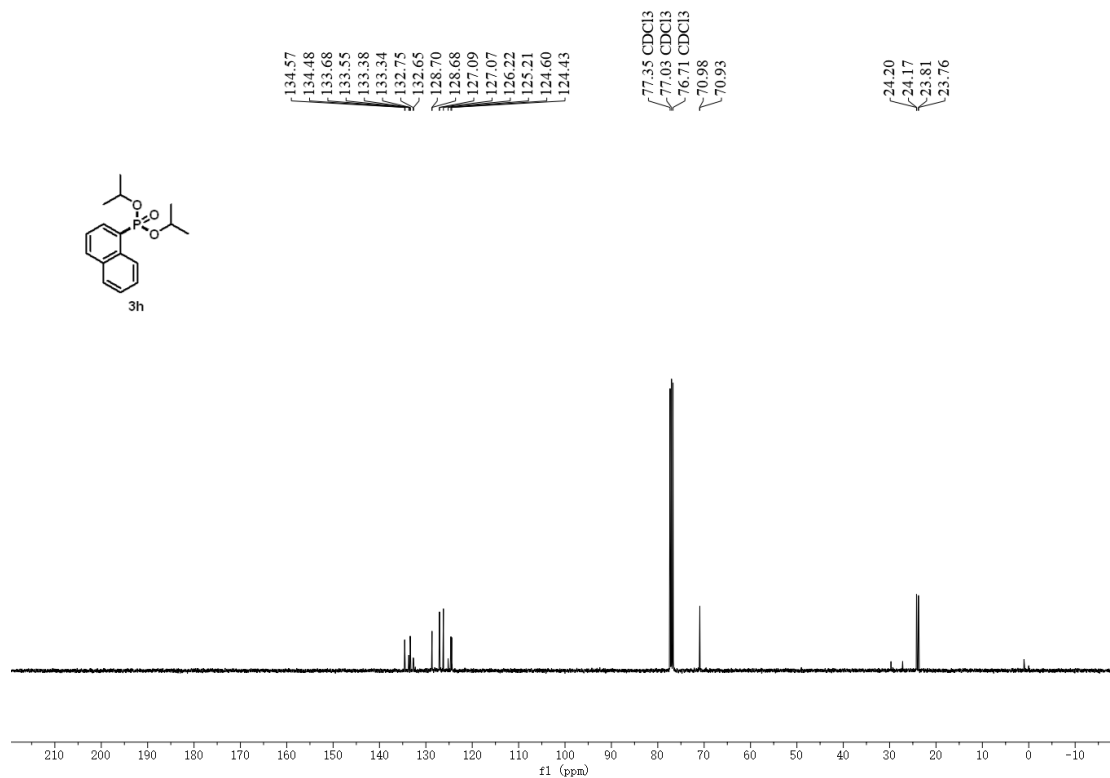
^{31}P NMR (121 MHz, CDCl_3) spectrum for 3g



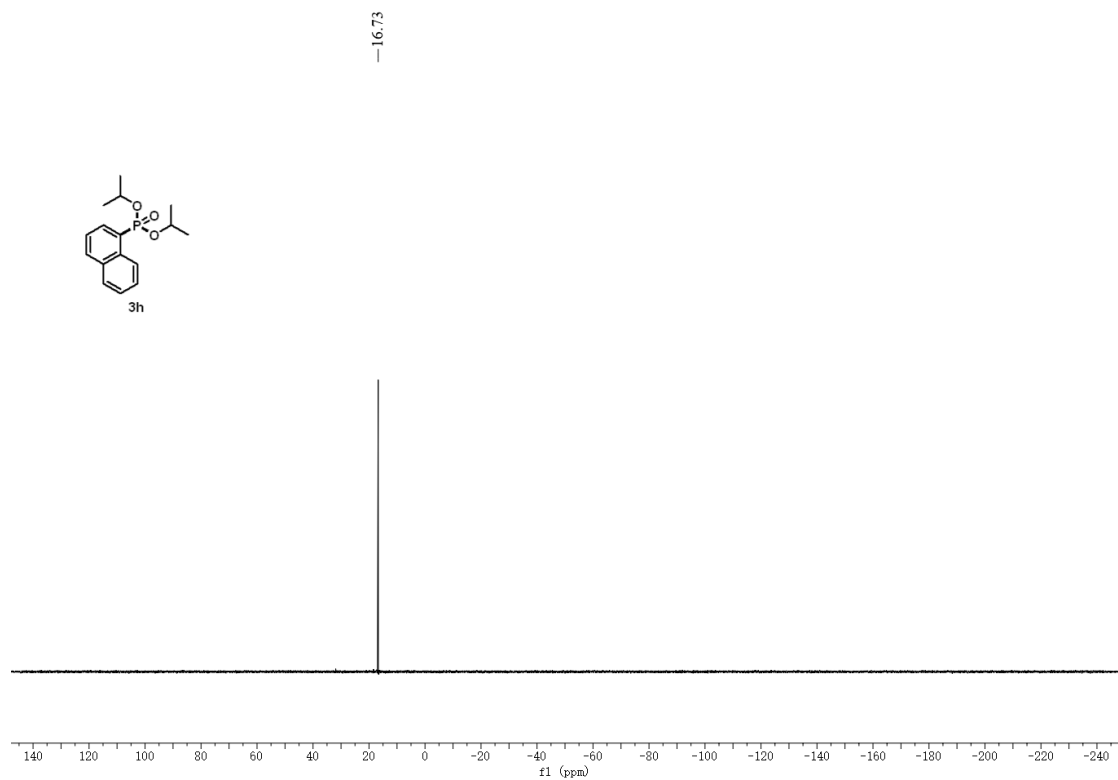
¹H NMR (400 MHz, CDCl₃) spectrum for 3h



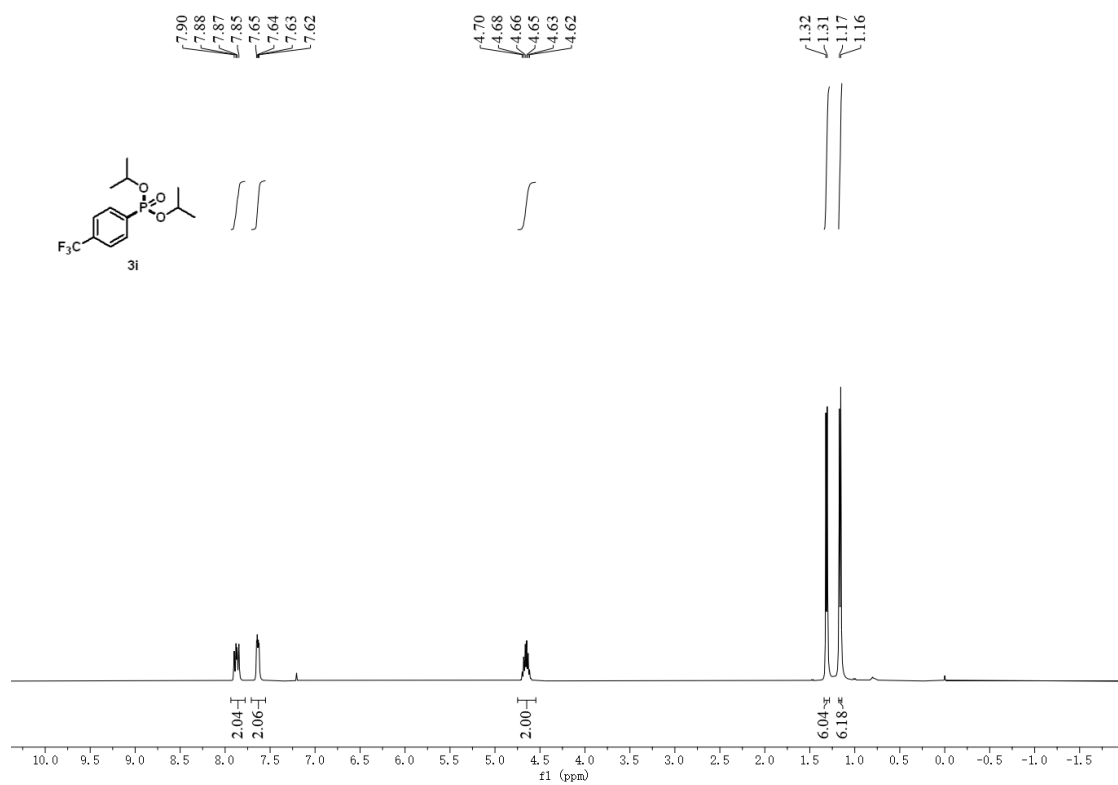
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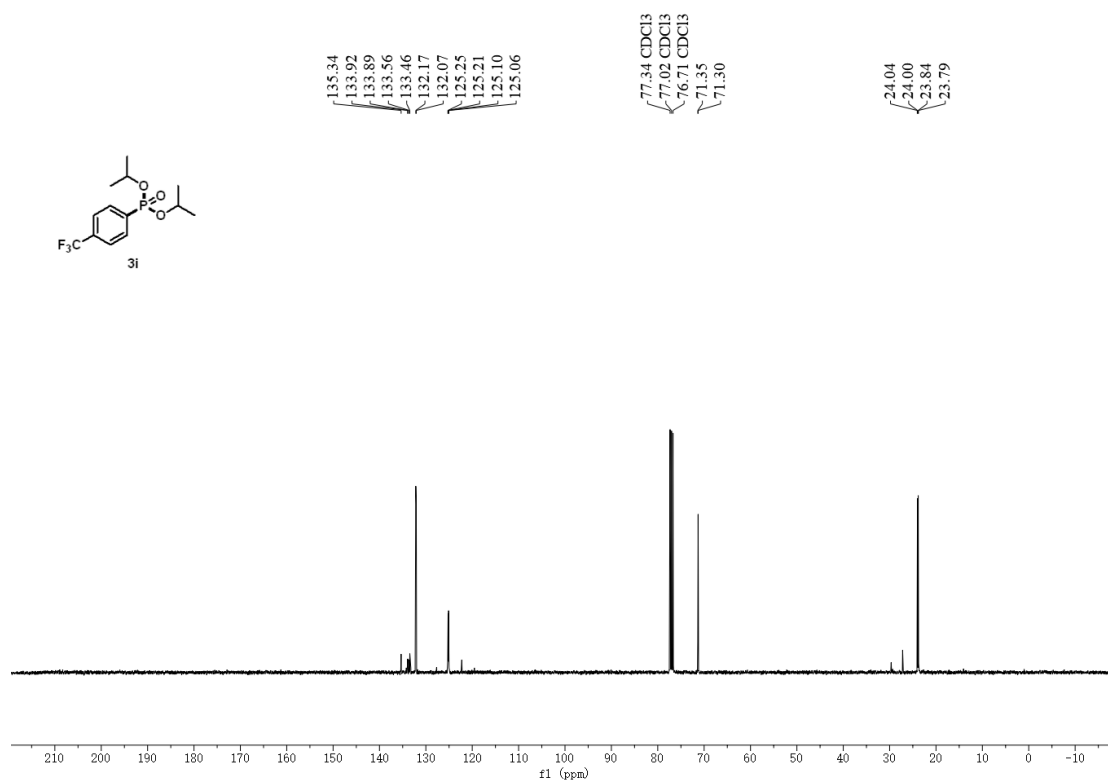
^{31}P NMR (121 MHz, CDCl_3) spectrum for 3h



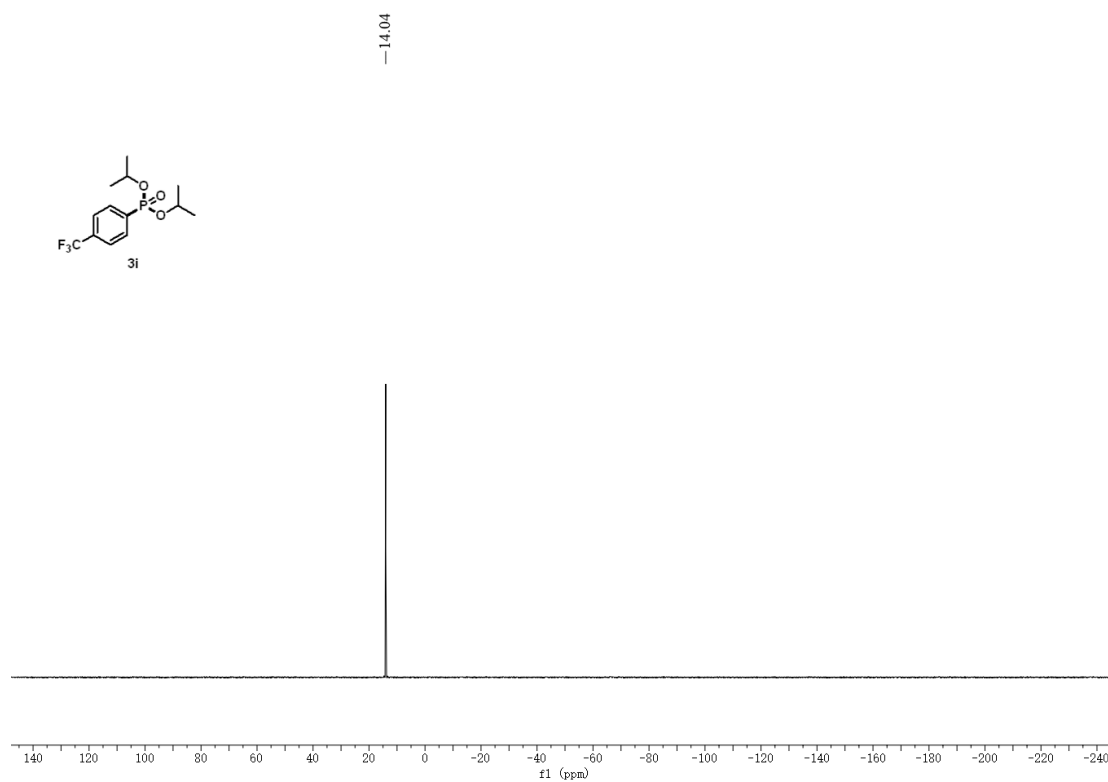
^1H NMR (400 MHz, CDCl_3) spectrum for 3i



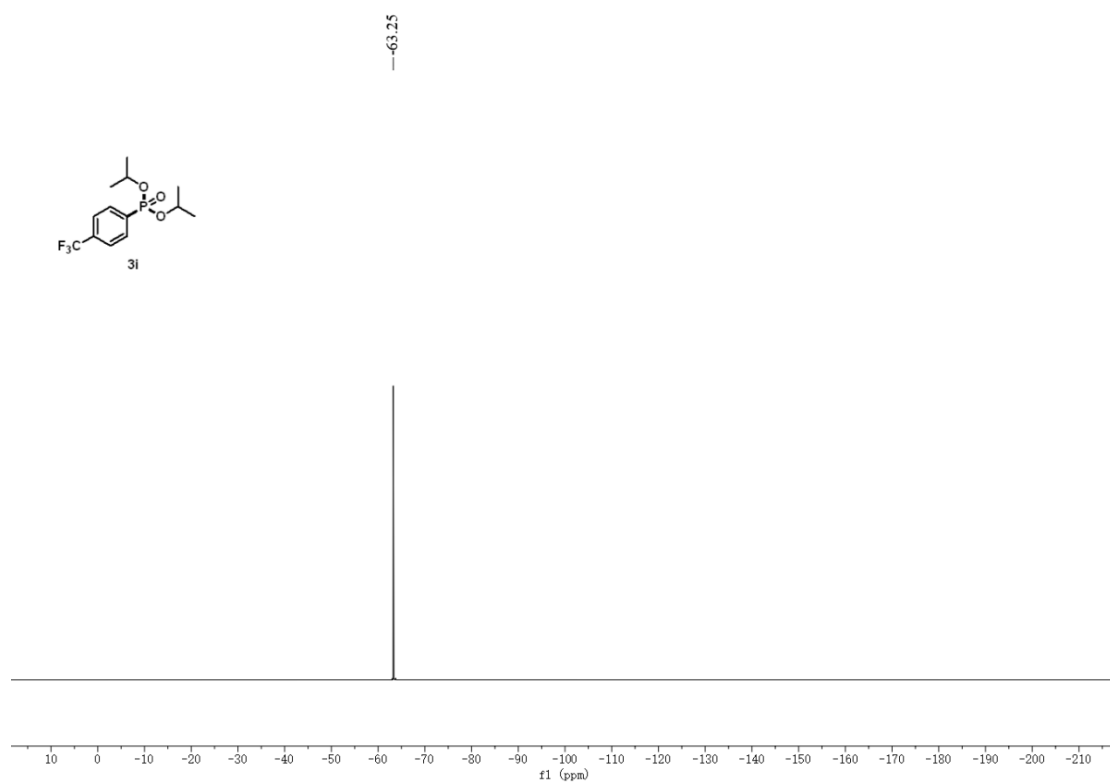
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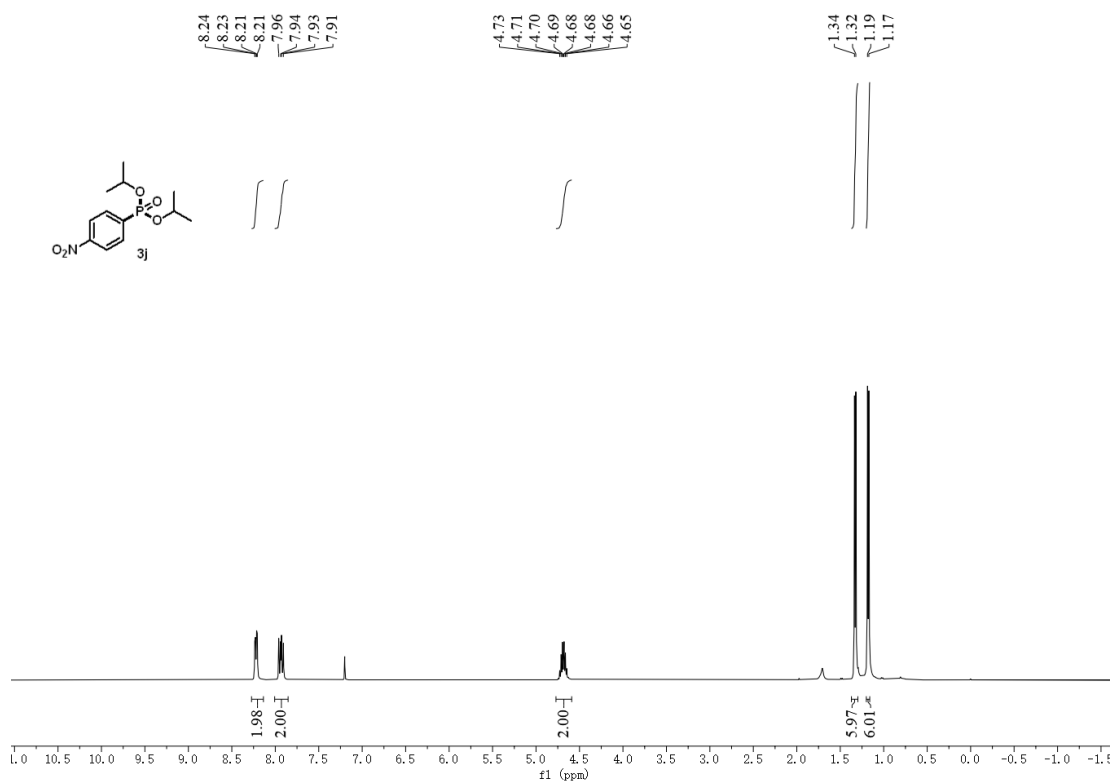
³¹P NMR (121 MHz, CDCl₃) spectrum for 3i



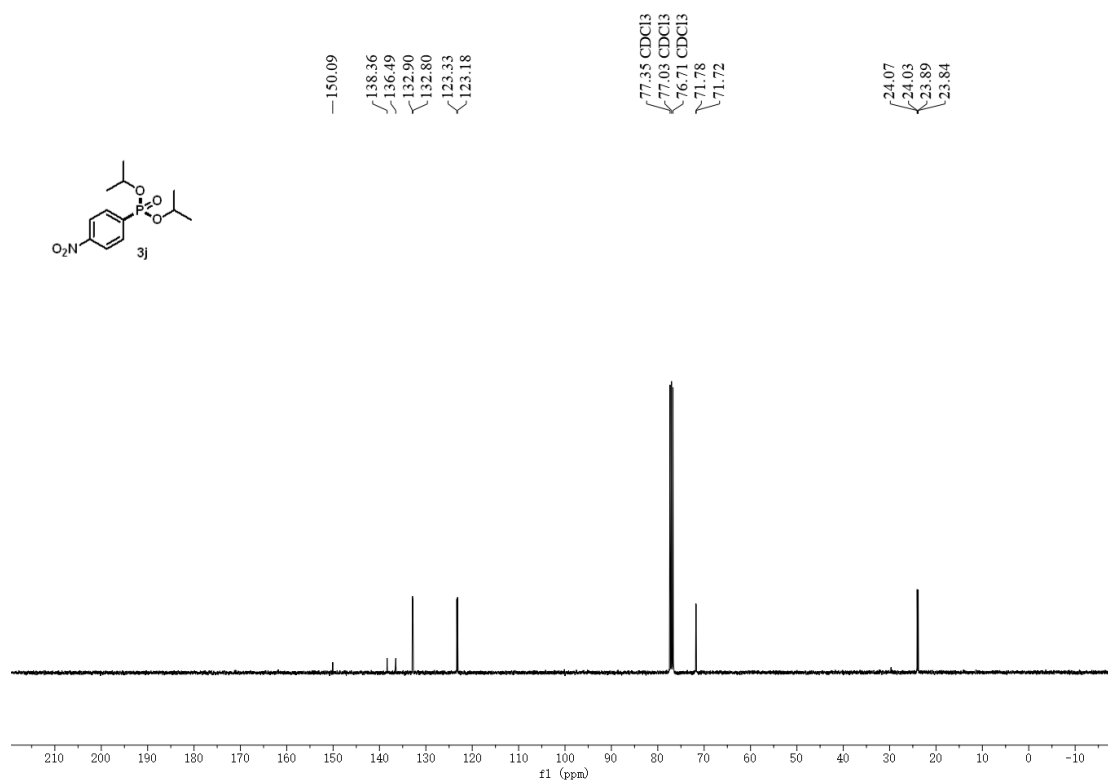
¹⁹F NMR (282 MHz, CDCl₃) spectrum for 3i



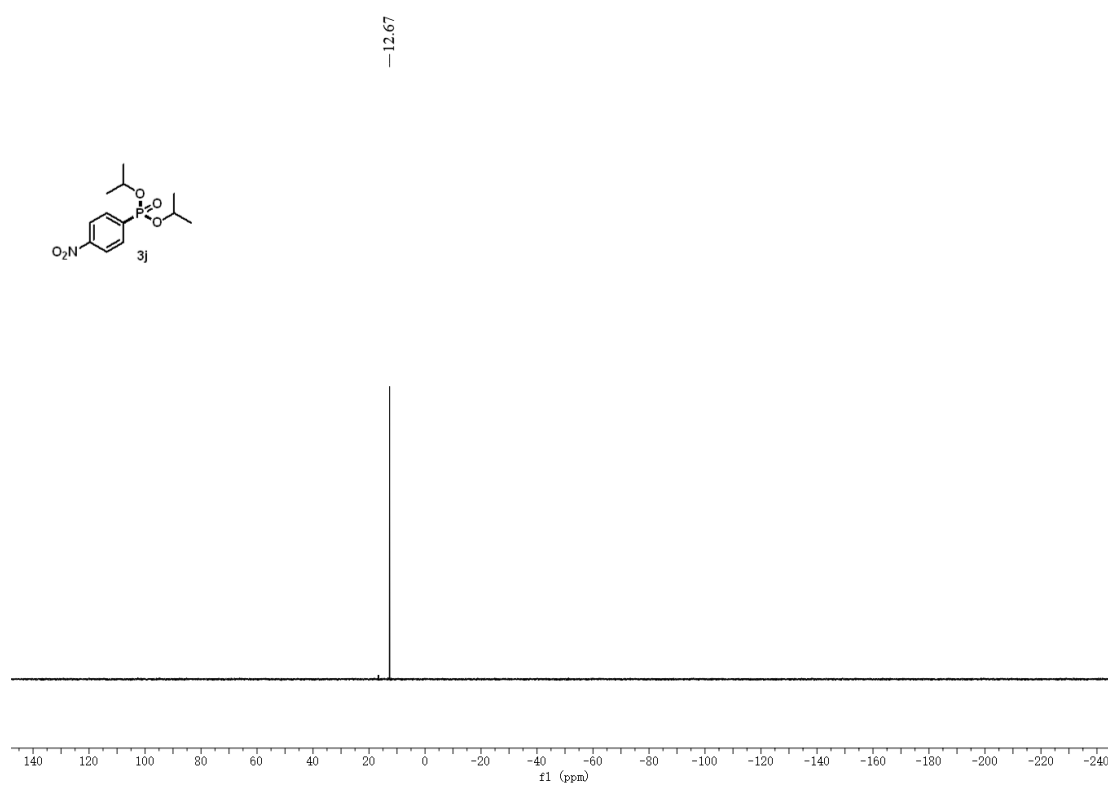
¹H NMR (400 MHz, CDCl₃) spectrum for 3j



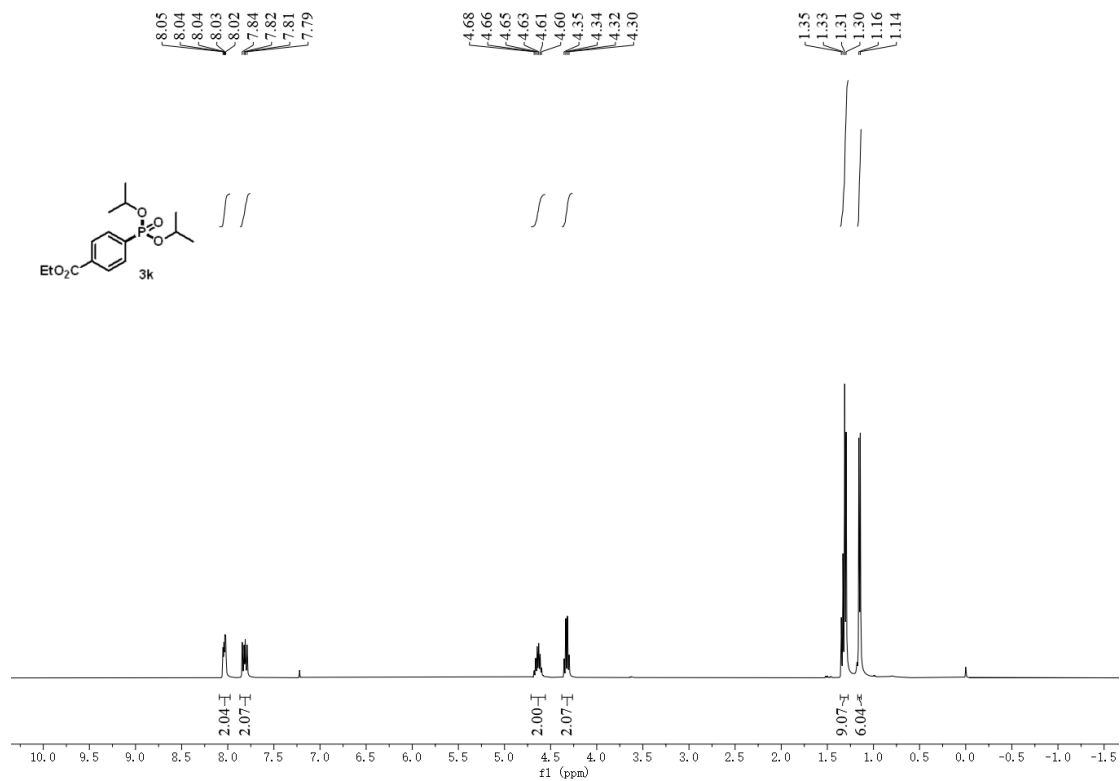
¹³C NMR (101 MHz, CDCl₃) spectrum for 3j



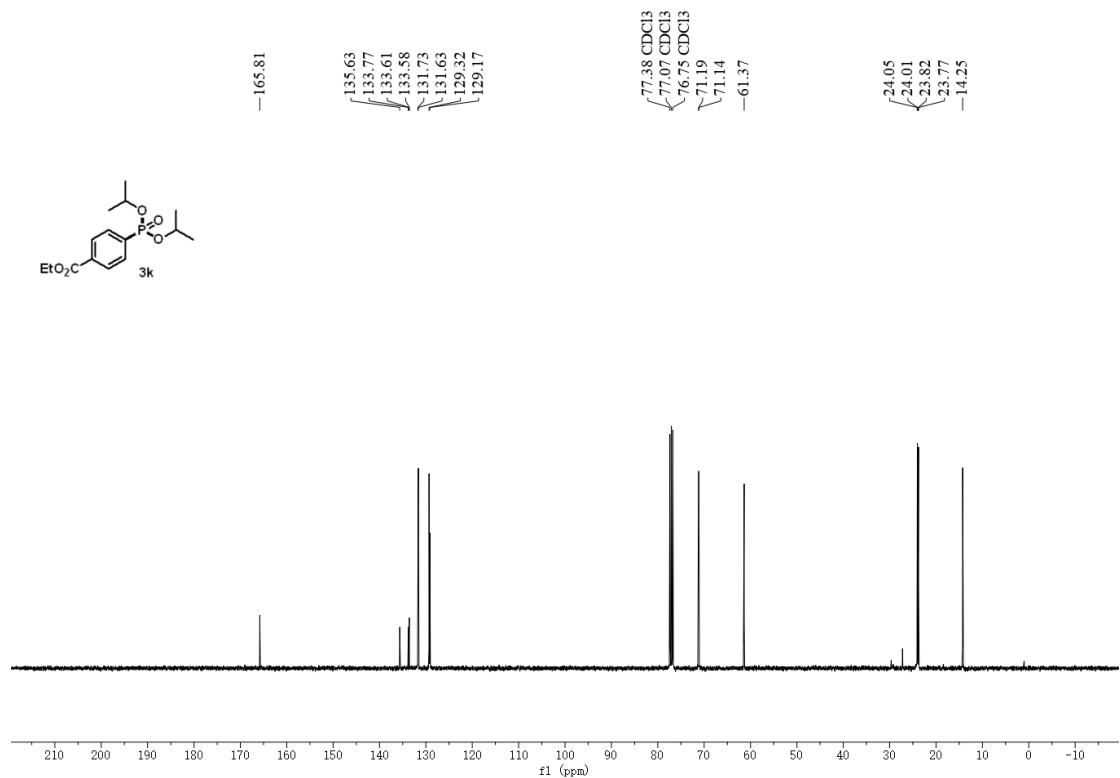
³¹P NMR (121 MHz, CDCl₃) spectrum for 3j



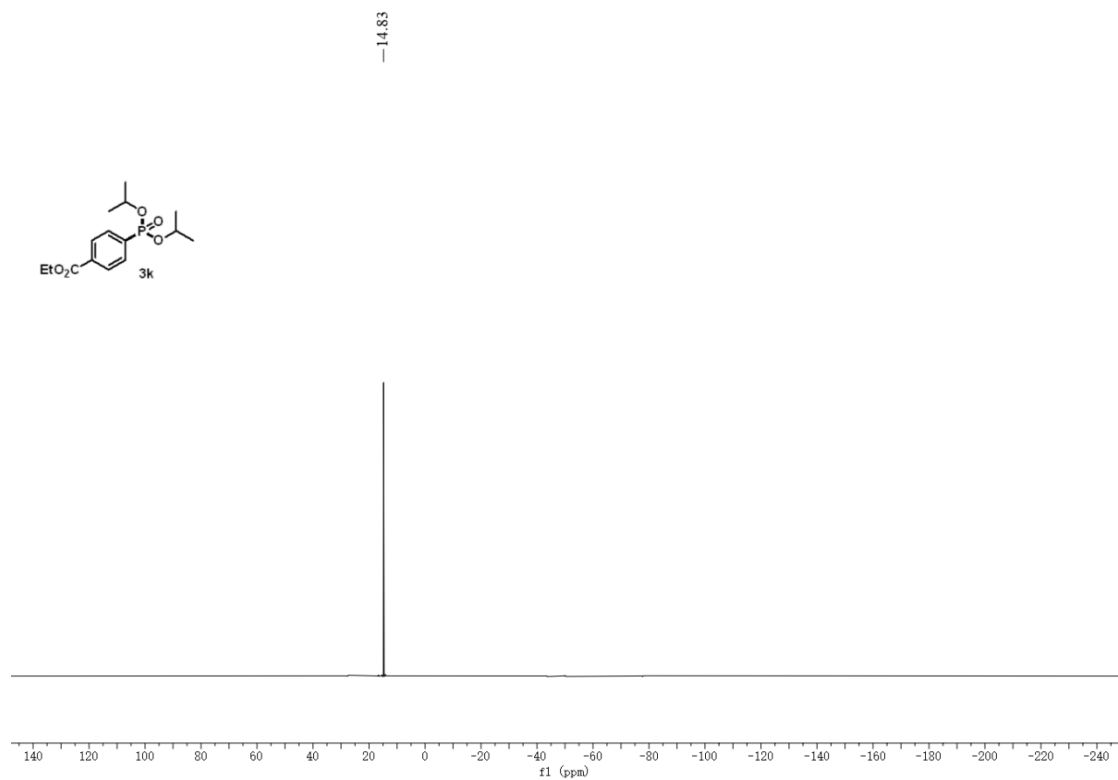
¹H NMR (400 MHz, CDCl₃) spectrum for 3k



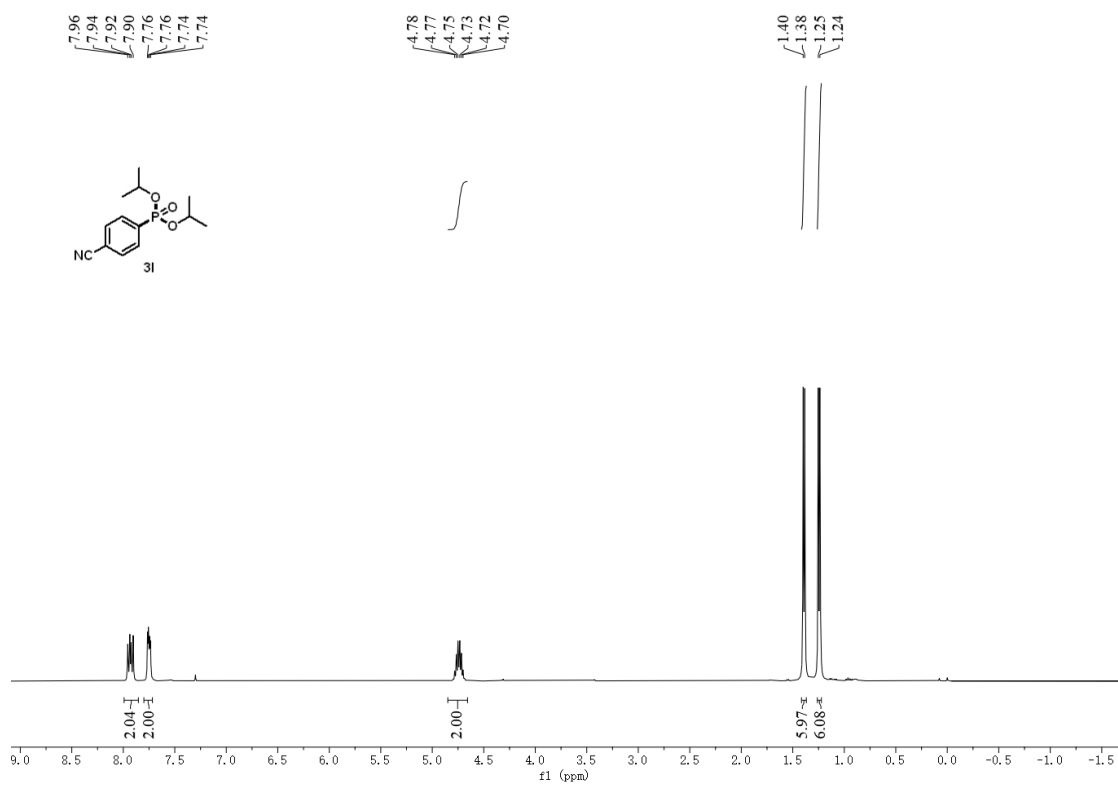
¹³C NMR (101 MHz, CDCl₃) spectrum for 3k



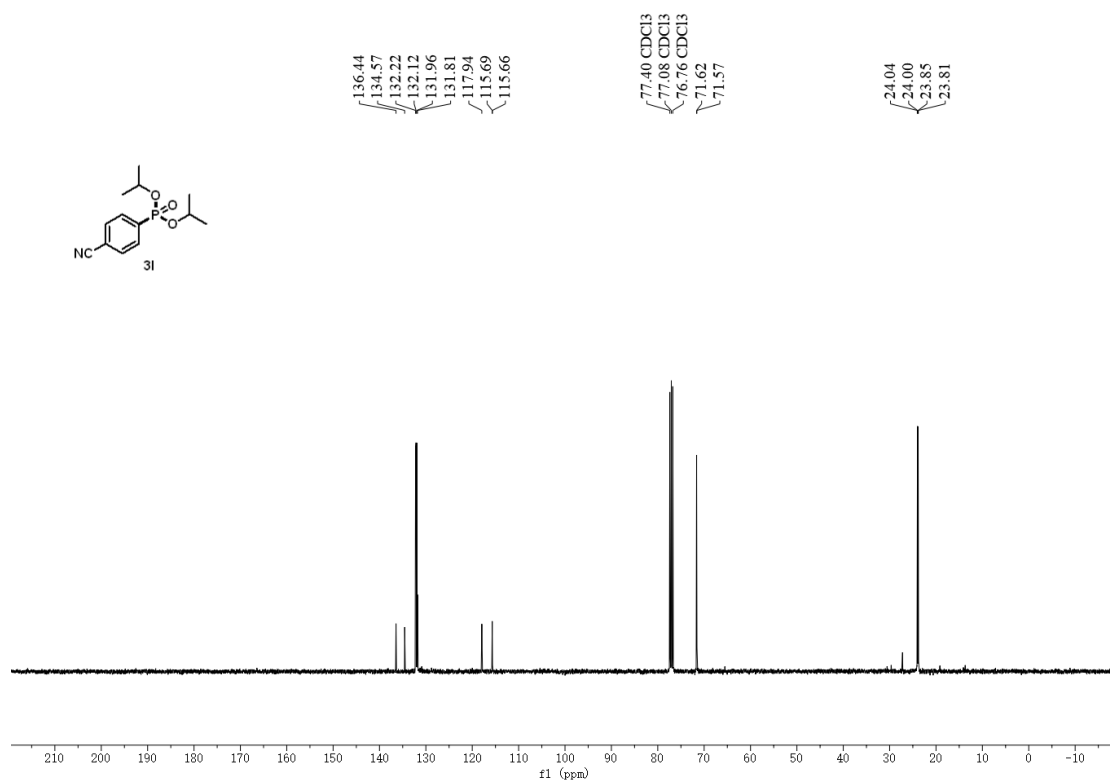
³¹P NMR (121 MHz, CDCl₃) spectrum for 3k



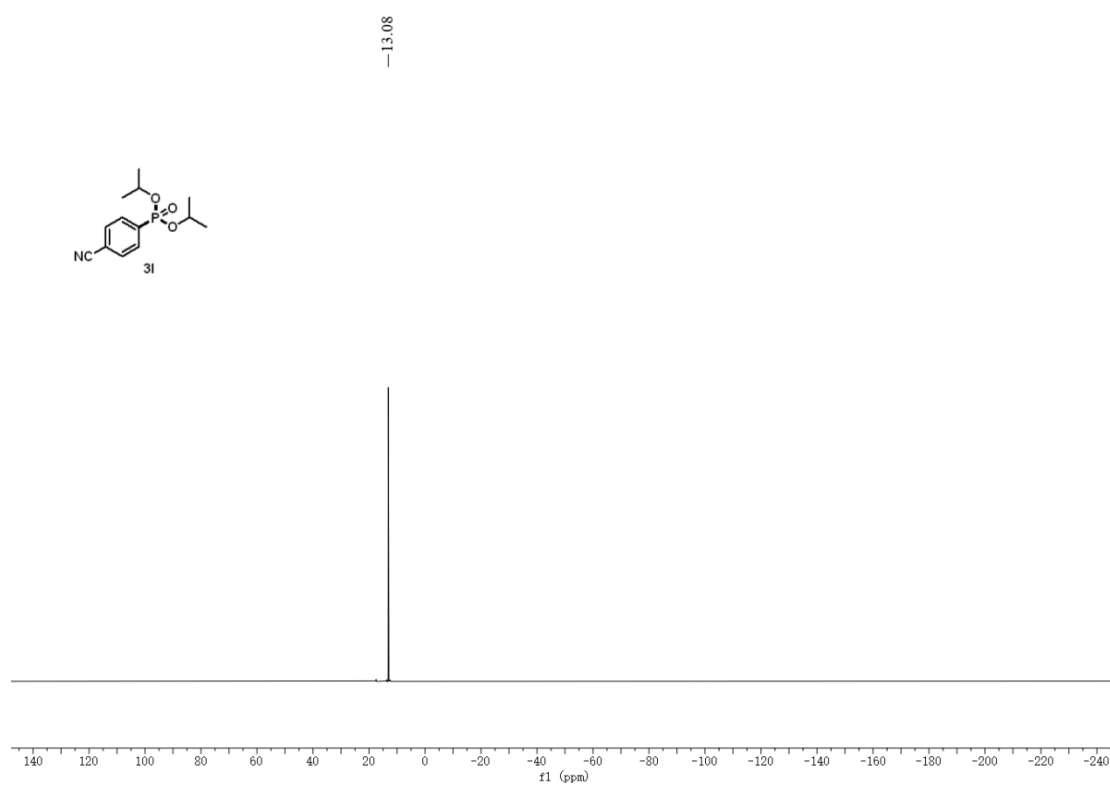
¹H NMR (400 MHz, CDCl₃) spectrum for 3l



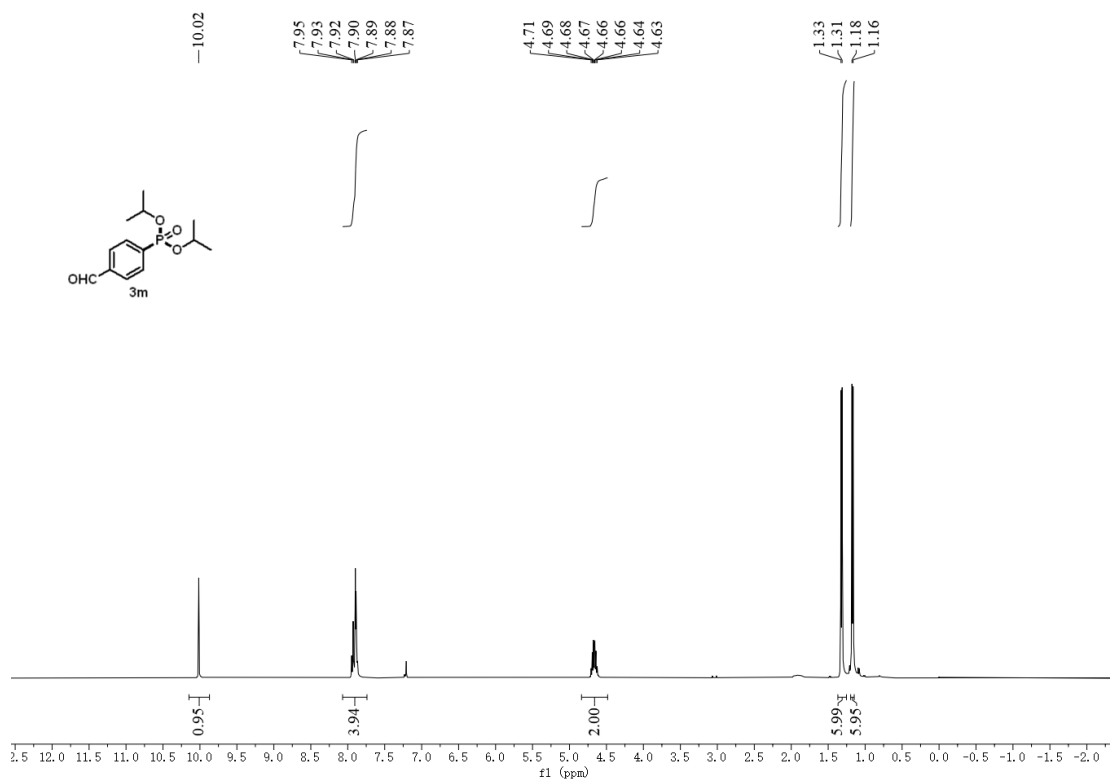
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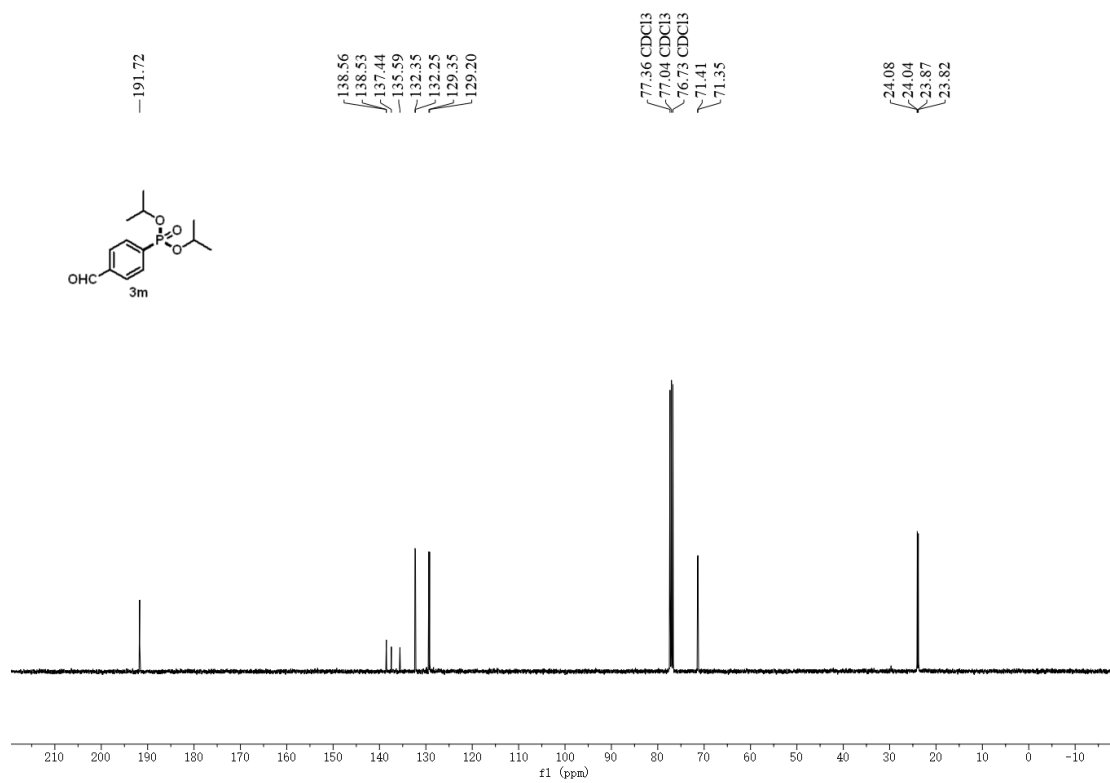
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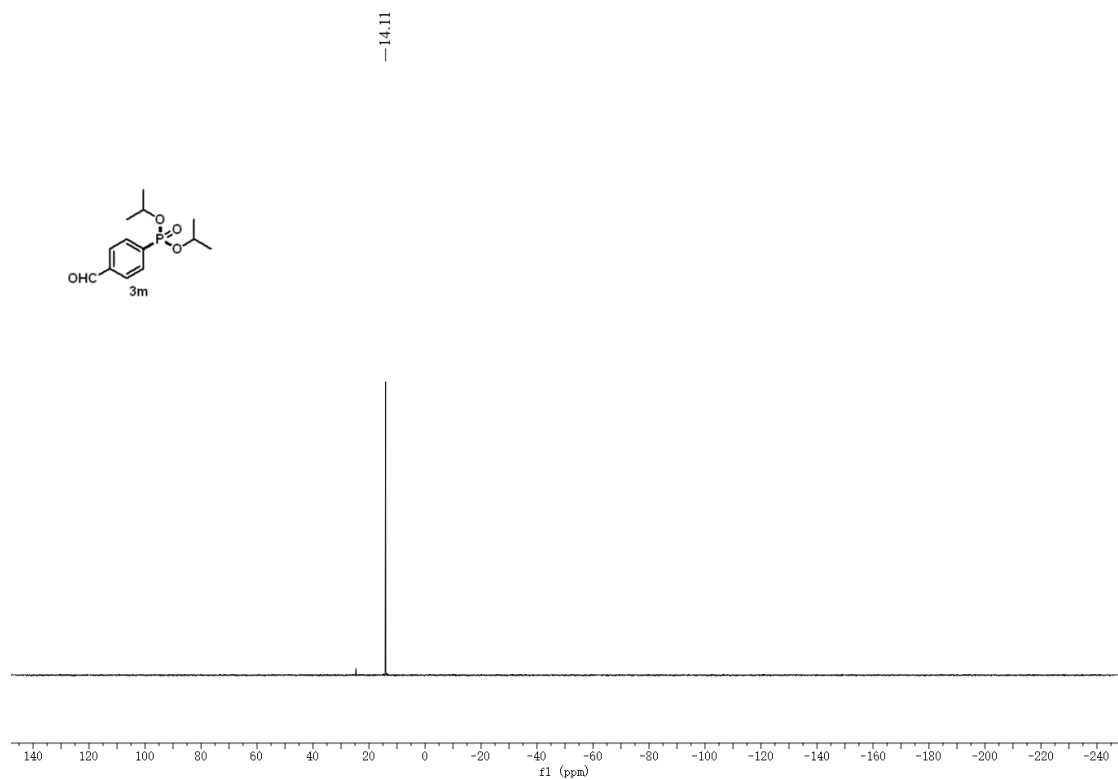
^1H NMR (400 MHz, CDCl_3) spectrum for 3m



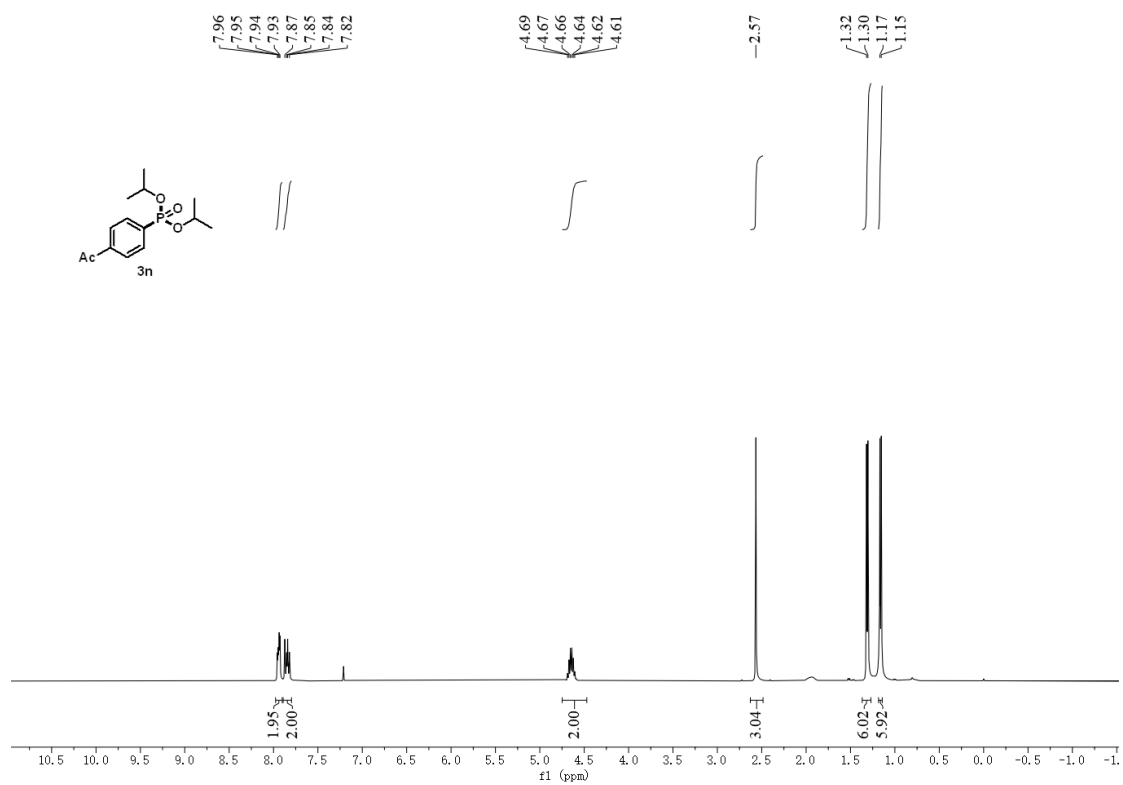
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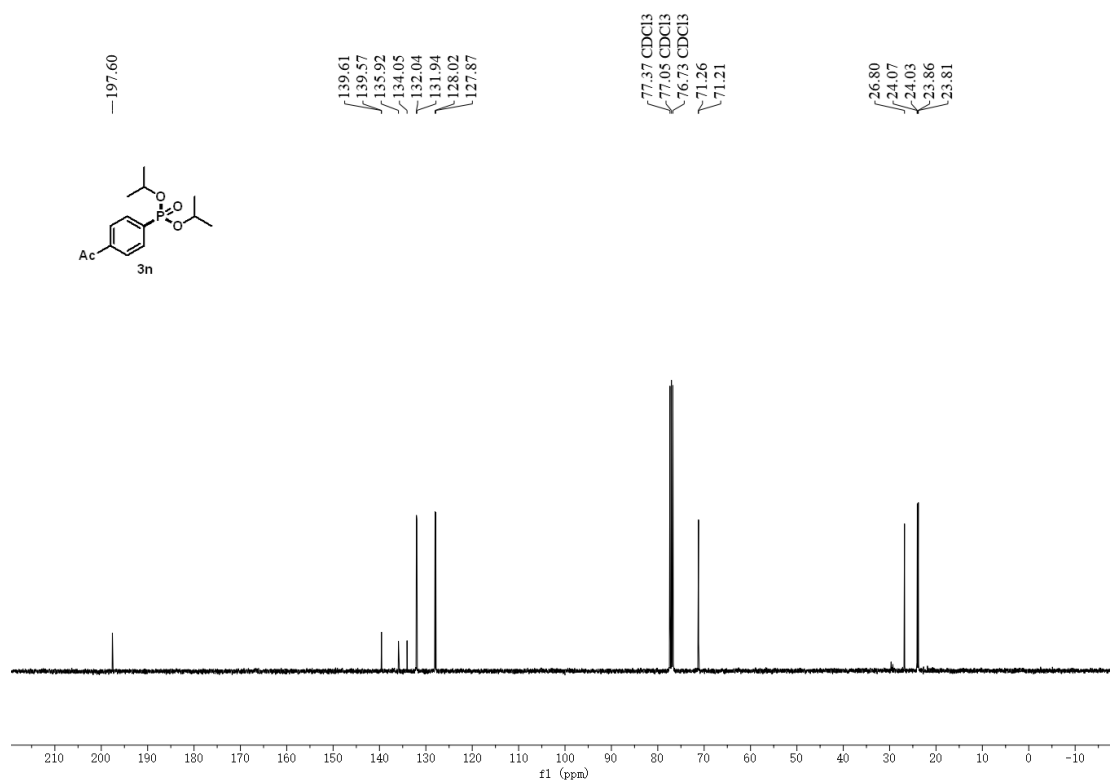
³¹P NMR (121 MHz, CDCl₃) spectrum for 3m



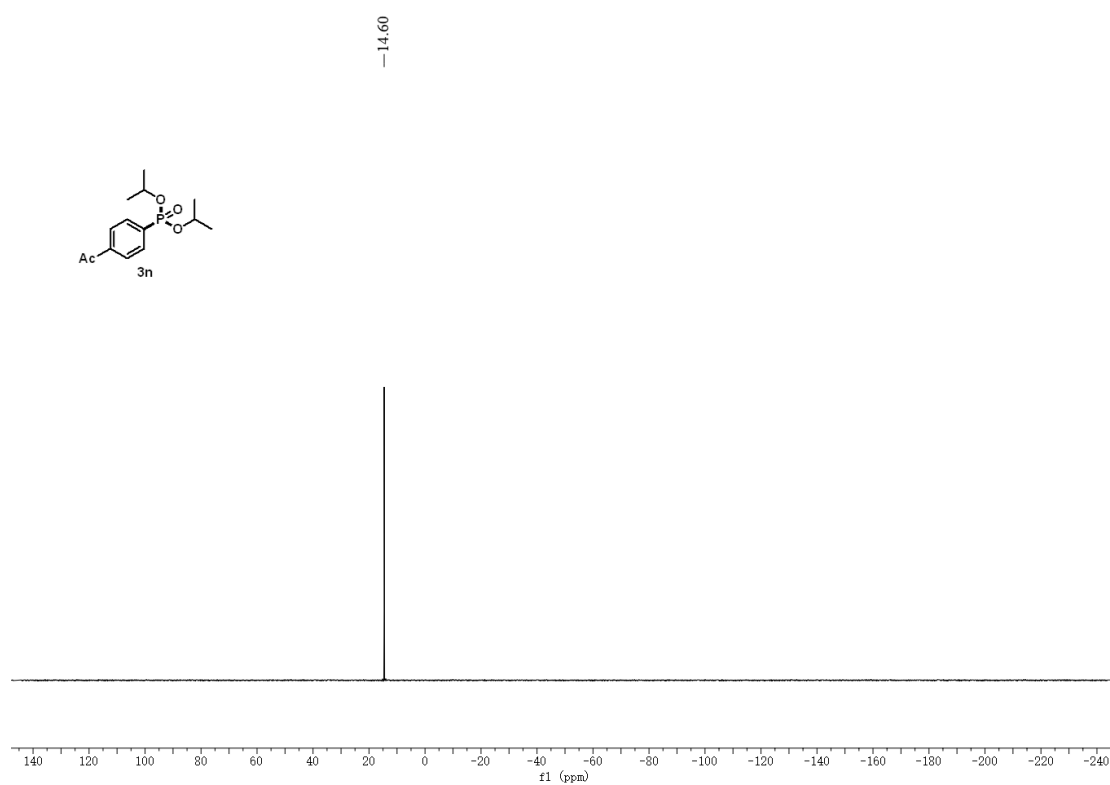
¹H NMR (400 MHz, CDCl₃) spectrum for 3n



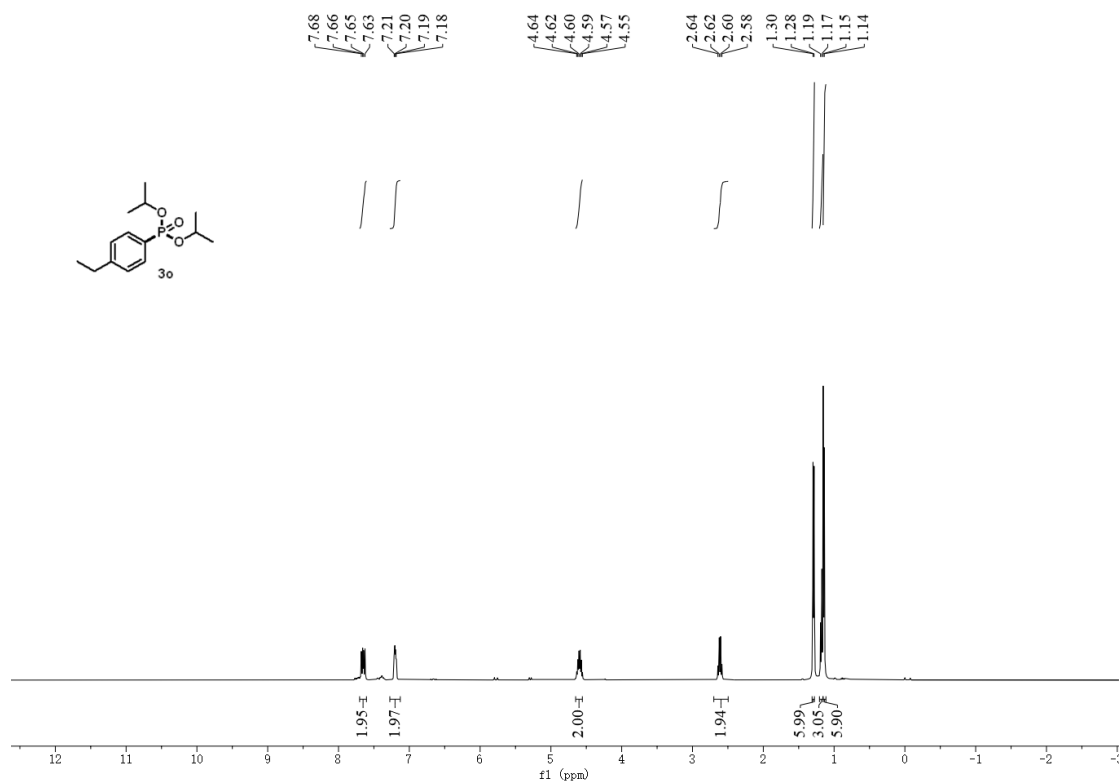
¹³C NMR (101 MHz, CDCl₃) spectrum for 3n



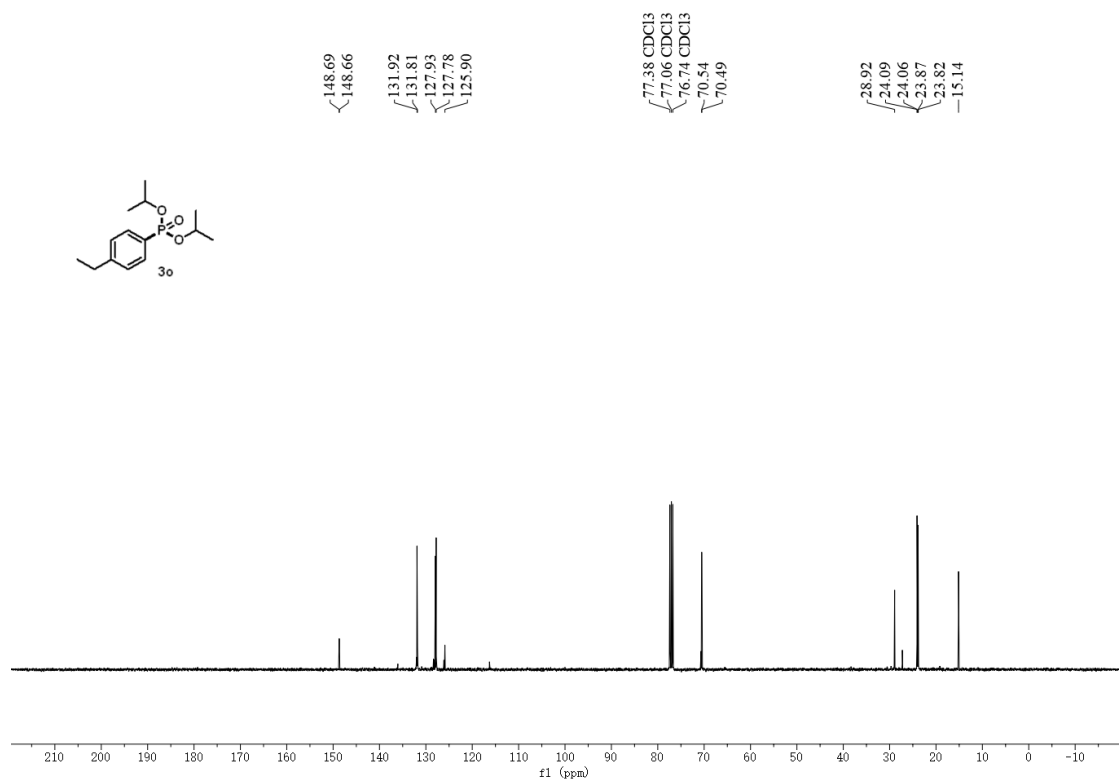
³¹P NMR (121 MHz, CDCl₃) spectrum for 3n



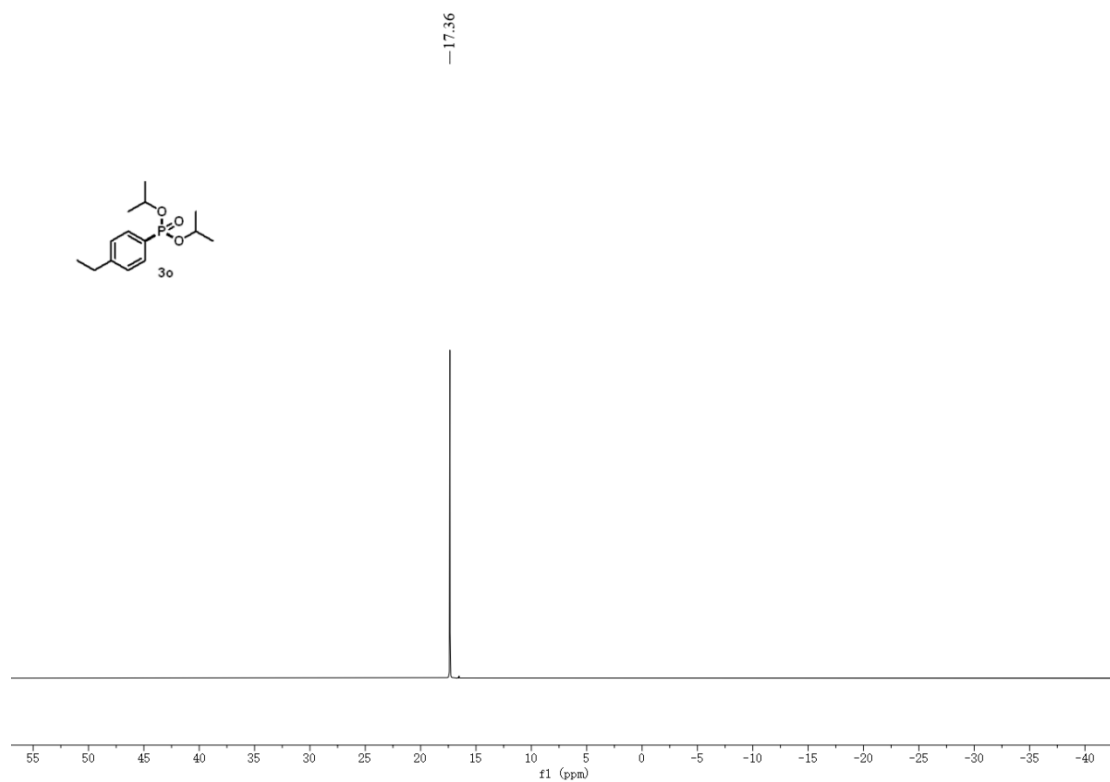
¹H NMR (400 MHz, CDCl₃) spectrum for 3o



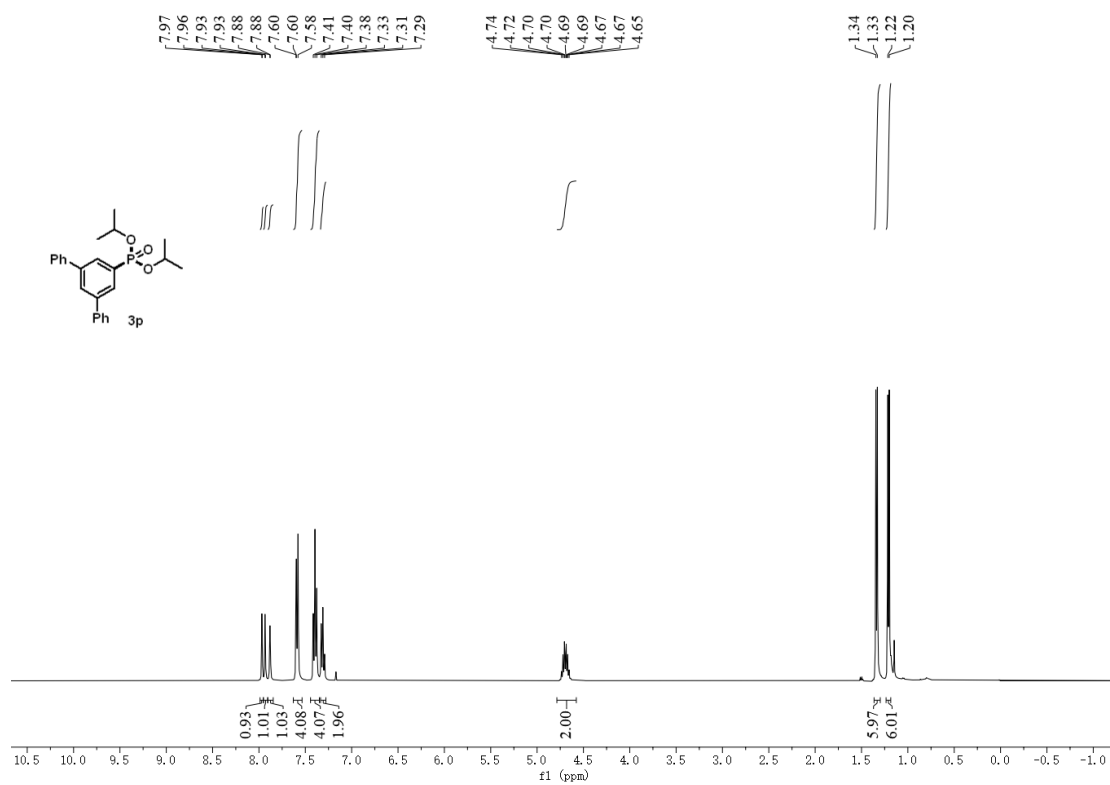
¹³C NMR (101 MHz, CDCl₃) spectrum for 3o



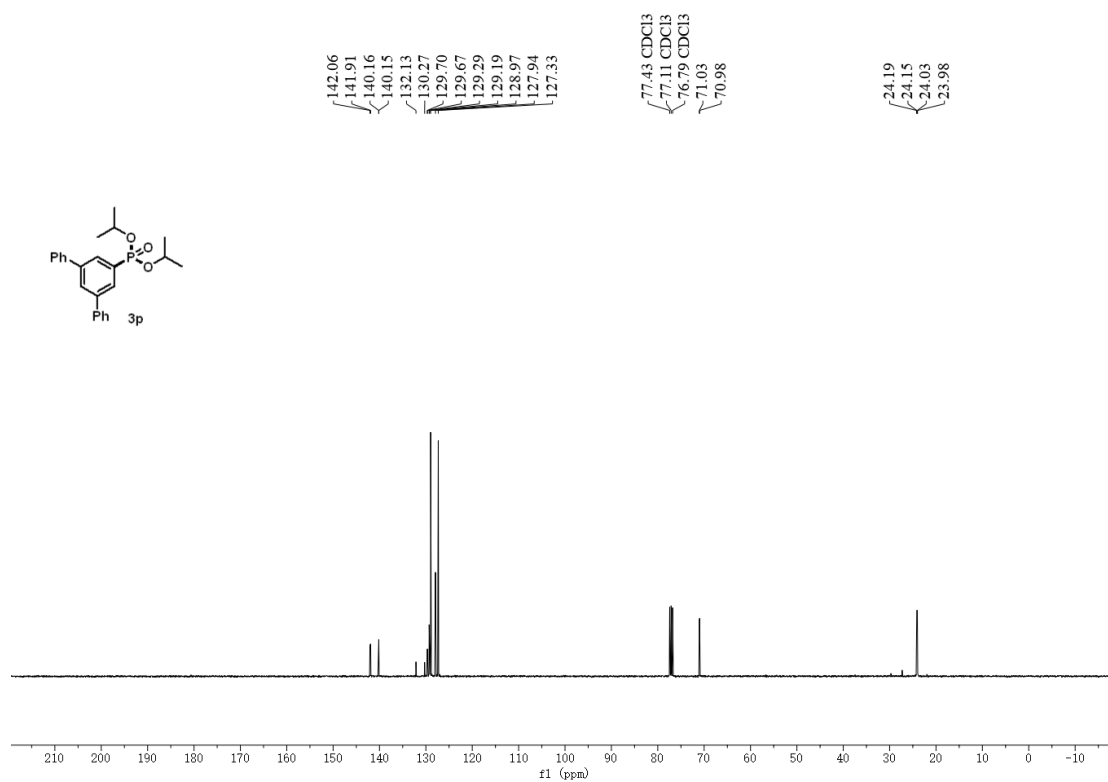
^{31}P NMR (121 MHz, CDCl_3) spectrum for 3o



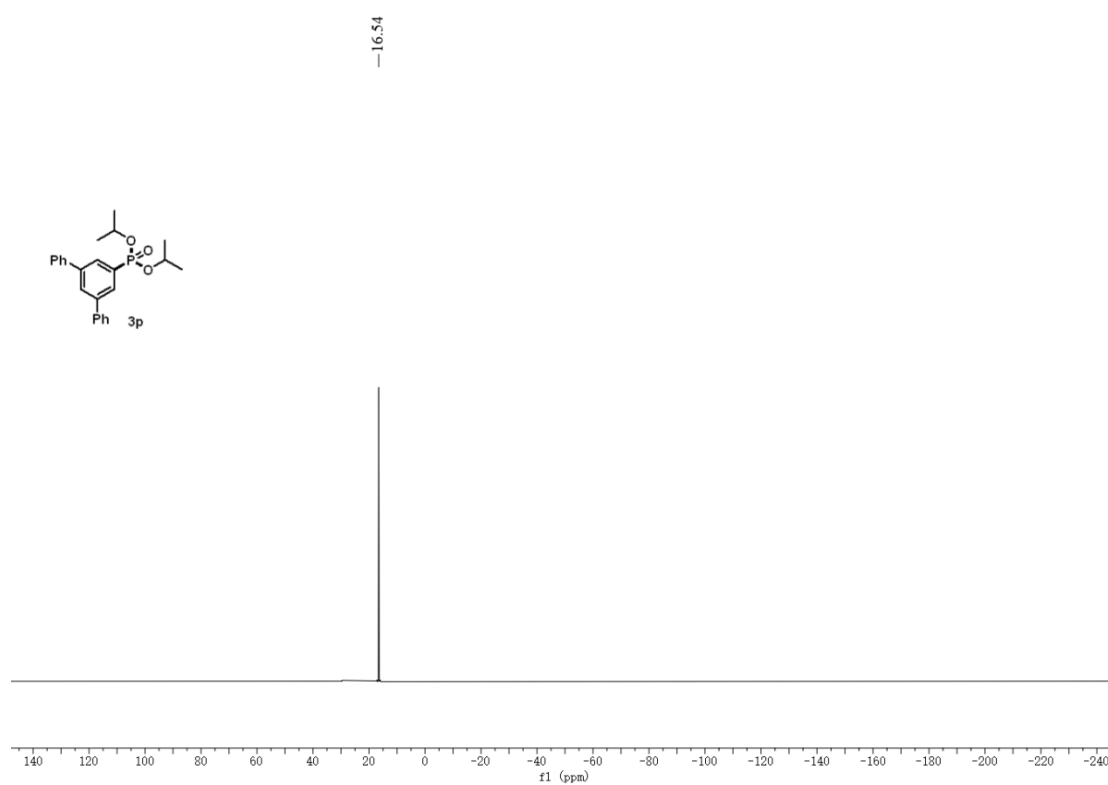
^1H NMR (400 MHz, CDCl_3) spectrum for 3p



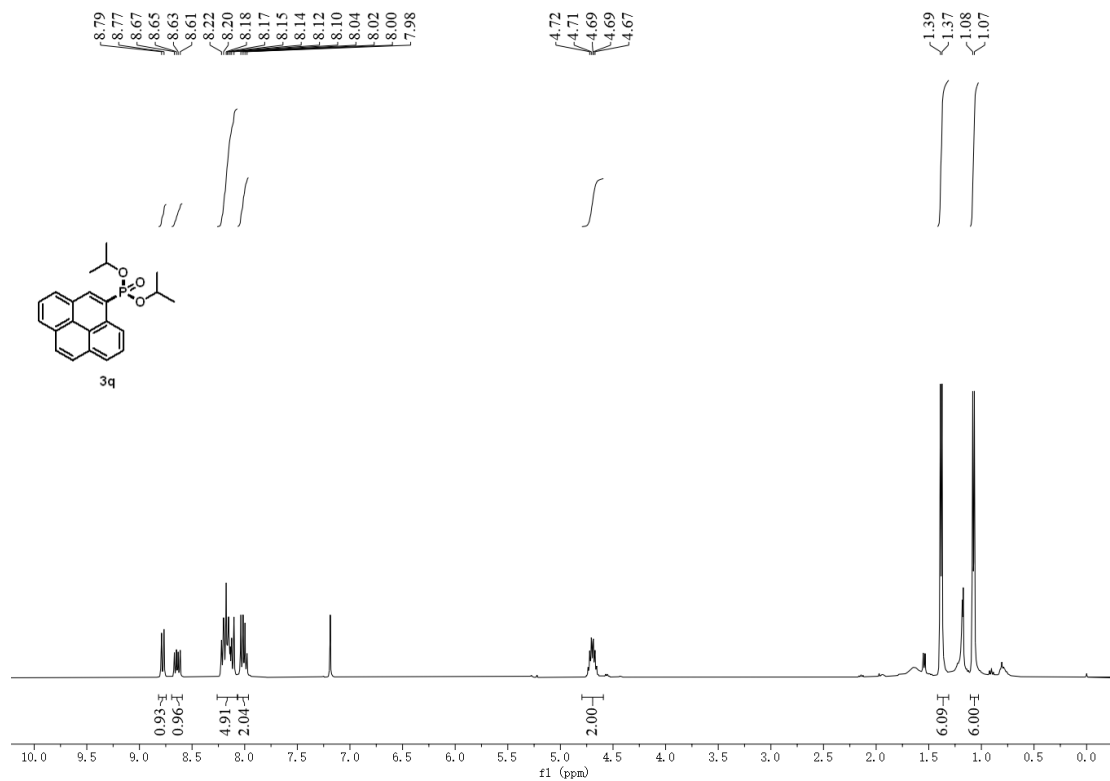
¹³C NMR (101 MHz, CDCl₃) spectrum for 3p



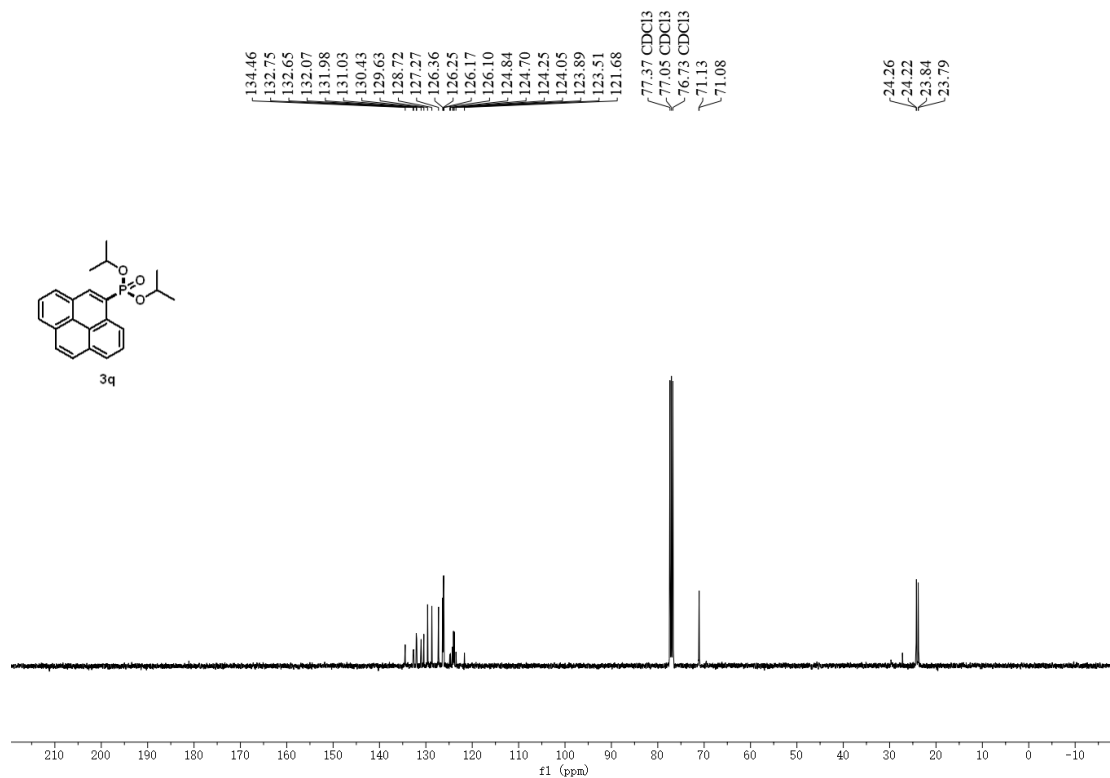
³¹P NMR (121 MHz, CDCl₃) spectrum for 3p



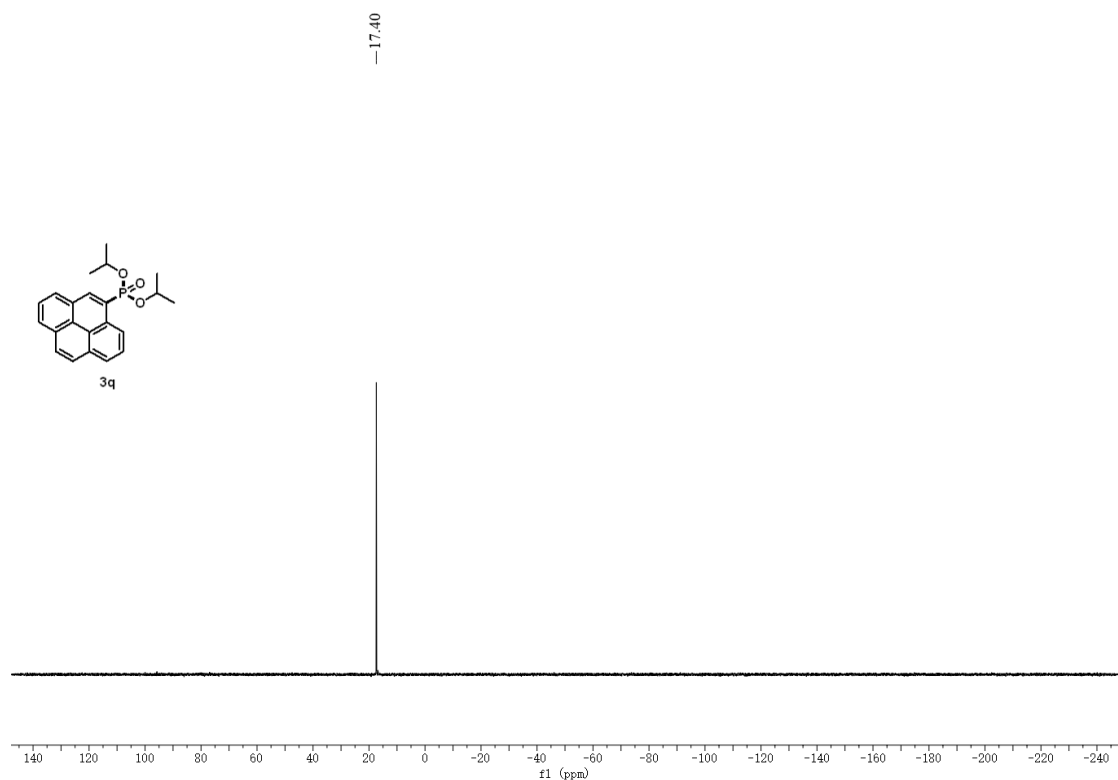
^1H NMR (400 MHz, CDCl_3) spectrum for 3q



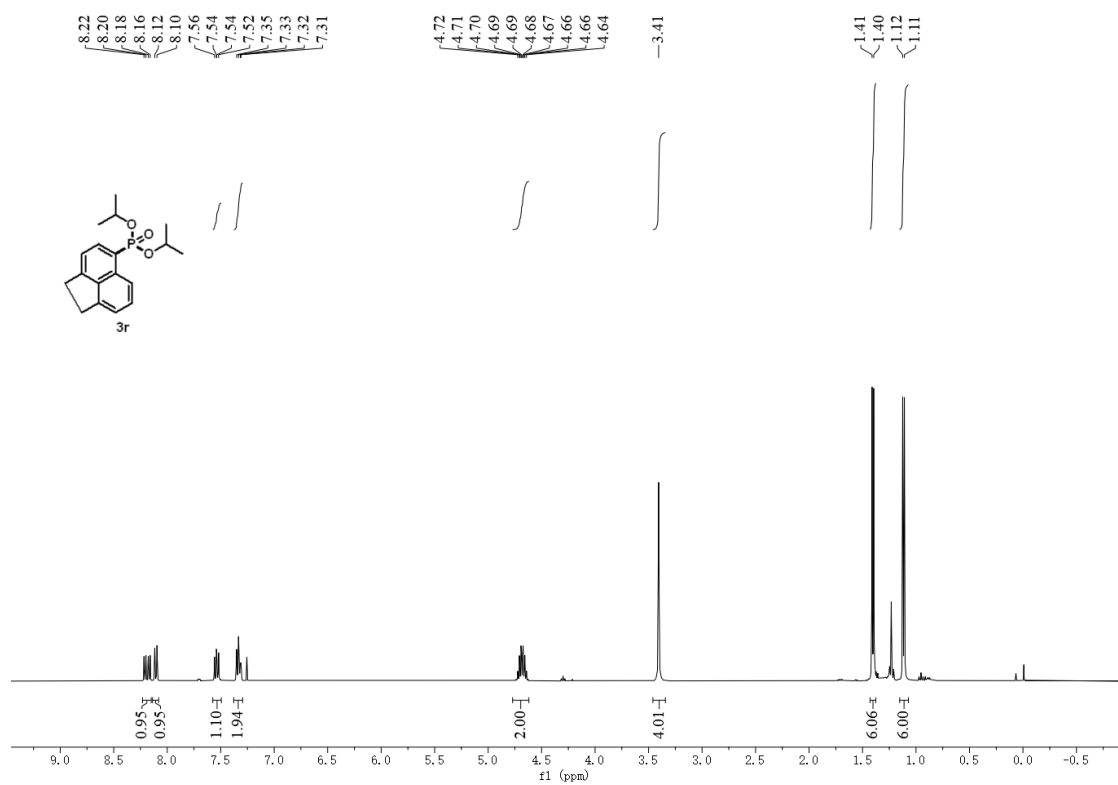
^{13}C NMR (101 MHz, CDCl_3) spectrum for 3q



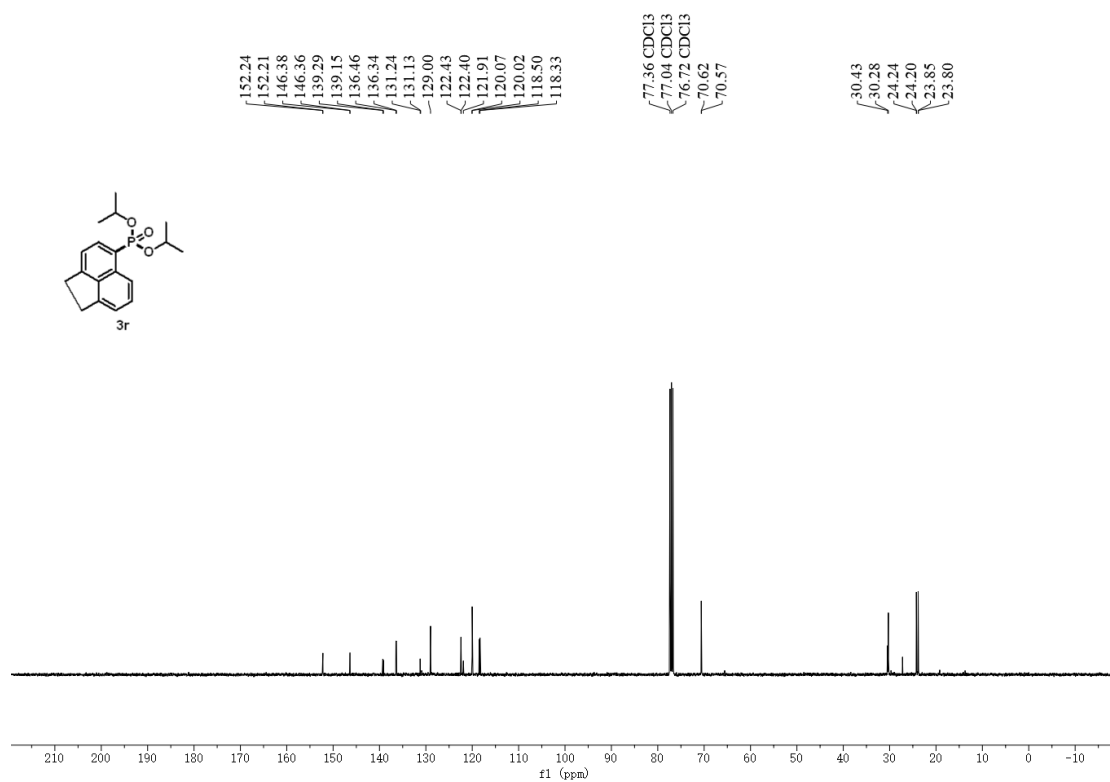
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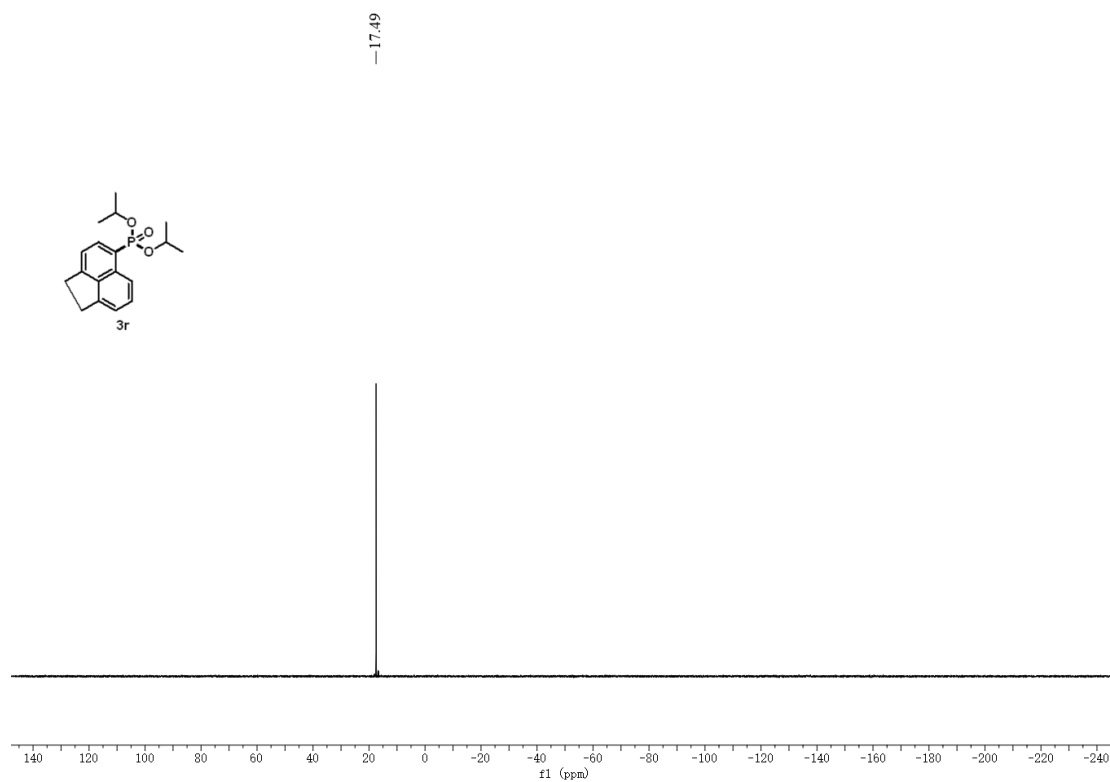
^1H NMR (400 MHz, CDCl_3) spectrum for 3r



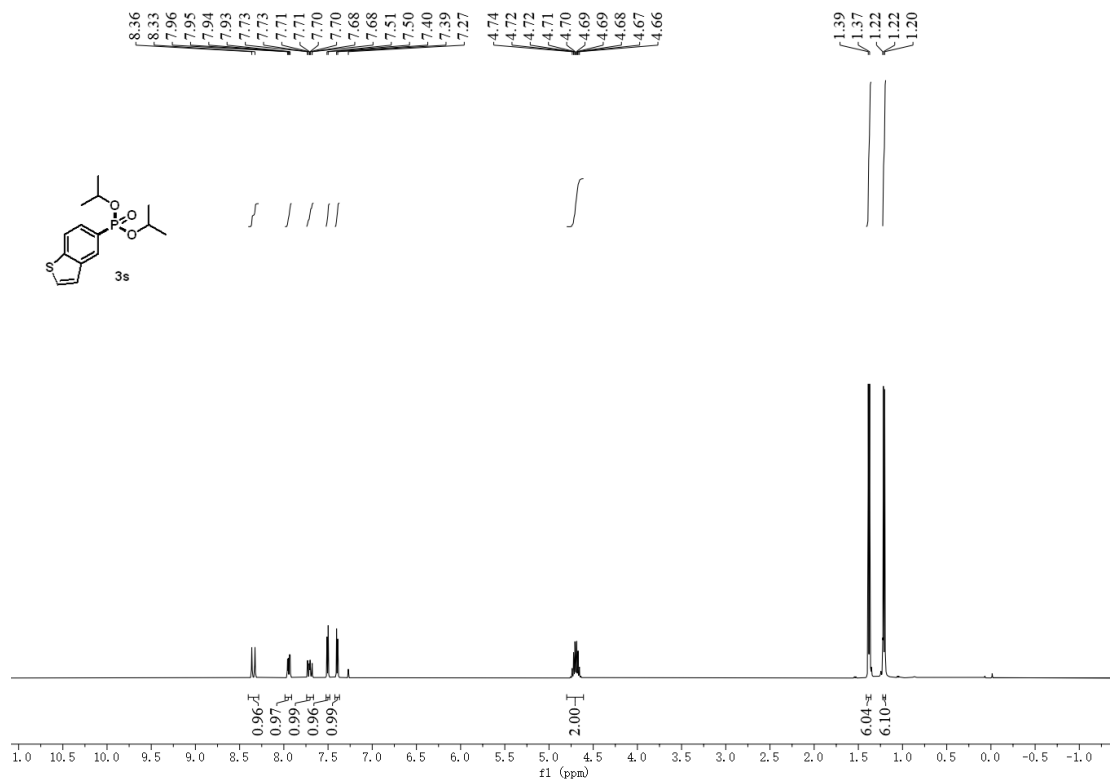
¹³C NMR (101 MHz, CDCl₃) spectrum for 3r



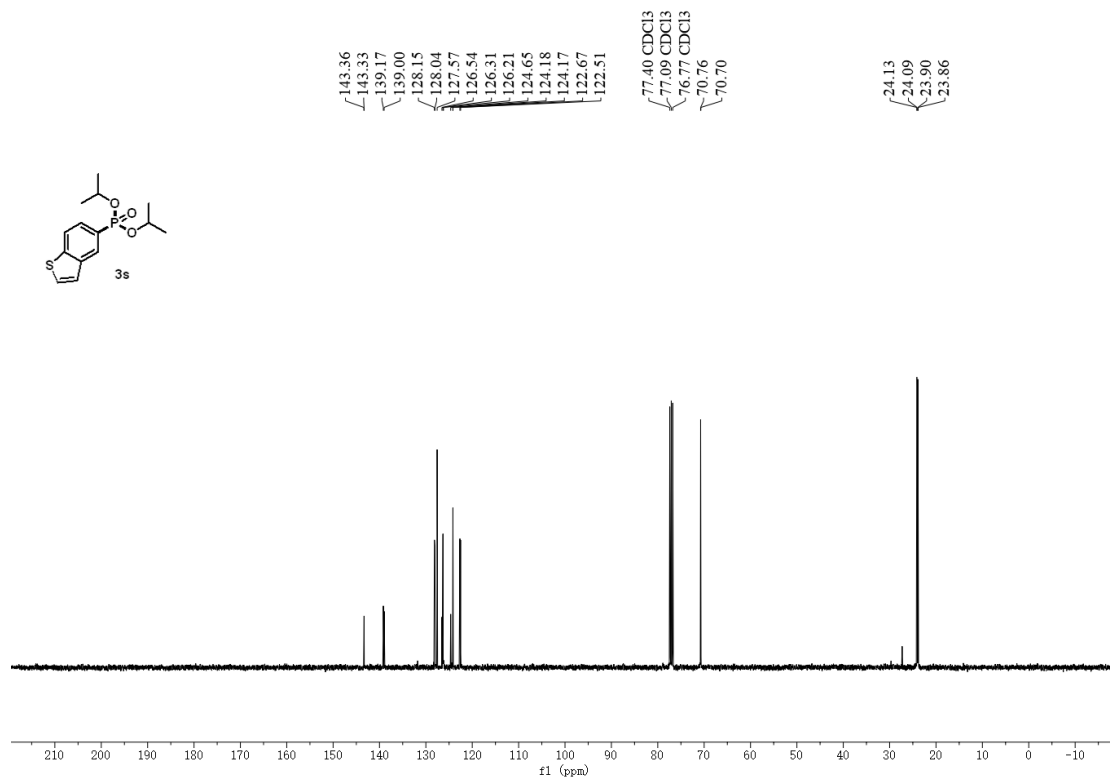
³¹P NMR (121 MHz, CDCl₃) spectrum for 3r



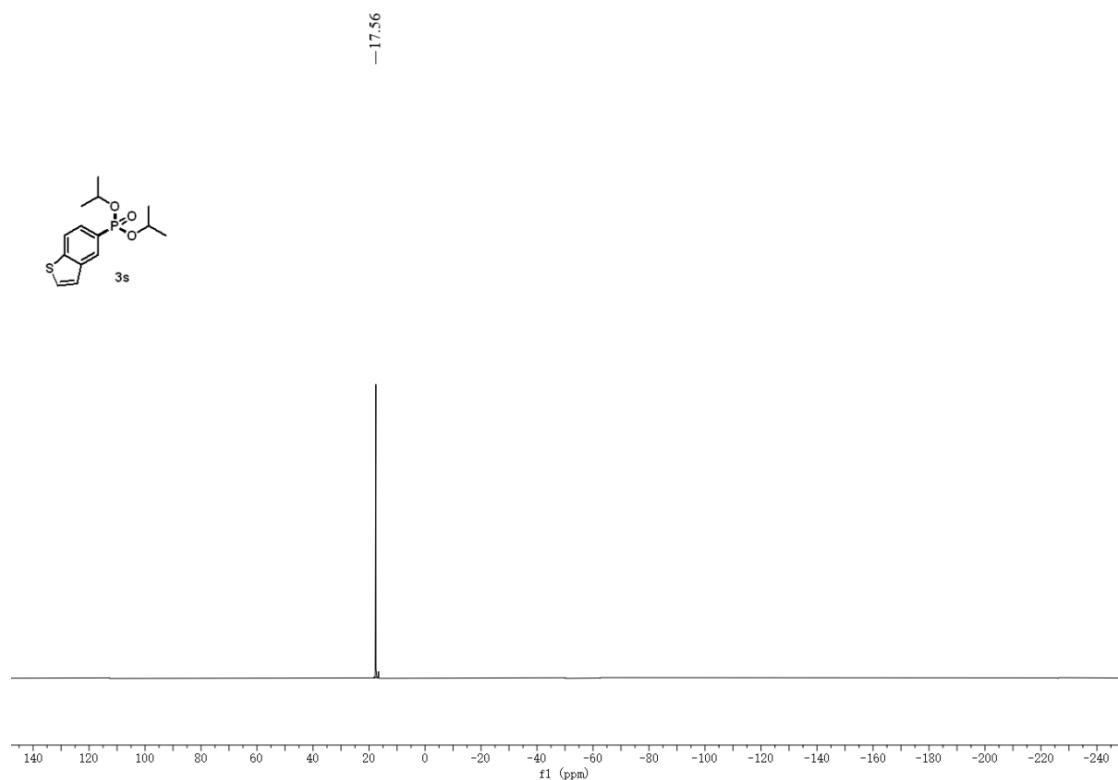
¹H NMR (400 MHz, CDCl₃) spectrum for 3s



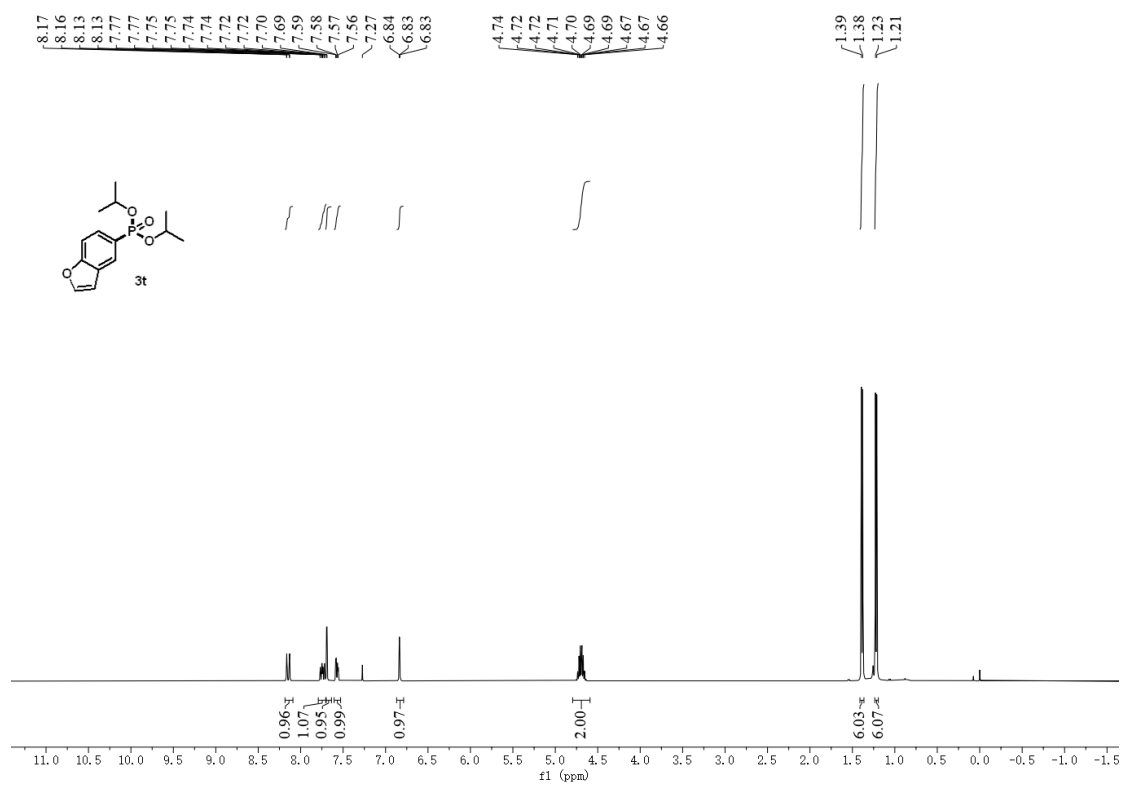
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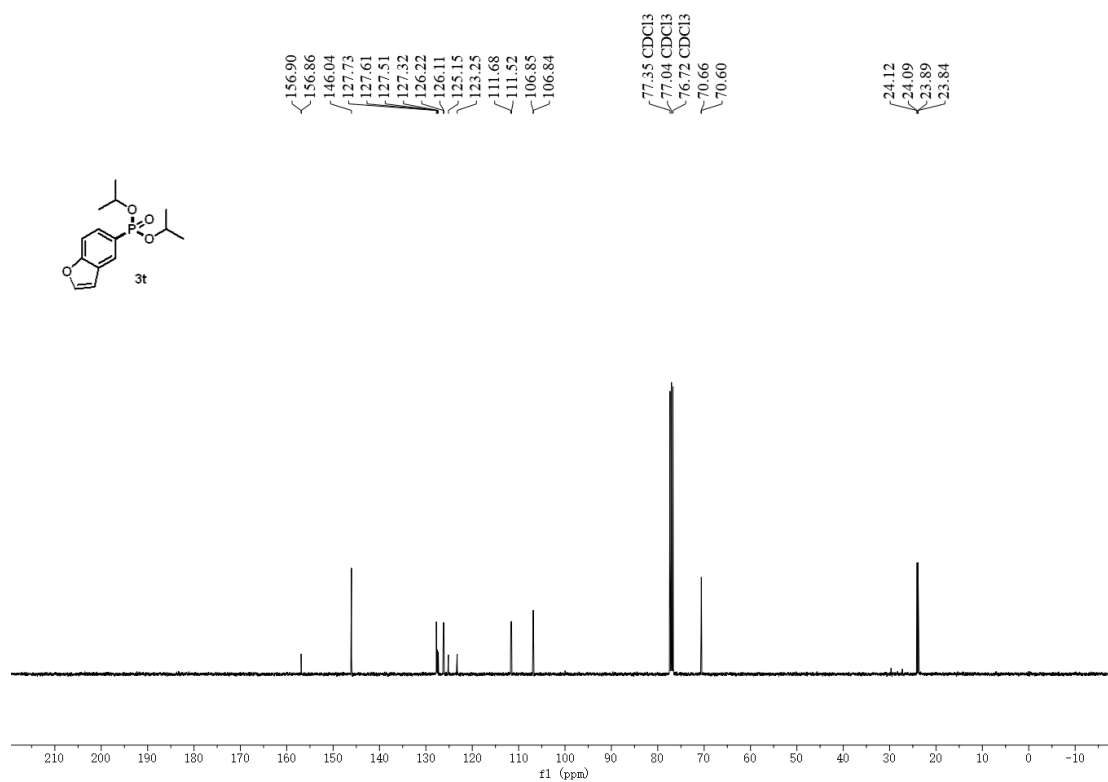
³¹P NMR (121 MHz, CDCl₃) spectrum for 3s



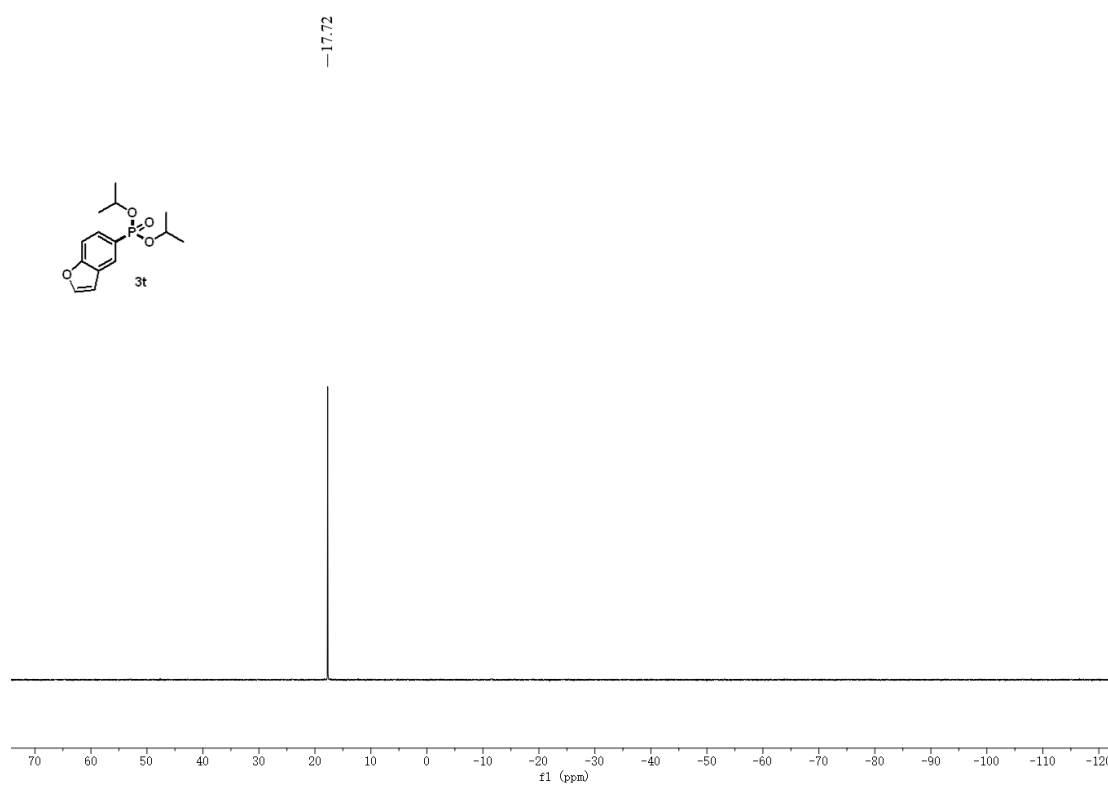
¹H NMR (400 MHz, CDCl₃) spectrum for 3t



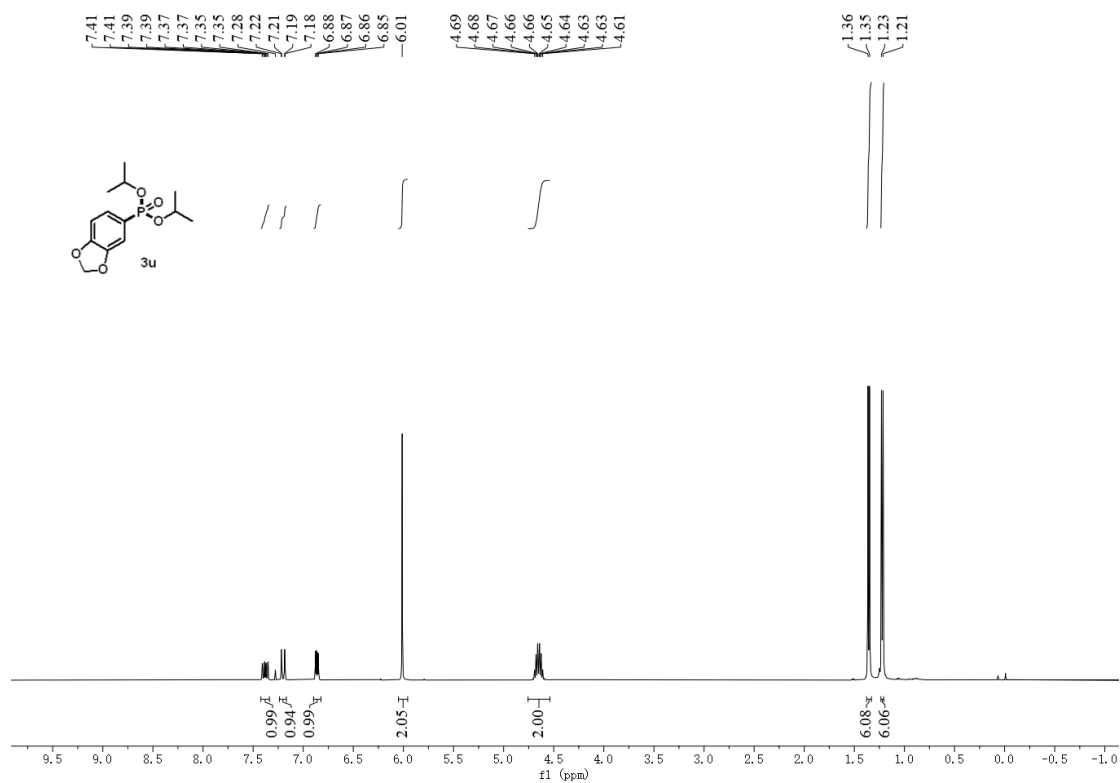
^{13}C NMR (101 MHz, CDCl_3) spectrum for 3t



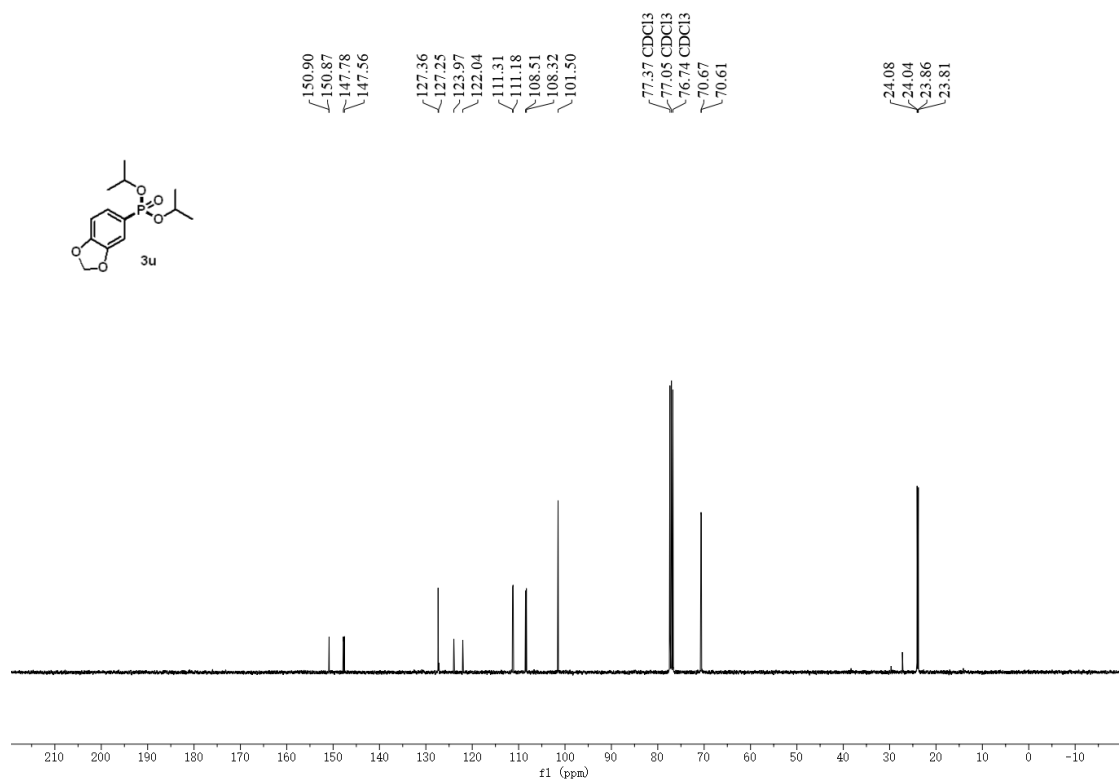
^{31}P NMR (121 MHz, CDCl_3) spectrum for 3t



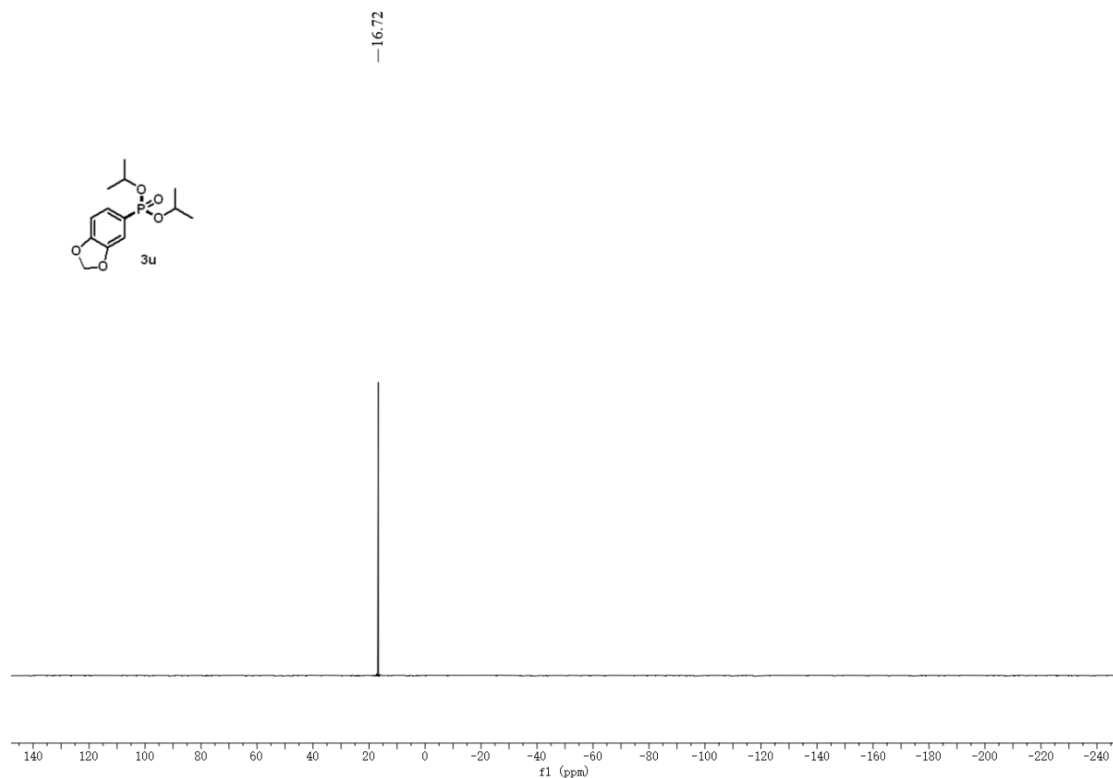
¹H NMR (400 MHz, CDCl₃) spectrum for 3u



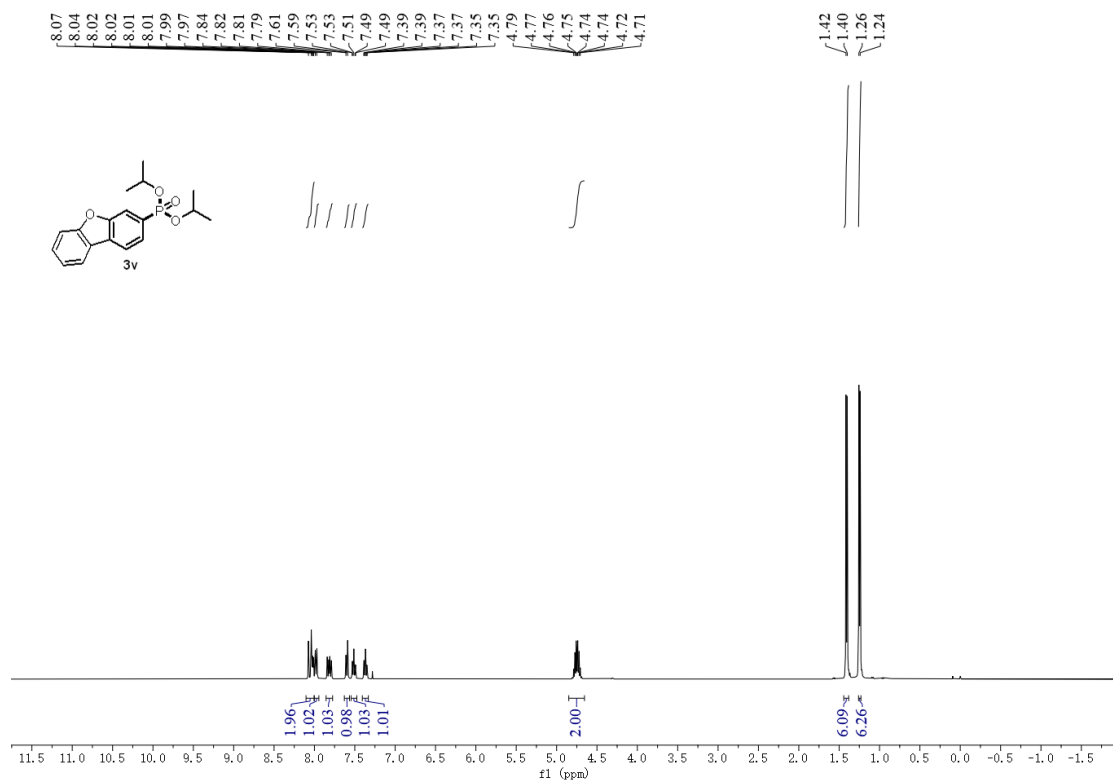
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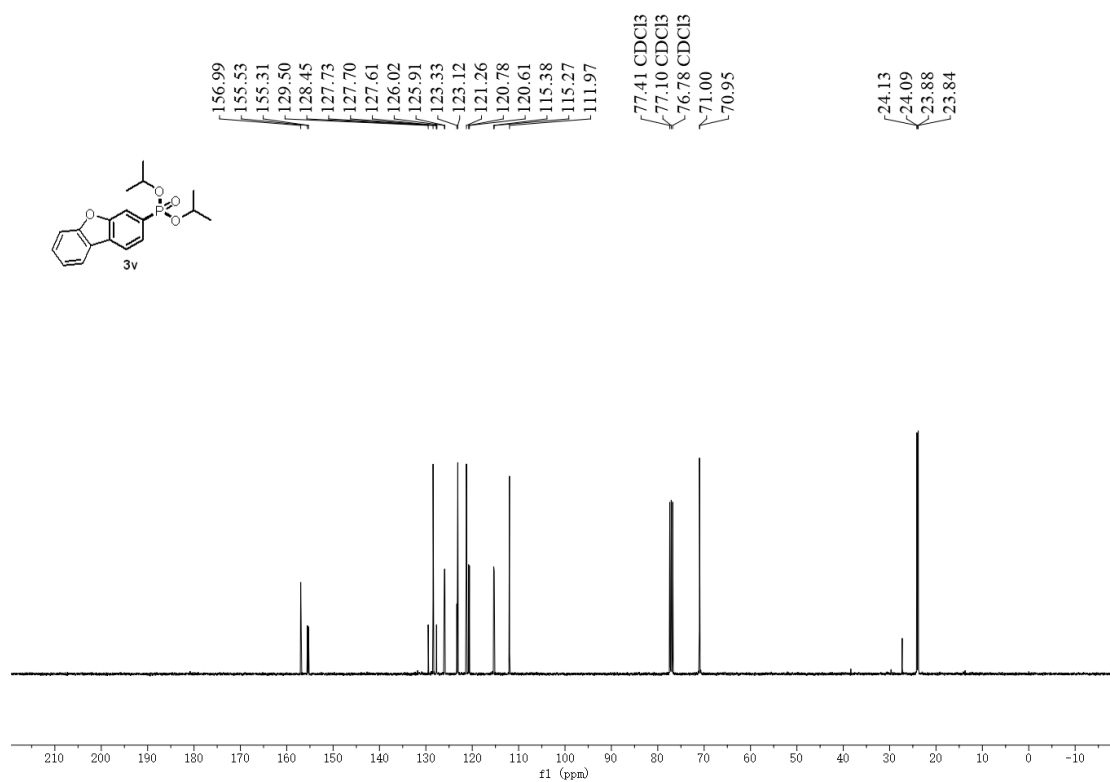
³¹P NMR (121 MHz, CDCl₃) spectrum for 3u



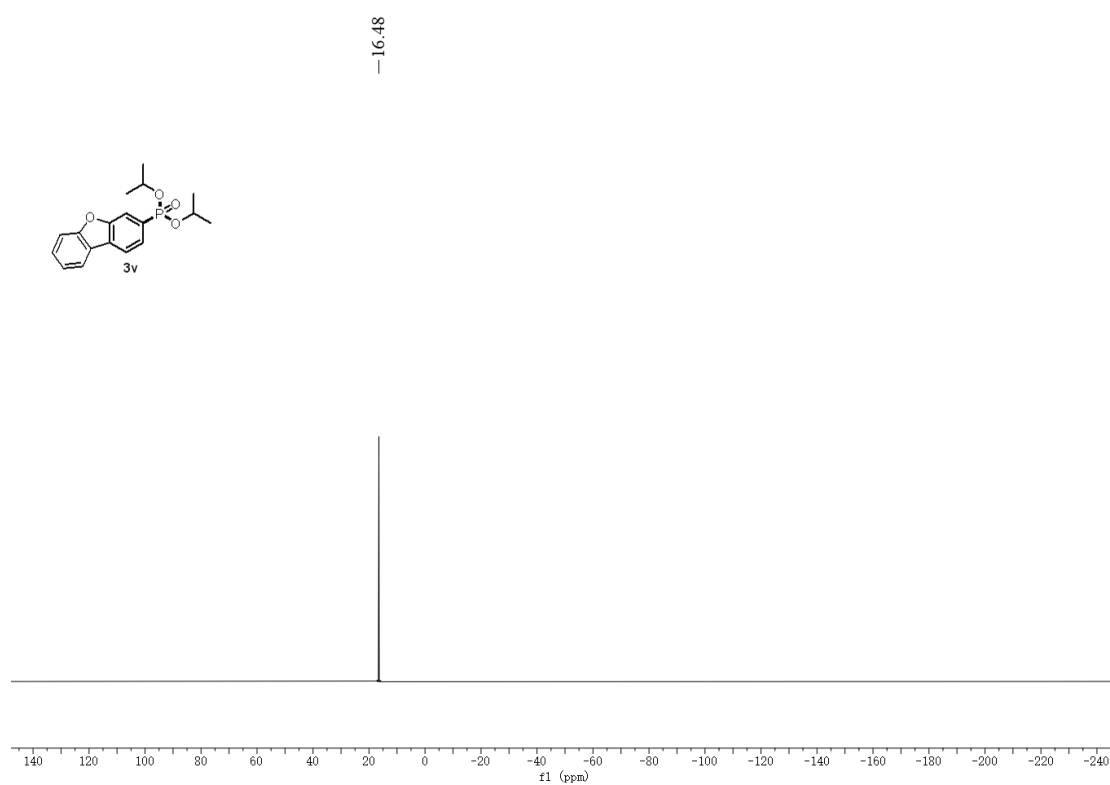
¹H NMR (400 MHz, CDCl₃) spectrum for 3v



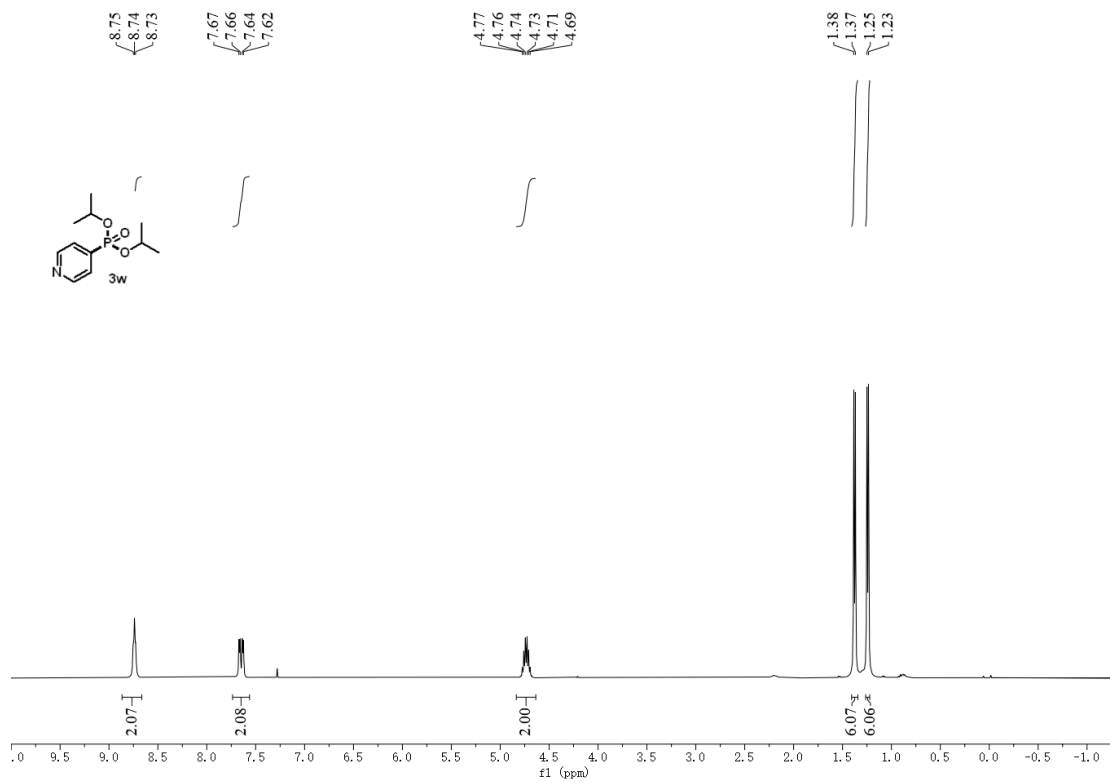
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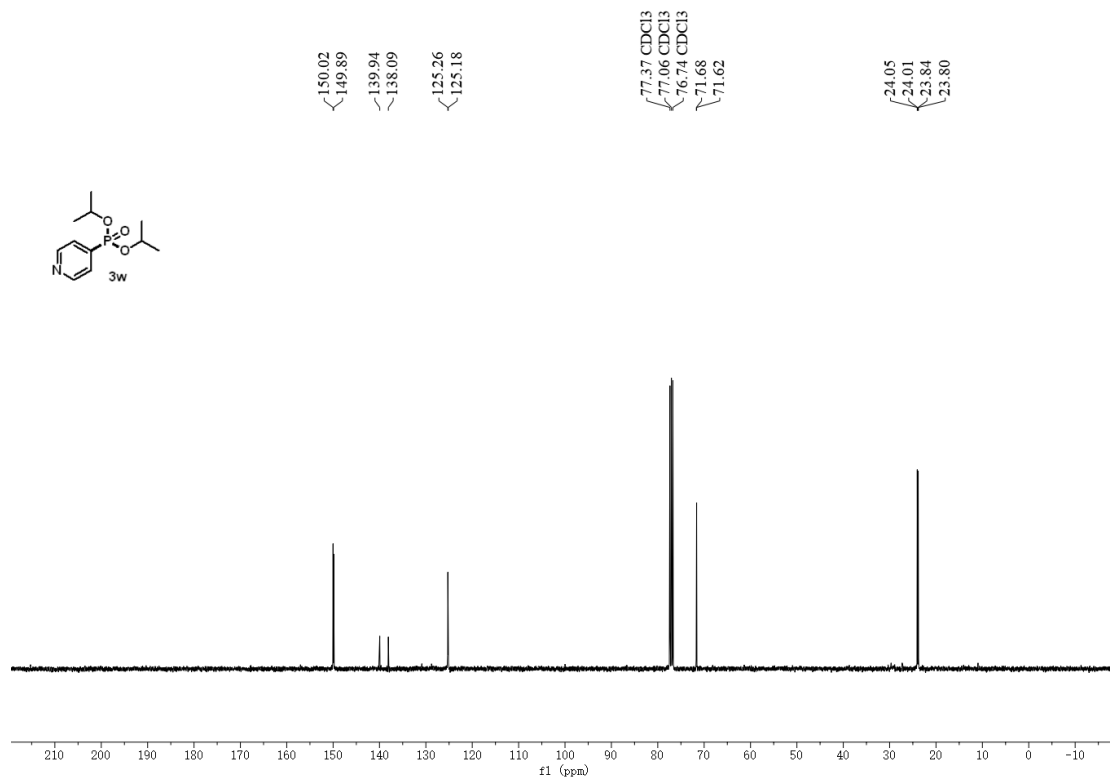
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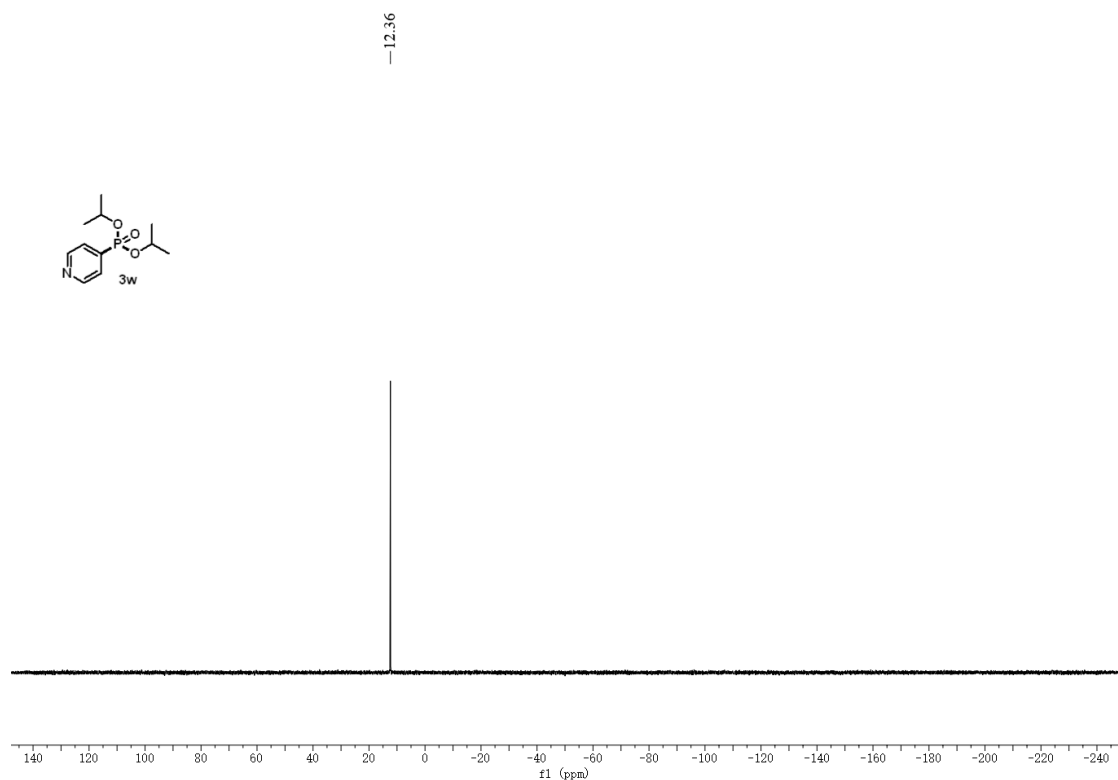
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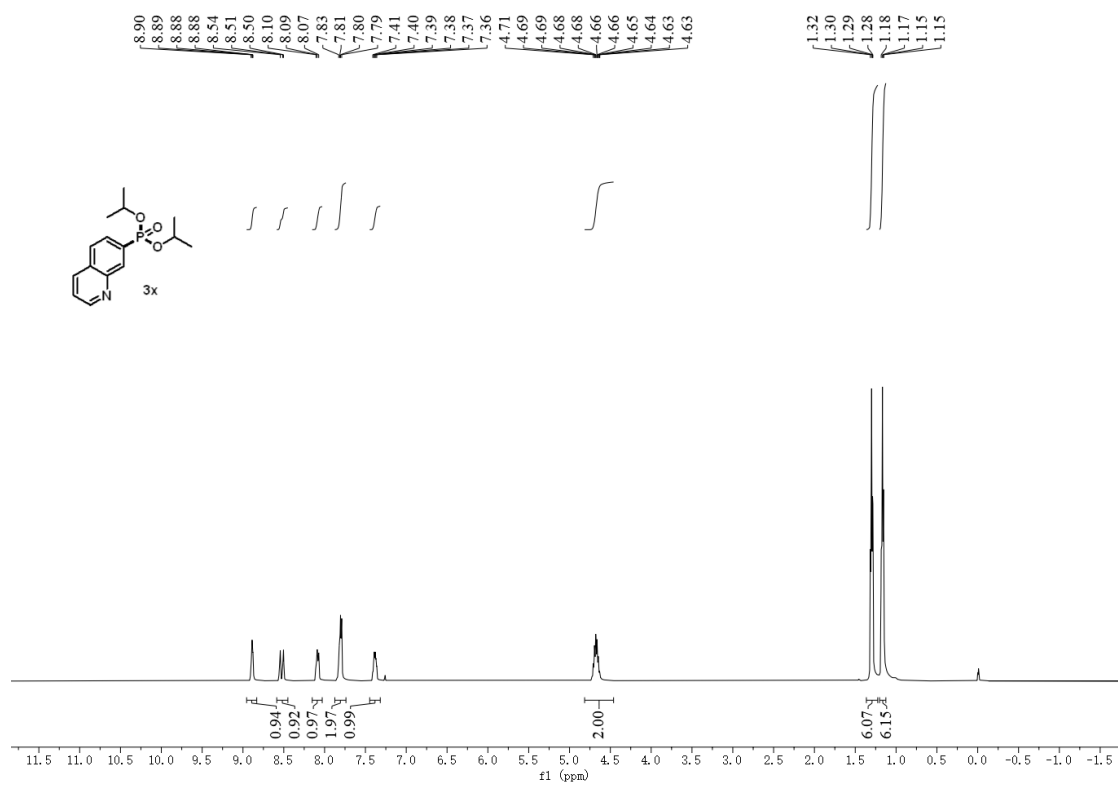
^{13}C NMR (101 MHz, CDCl_3) spectrum for 3w



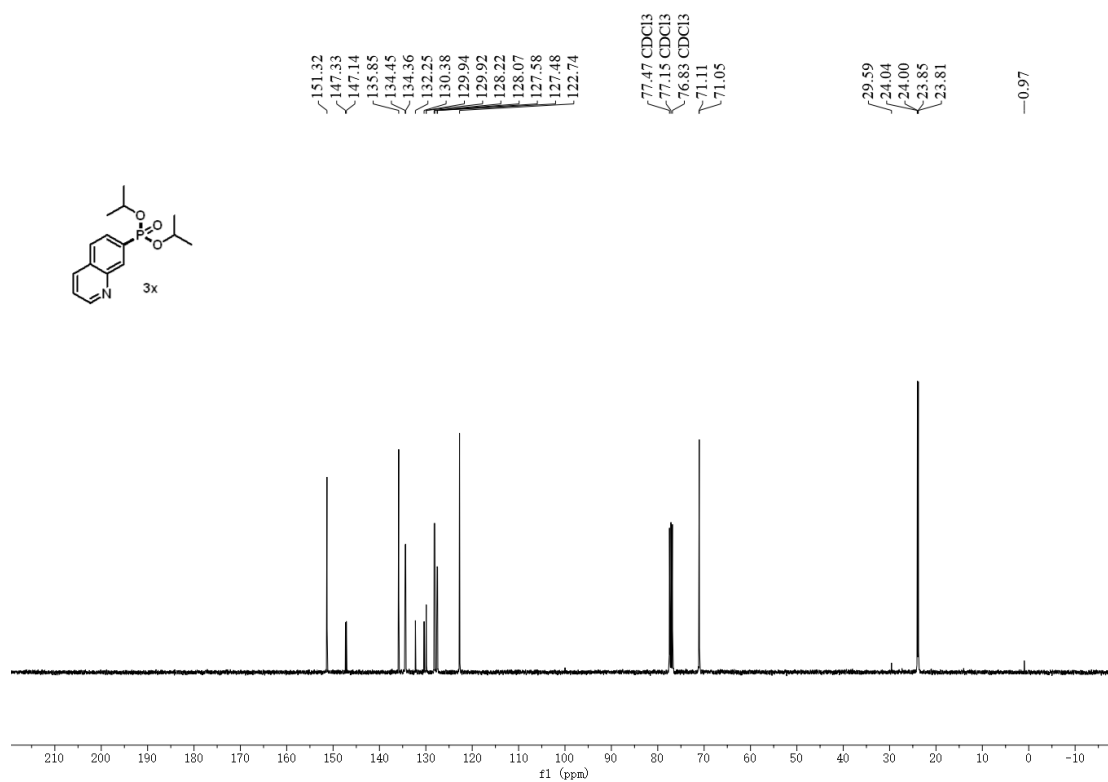
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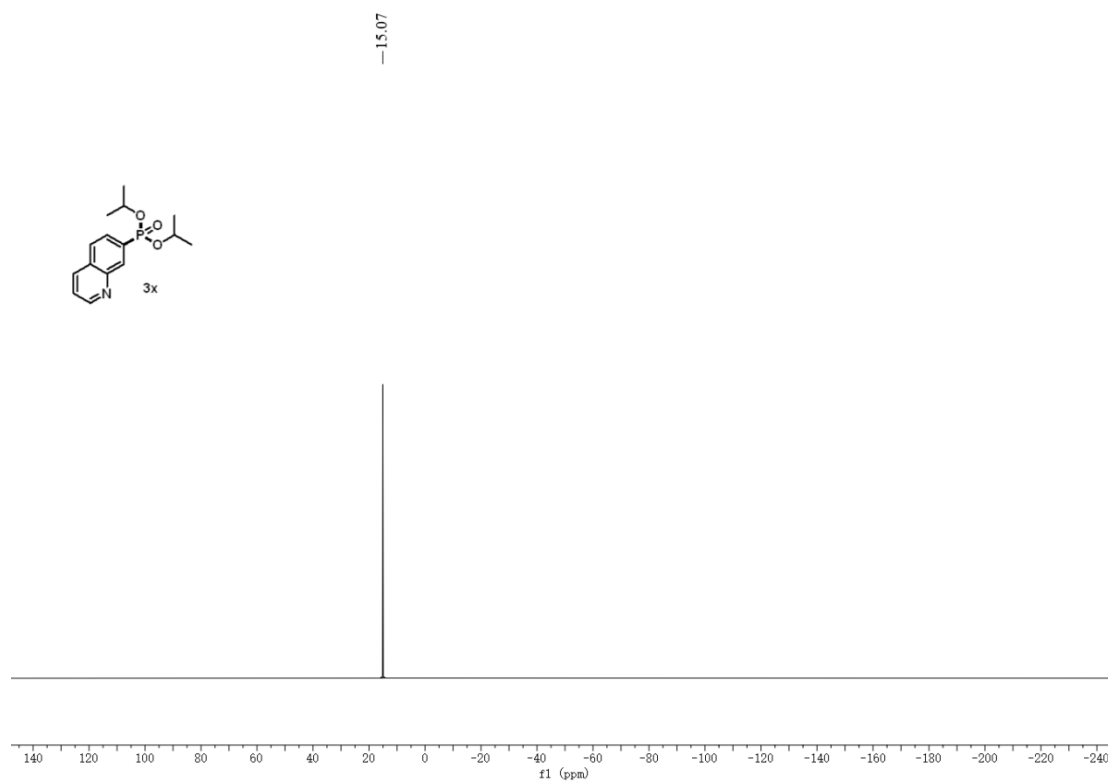
¹H NMR (400 MHz, CDCl₃) spectrum for 3x



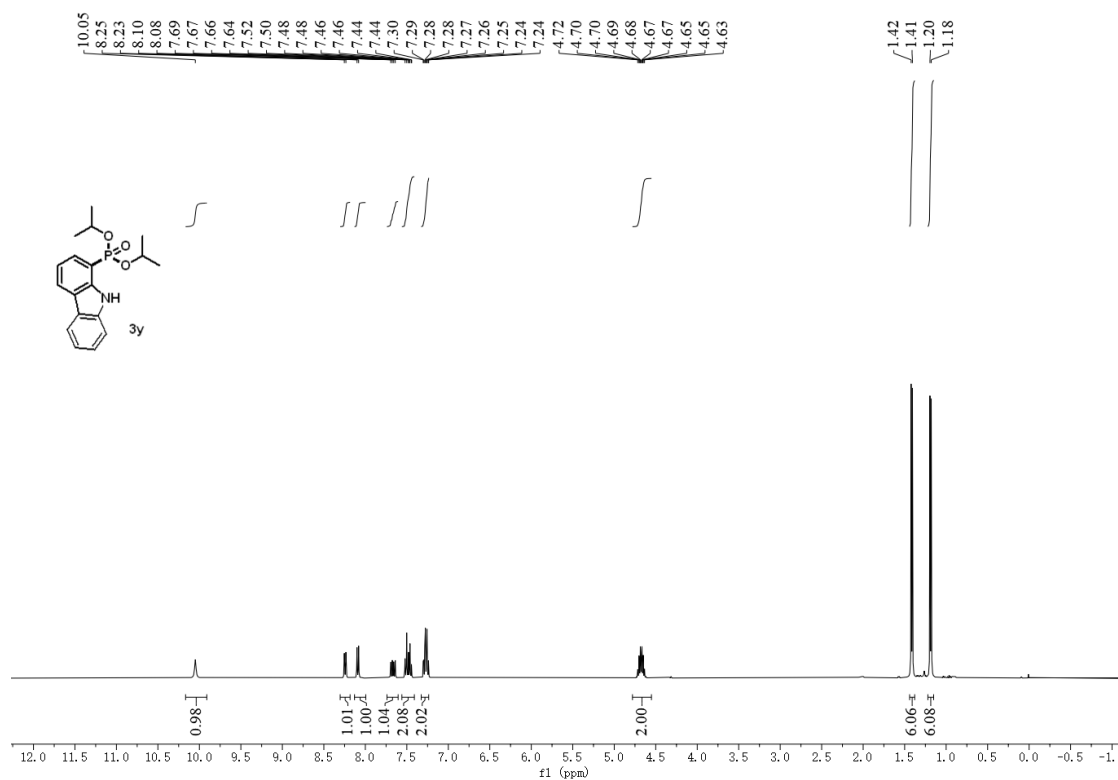
¹³C NMR (101 MHz, CDCl₃) spectrum for 3x



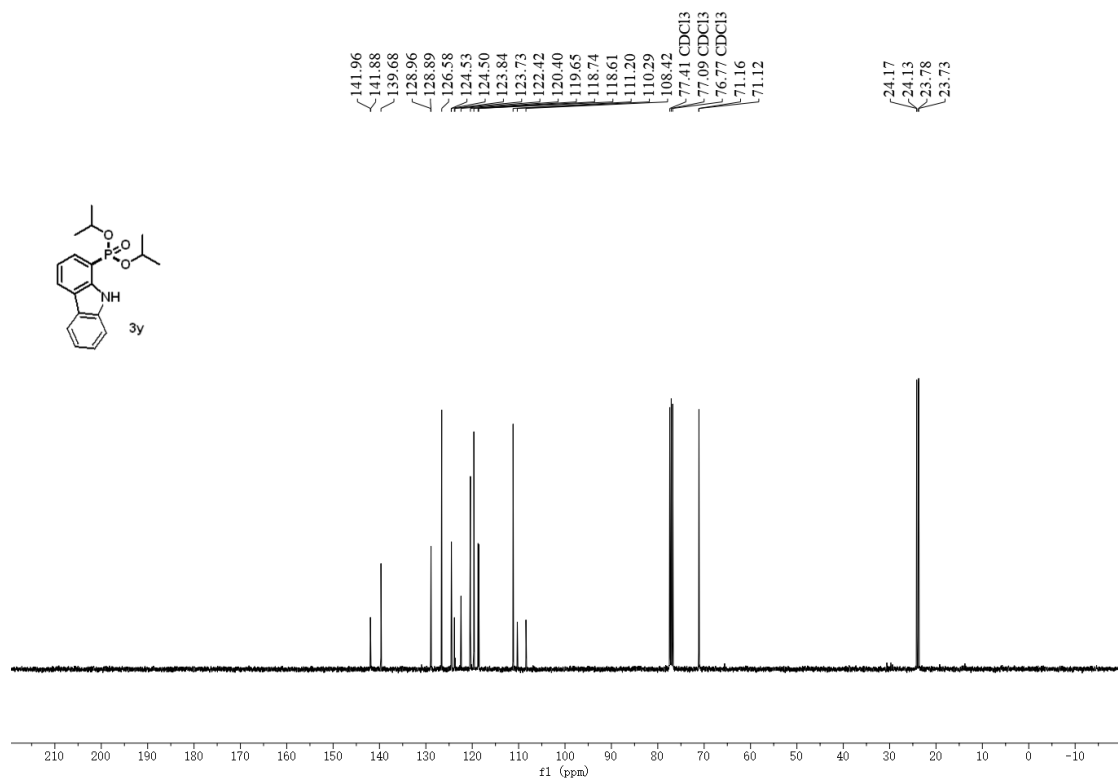
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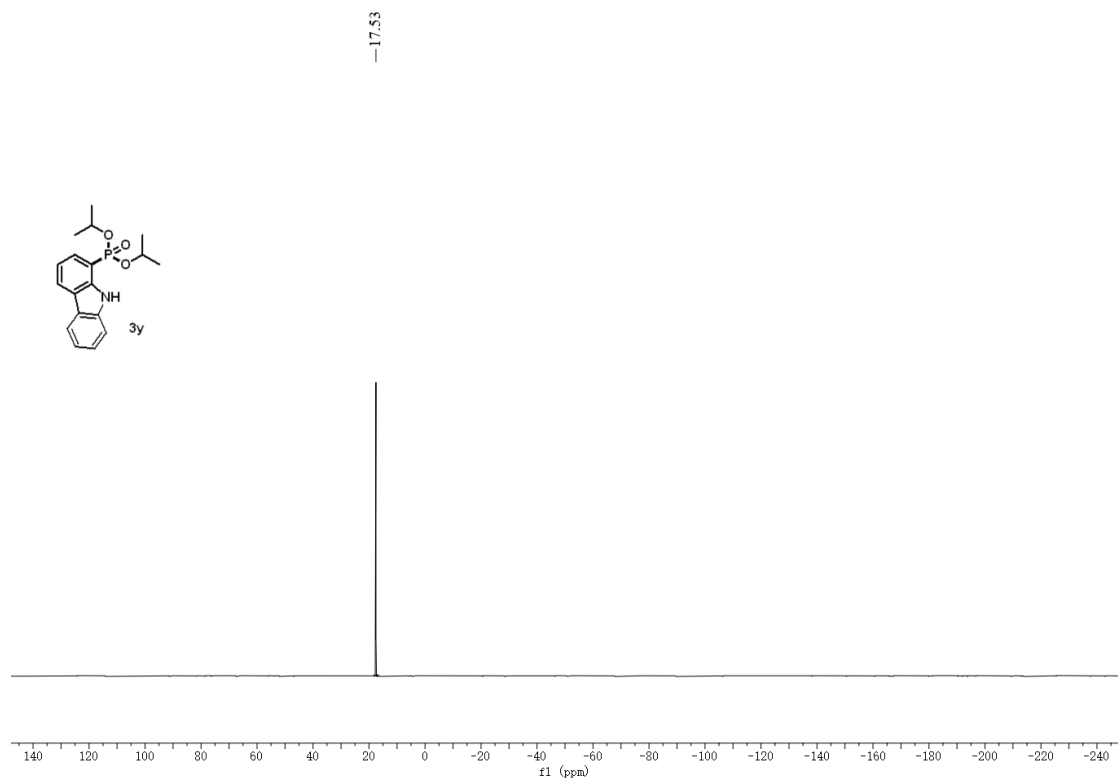
^1H NMR (400 MHz, CDCl_3) spectrum for **3y**



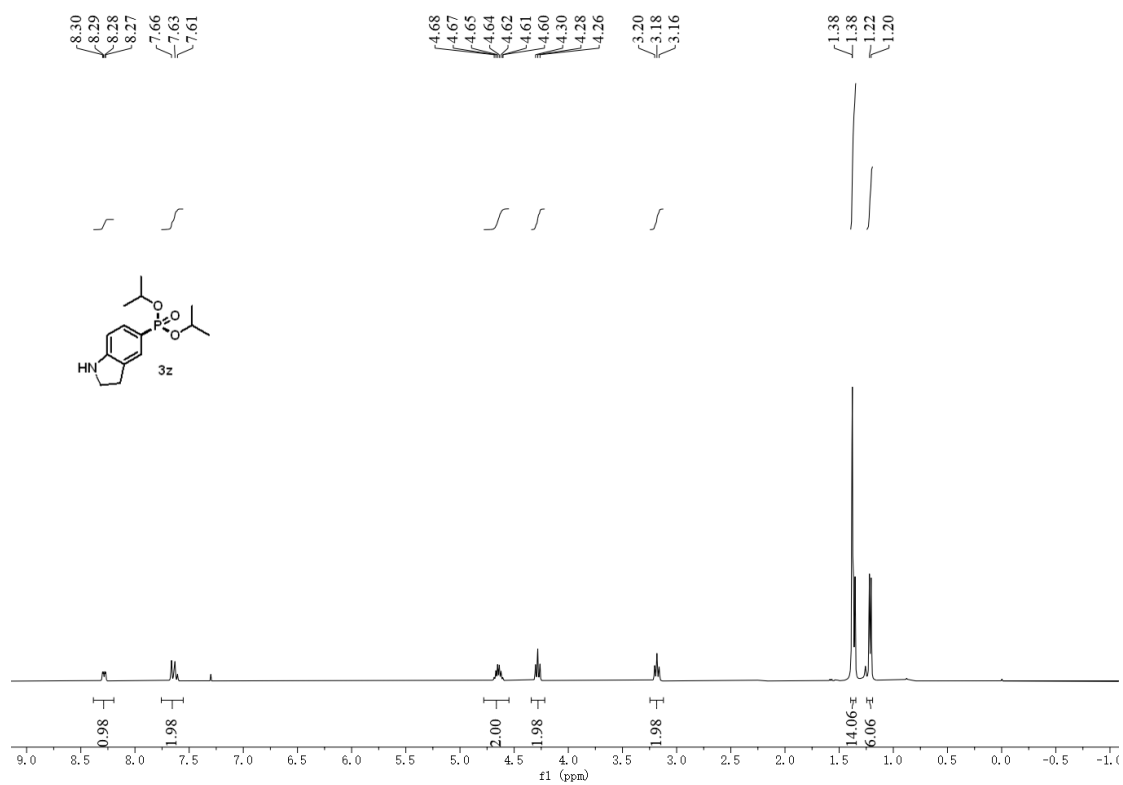
^{13}C NMR (101 MHz, CDCl_3) spectrum for **3y**



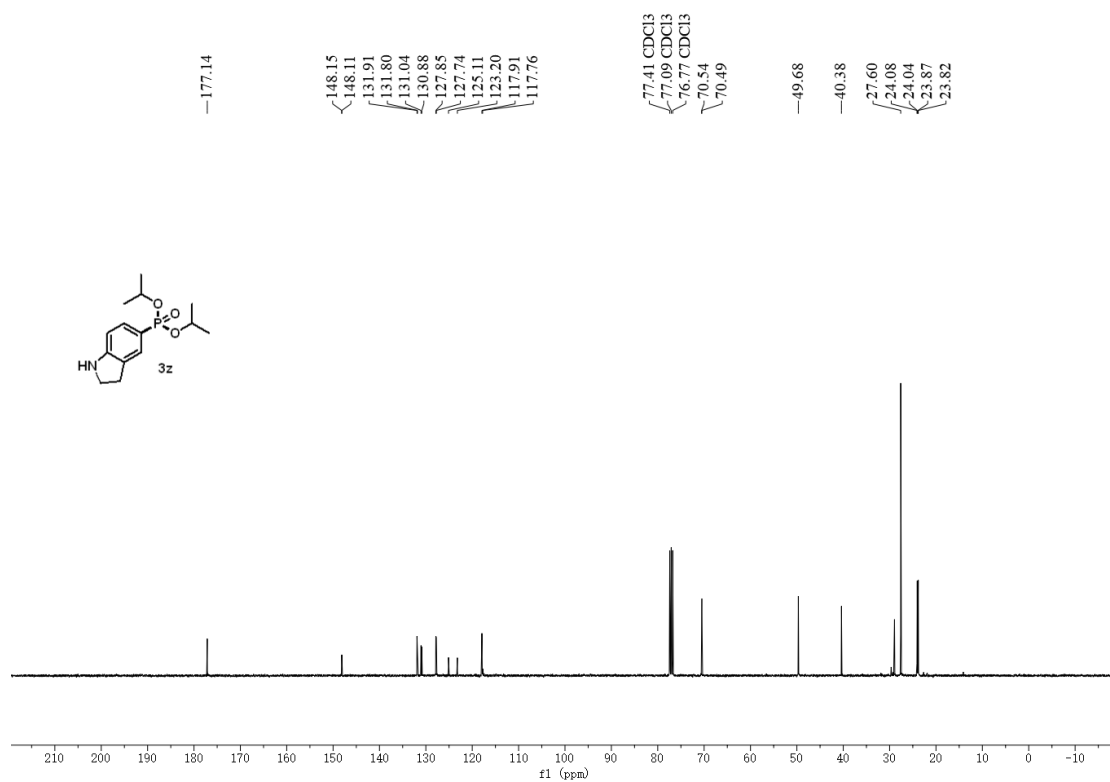
^{31}P NMR (121 MHz, CDCl_3) spectrum for 3y



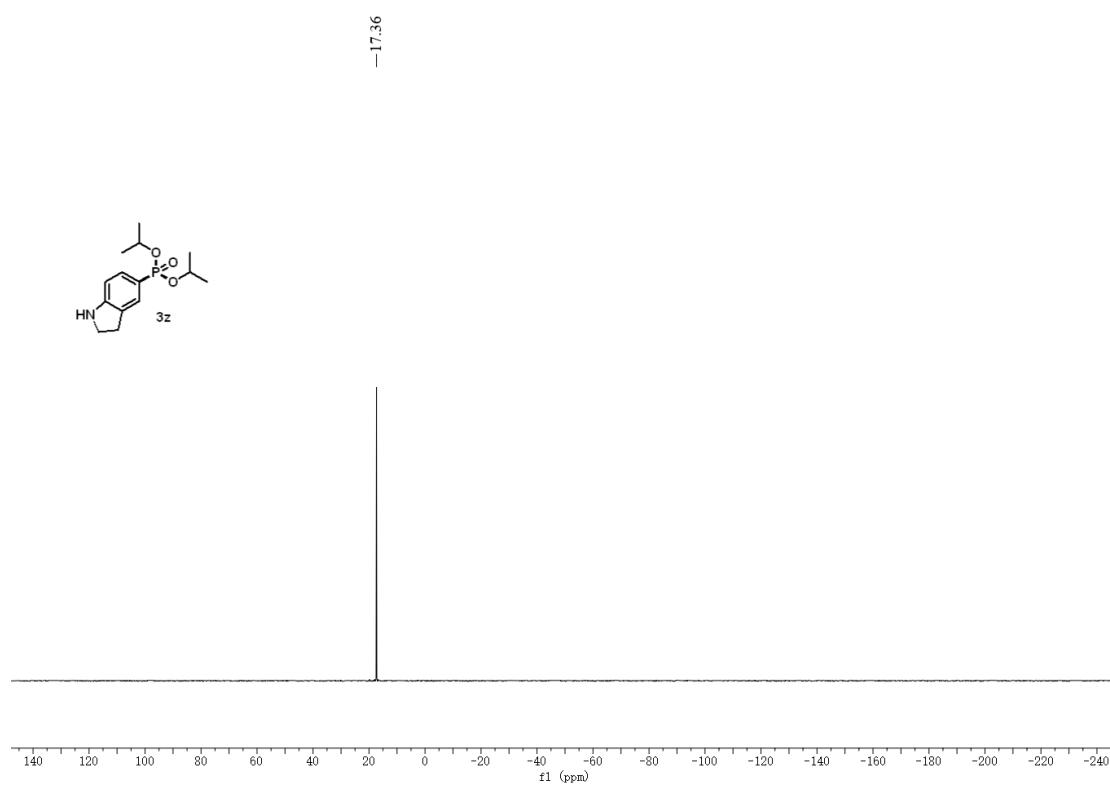
^1H NMR (400 MHz, CDCl_3) spectrum for 3z



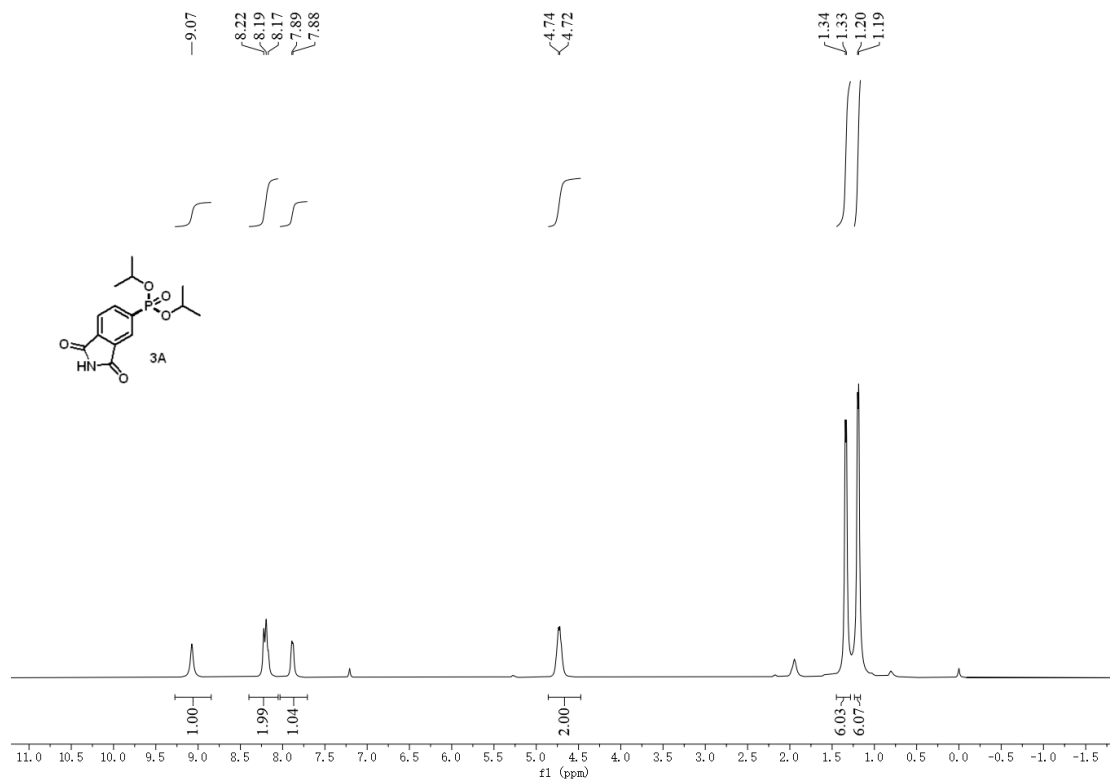
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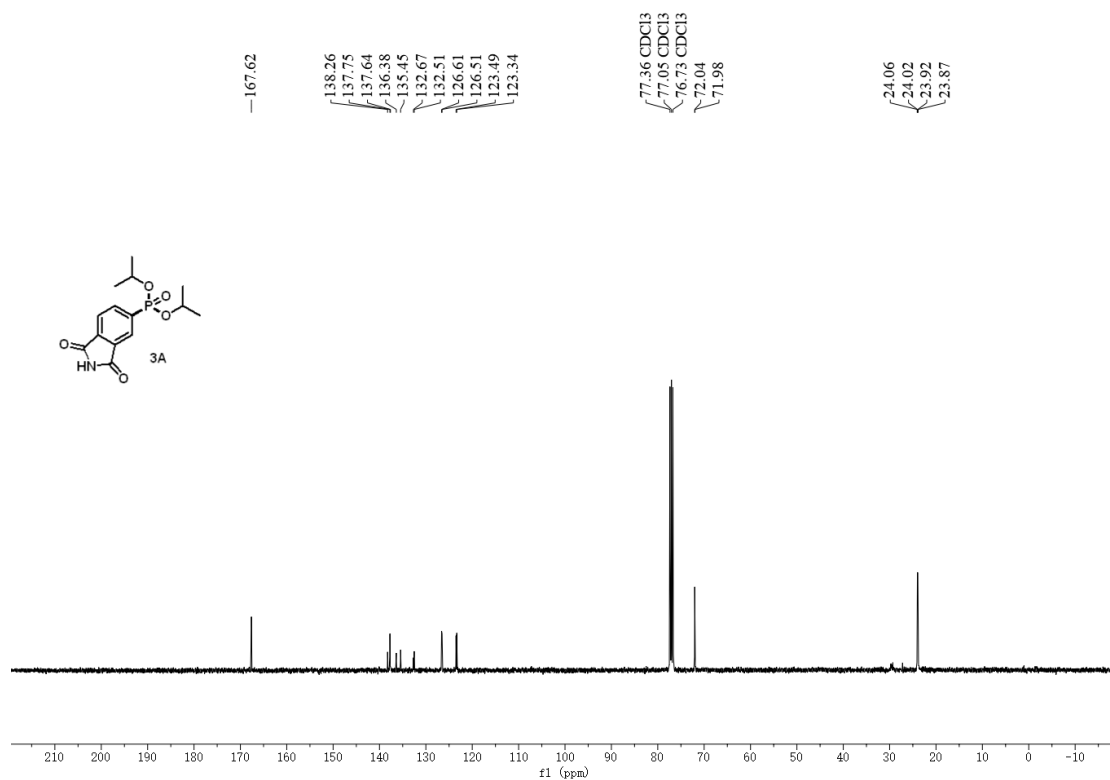
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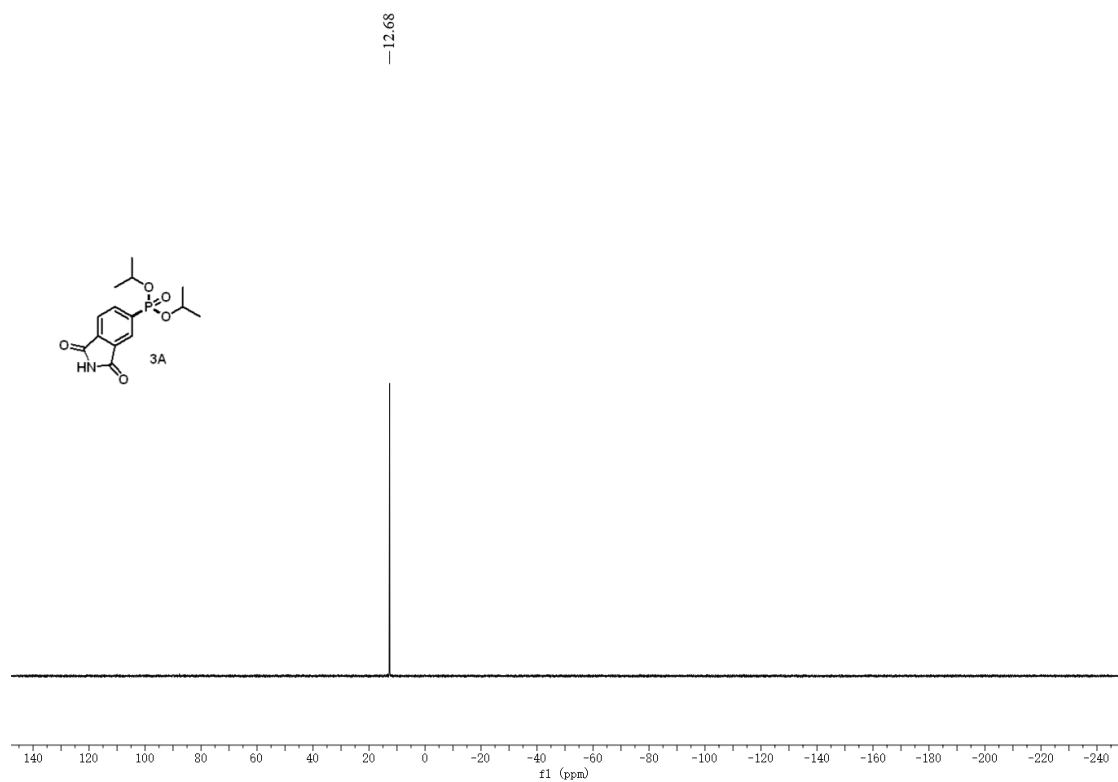
^1H NMR (400 MHz, CDCl_3) spectrum for 3A



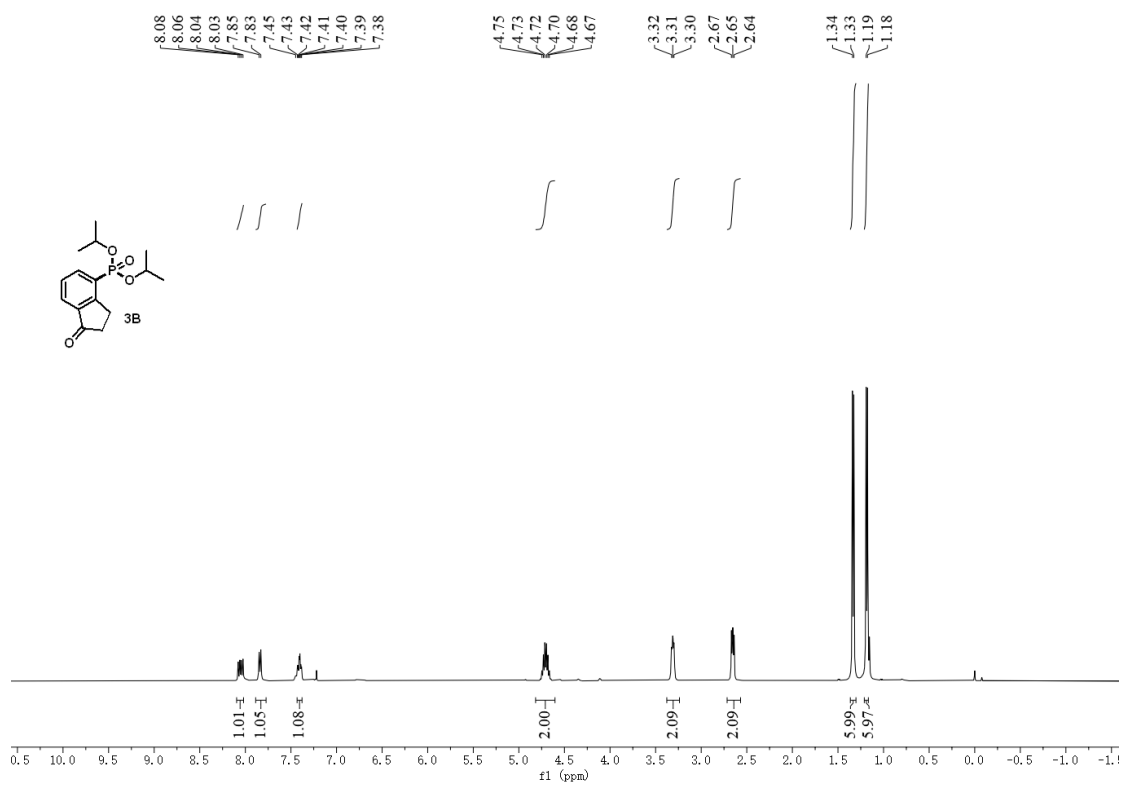
^{13}C NMR (101 MHz, CDCl_3) spectrum for 3A



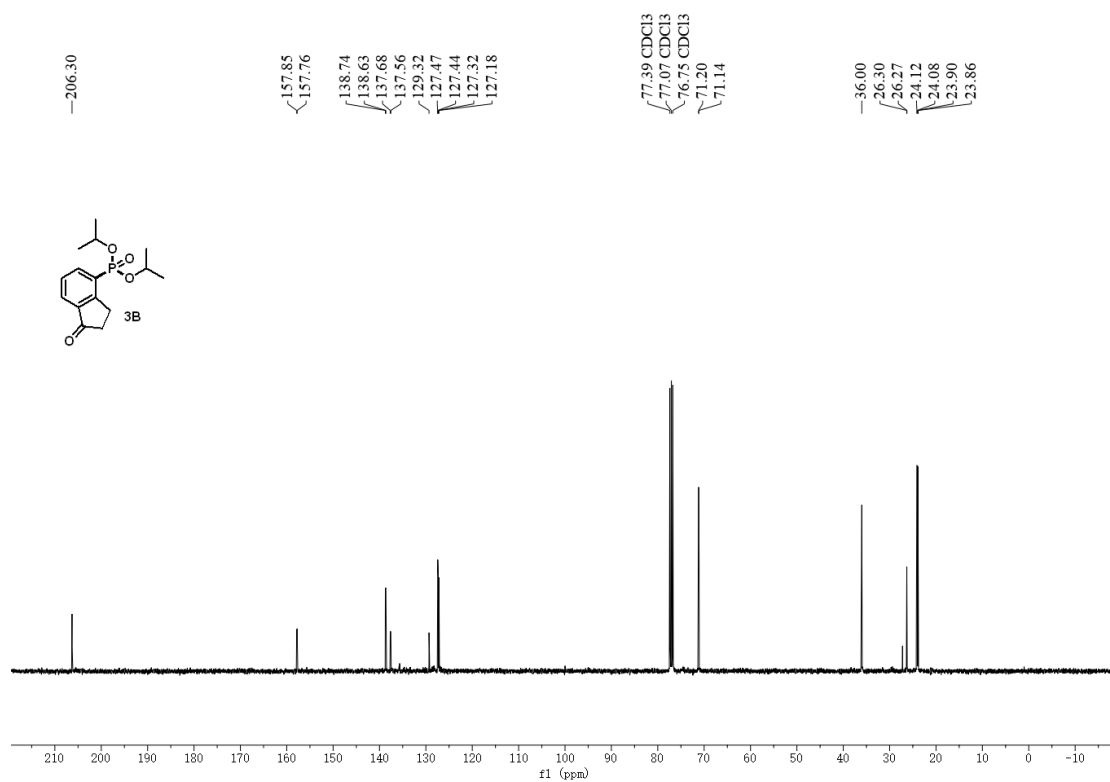
^{31}P NMR (121 MHz, CDCl_3) spectrum for 3A



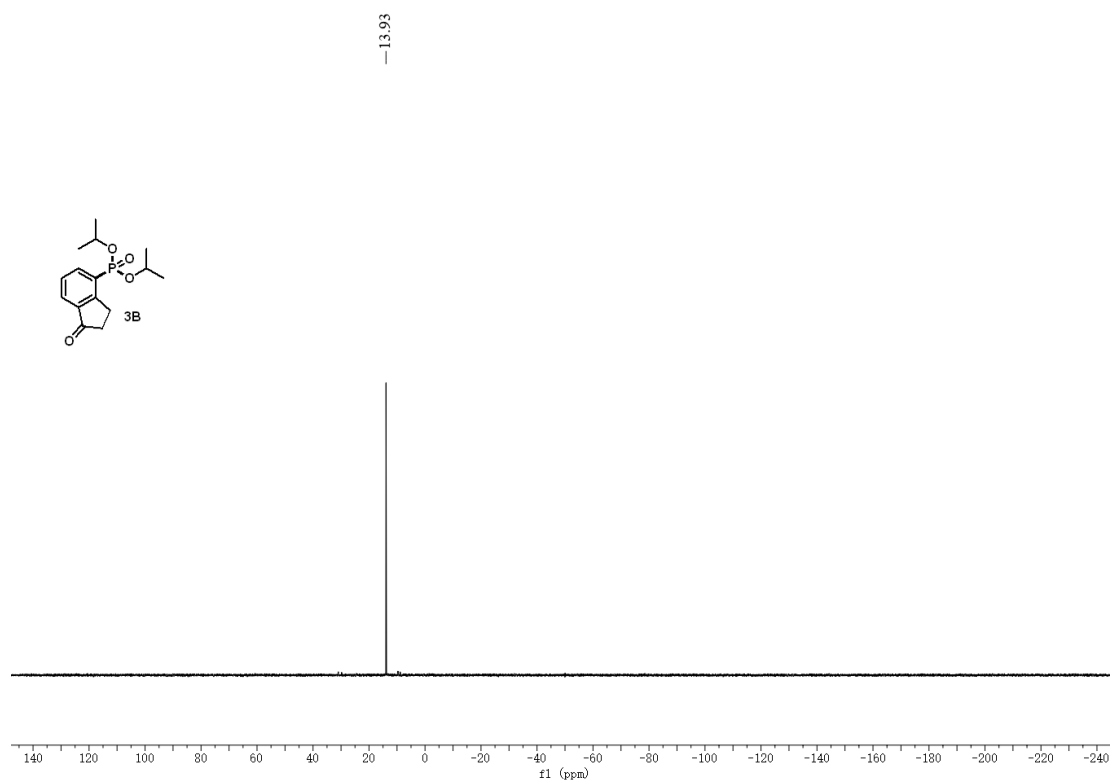
^1H NMR (400 MHz, CDCl_3) spectrum for 3B



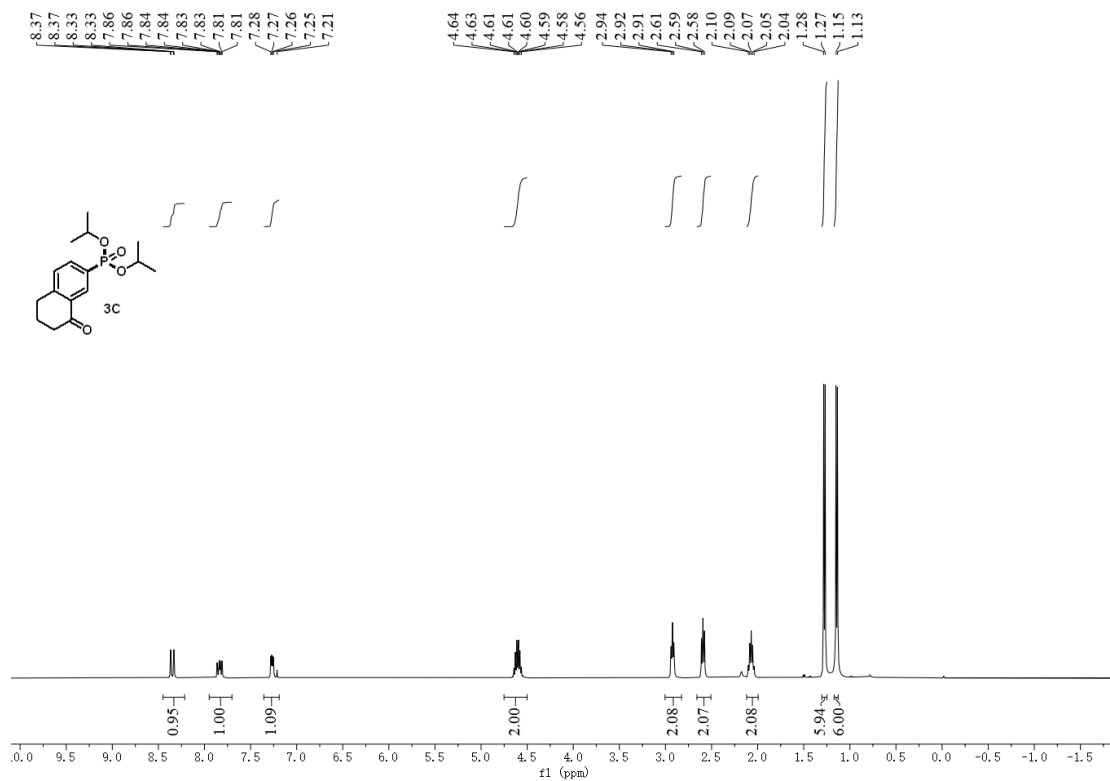
¹³C NMR (101 MHz, CDCl₃) spectrum for 3B



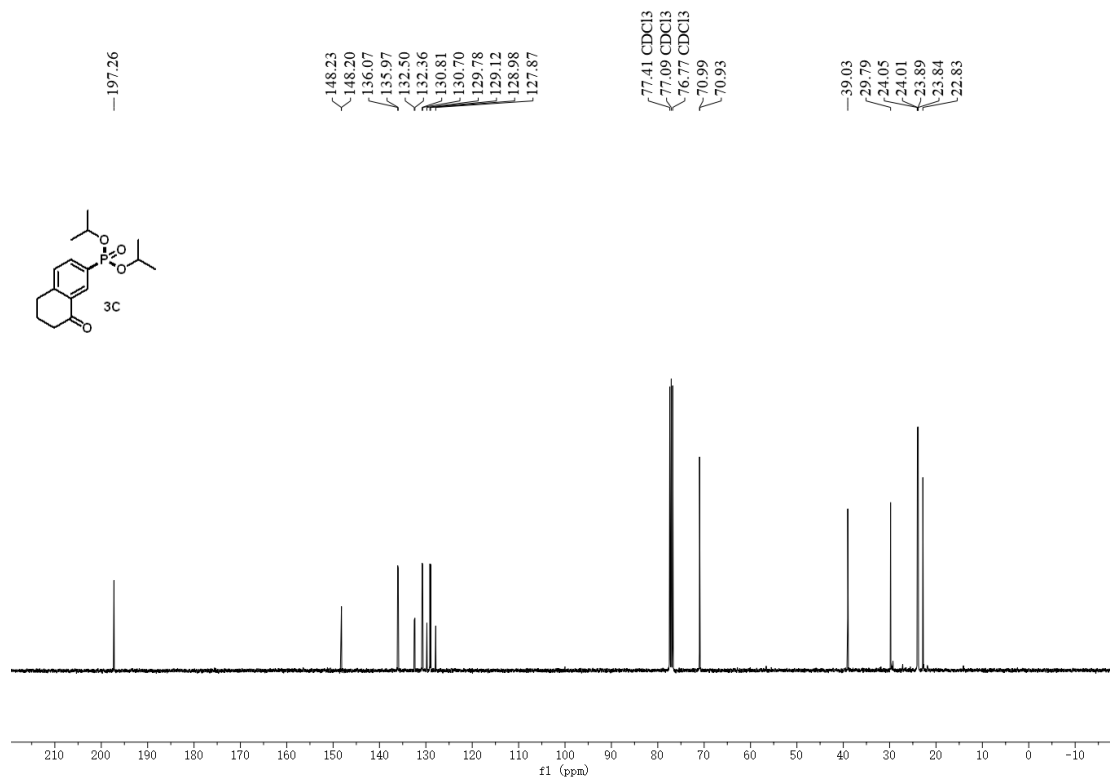
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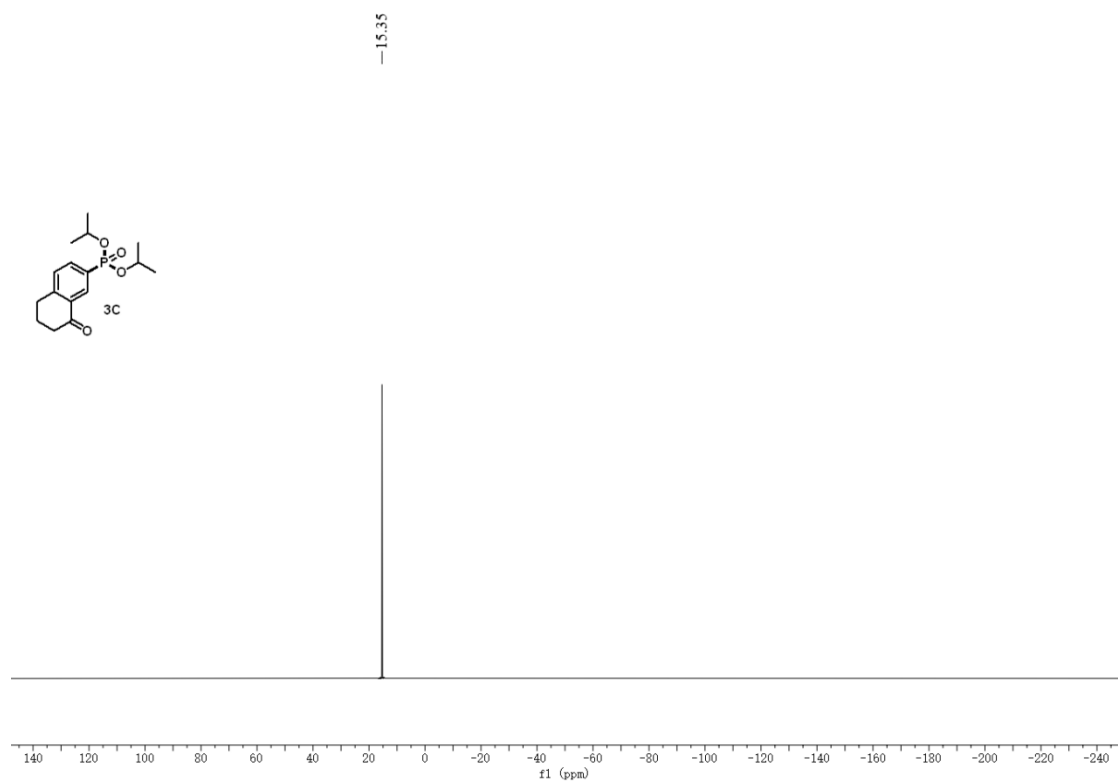
^1H NMR (400 MHz, CDCl_3) spectrum for 3C



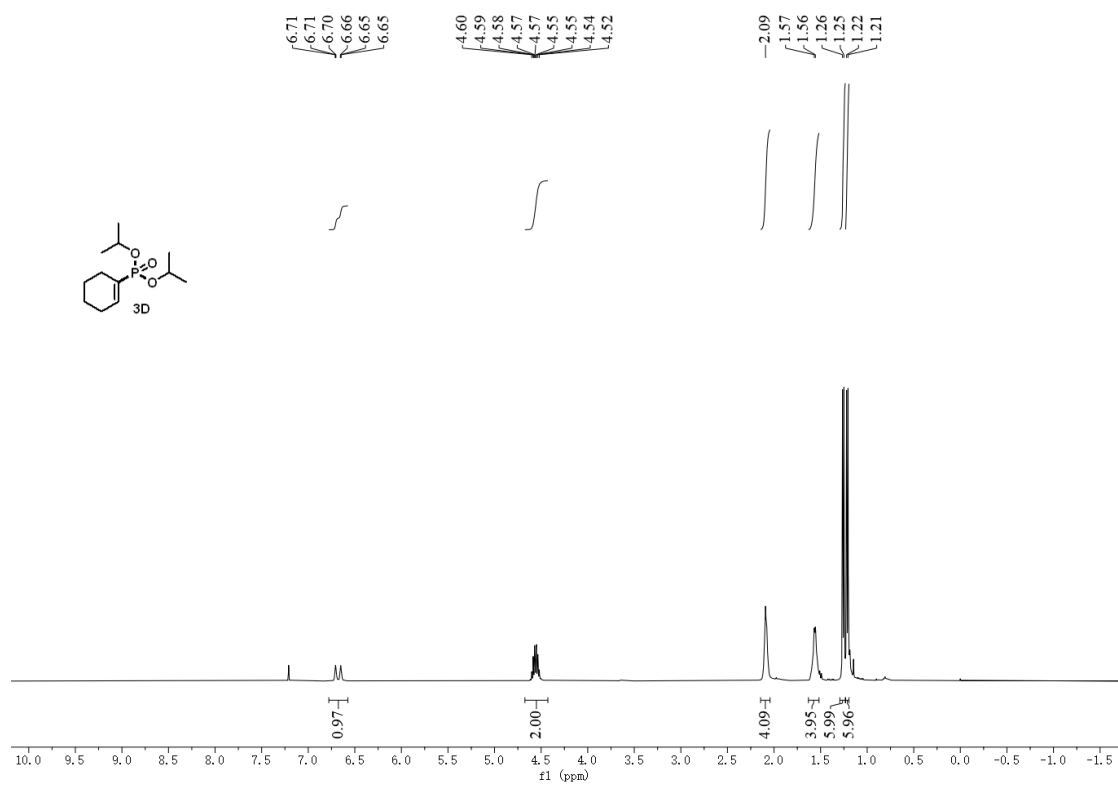
^{13}C NMR (101 MHz, CDCl_3) spectrum for 3C



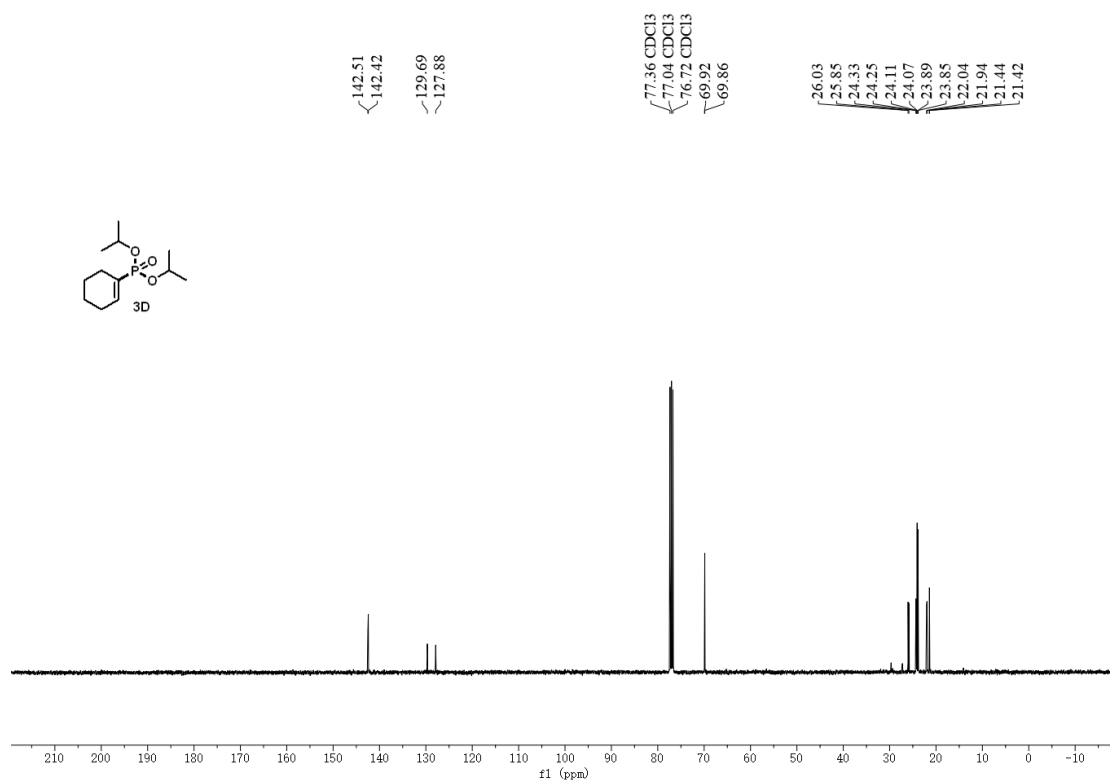
³¹P NMR (121 MHz, CDCl₃) spectrum for 3C



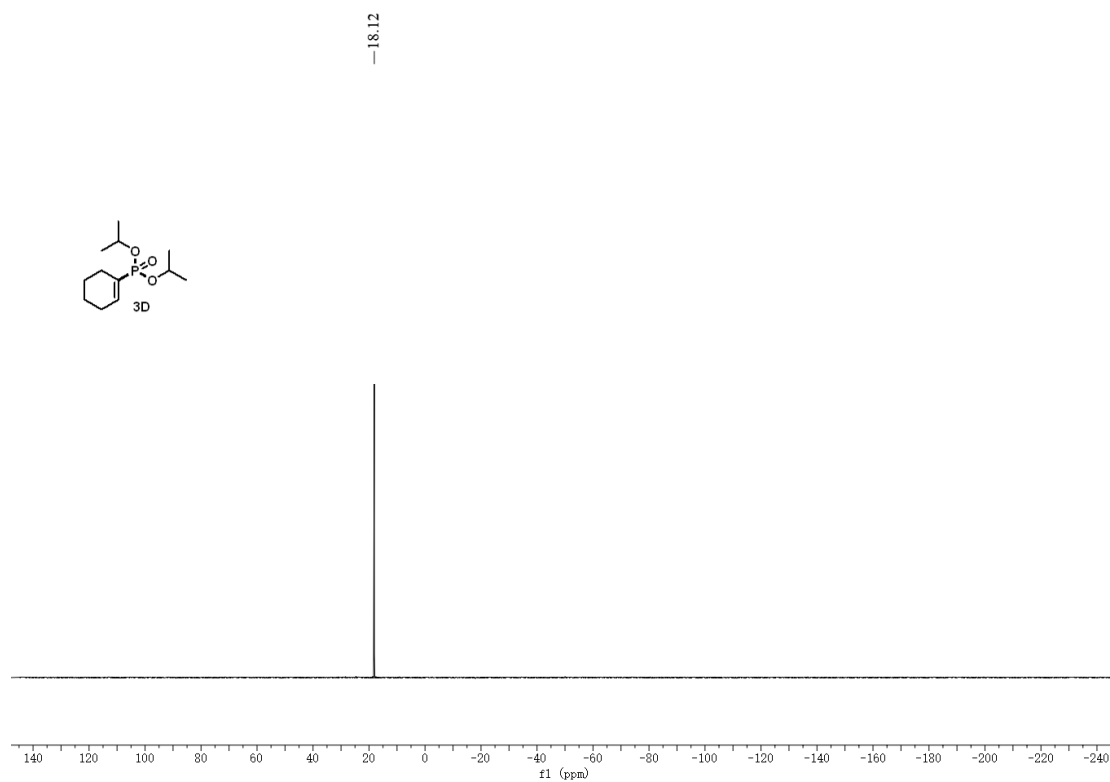
¹H NMR (400 MHz, CDCl₃) spectrum for 3D



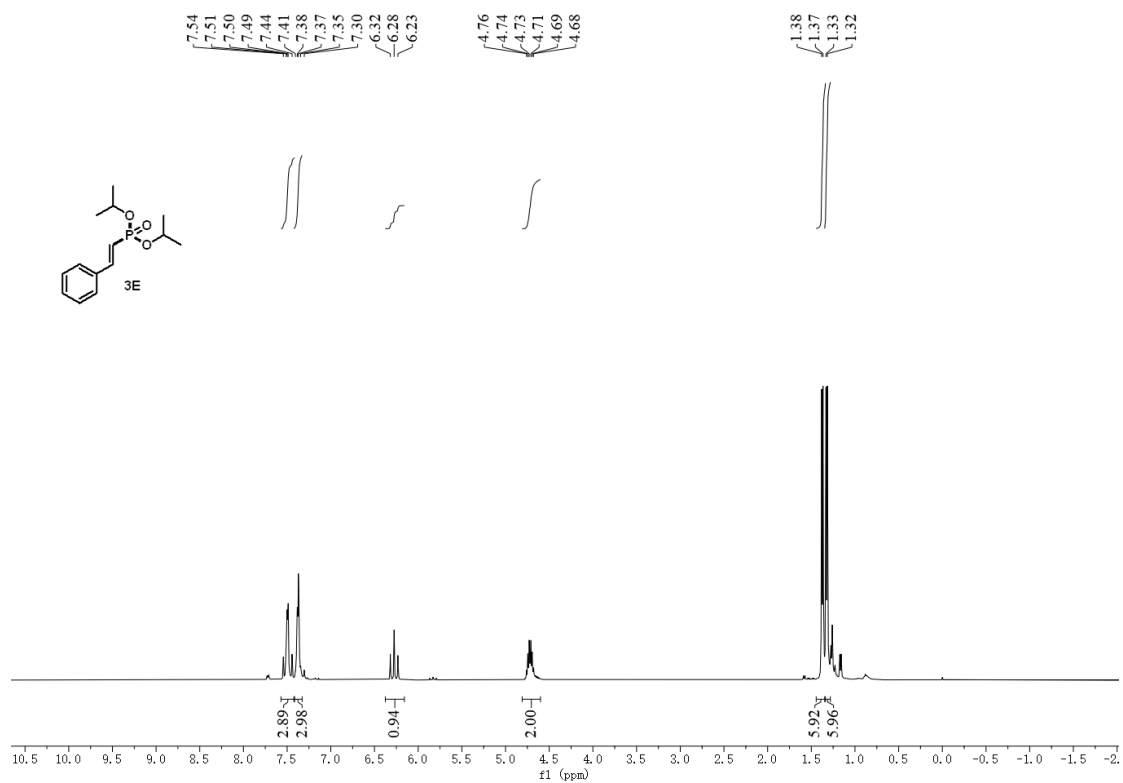
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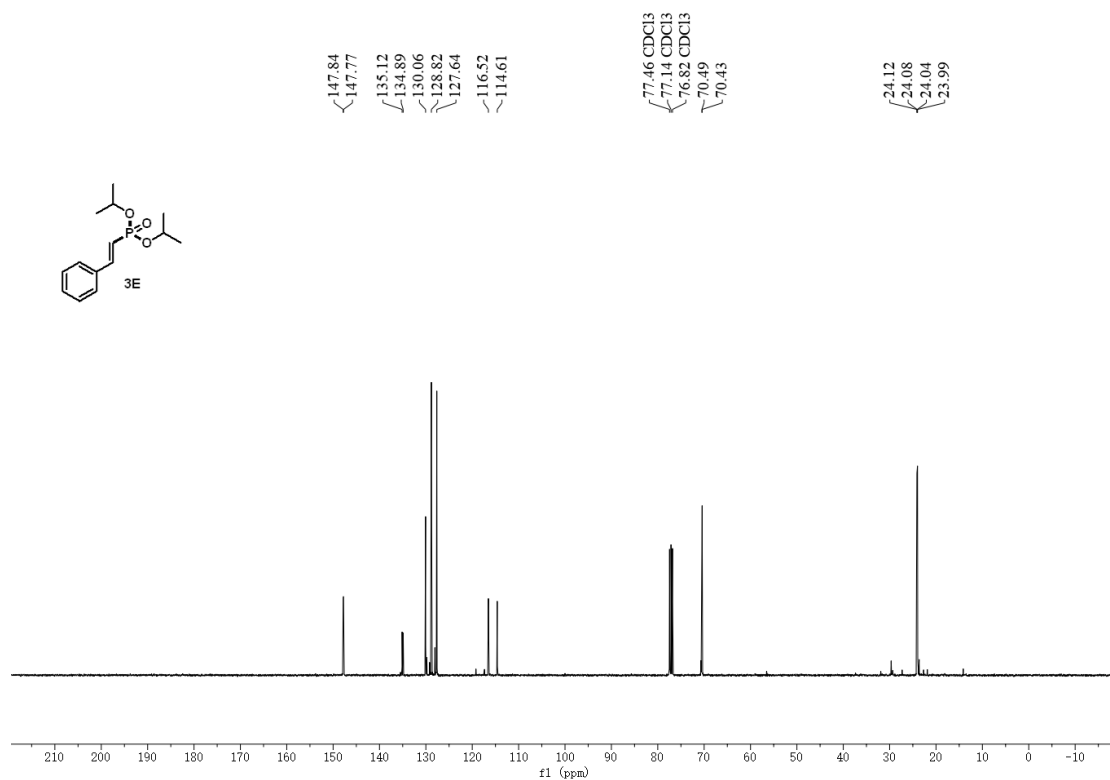
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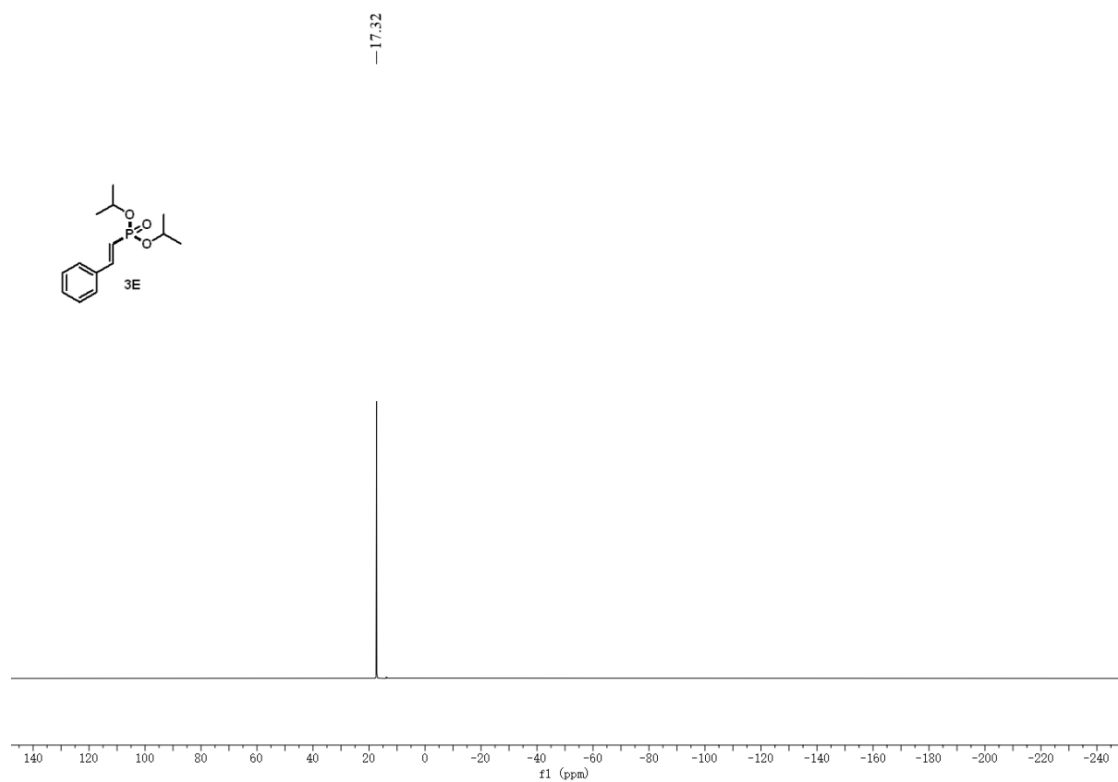
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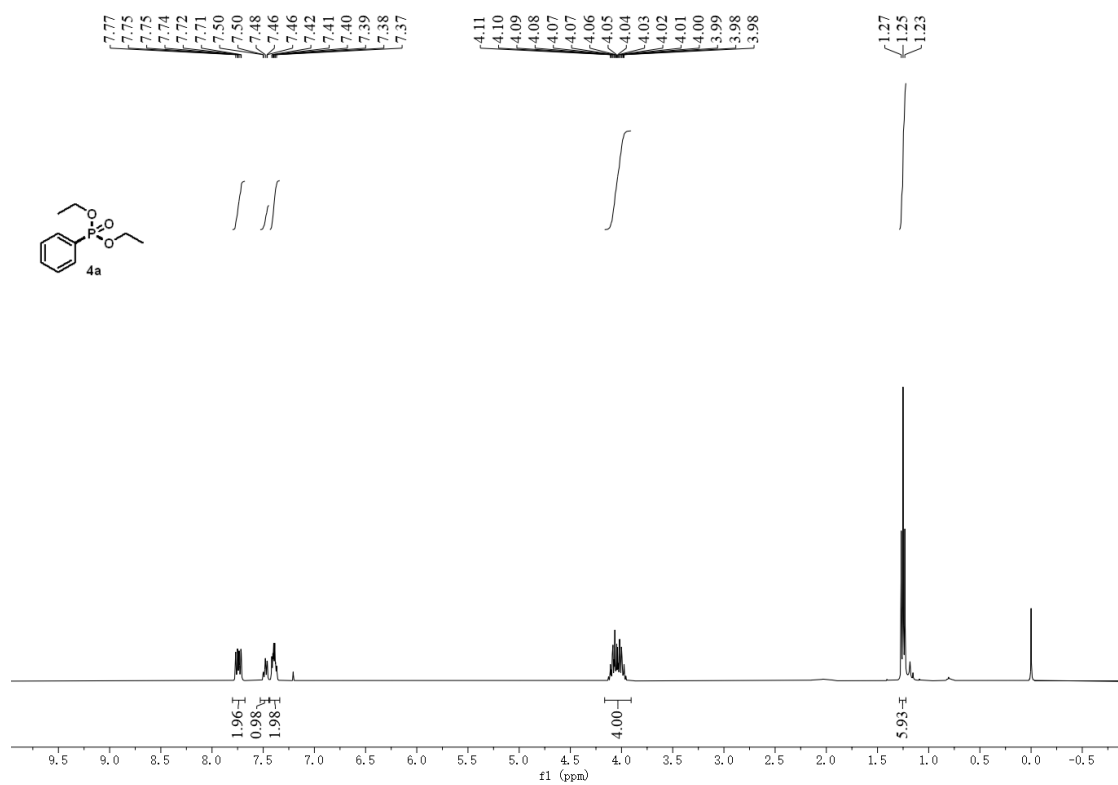
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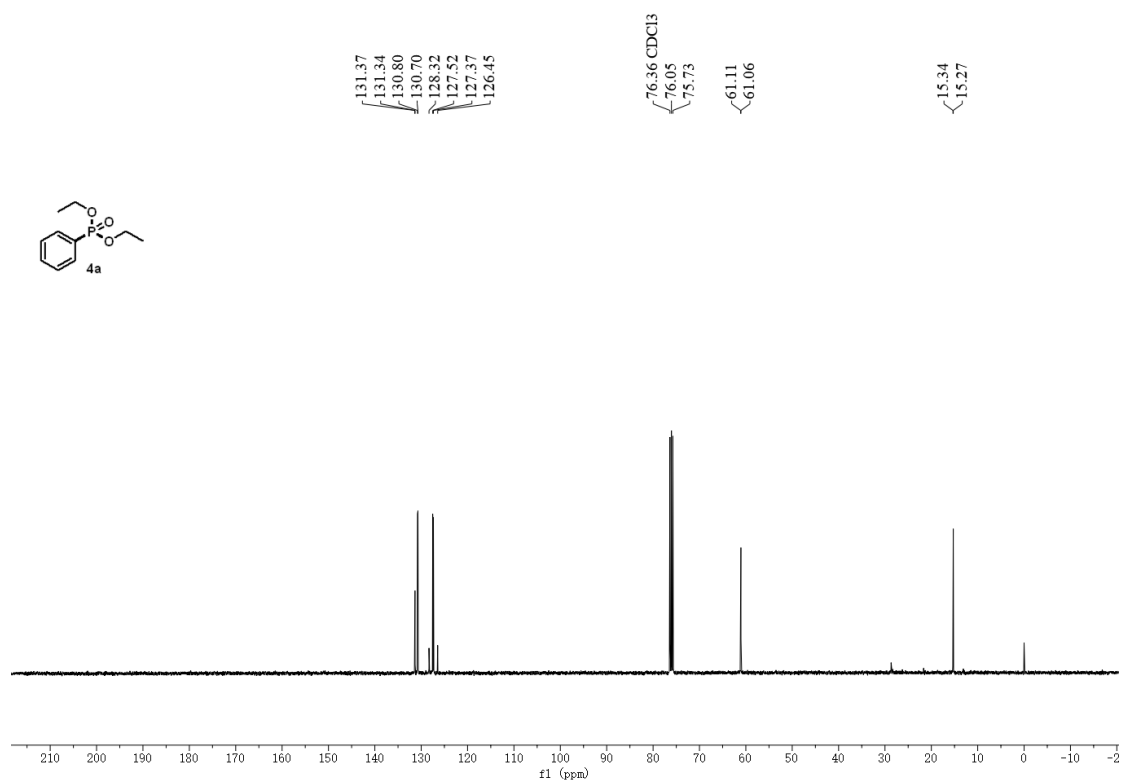
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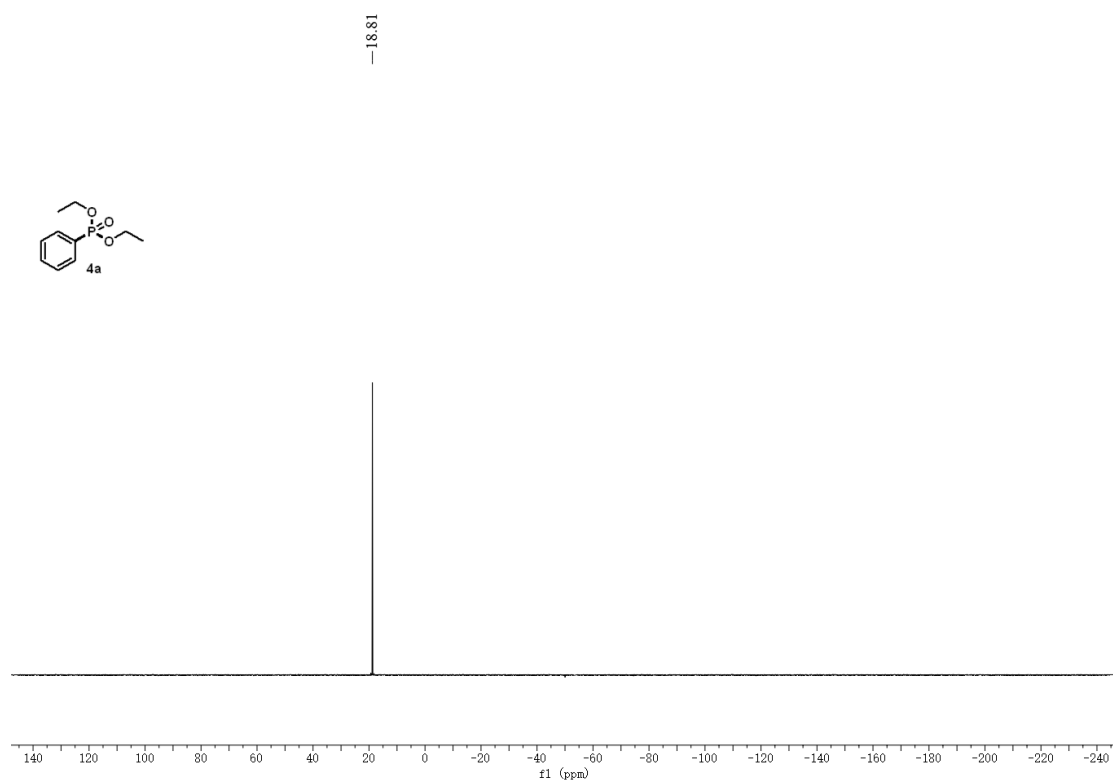
¹H NMR (400 MHz, CDCl₃) spectrum for 4a



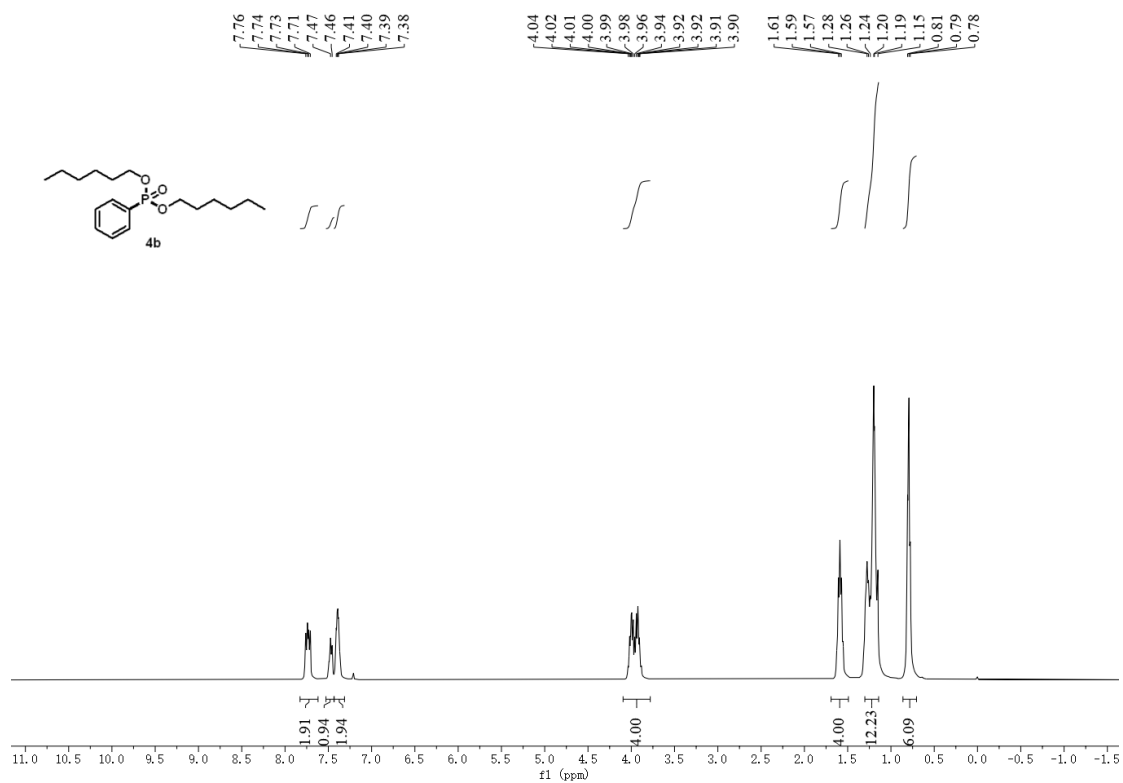
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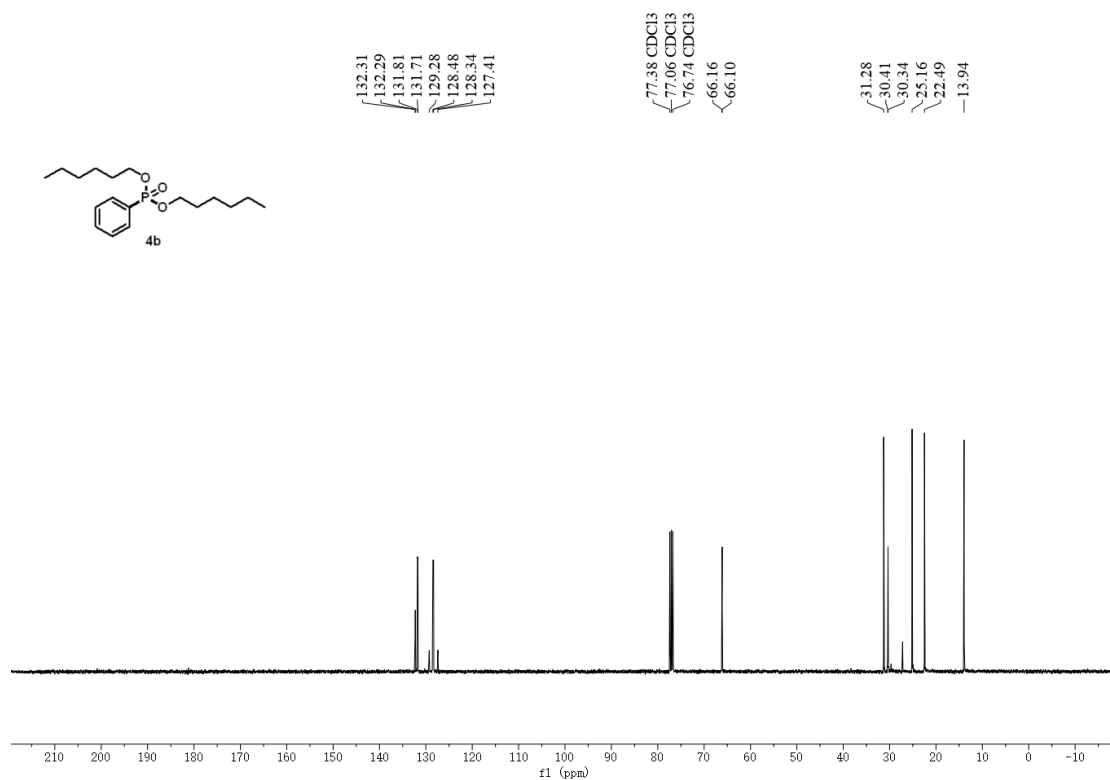
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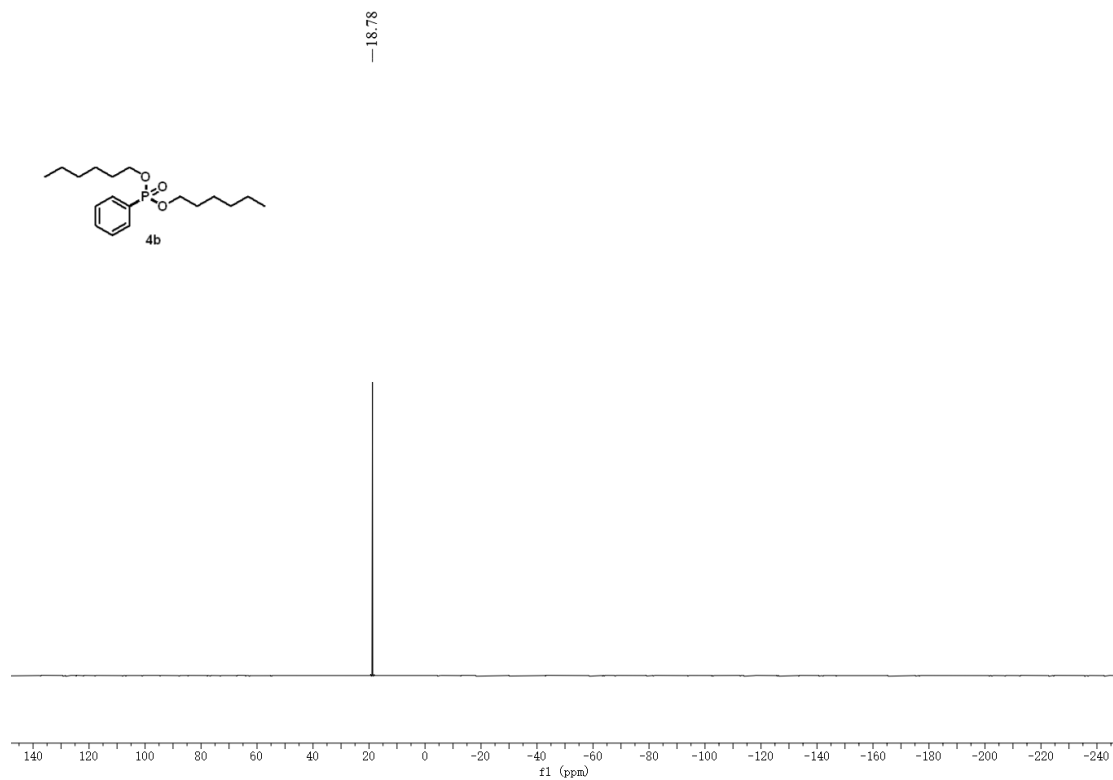
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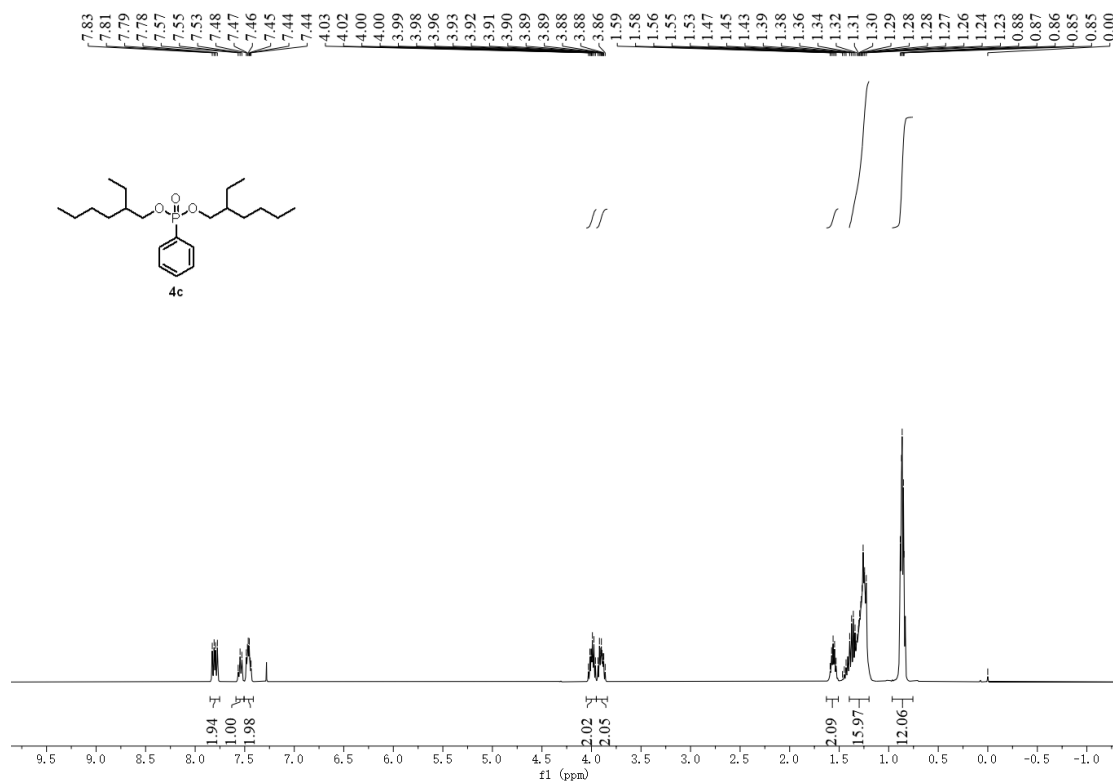
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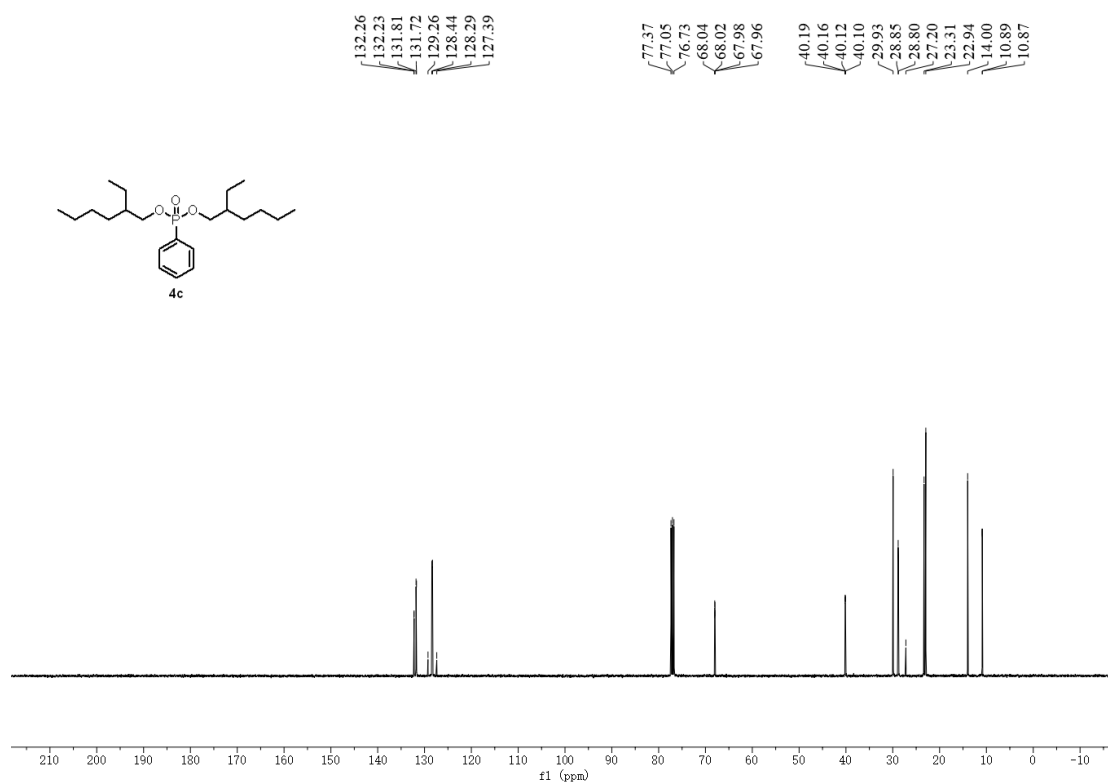
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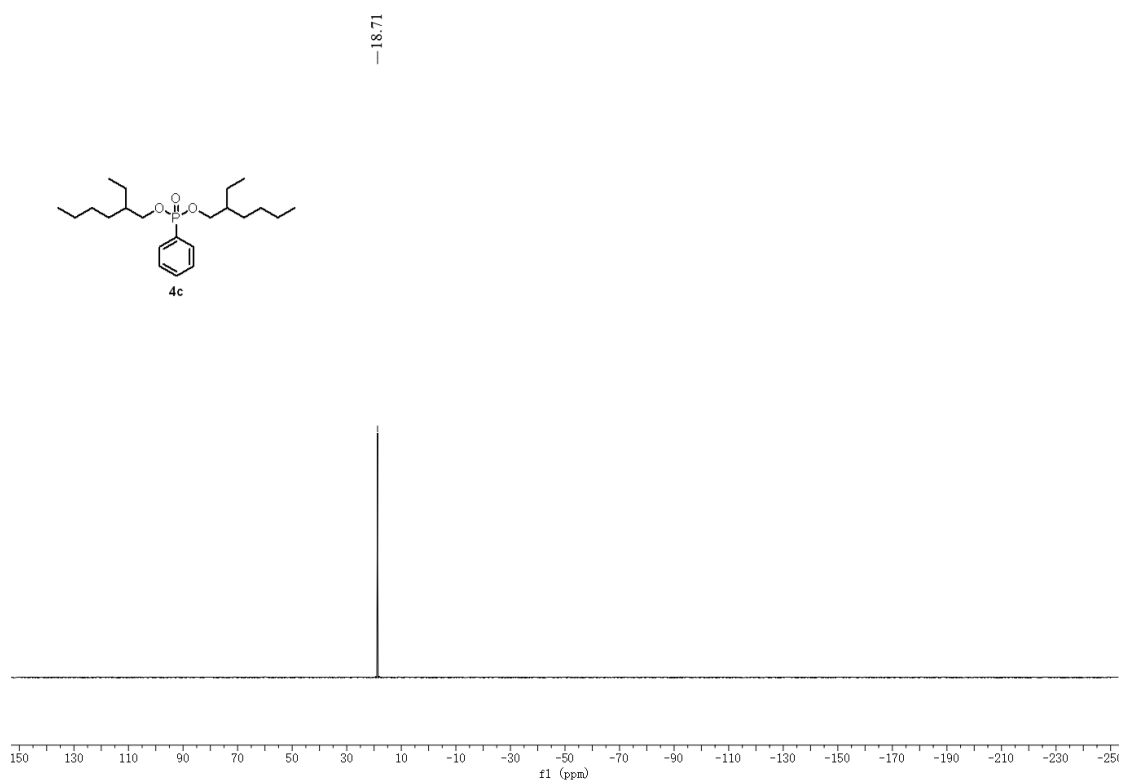
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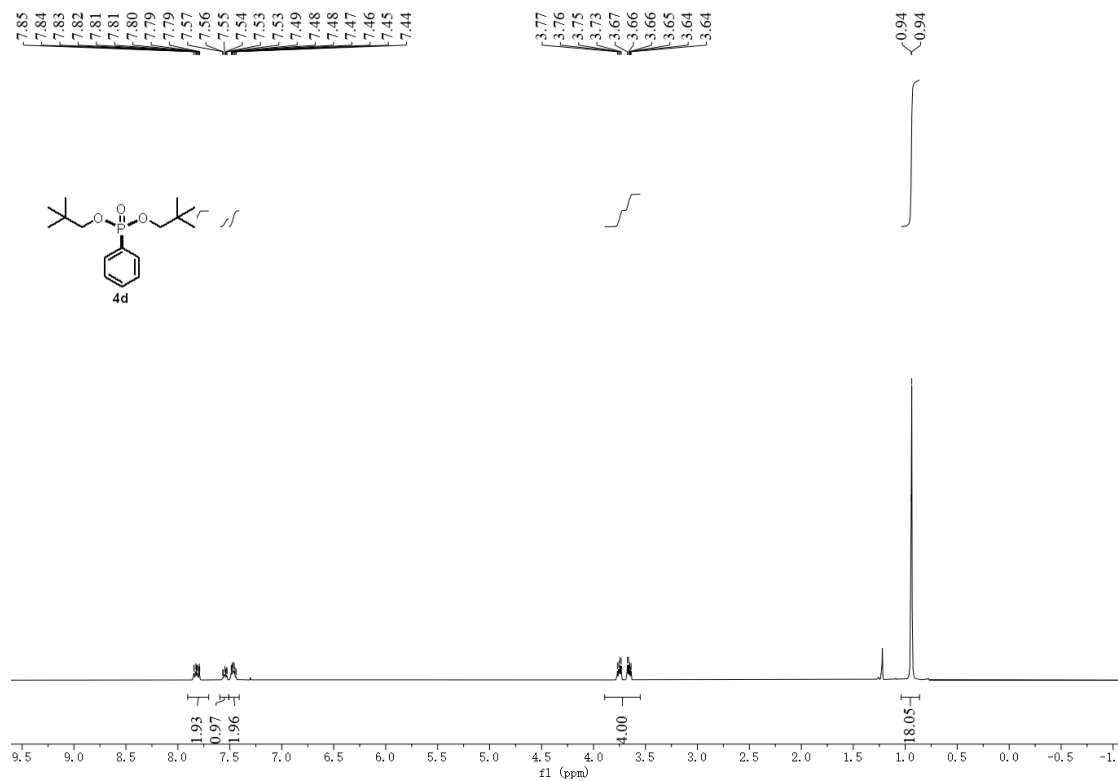
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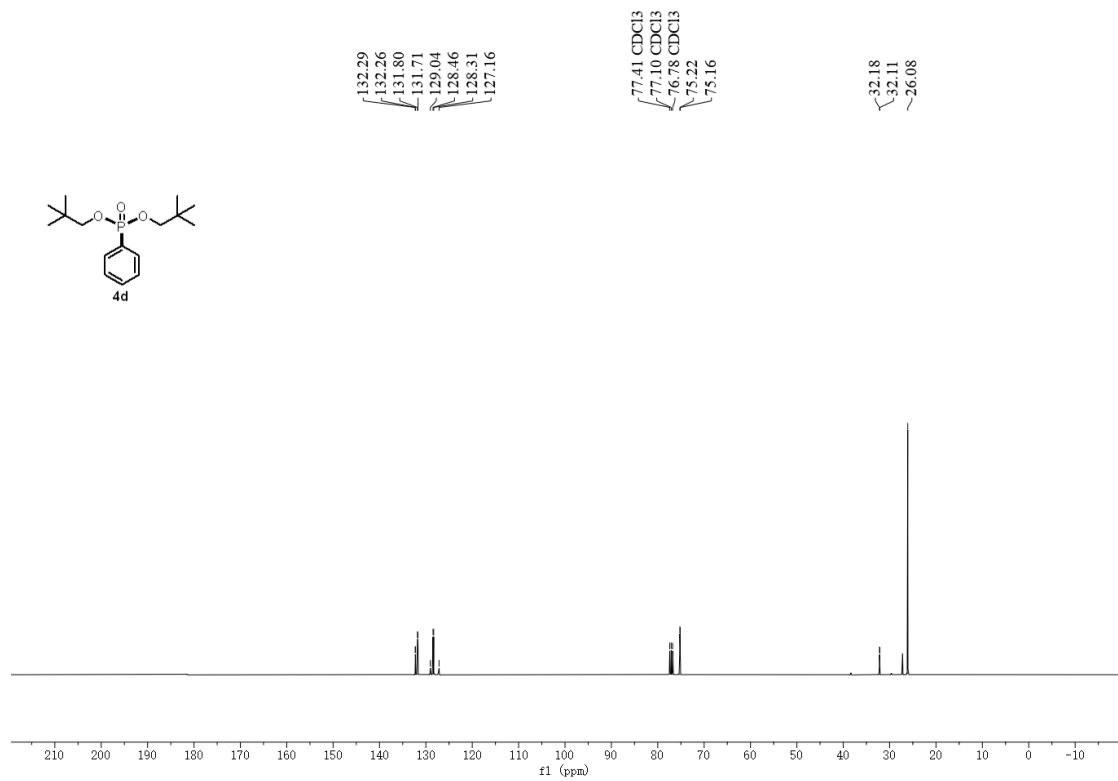
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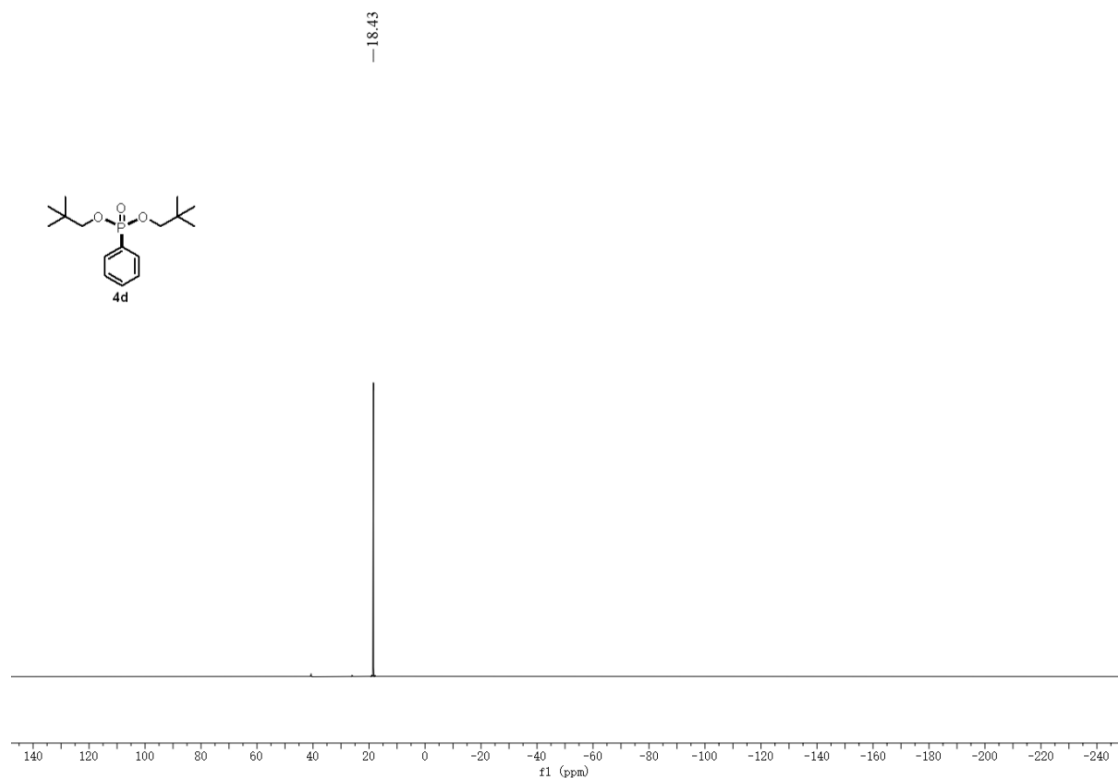
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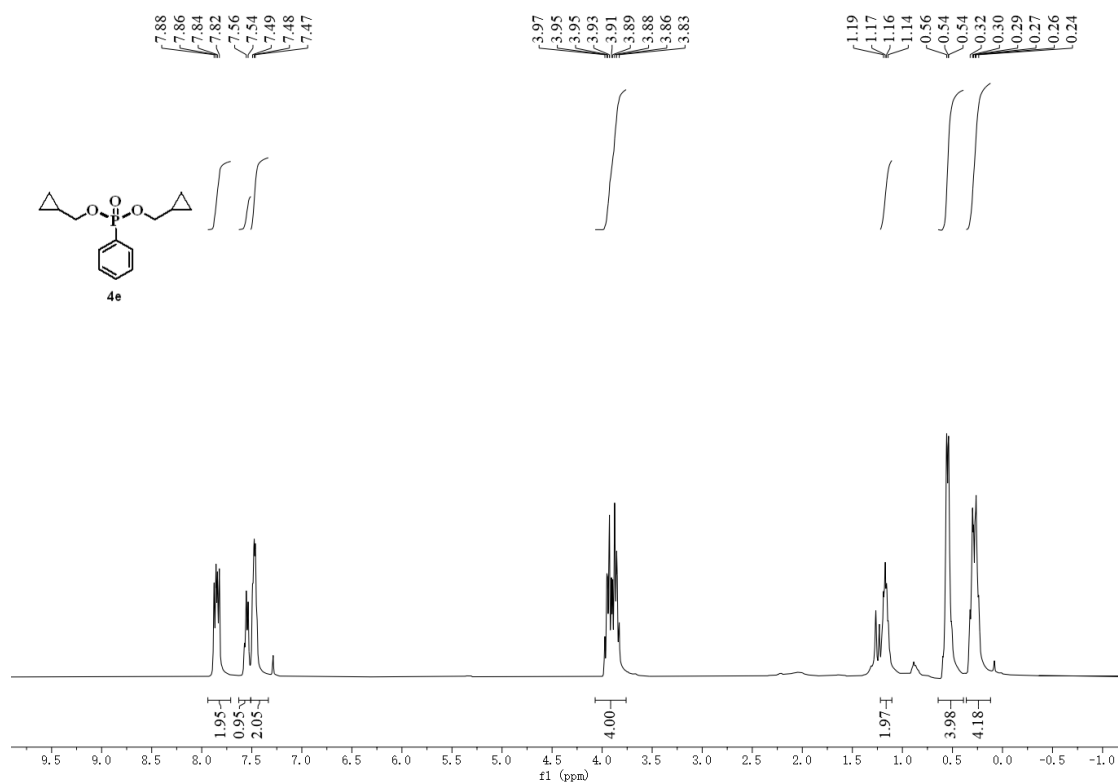
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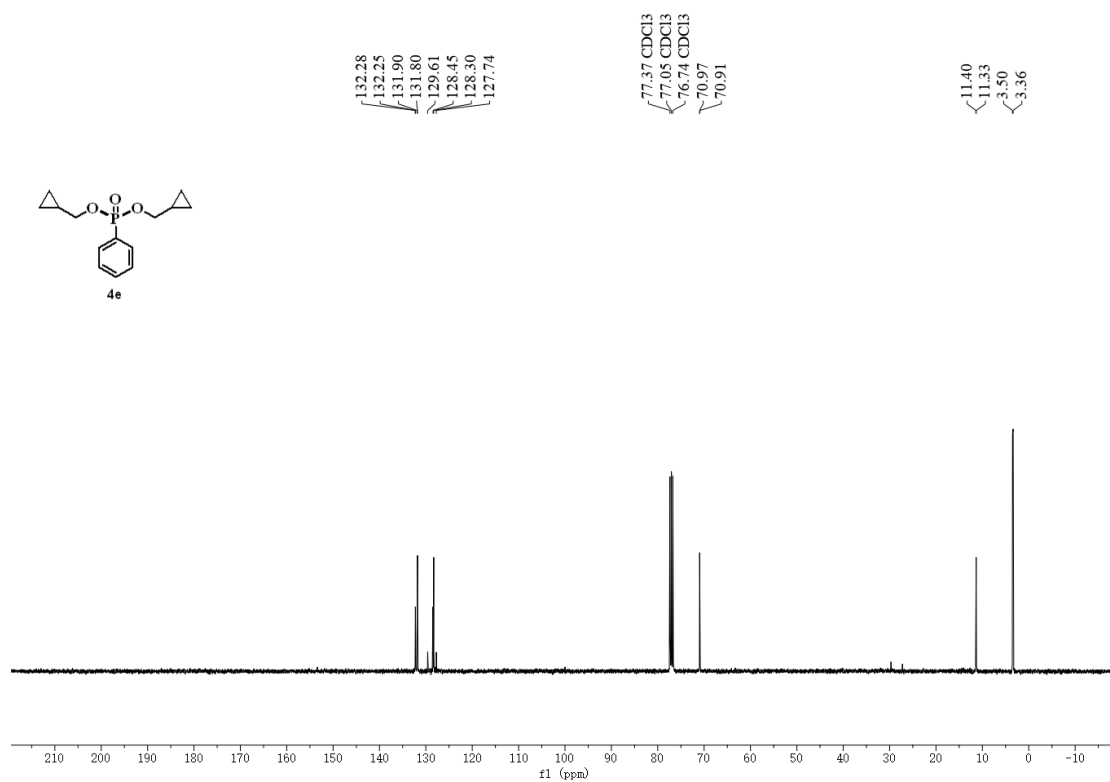
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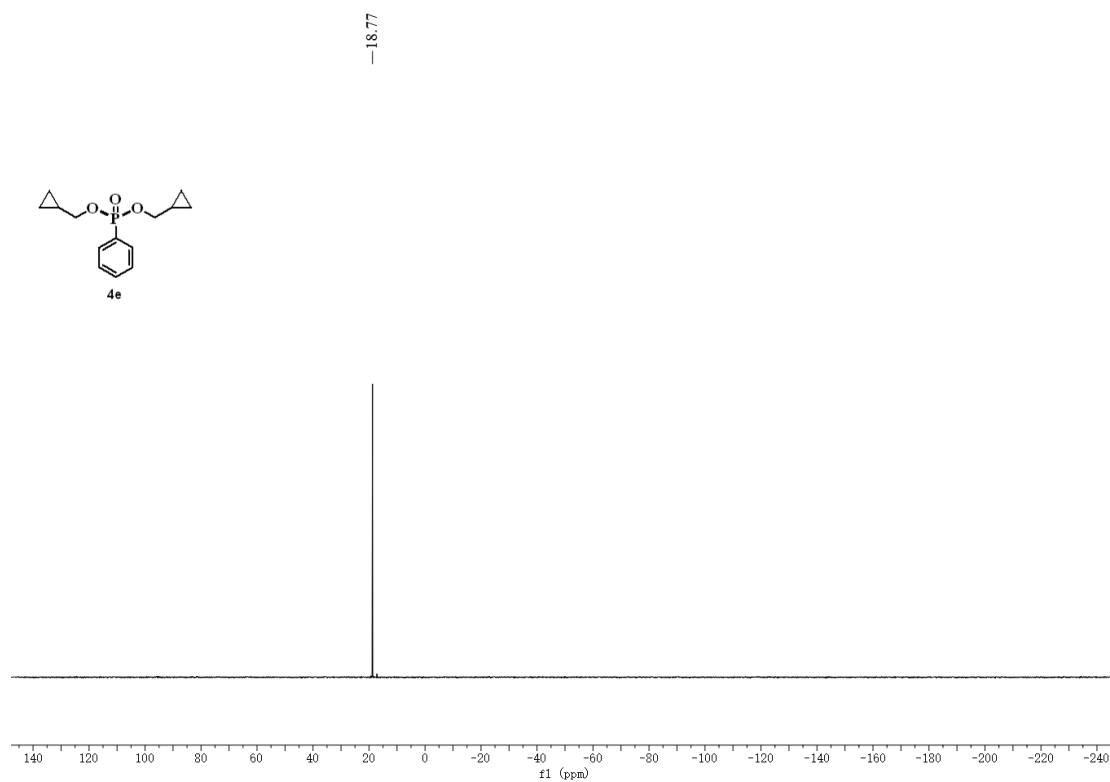
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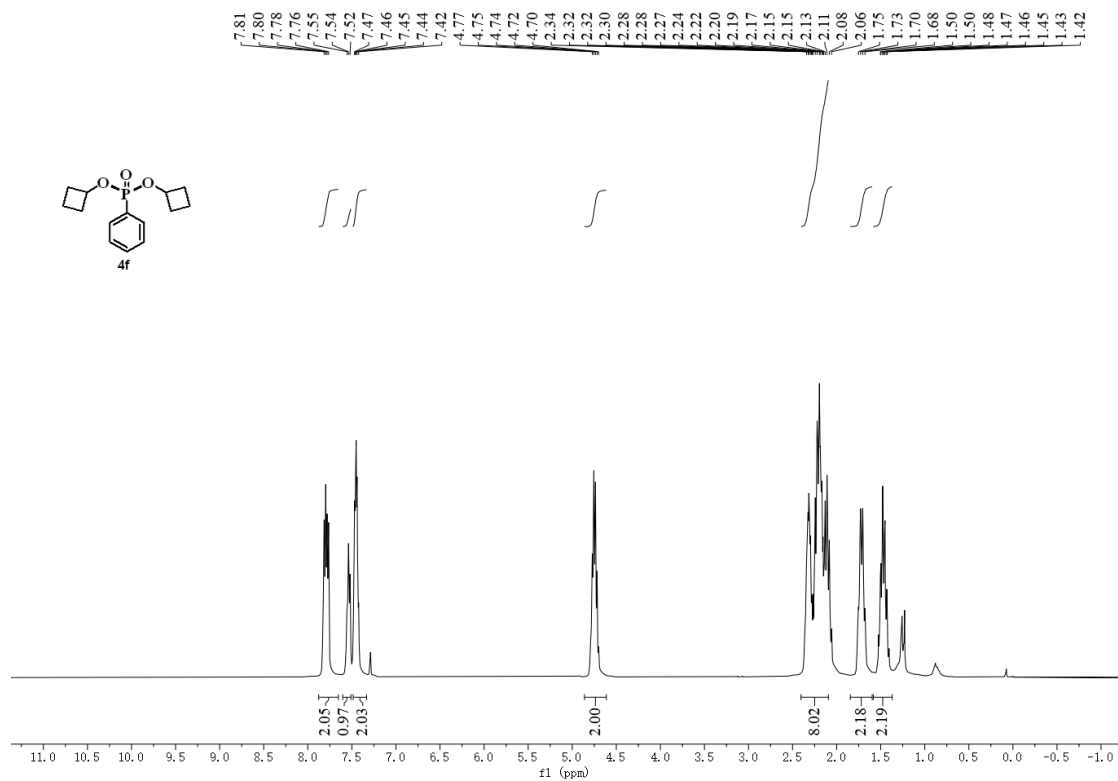
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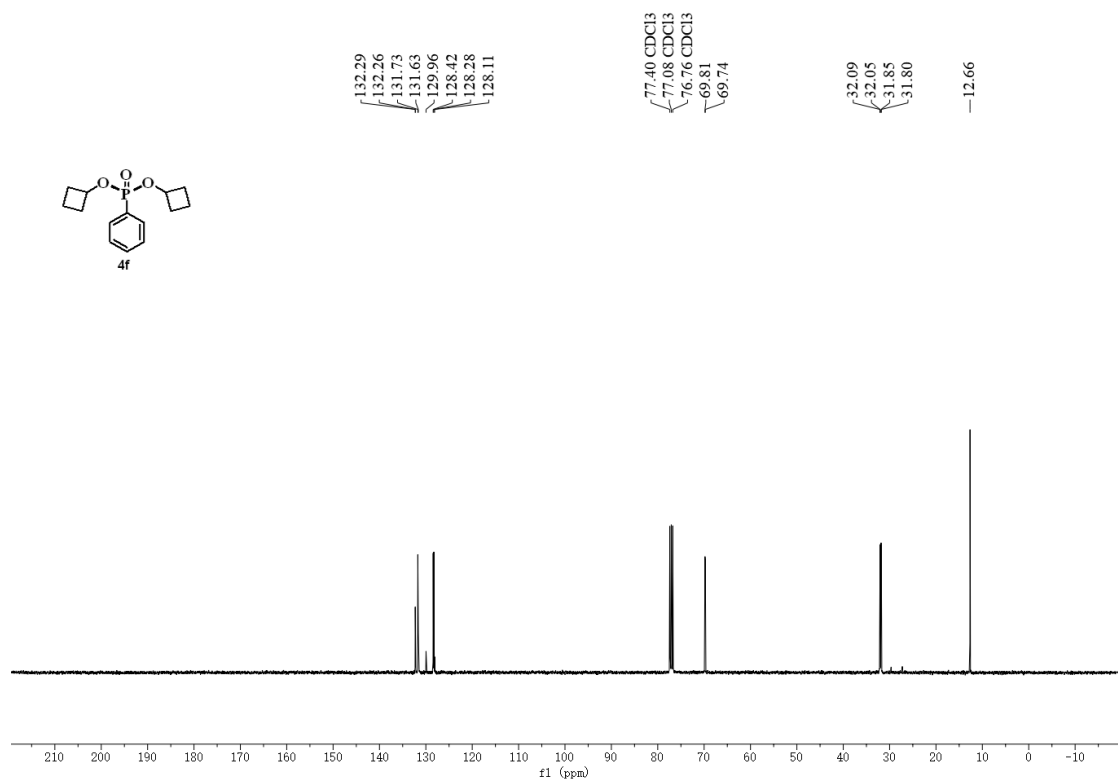
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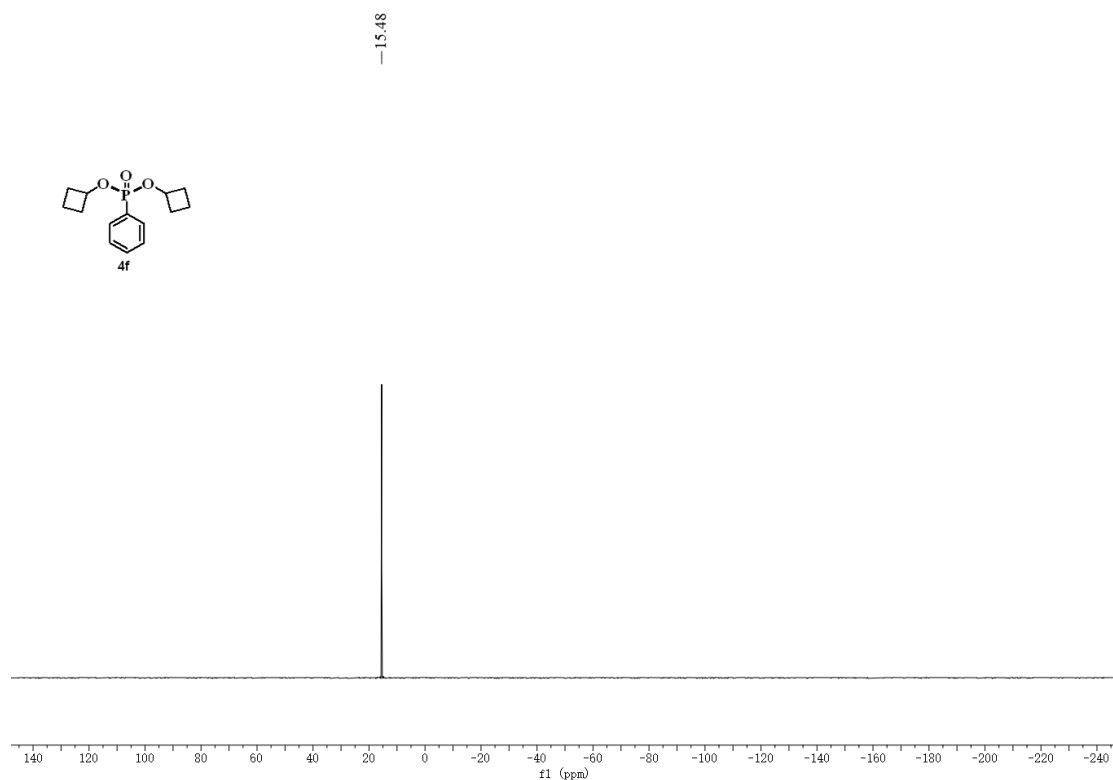
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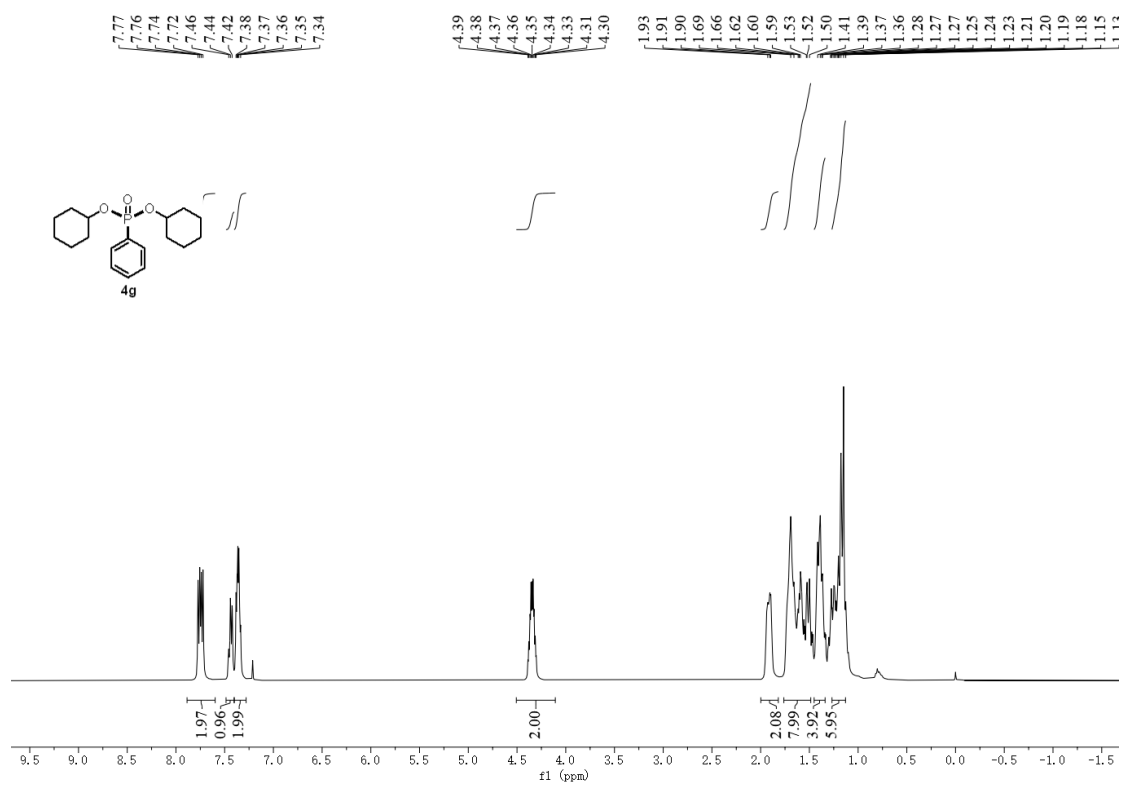
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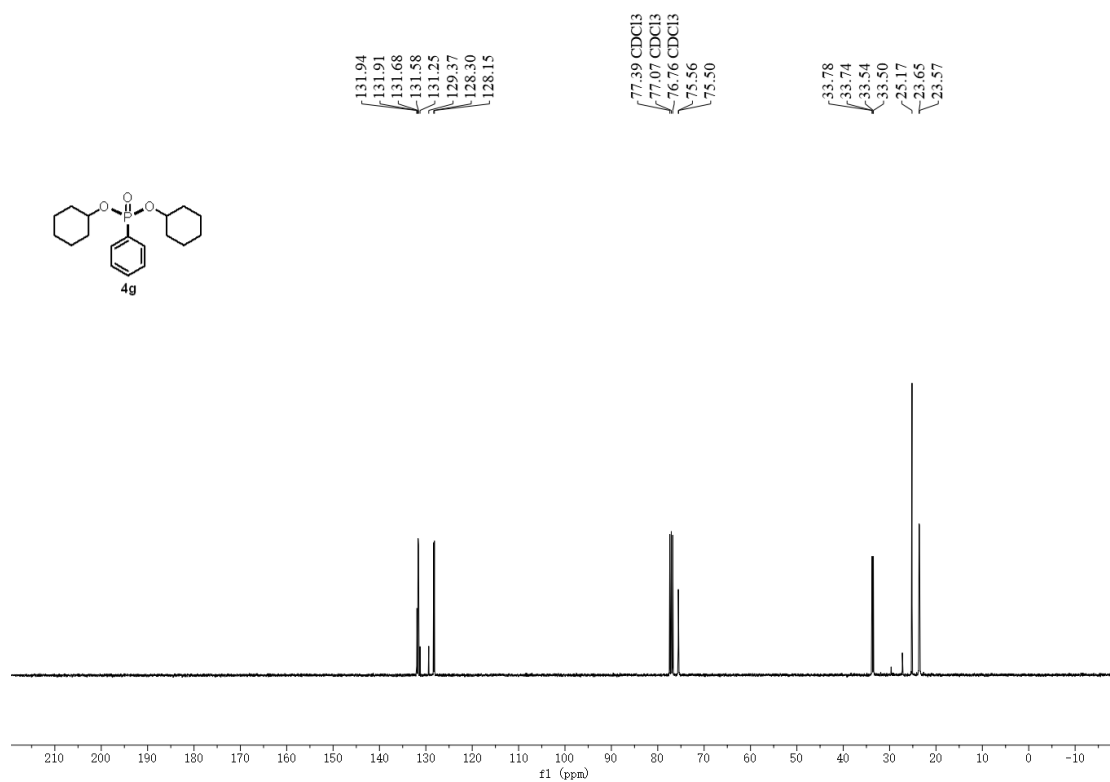
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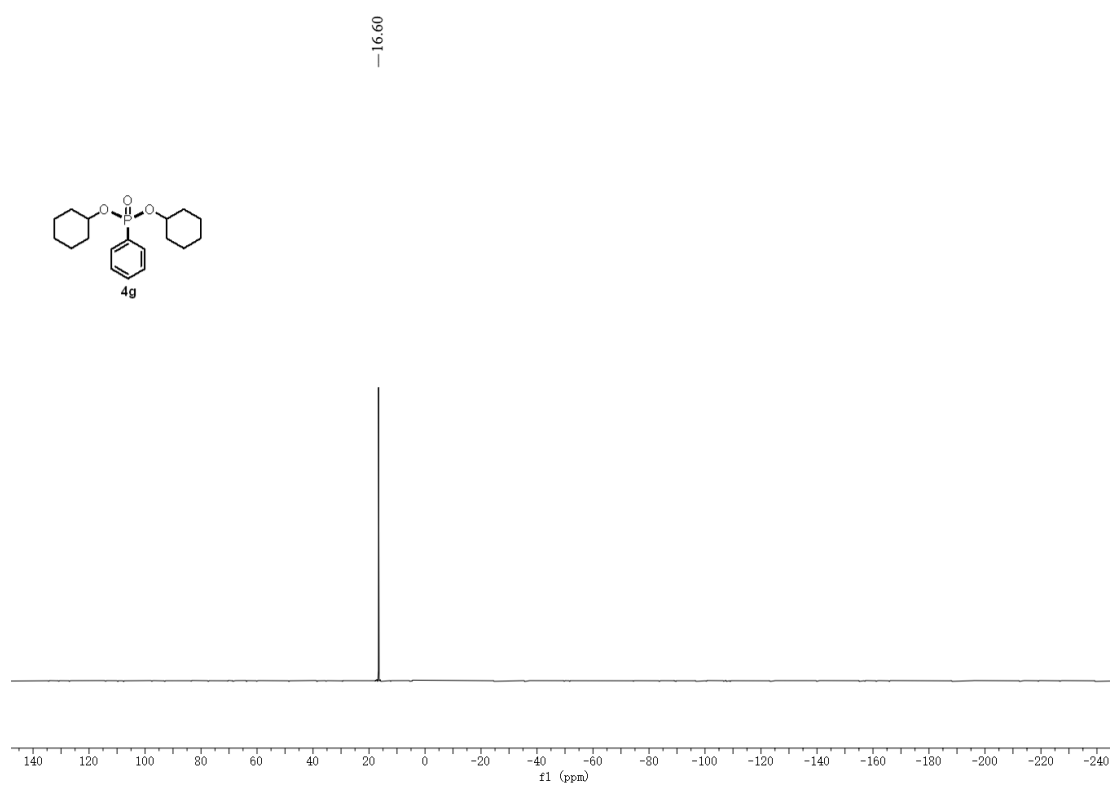
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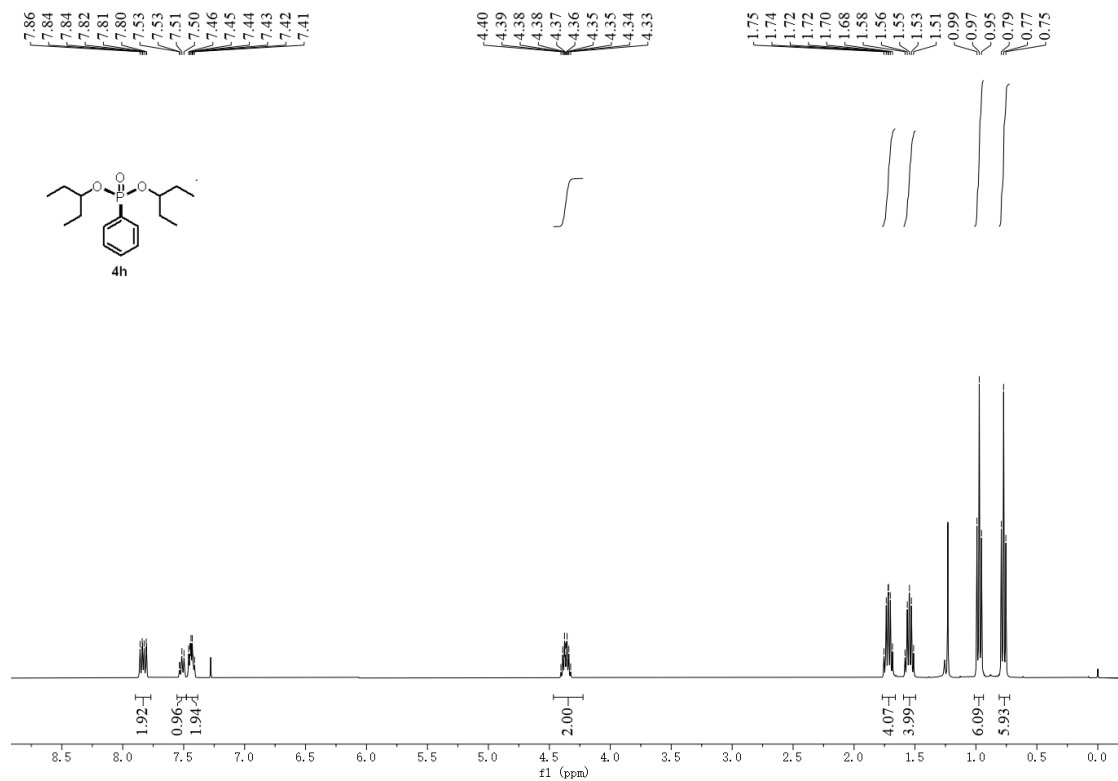
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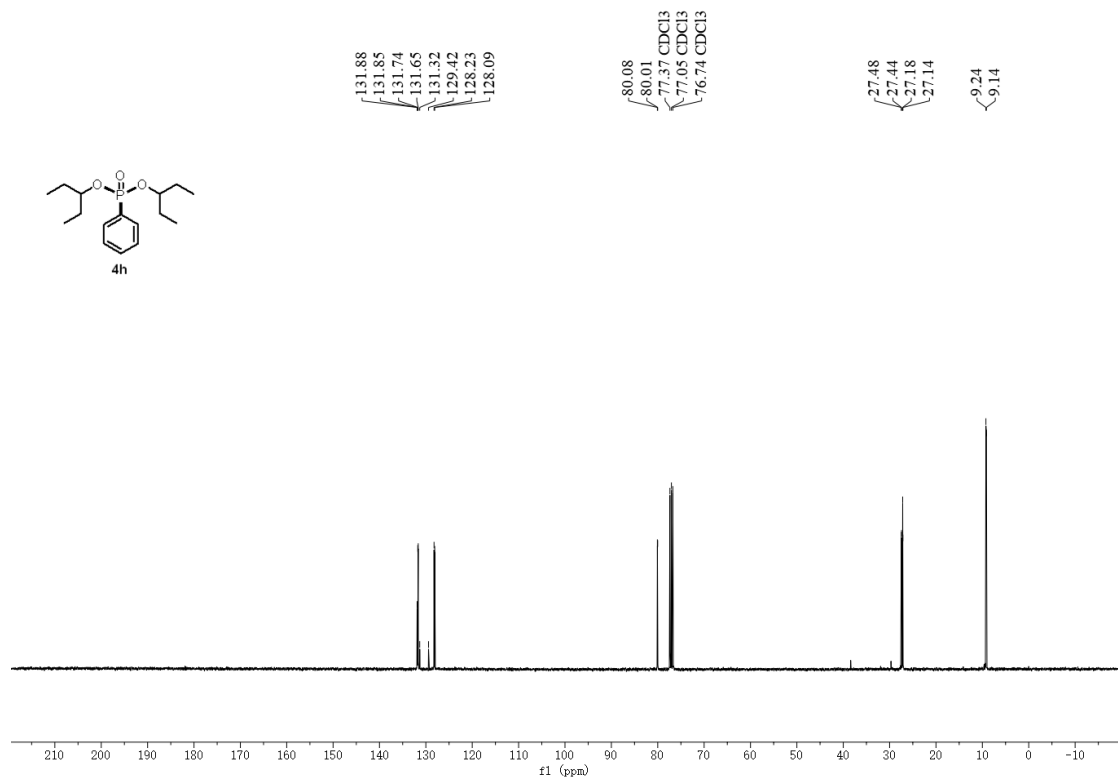
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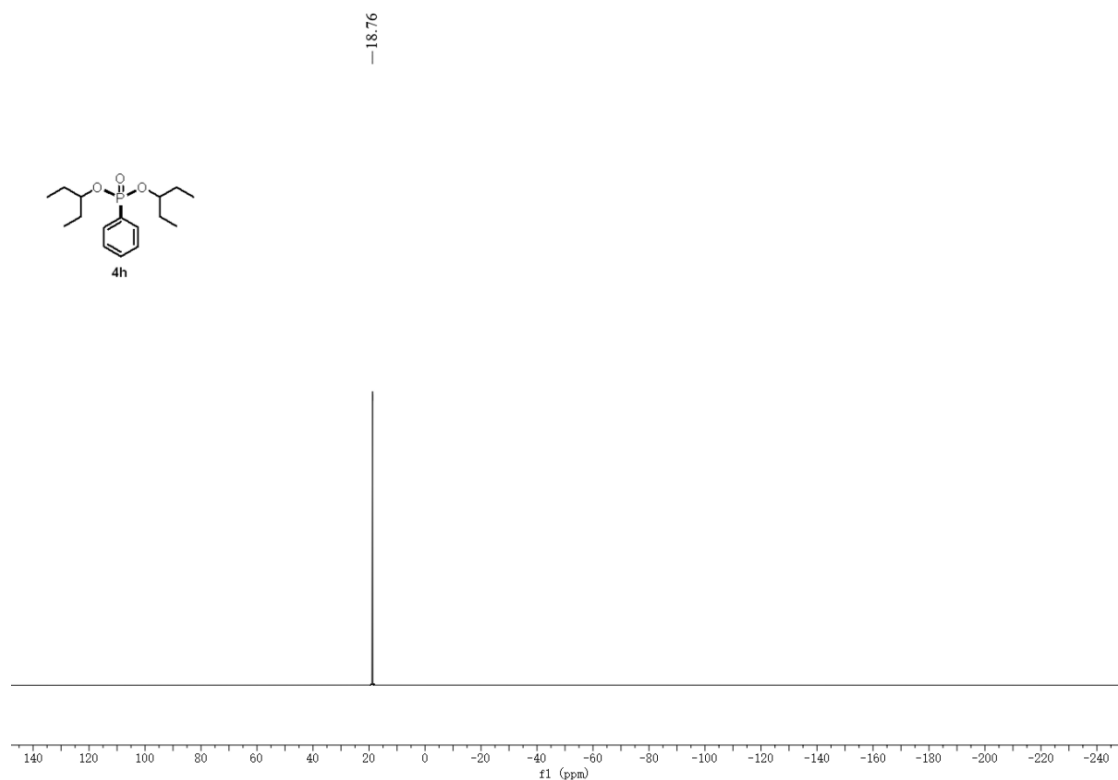
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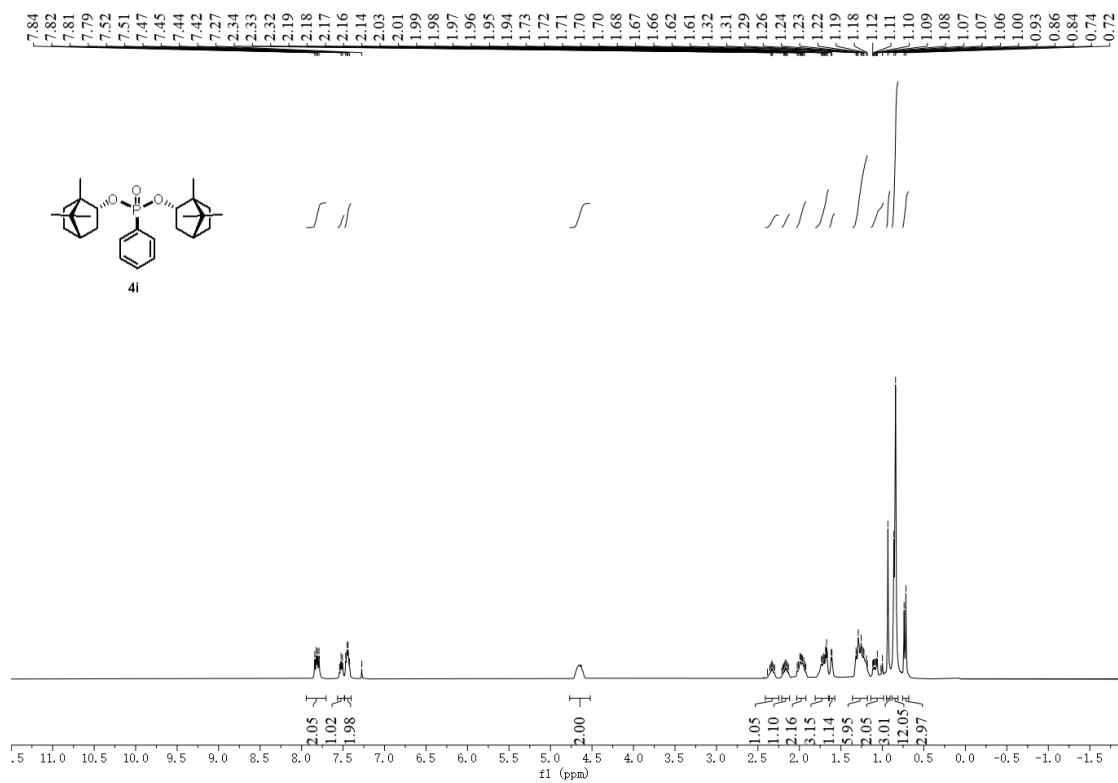
¹³C NMR (101 MHz, CDCl₃) spectrum for 4h



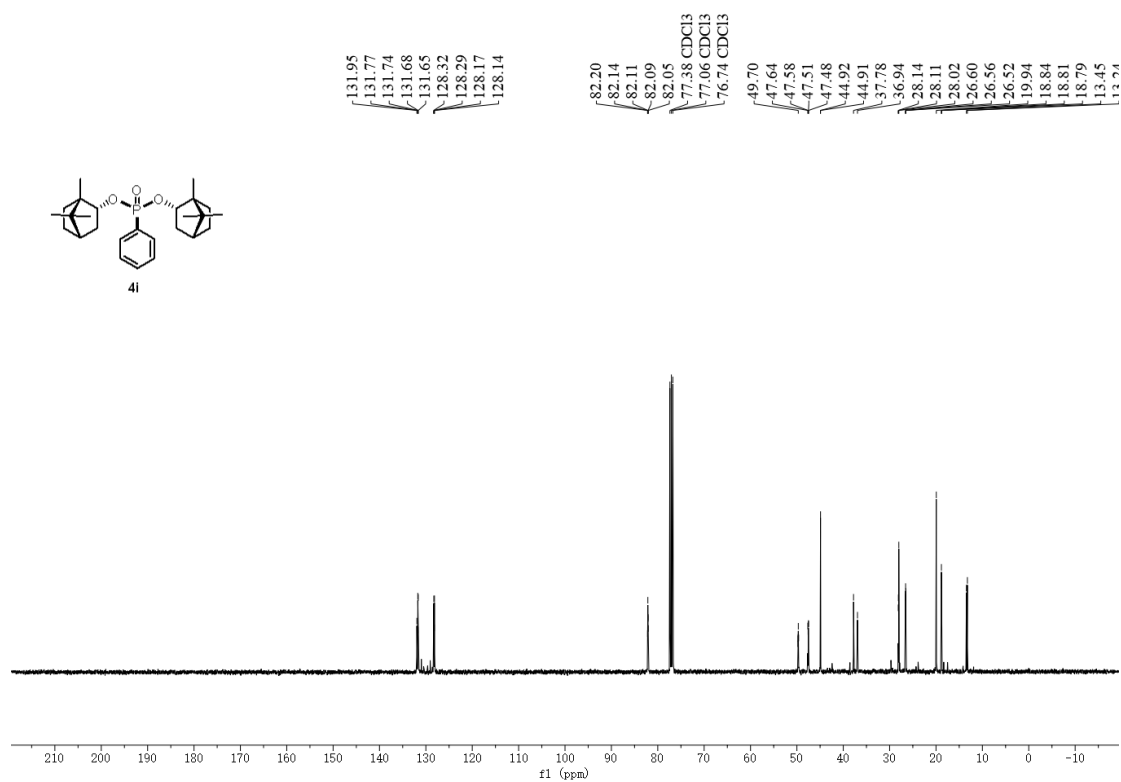
³¹P NMR (121 MHz, CDCl₃) spectrum for 4h



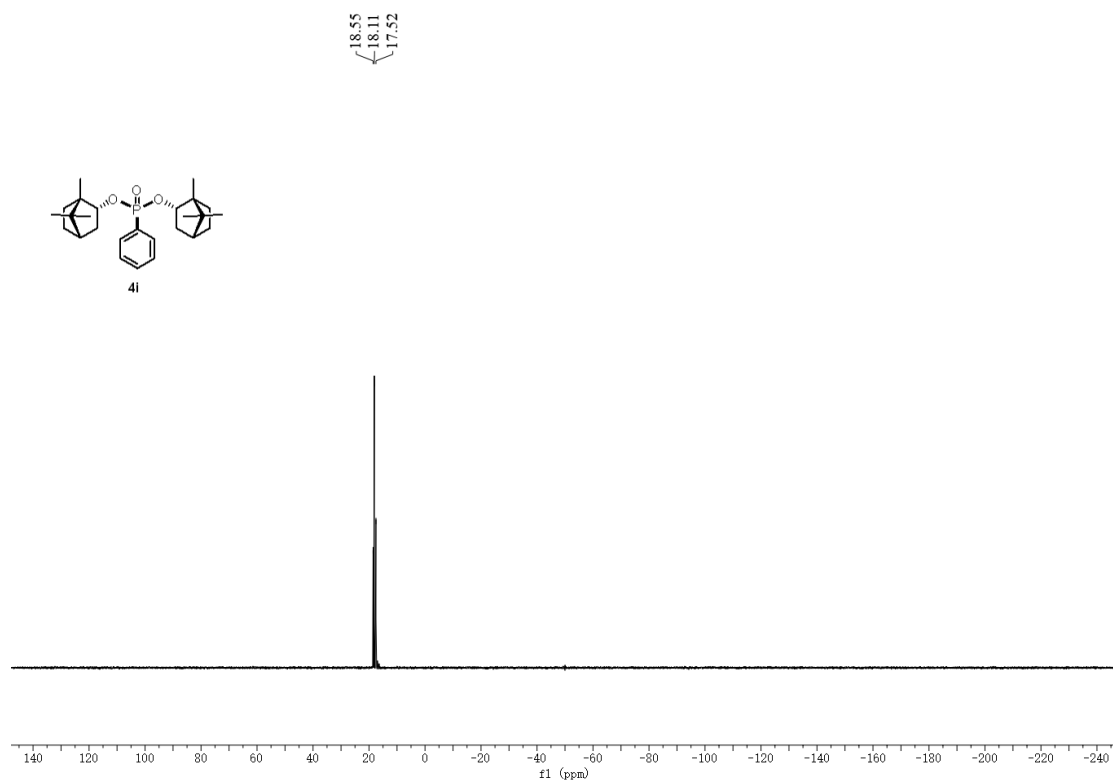
¹H NMR (400 MHz, CDCl₃) spectrum for 4i



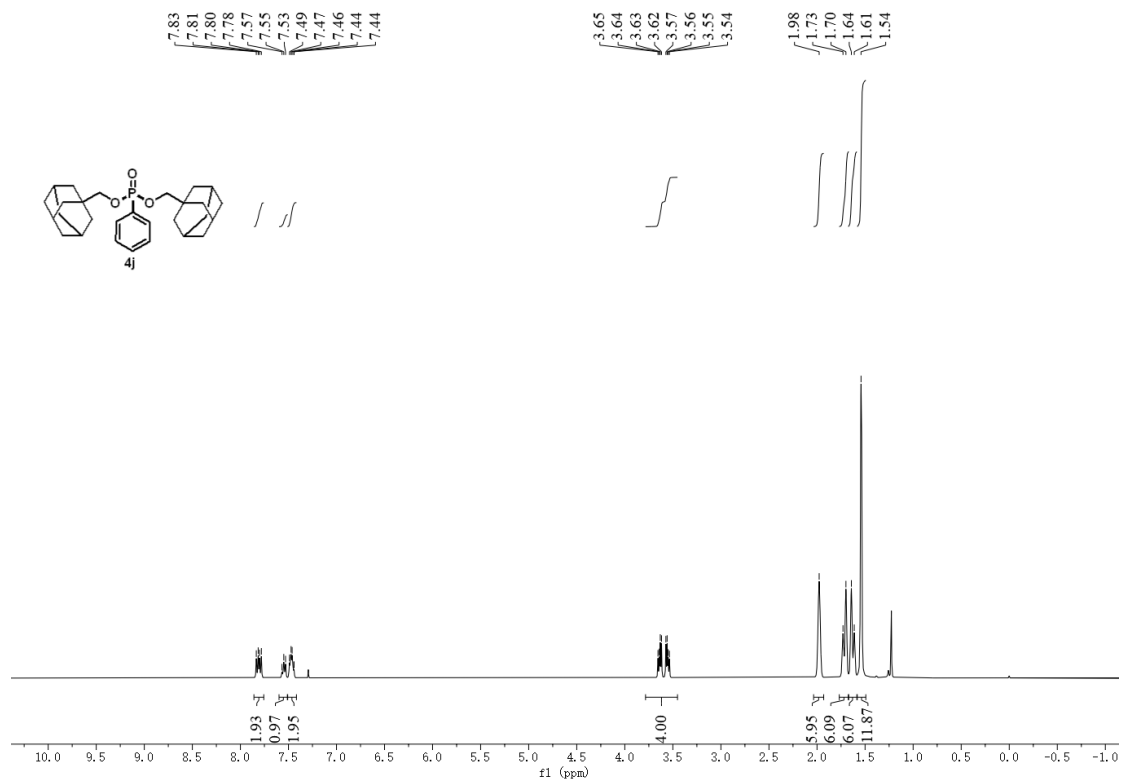
¹³C NMR (101 MHz, CDCl₃) spectrum for 4i



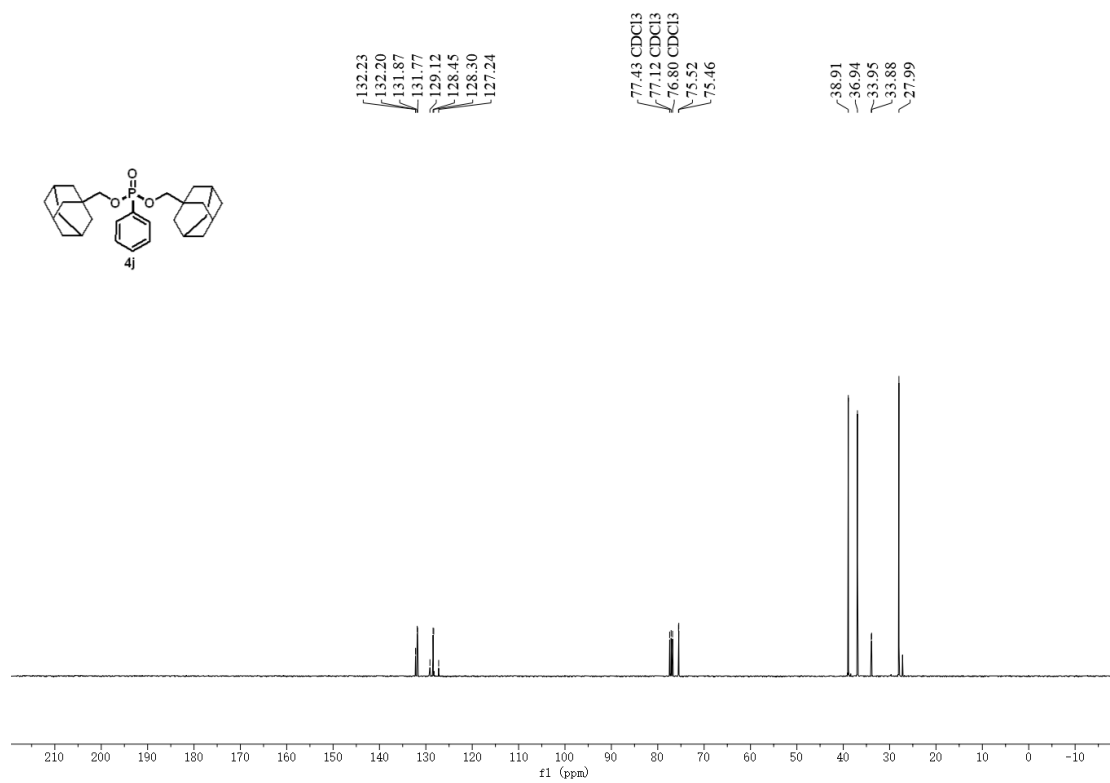
³¹P NMR (121 MHz, CDCl₃) spectrum for 4i



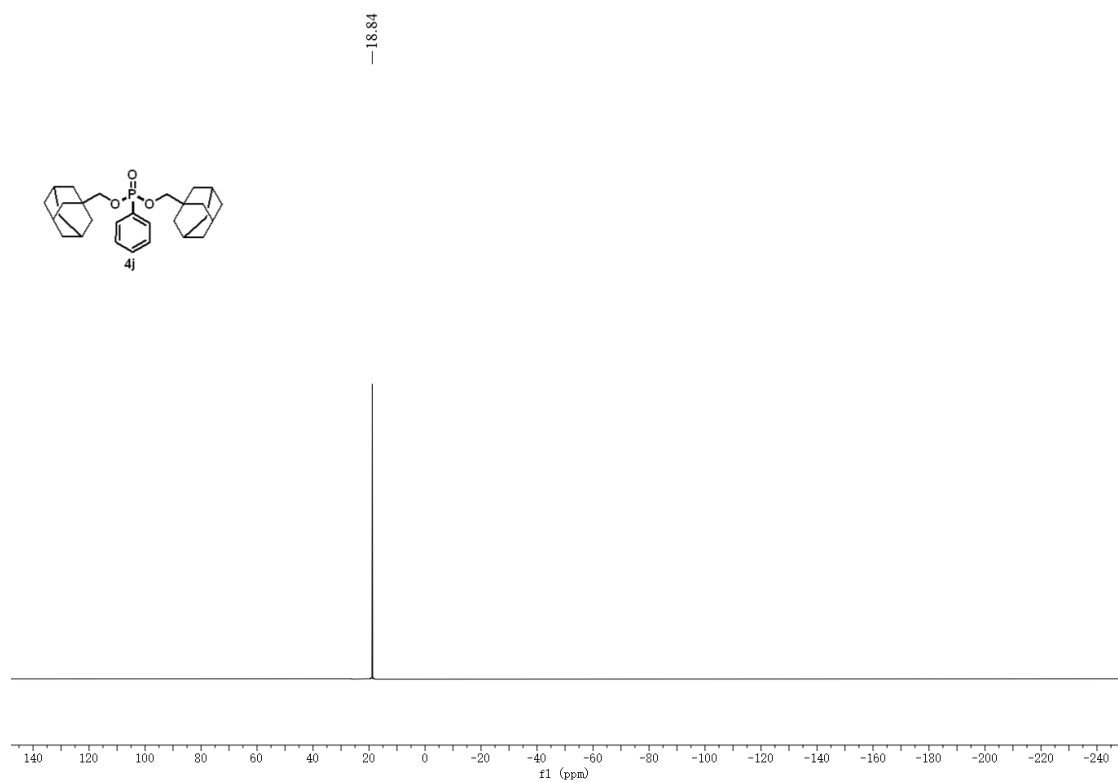
¹H NMR (400 MHz, CDCl₃) spectrum for 4j



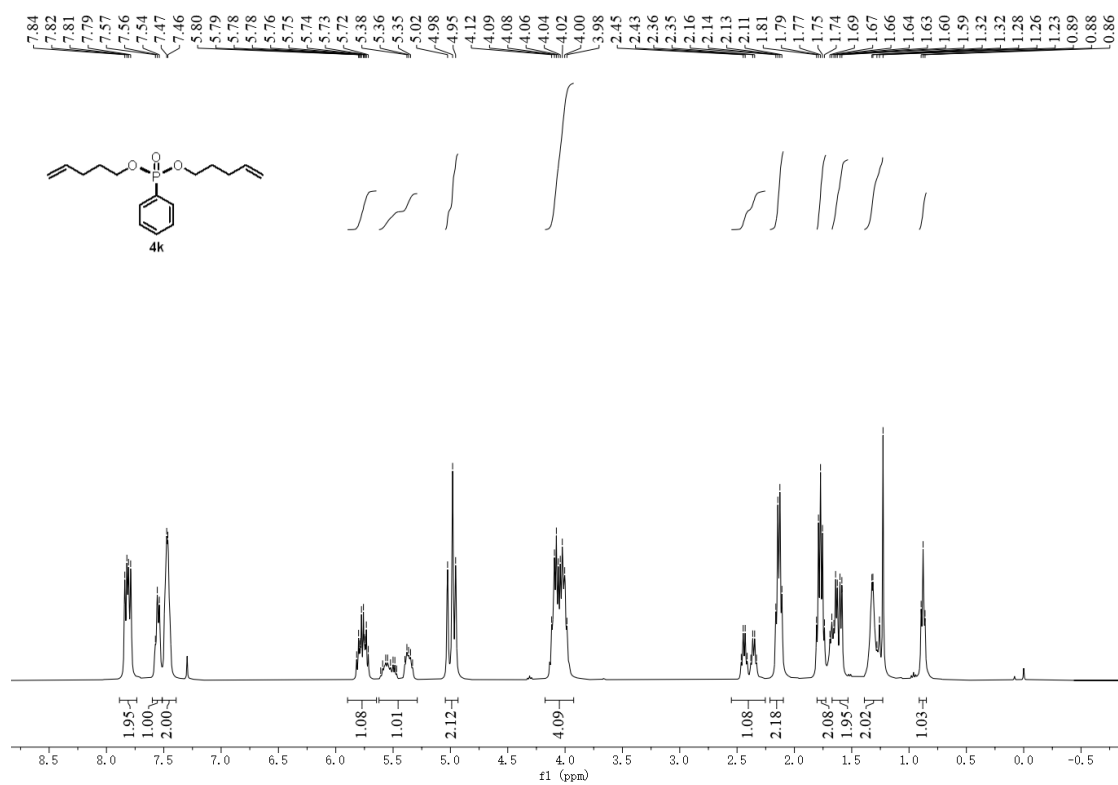
¹³C NMR (101 MHz, CDCl₃) spectrum for 4j



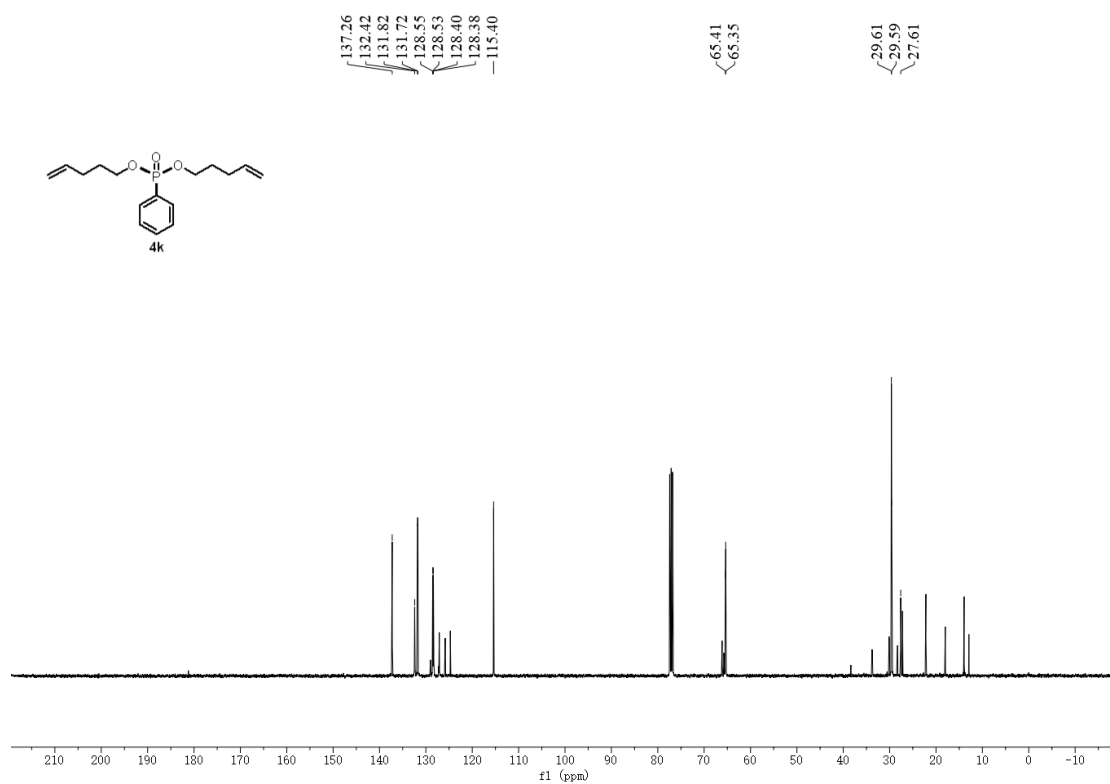
^{31}P NMR (121 MHz, CDCl_3) spectrum for 4j



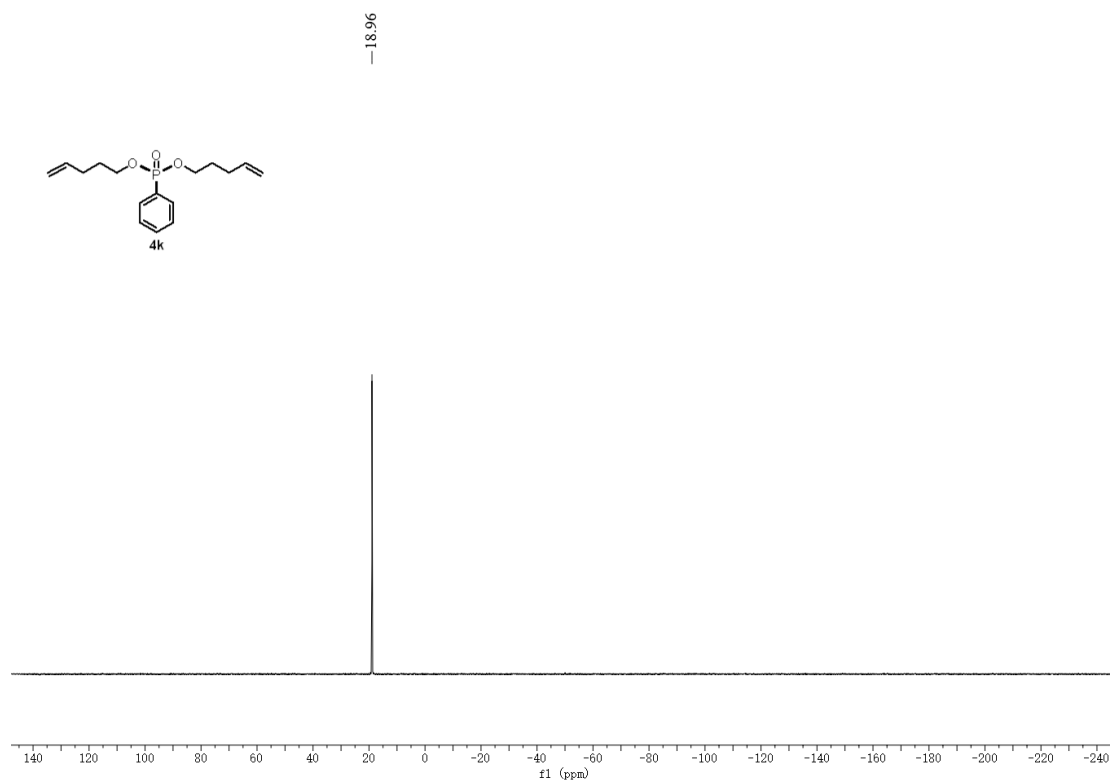
^1H NMR (400 MHz, CDCl_3) spectrum for 4k



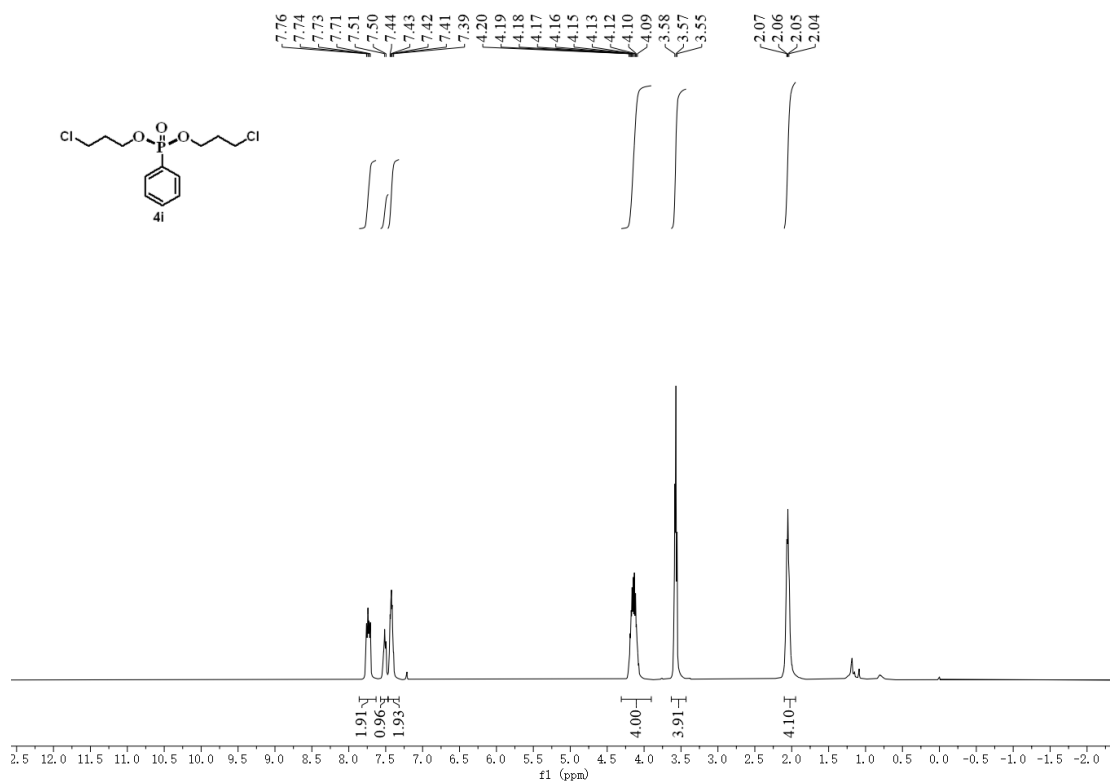
¹³C NMR (101 MHz, CDCl₃) spectrum for 4k



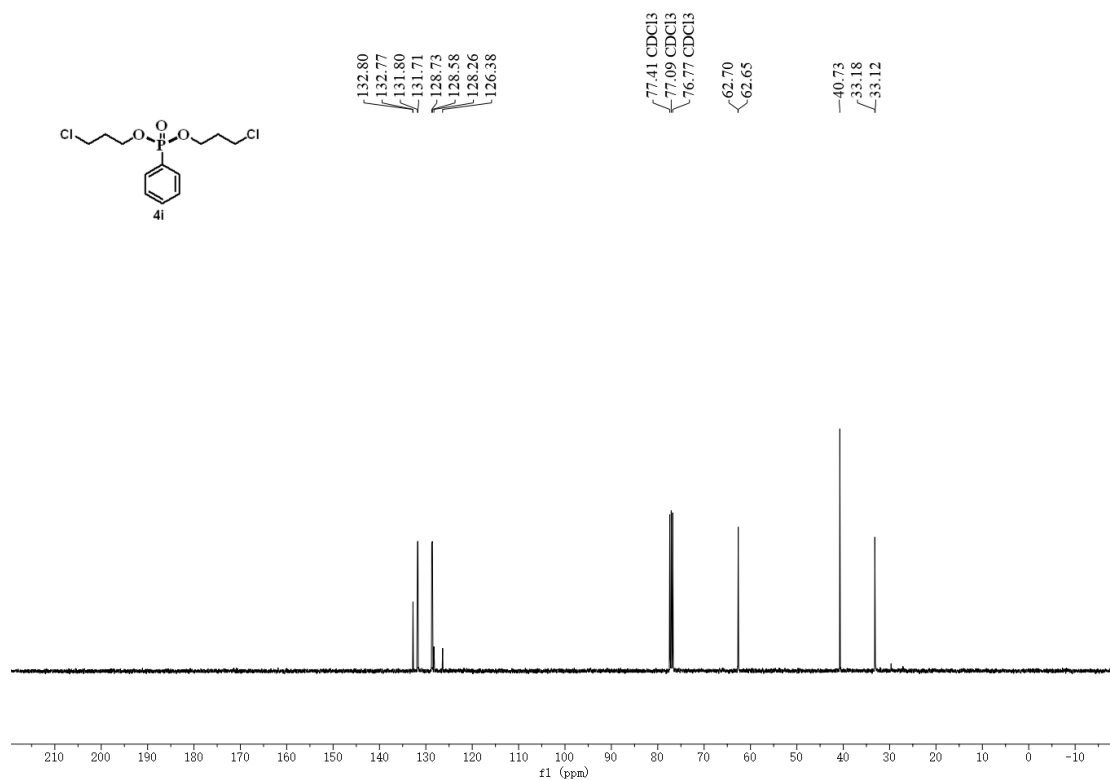
³¹P NMR (121 MHz, CDCl₃) spectrum for 4k



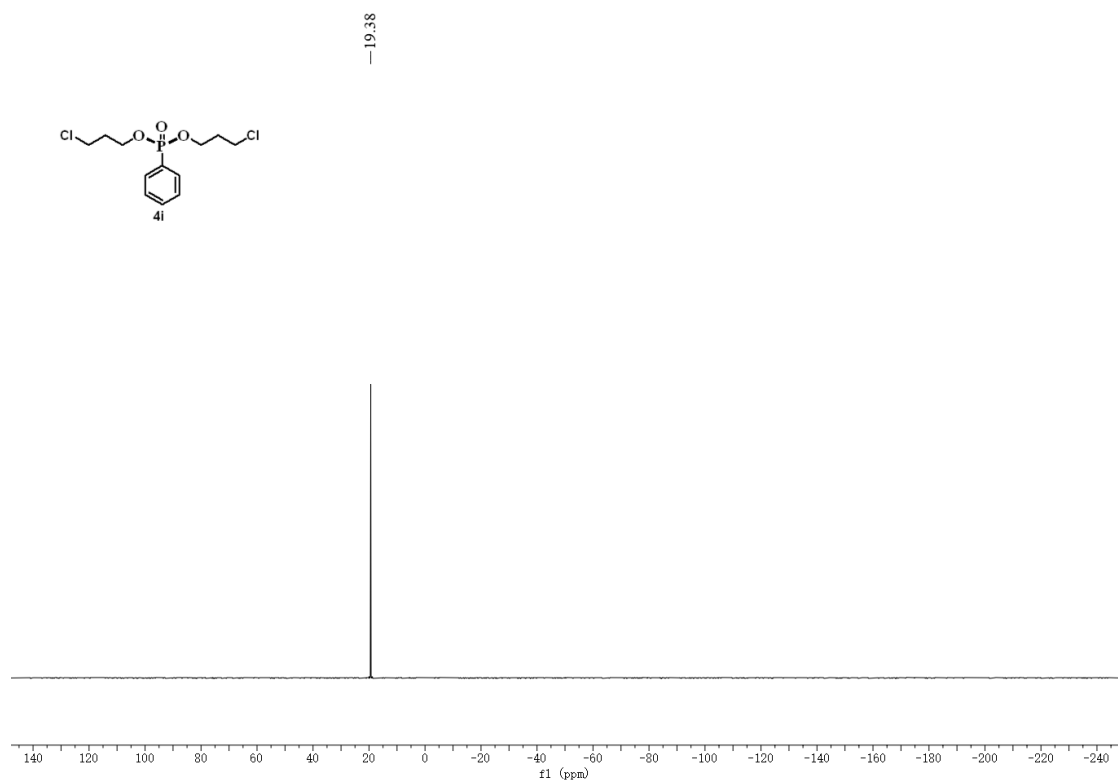
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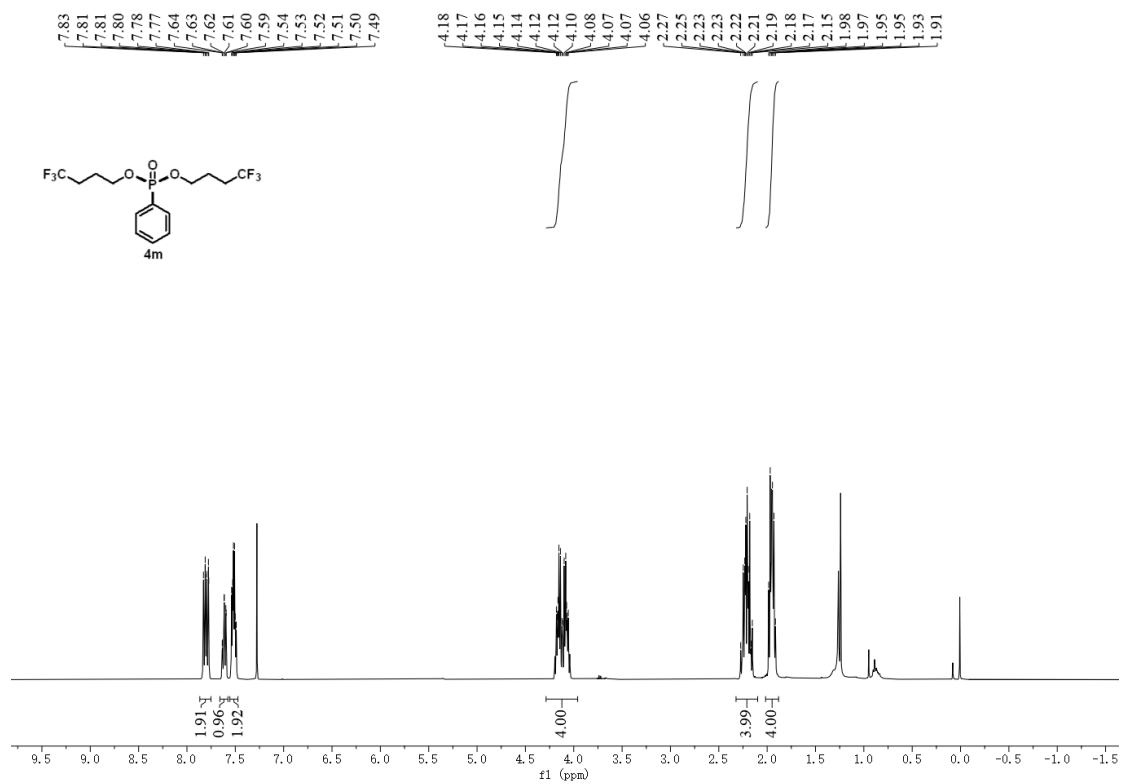
¹³C NMR (101 MHz, CDCl₃) spectrum for 4l



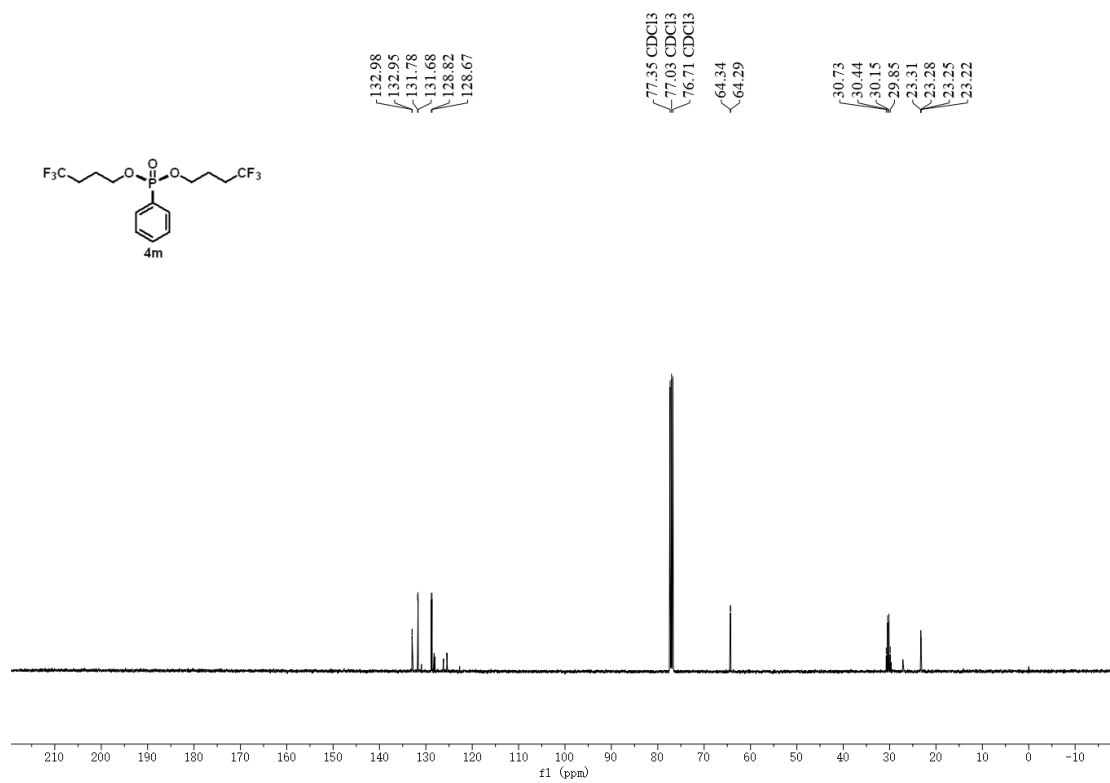
³¹P NMR (121 MHz, CDCl₃) spectrum for 4l



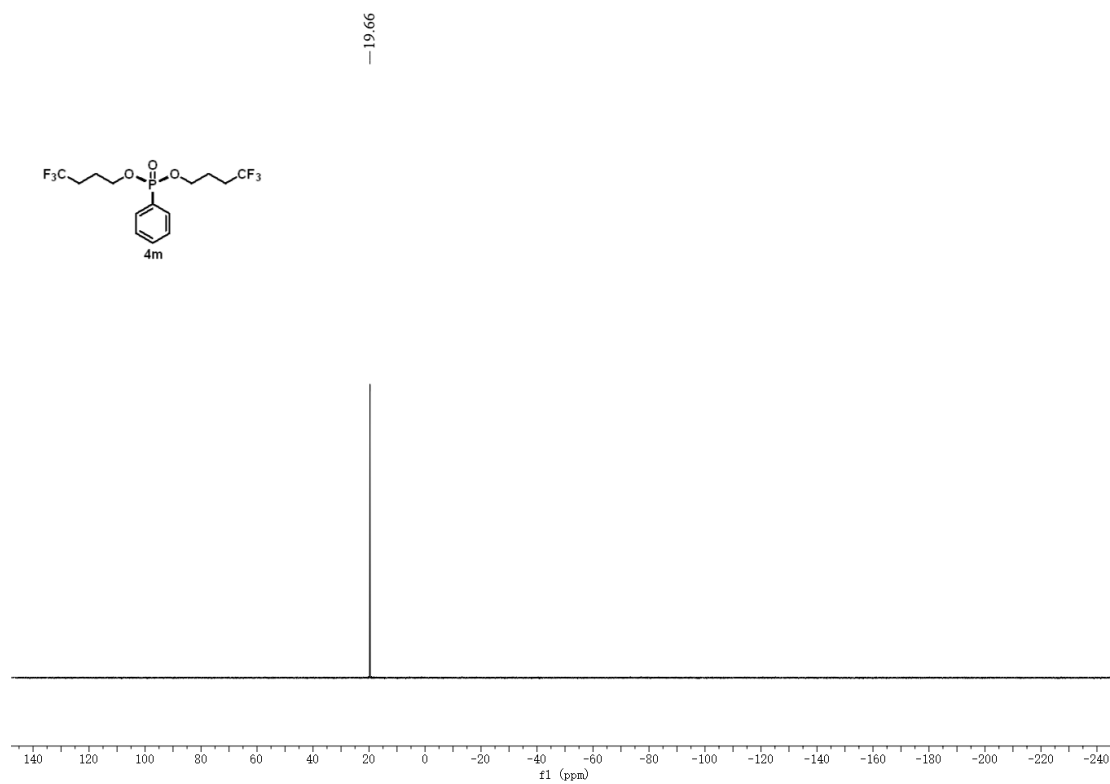
¹H NMR (400 MHz, CDCl₃) spectrum for 4m



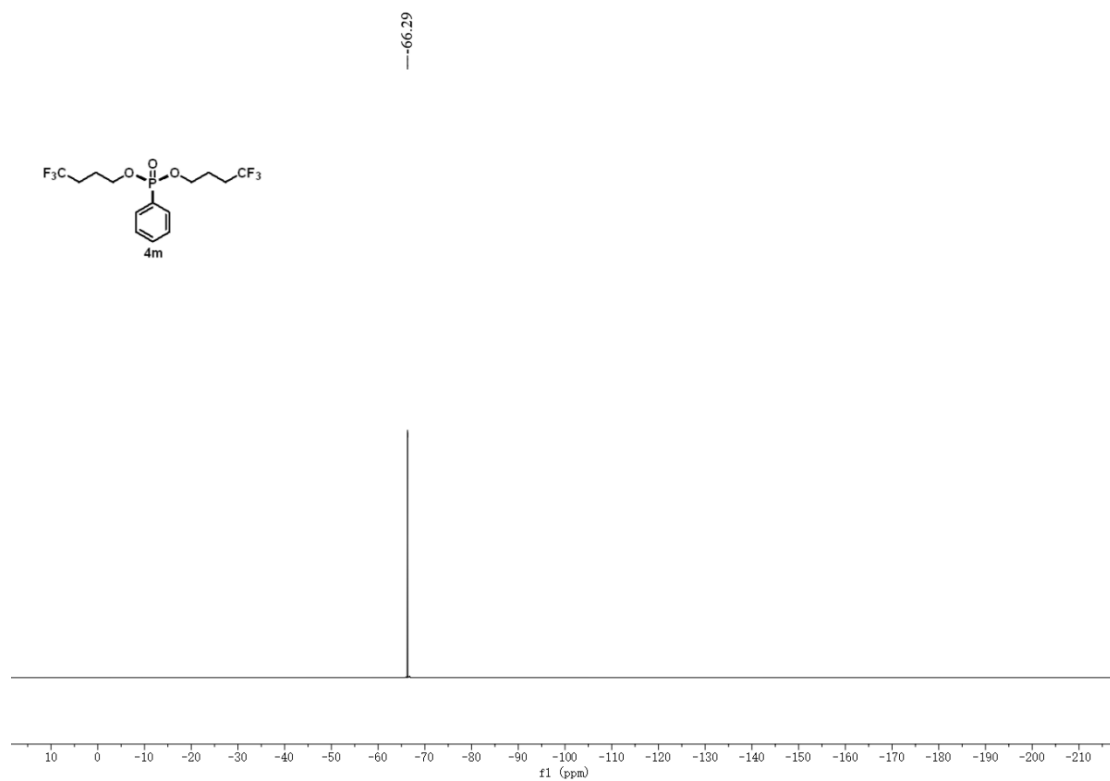
¹³C NMR (101 MHz, CDCl₃) spectrum for 4m



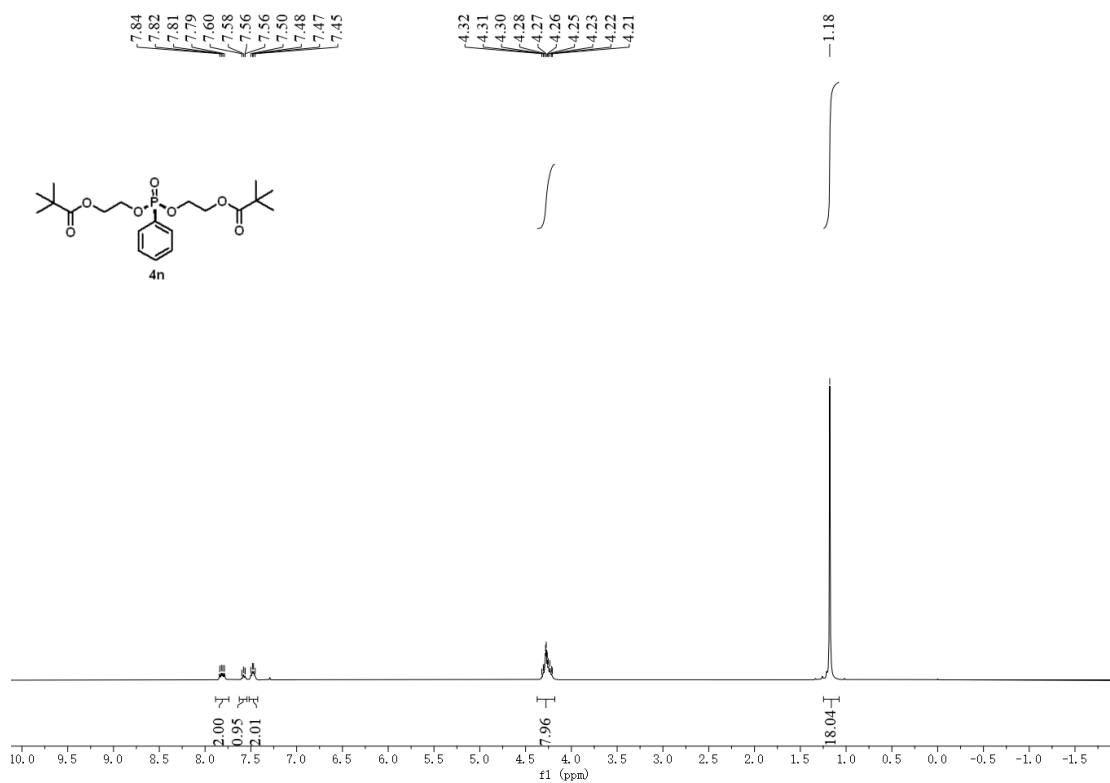
³¹P NMR (121 MHz, CDCl₃) spectrum for 4m



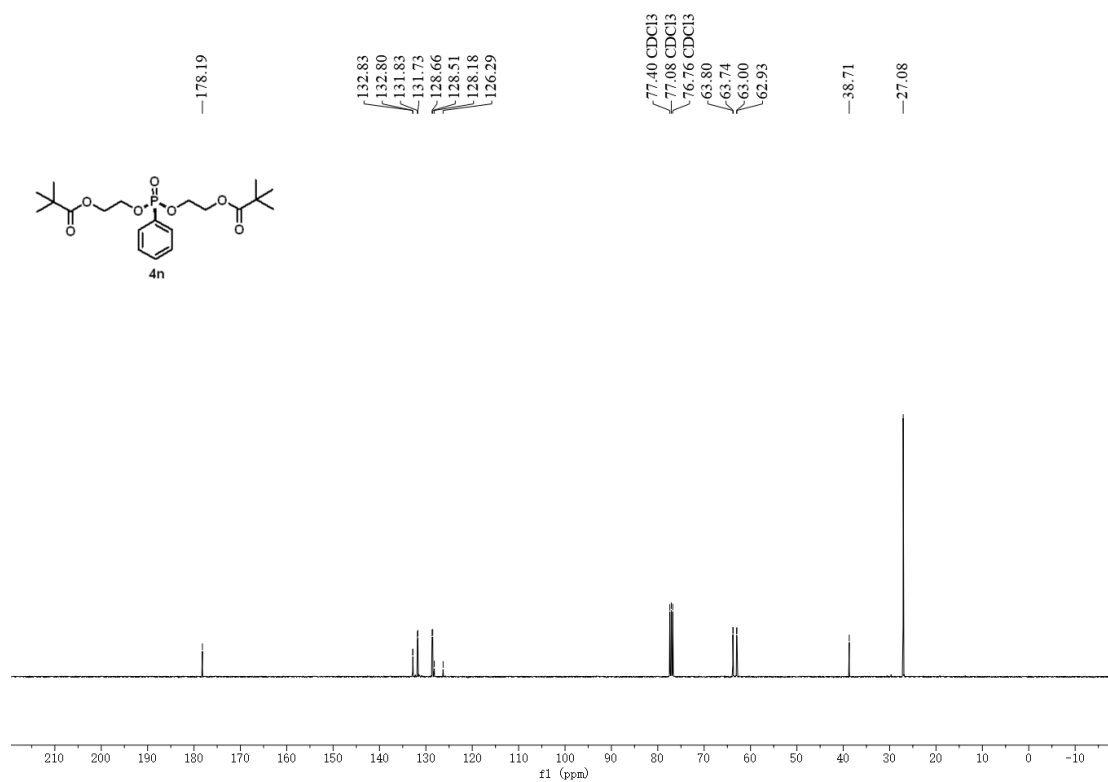
¹⁹F NMR (282 MHz, CDCl₃) spectrum for 4m



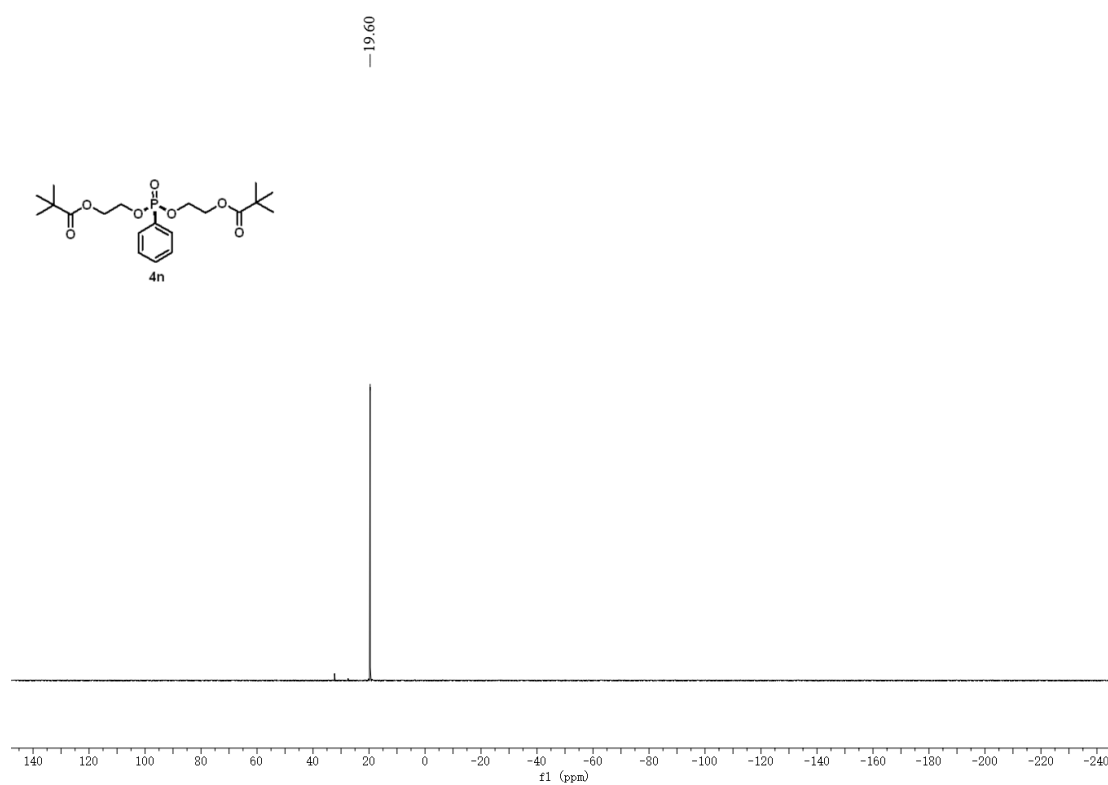
¹H NMR (400 MHz, CDCl₃) spectrum for 4n



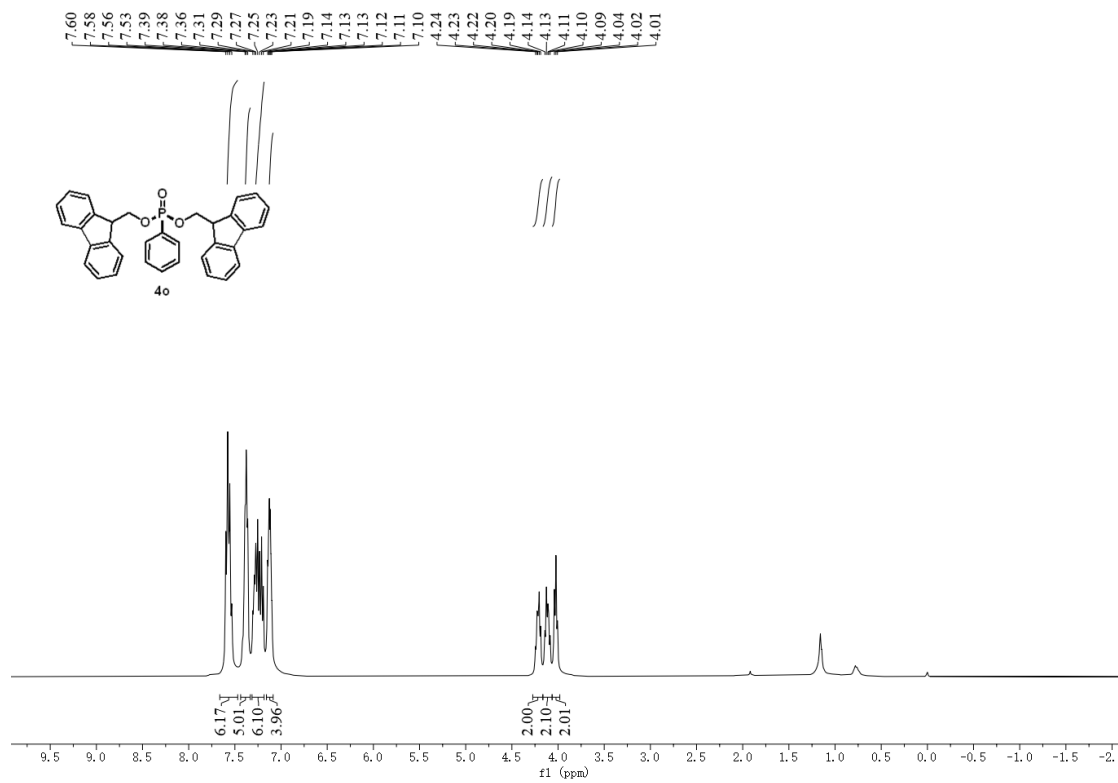
^{13}C NMR (101 MHz, CDCl_3) spectrum for 4n



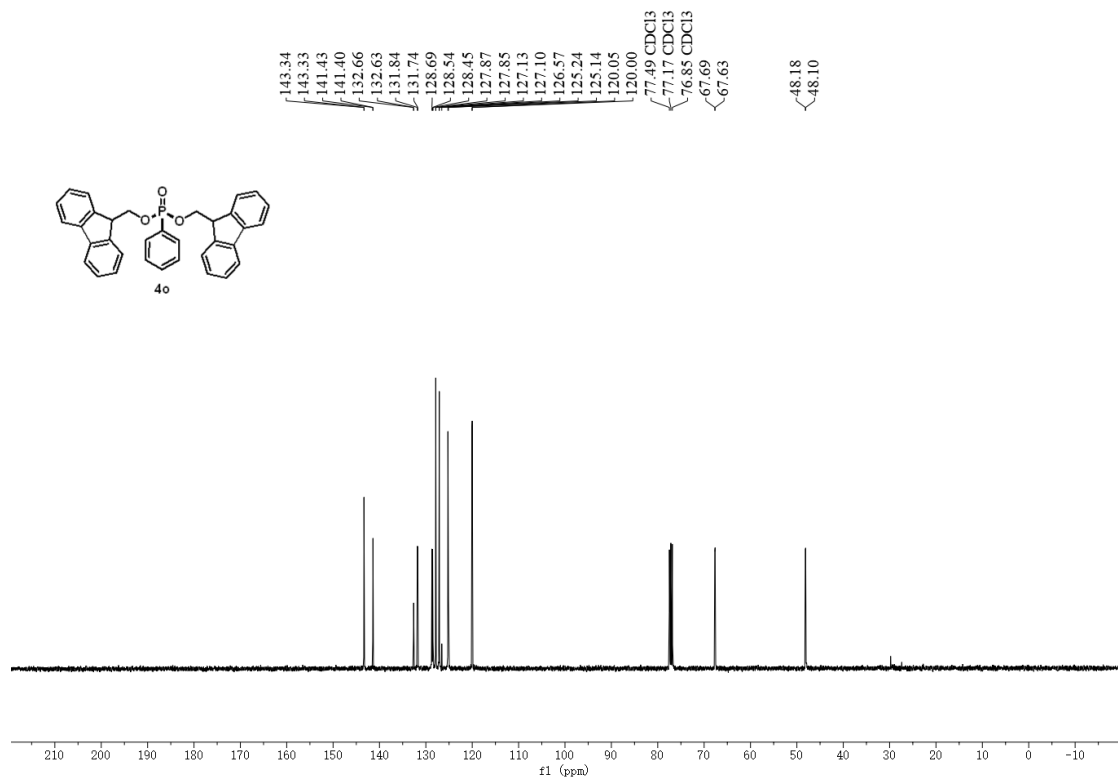
^{31}P NMR (121 MHz, CDCl_3) spectrum for 4n



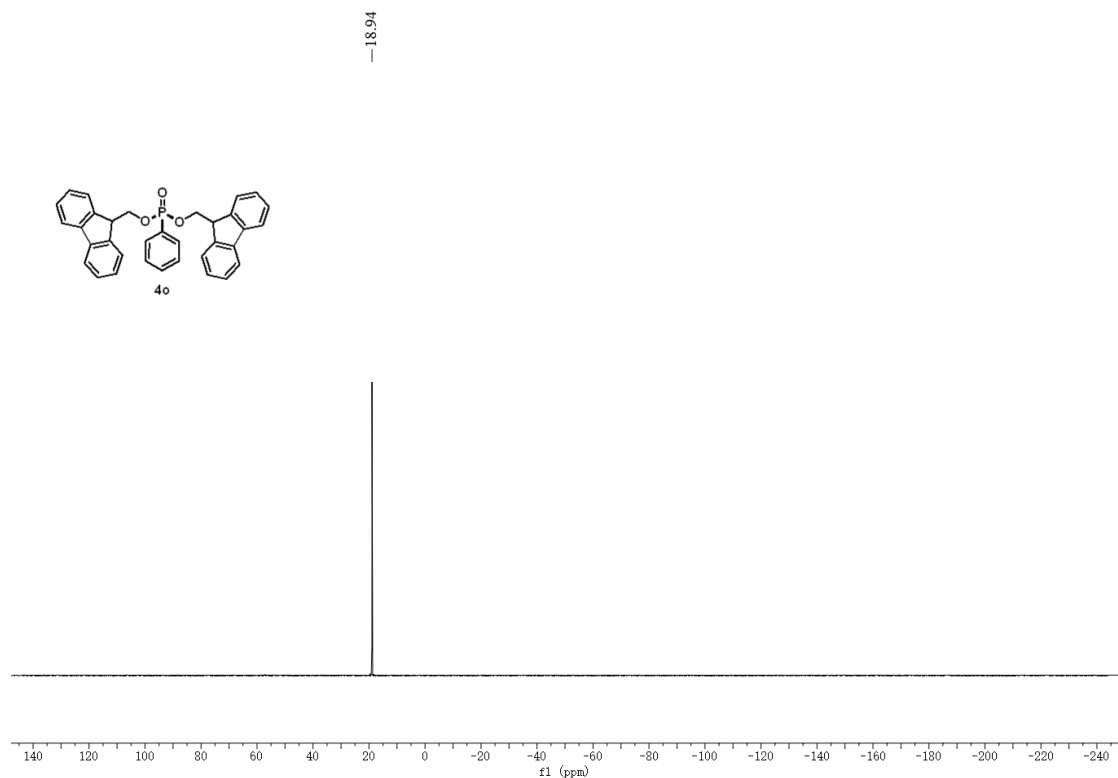
¹H NMR (400 MHz, CDCl₃) spectrum for 4o



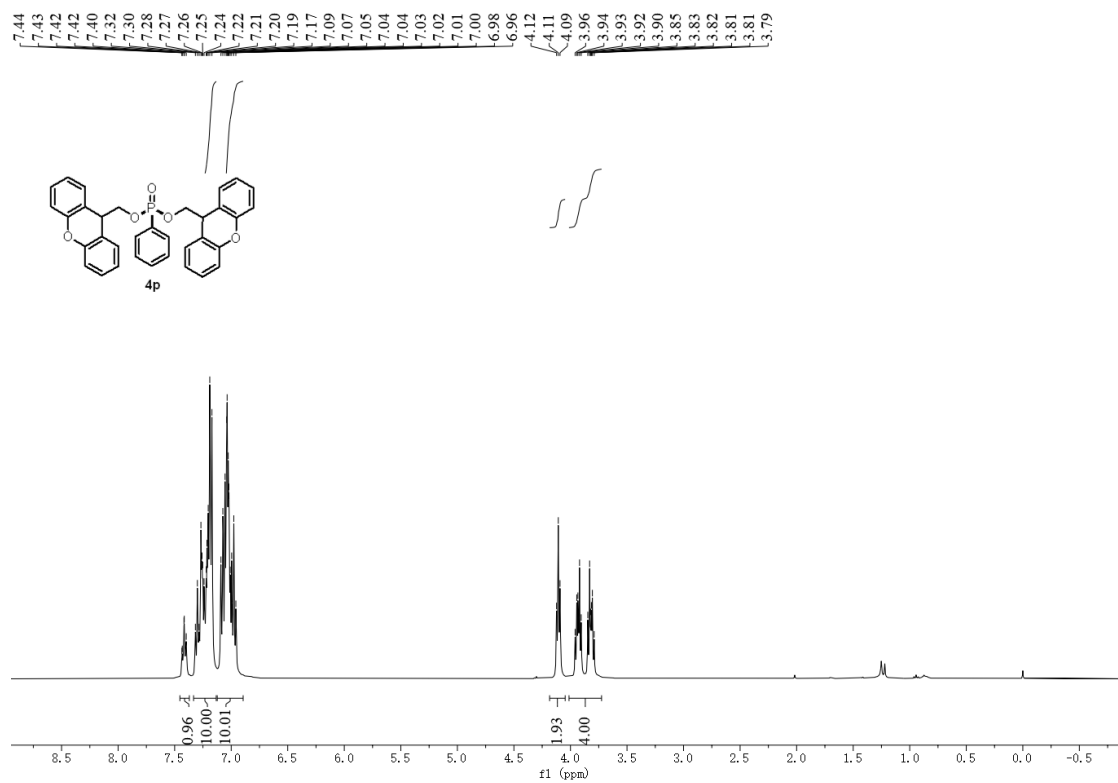
¹³C NMR (101 MHz, CDCl₃) spectrum for 4o



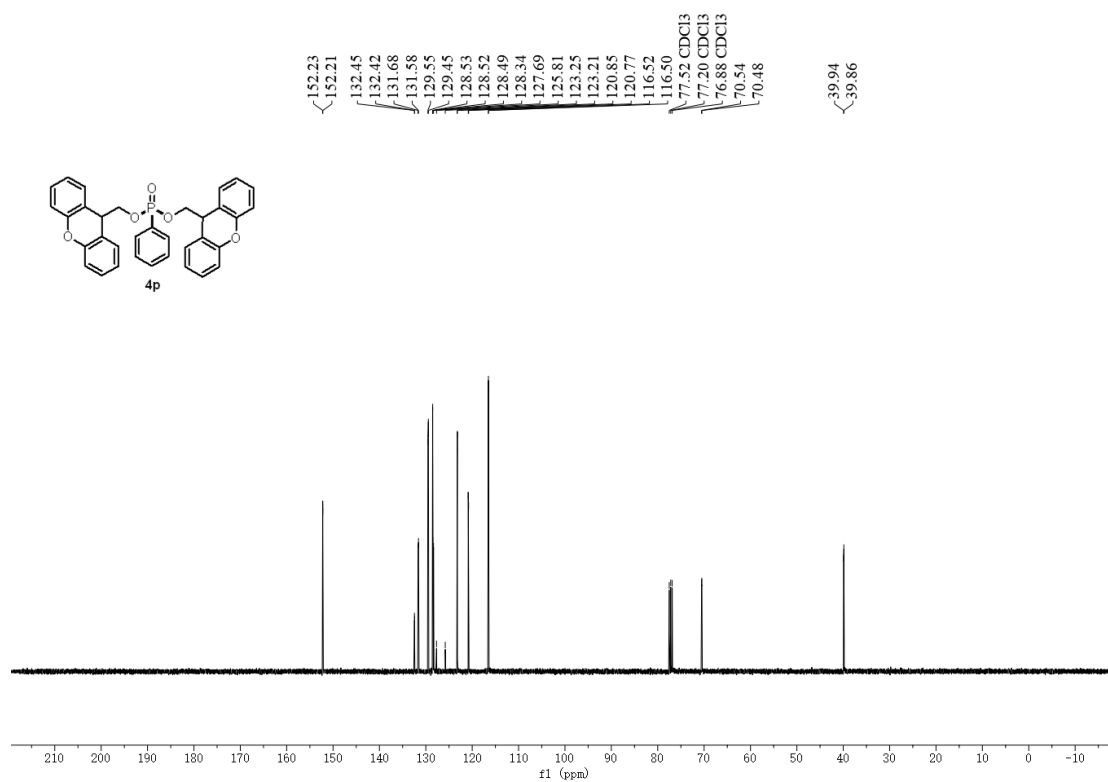
³¹P NMR (121 MHz, CDCl₃) spectrum for 4o



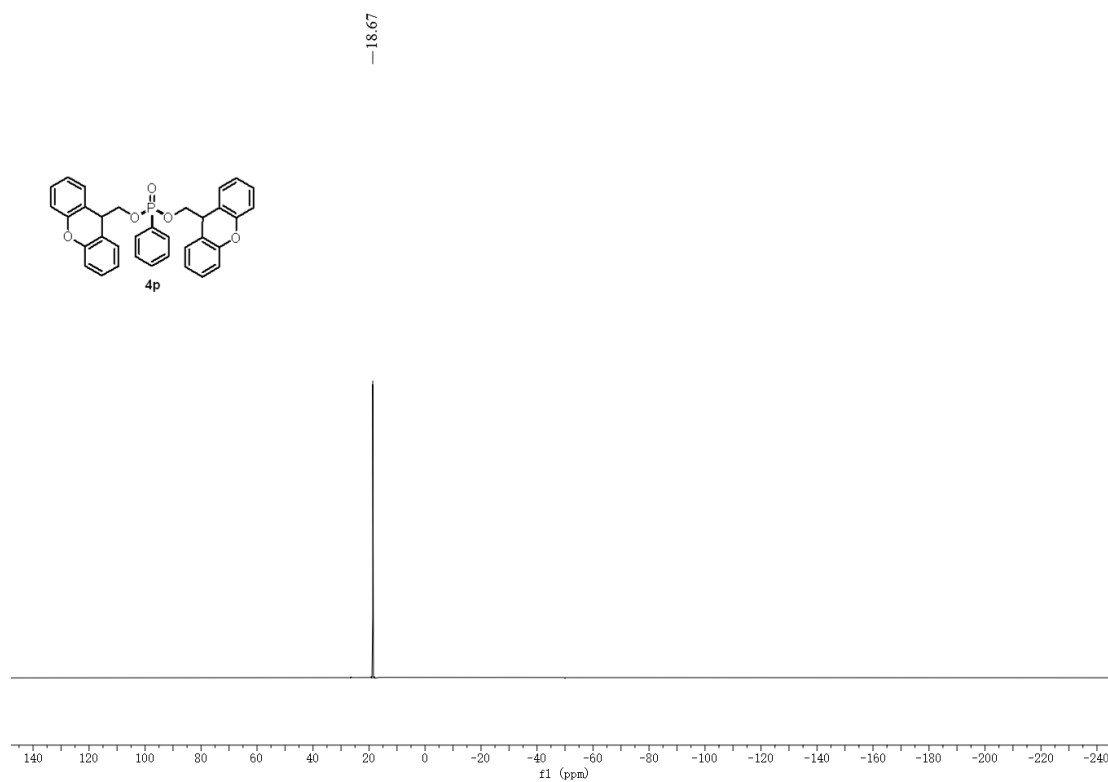
¹H NMR (400 MHz, CDCl₃) spectrum for 4p



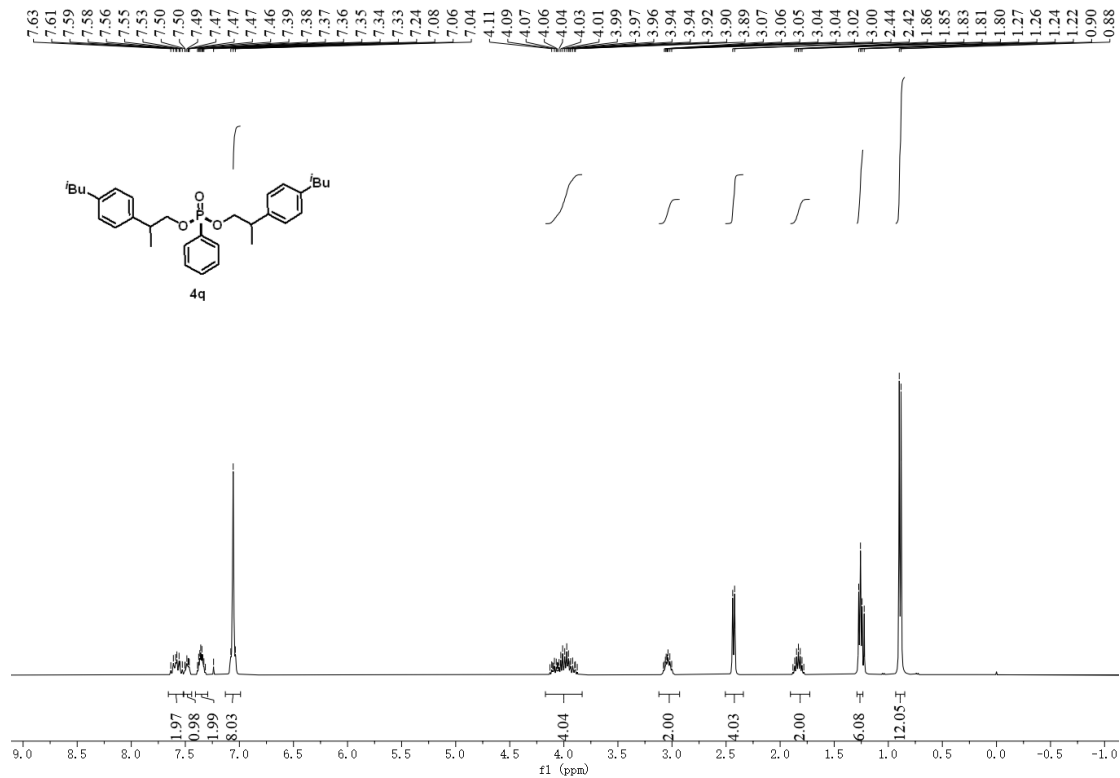
¹³C NMR (101 MHz, CDCl₃) spectrum for 4p



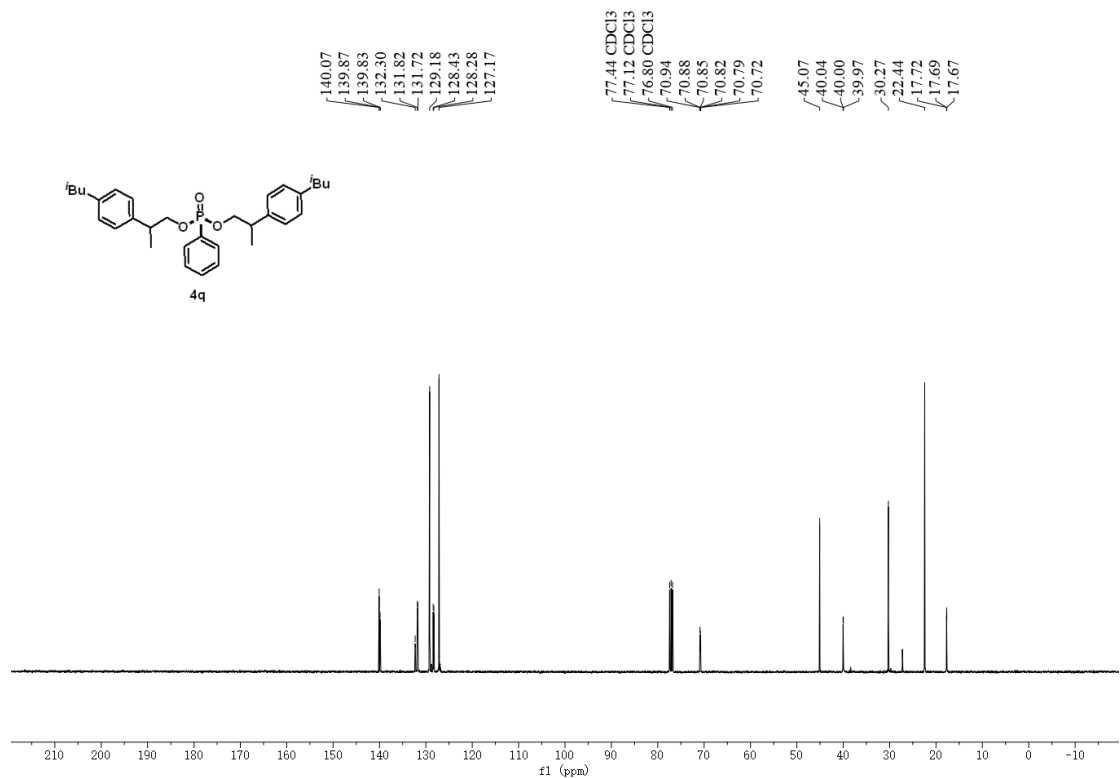
³¹P NMR (121 MHz, CDCl₃) spectrum for 4p



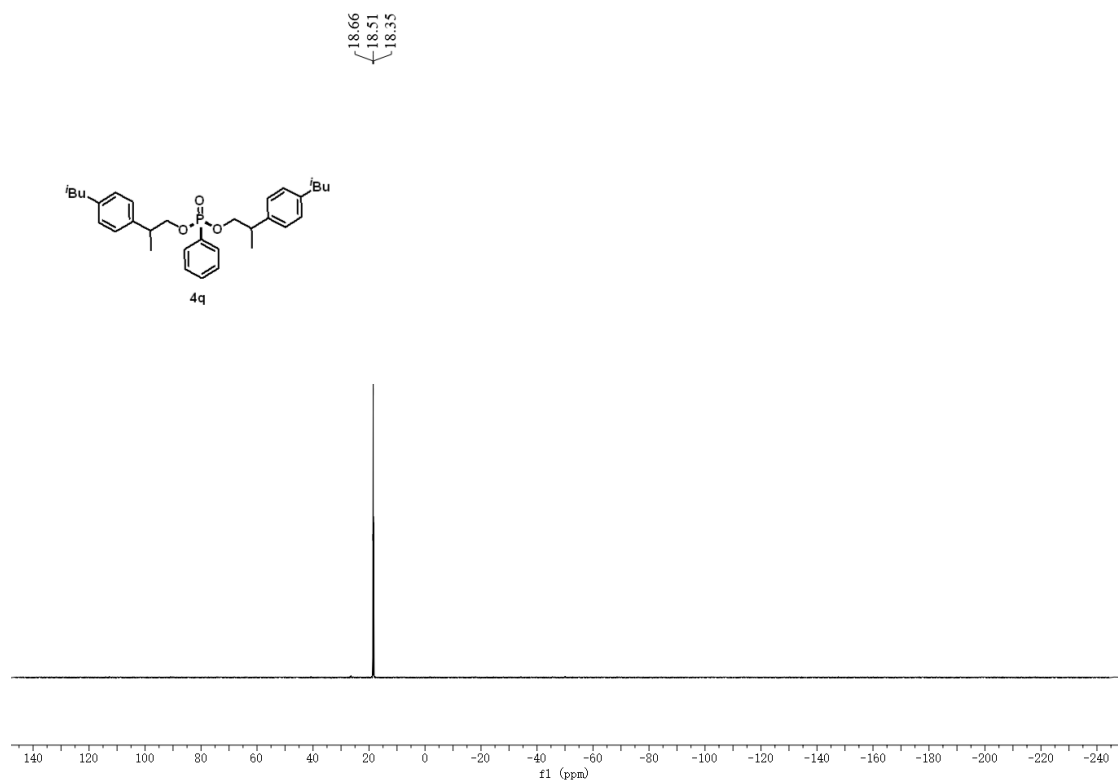
¹H NMR (400 MHz, CDCl₃) spectrum for 4q



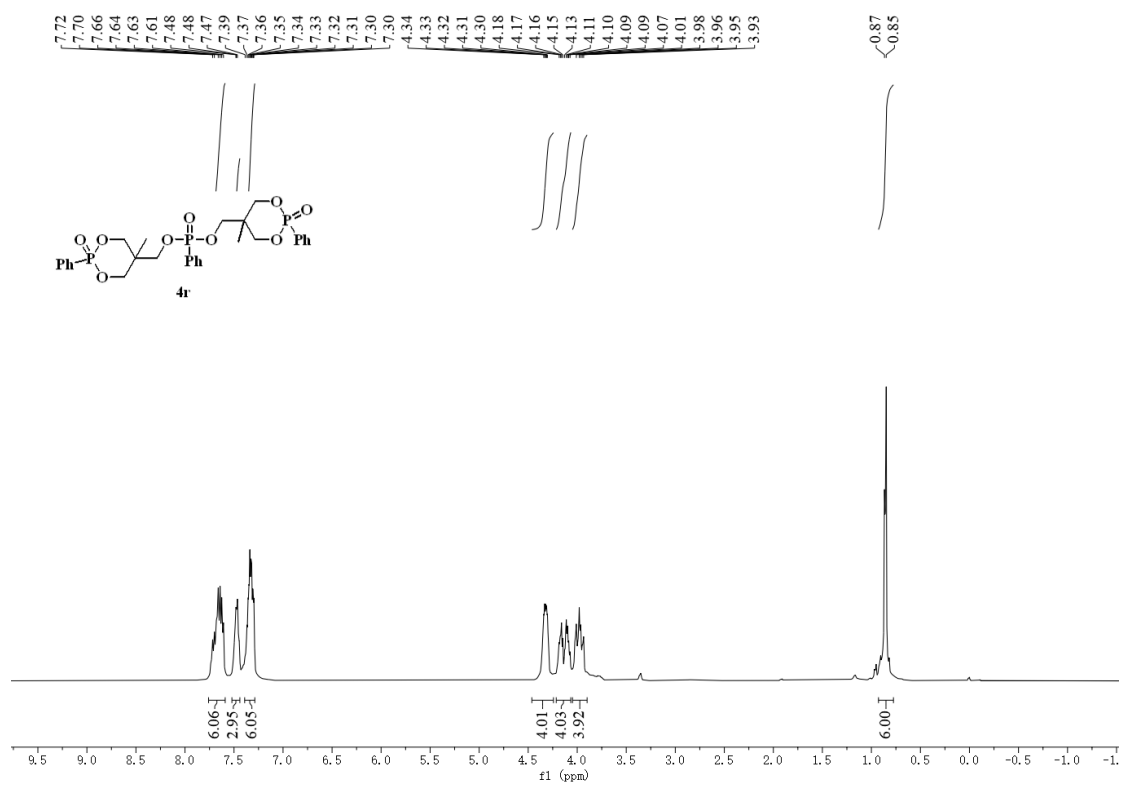
¹³C NMR (101 MHz, CDCl₃) spectrum for 4q



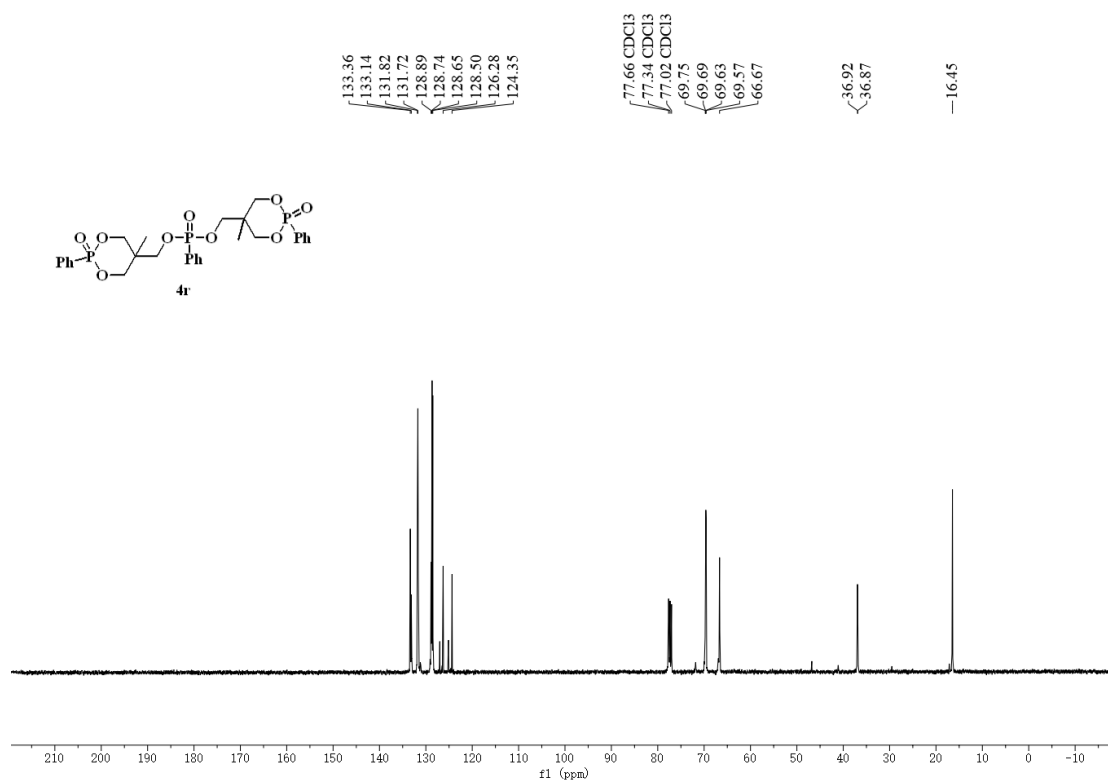
^{31}P NMR (121 MHz, CDCl_3) spectrum for 4q



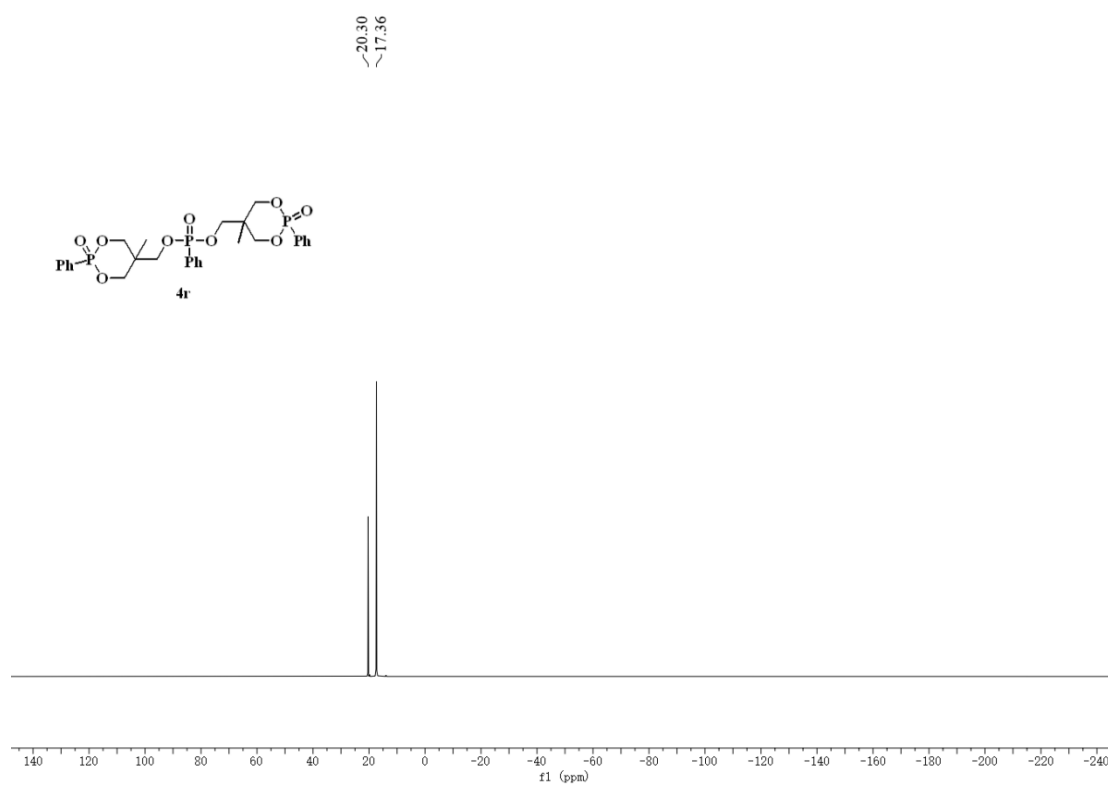
^1H NMR (400 MHz, CDCl_3) spectrum for 4r



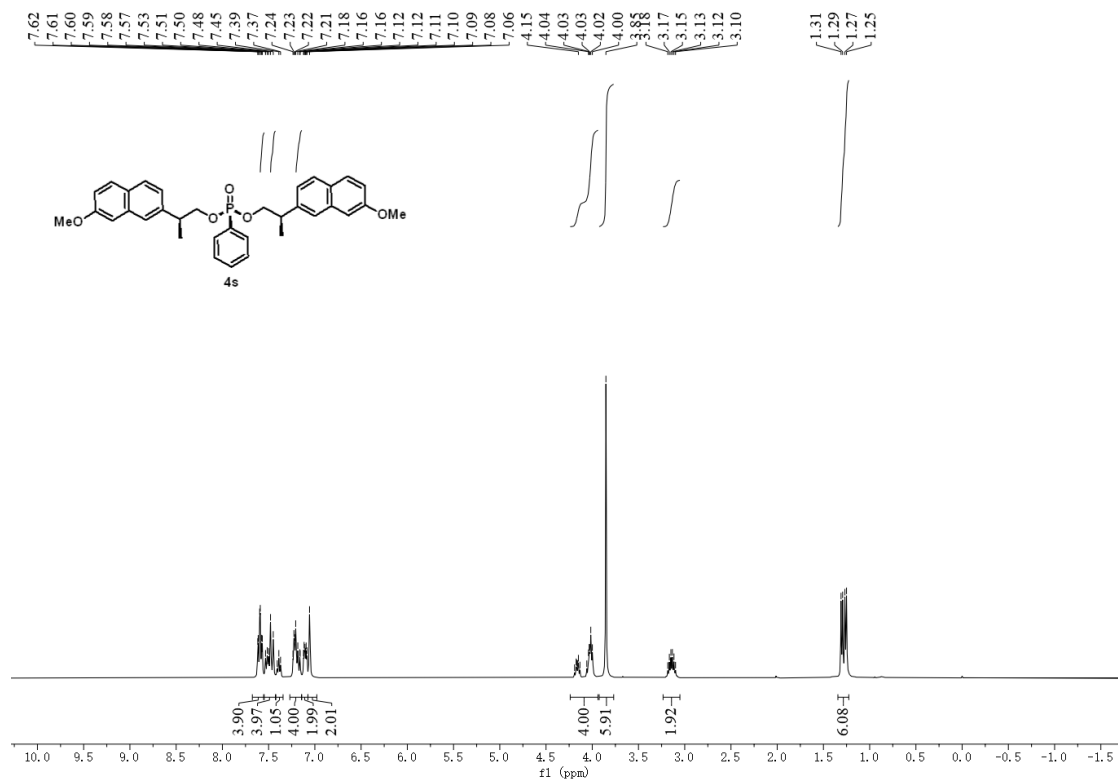
^{13}C NMR (101 MHz, CDCl_3) spectrum for 4r



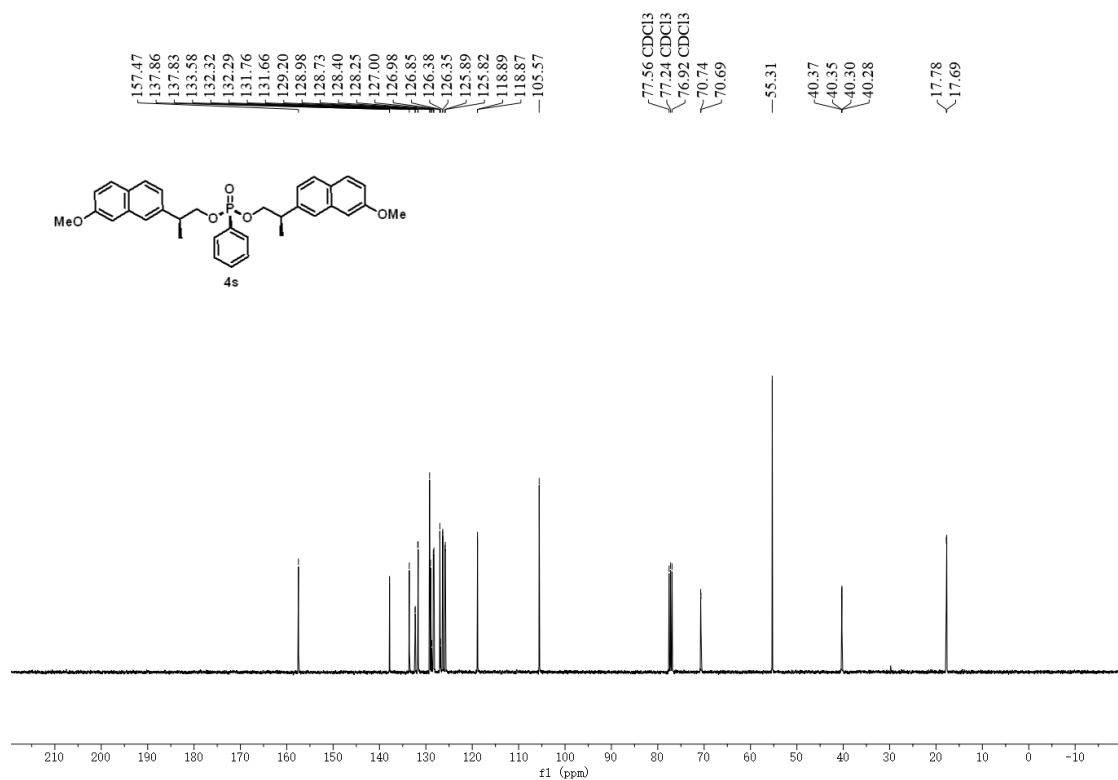
^{31}P NMR (121 MHz, CDCl_3) spectrum for 4r



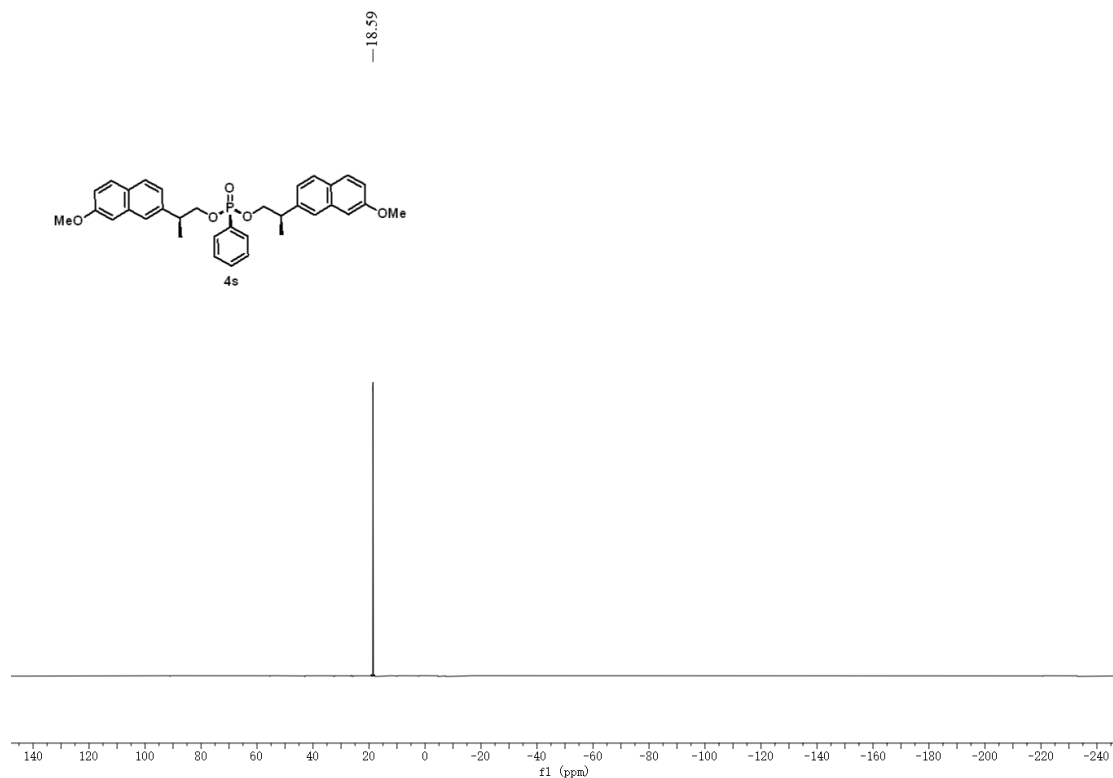
^1H NMR (400 MHz, CDCl_3) spectrum for 4s



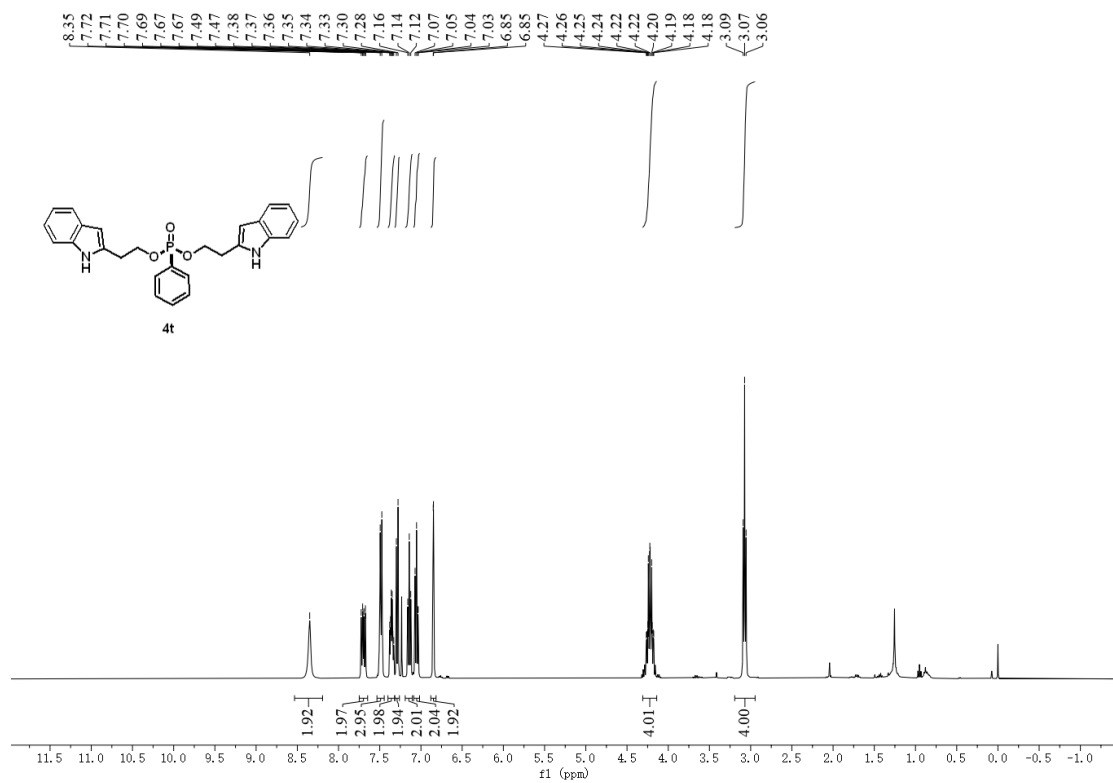
^{13}C NMR (101 MHz, CDCl_3) spectrum for 4s



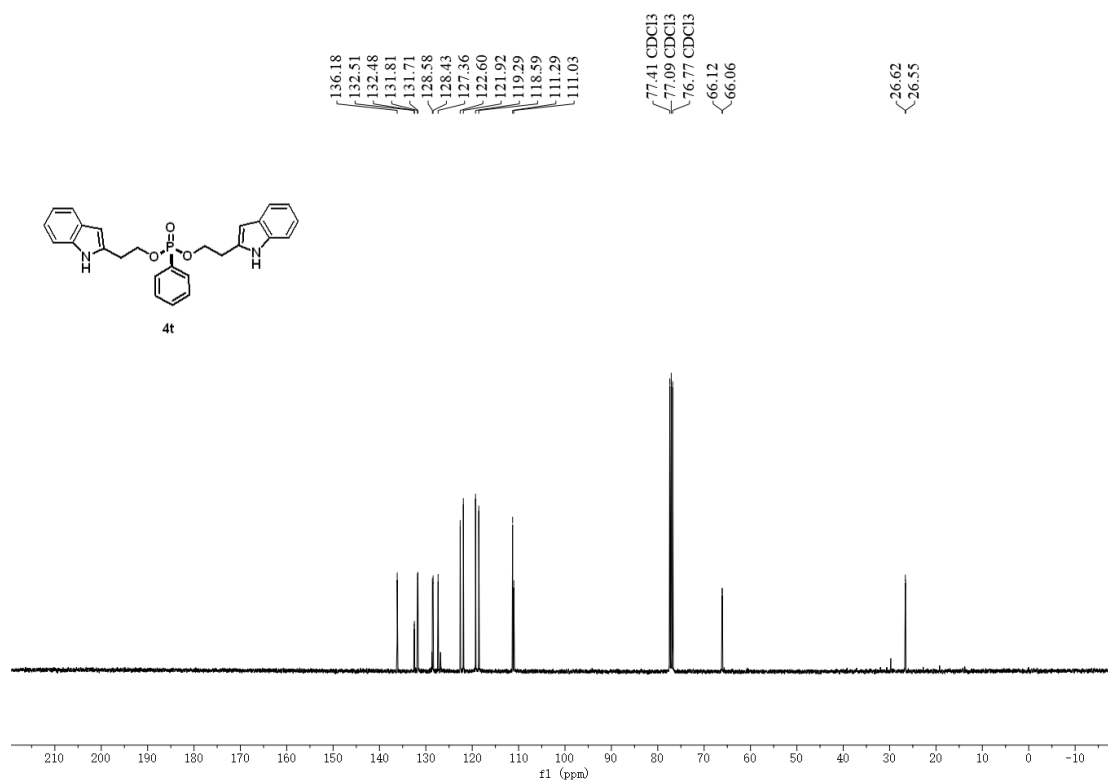
³¹P NMR (121 MHz, CDCl₃) spectrum for 4s



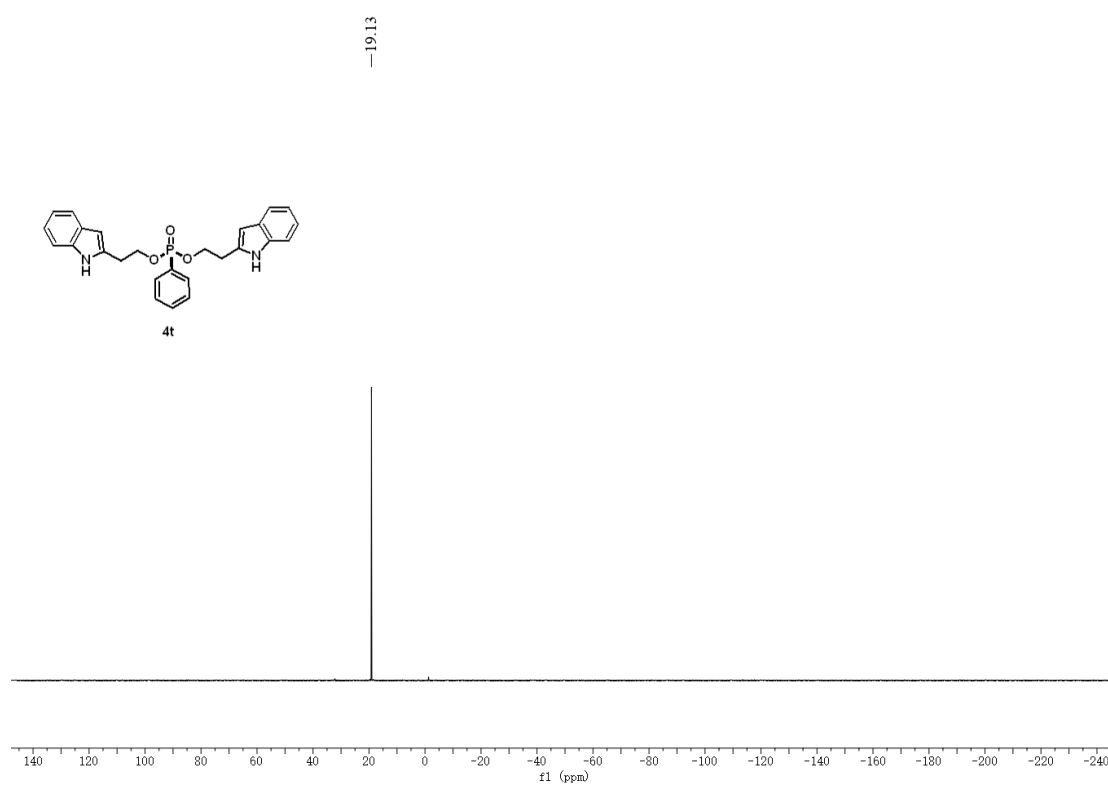
¹H NMR (400 MHz, CDCl₃) spectrum for 4t



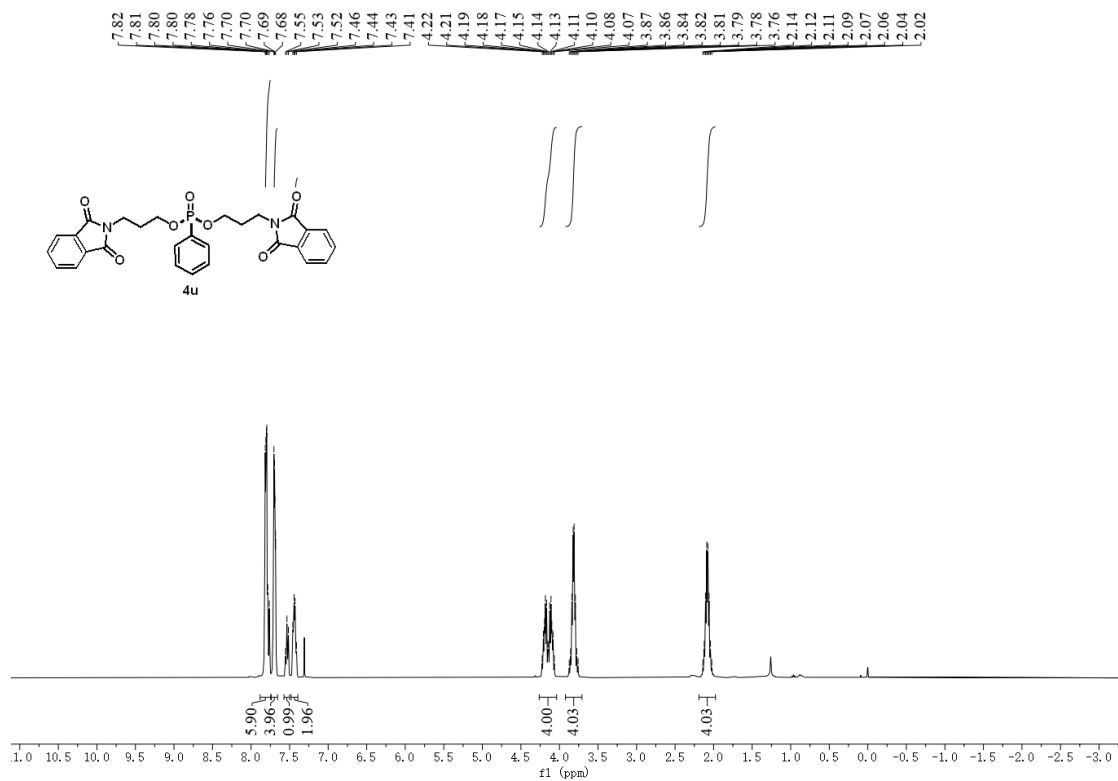
¹³C NMR (101 MHz, CDCl₃) spectrum for 4t



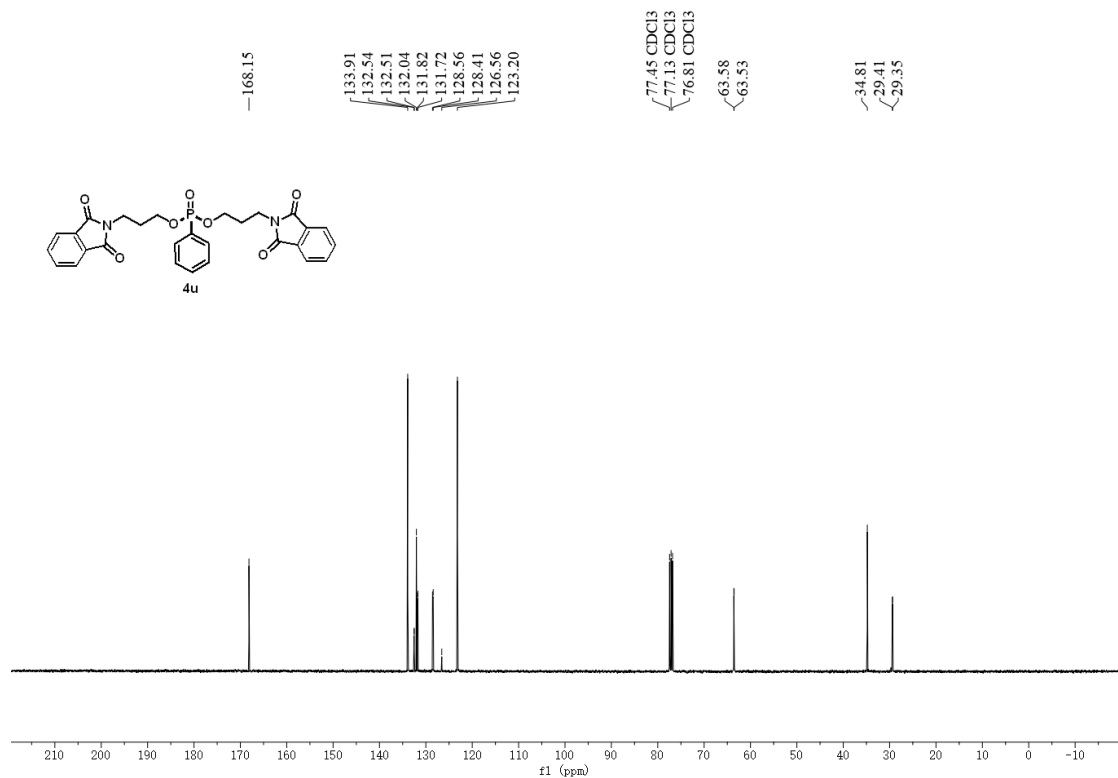
³¹P NMR (121 MHz, CDCl₃) spectrum for 4t



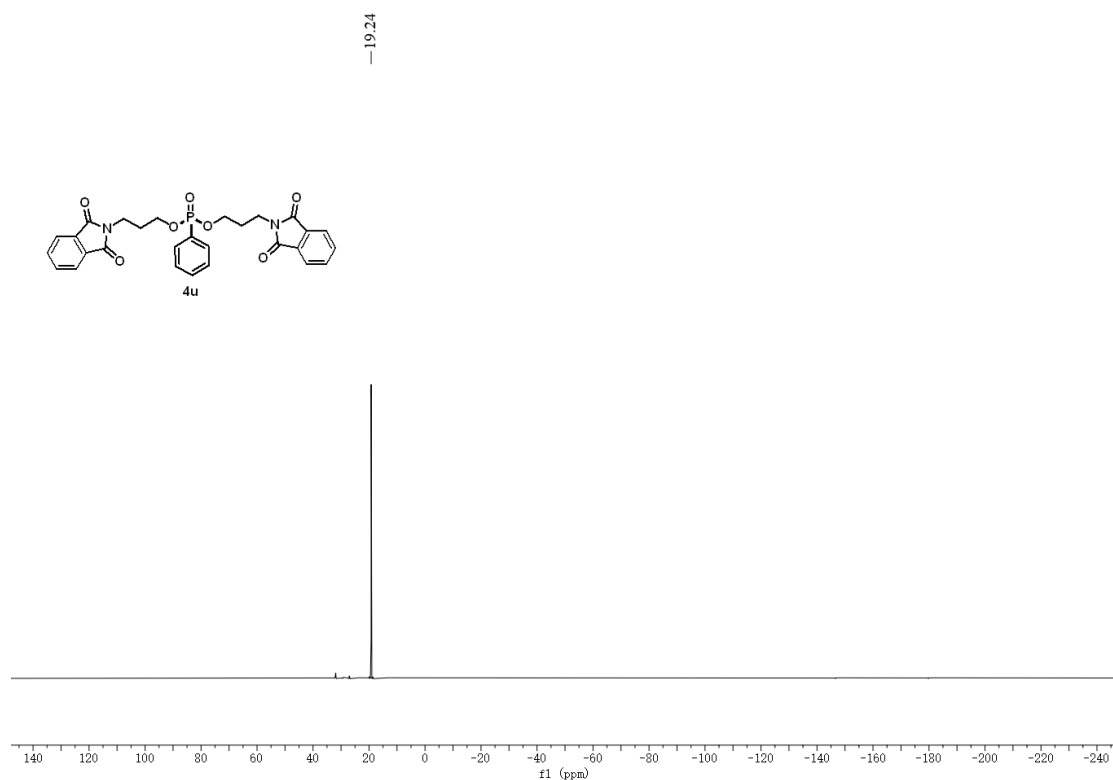
¹H NMR (400 MHz, CDCl₃) spectrum for 4u



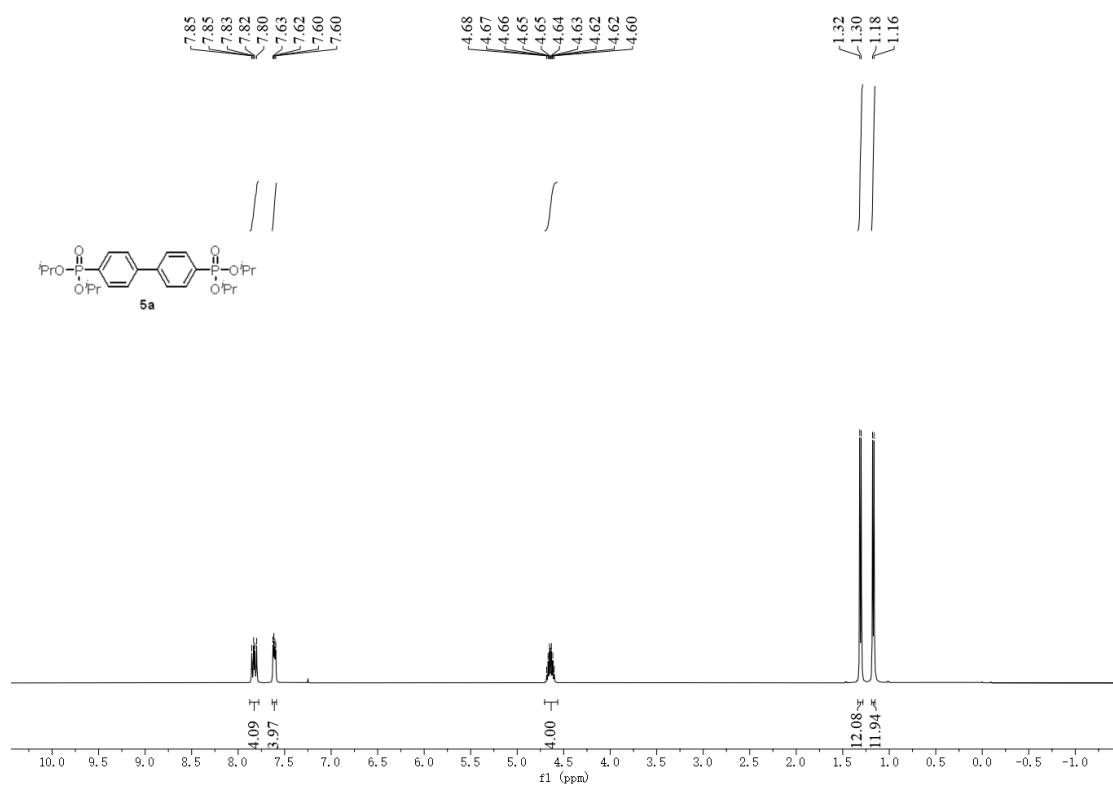
¹³C NMR (101 MHz, CDCl₃) spectrum for 4u



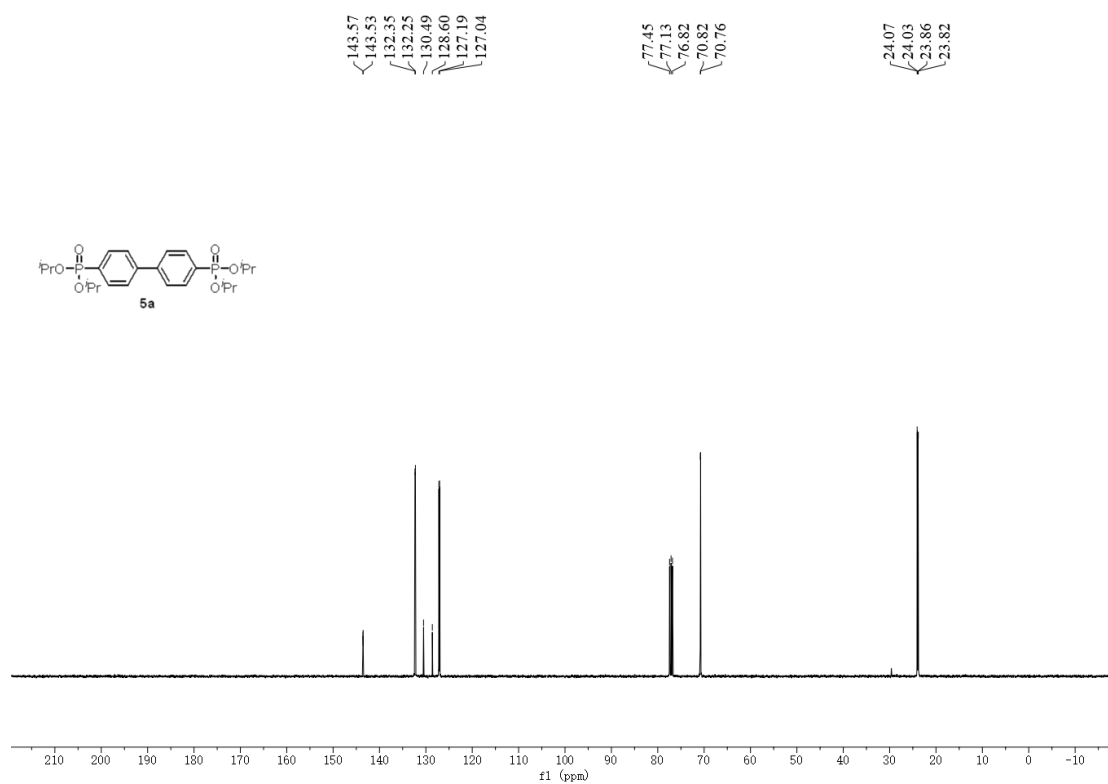
³¹P NMR (121 MHz, CDCl₃) spectrum for 4u



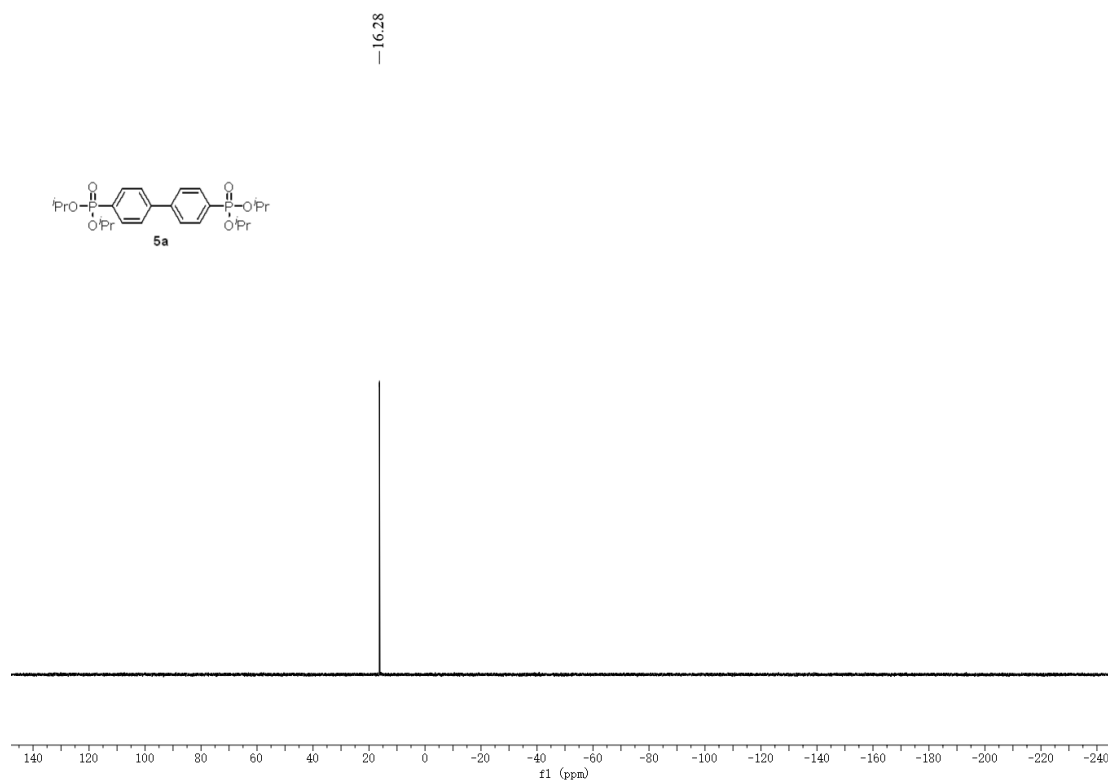
¹H NMR (400 MHz, CDCl₃) spectrum for 5a



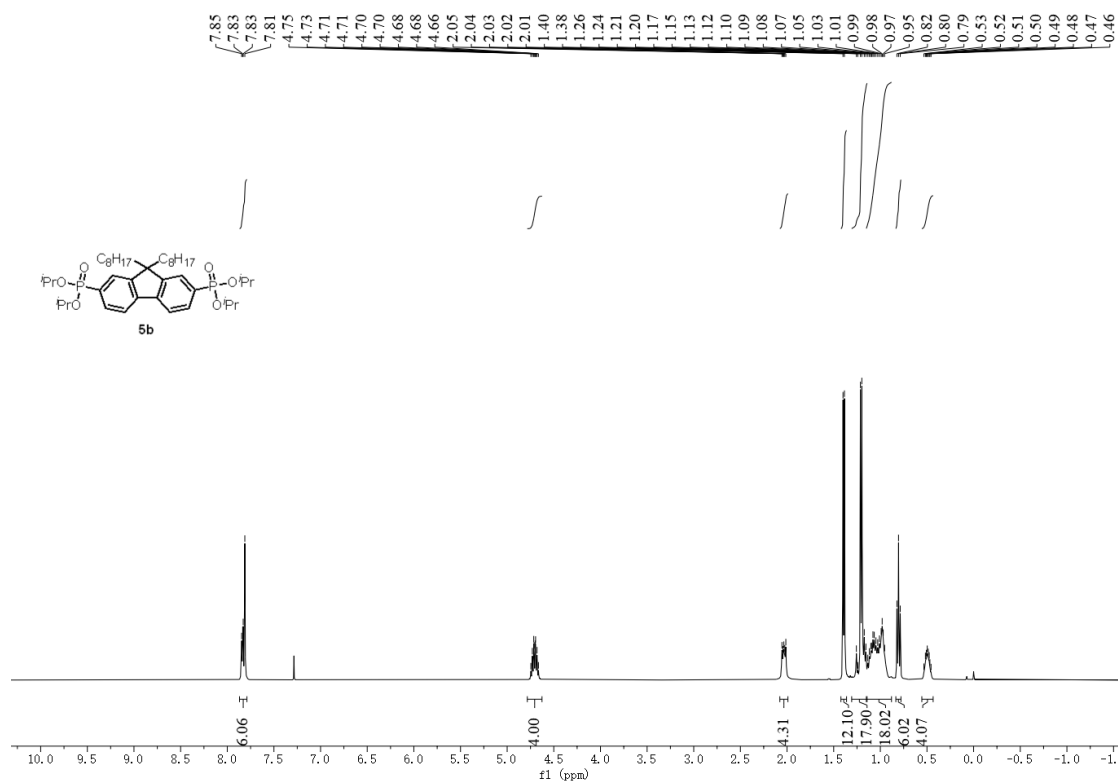
¹³C NMR (101 MHz, CDCl₃) spectrum for 5a



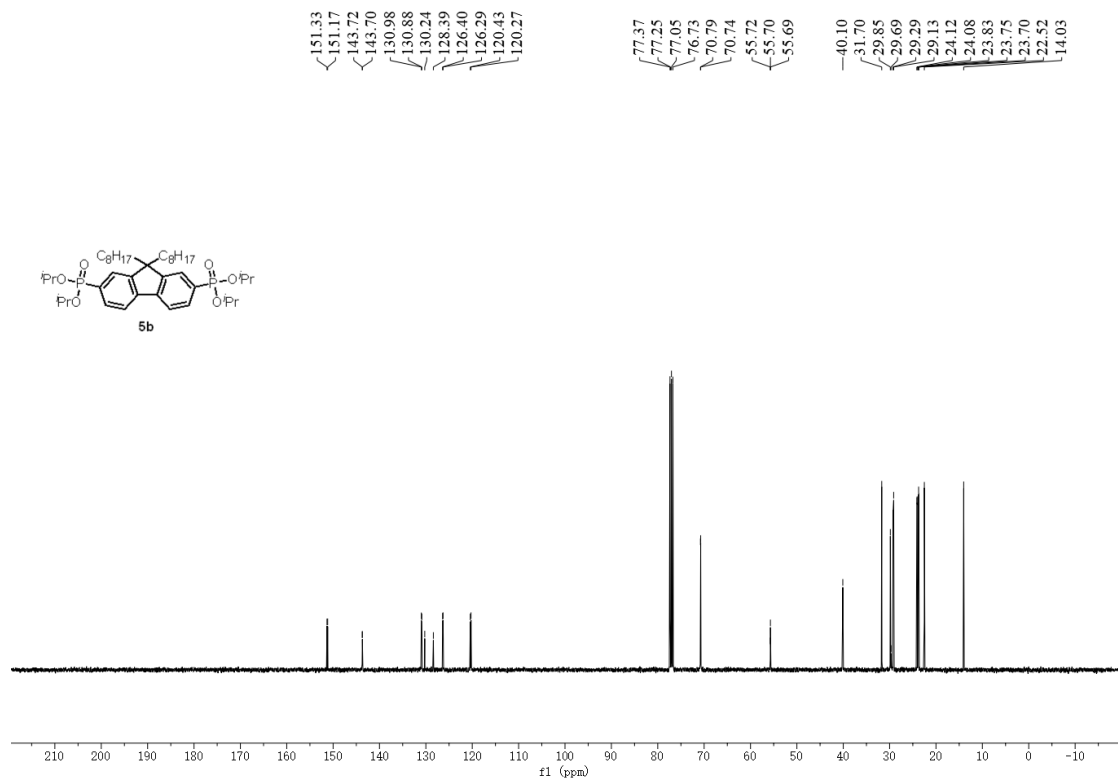
³¹P NMR (121 MHz, CDCl₃) spectrum for 5a



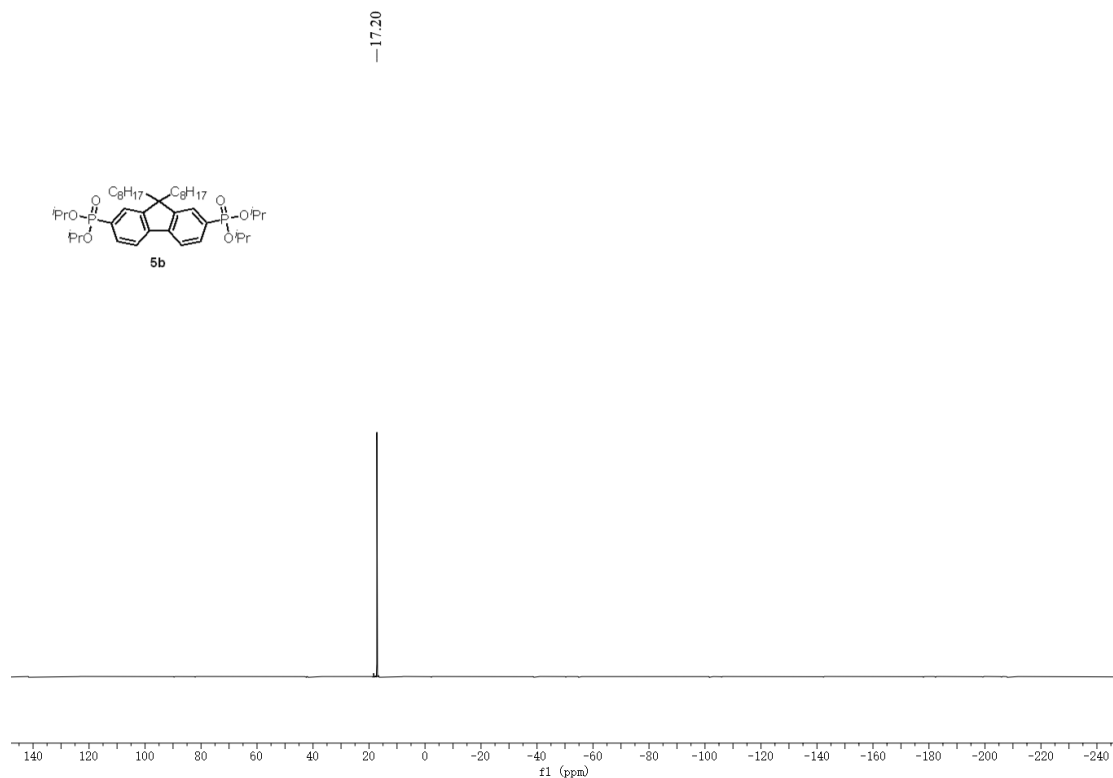
¹H NMR (400 MHz, CDCl₃) spectrum for 5b



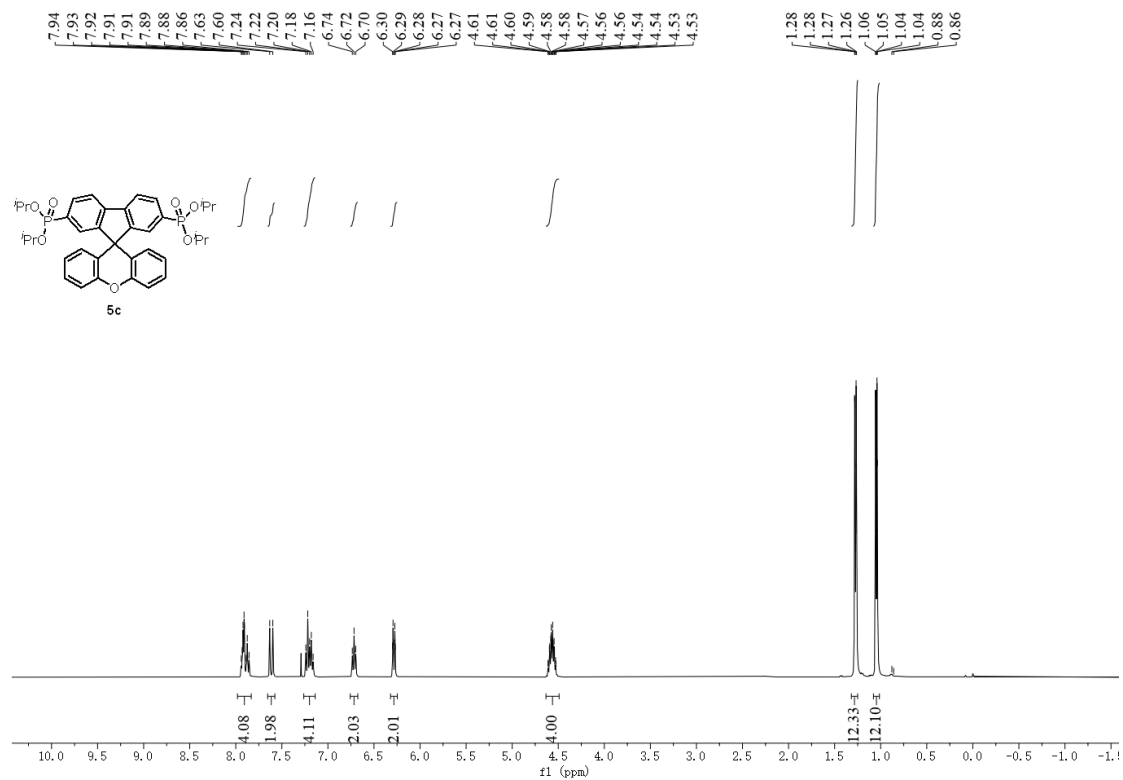
¹³C NMR (101 MHz, CDCl₃) spectrum for 5b



^{31}P NMR (121 MHz, CDCl_3) spectrum for 5b

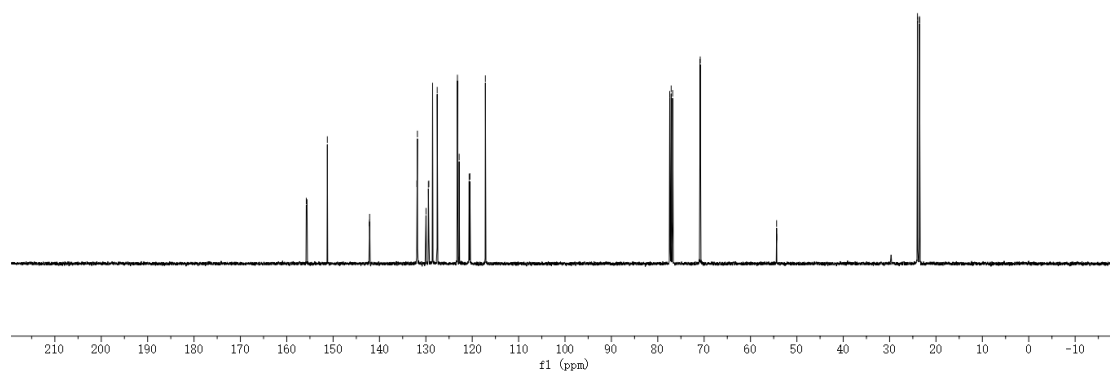
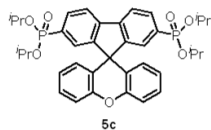


^1H NMR (400 MHz, CDCl_3) spectrum for 5c



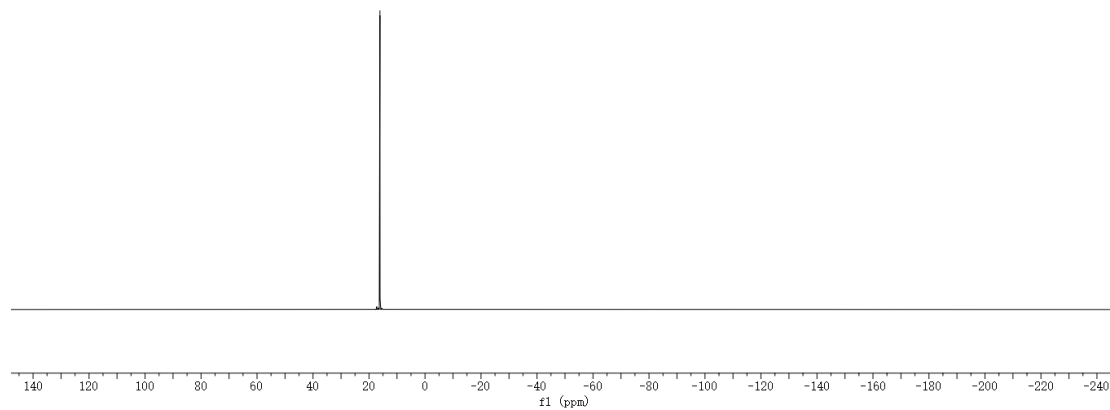
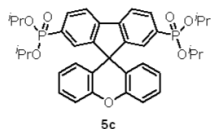
^{13}C NMR (101 MHz, CDCl_3) spectrum for **5c**

155.78, 155.63, 151.24, 142.16, 142.13, 131.93, 131.83, 129.97, 129.46, 129.35, 128.55, 127.55, 123.20, 122.81, 120.67, 120.51, 117.16, 77.42, 77.30, 77.10, 76.79, 70.89, 70.84, 54.39, 54.37, 54.35, 24.00, 23.96, 23.56, 23.51

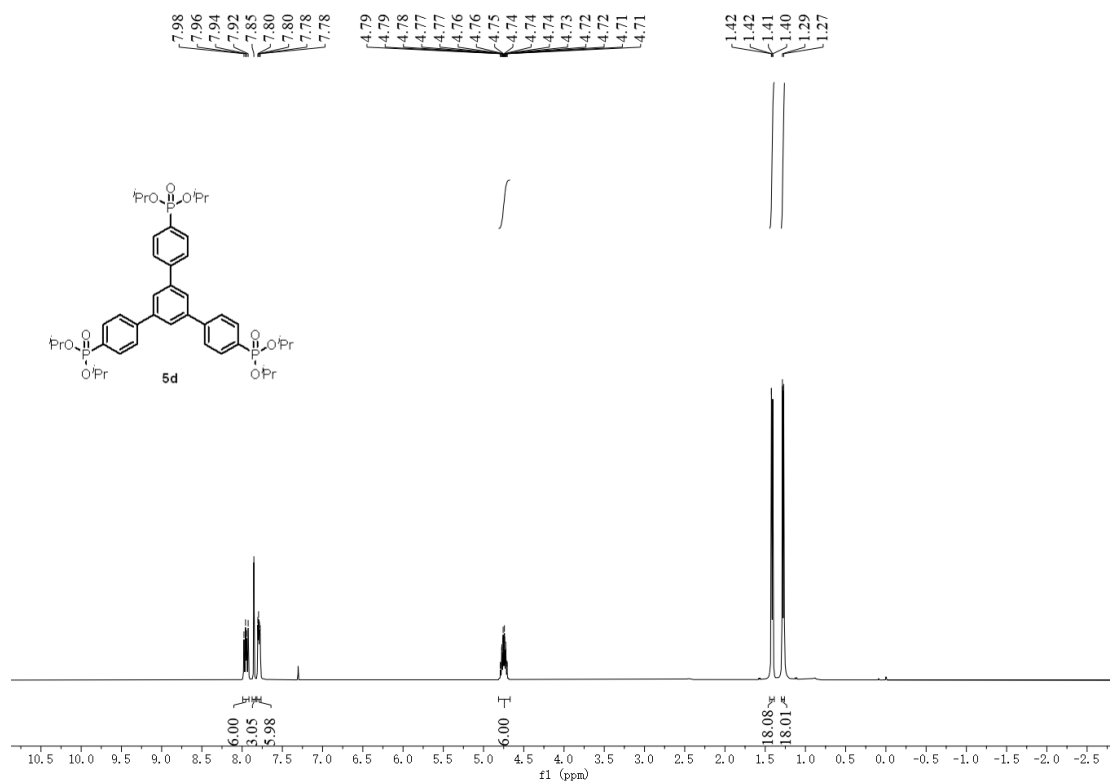


^{31}P NMR (121 MHz, CDCl_3) spectrum for **5c**

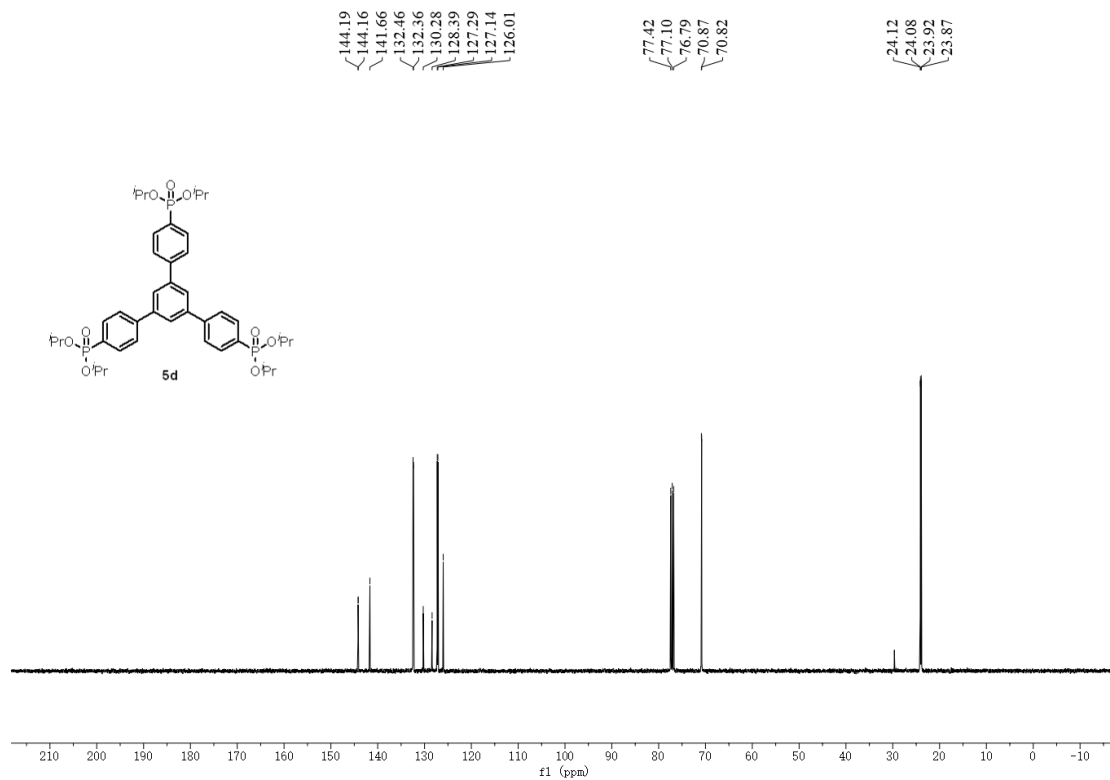
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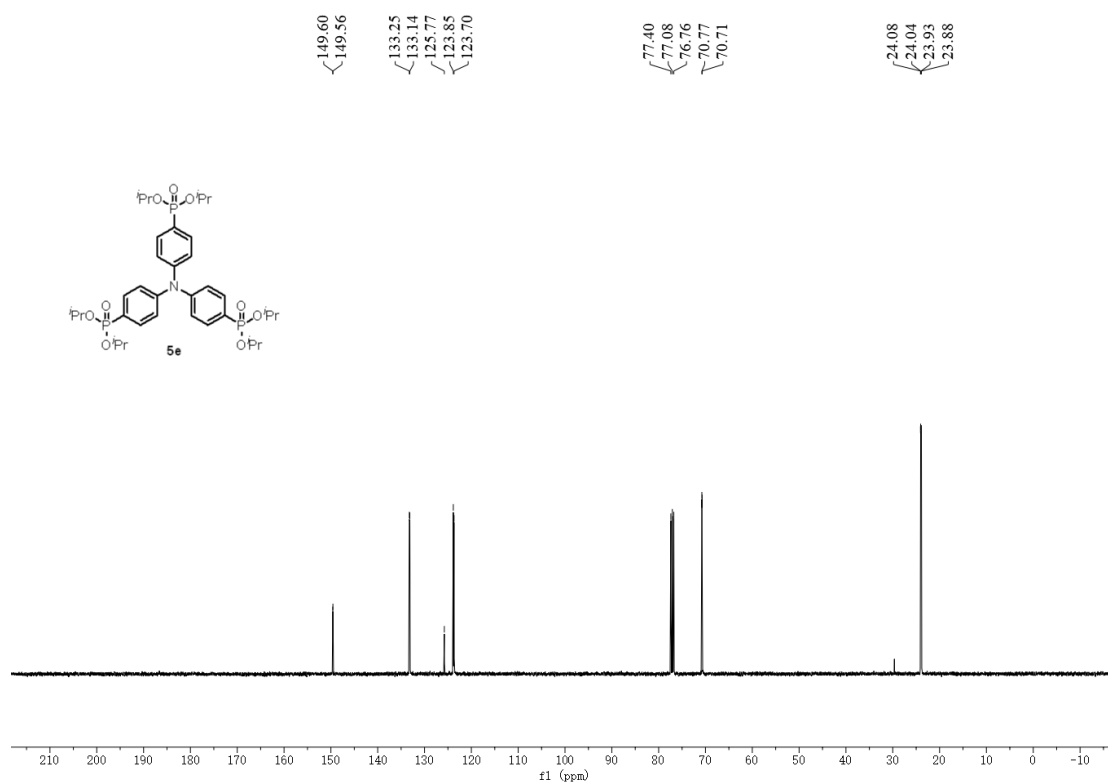
¹H NMR (400 MHz, CDCl₃) spectrum for 5d



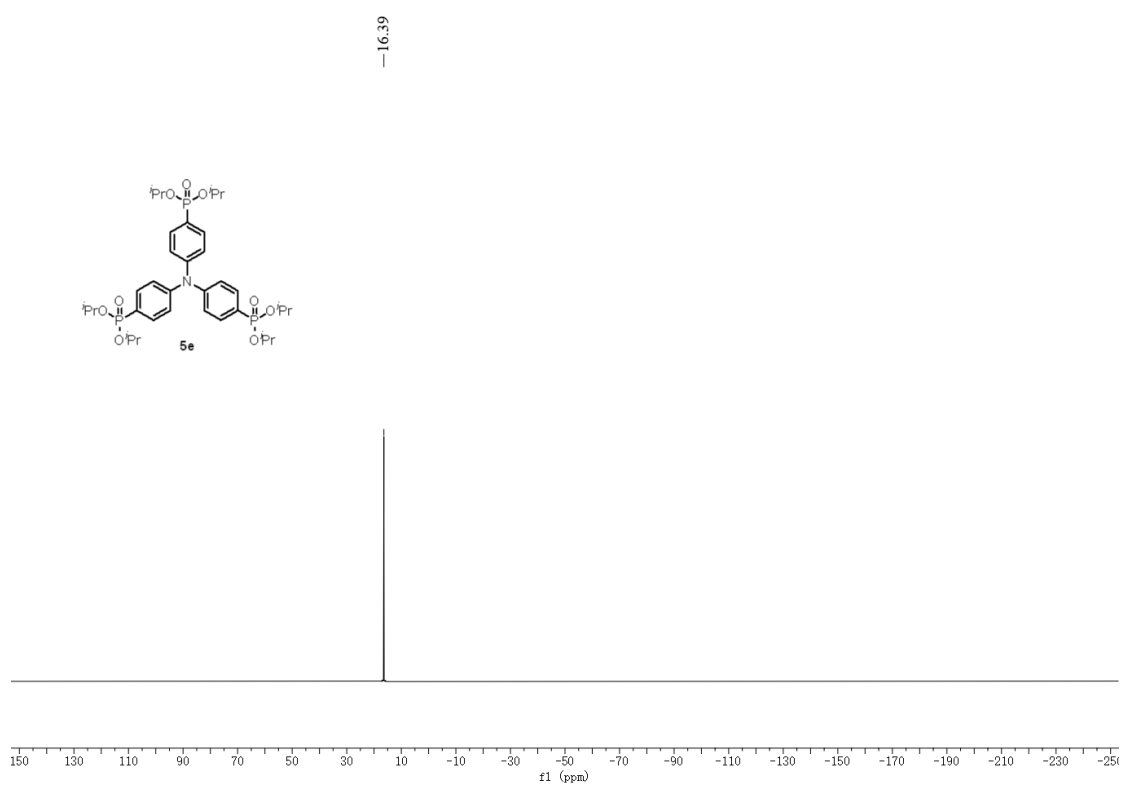
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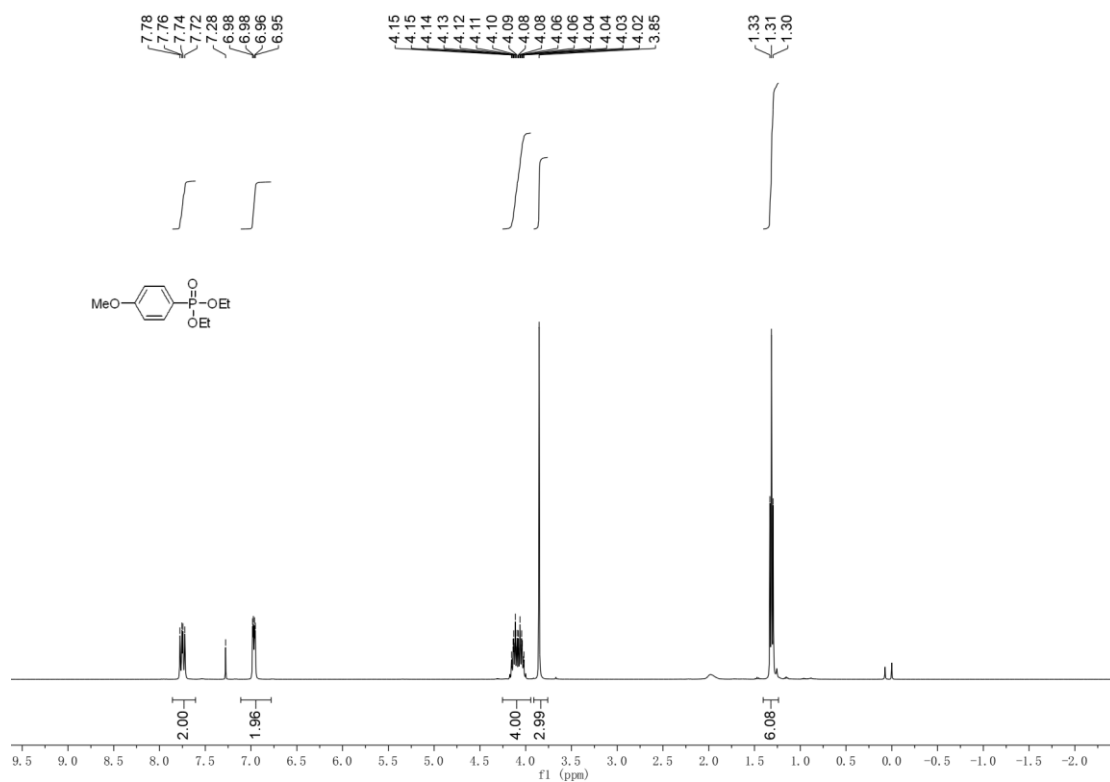
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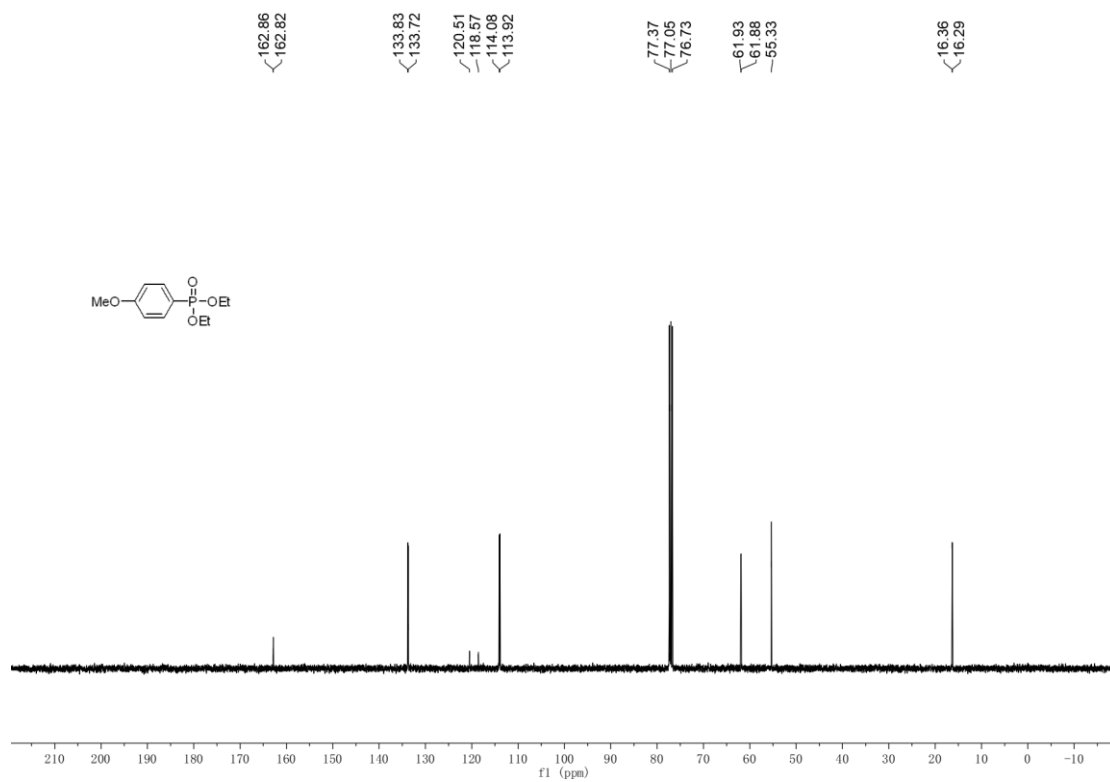
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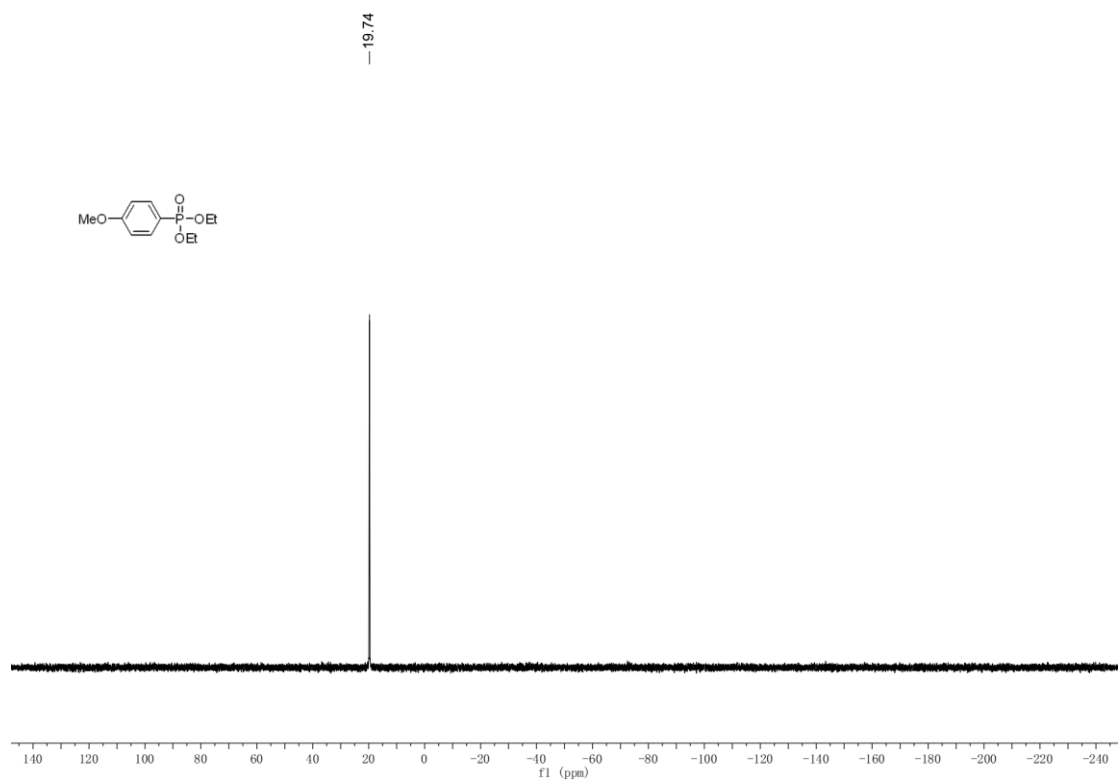
¹H NMR (400 MHz, CDCl₃) spectrum for 6



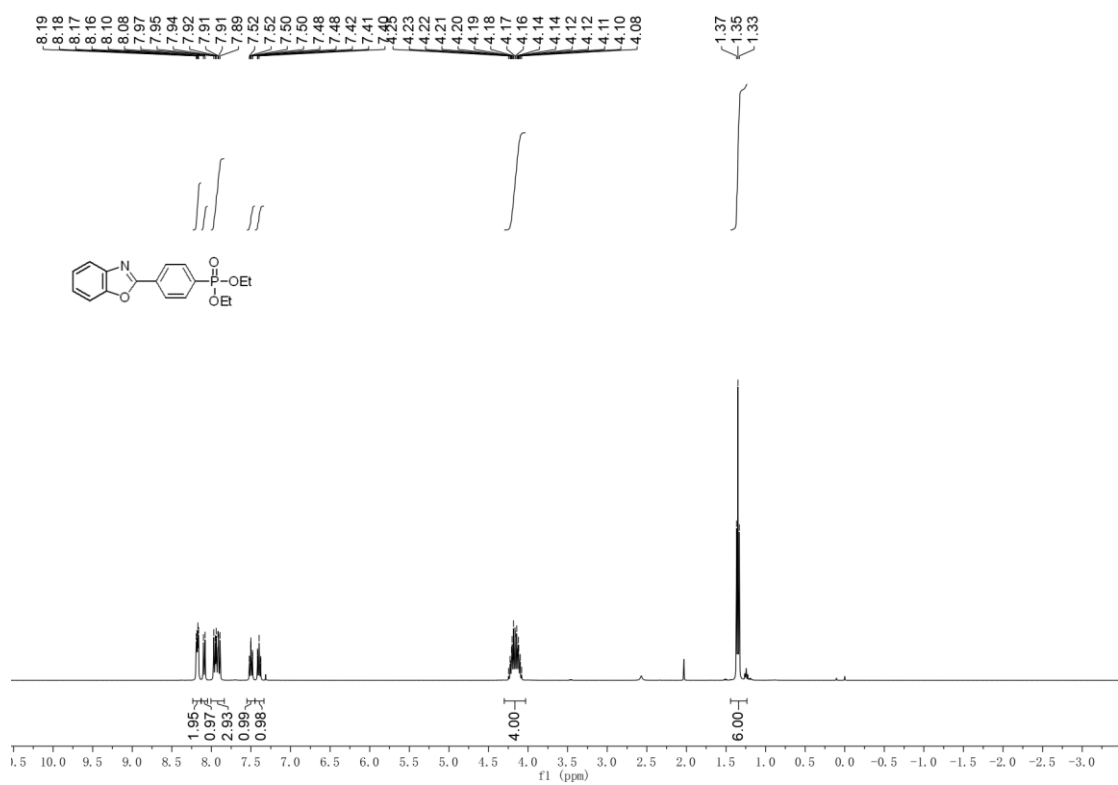
¹³C NMR (101 MHz, CDCl₃) spectrum for 6



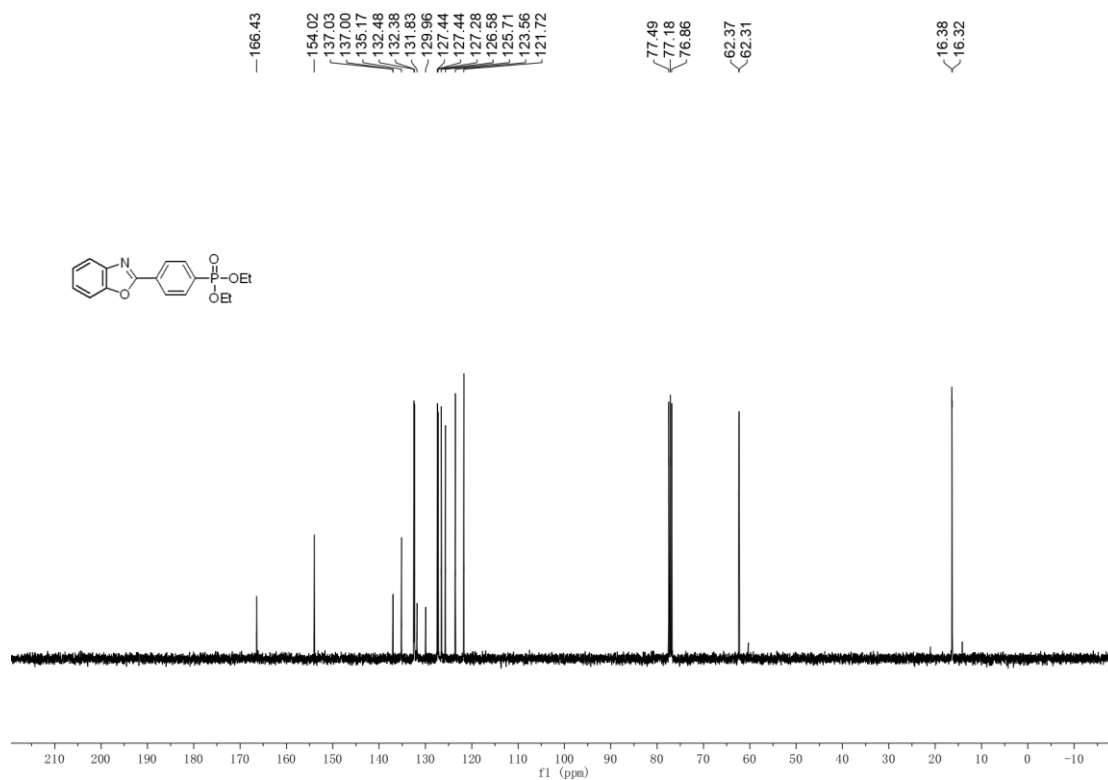
³¹P NMR (121 MHz, CDCl₃) spectrum for 6



¹H NMR (400 MHz, CDCl₃) spectrum for 7



¹³C NMR (101 MHz, CDCl₃) spectrum for 7



³¹P NMR (121 MHz, CDCl₃) spectrum for 7

