

## Supplementary Material

### Copper- and nickel- catalyzed C–P coupling reactions between P(O)–H compounds and alkyl radicals generated from alkylsilyl peroxides

Shiyong Liu,<sup>a,b</sup> Zhe Wang,<sup>a,b</sup> Terumasa Kato,<sup>\*a,b,c</sup> Yan Liu,<sup>\*a,b</sup> and Keiji Maruoka<sup>\*a,b,c</sup>

<sup>a</sup>*School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China*

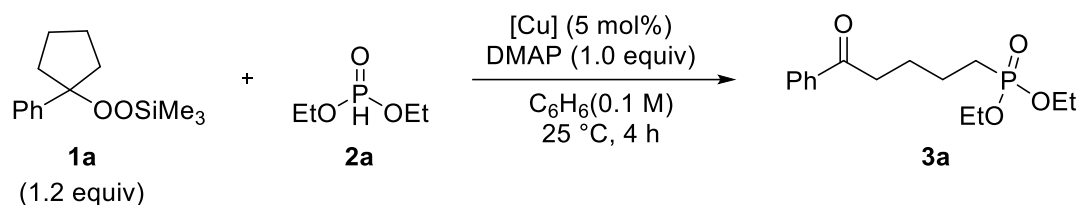
<sup>b</sup>*Guangdong Provincial Key Laboratory of Plant Resources Biorefinery, Guangdong University of Technology, Guangzhou, 510006, China*

<sup>c</sup>*Laboratory of Organocatalytic Chemistry, Graduate School of Pharmaceutical Sciences, Kyoto University, Sakyo, Kyoto 606-8501, Japan*  
Email: [maruoka.keiji.4w@kyoto-u.ac.jp](mailto:maruoka.keiji.4w@kyoto-u.ac.jp)

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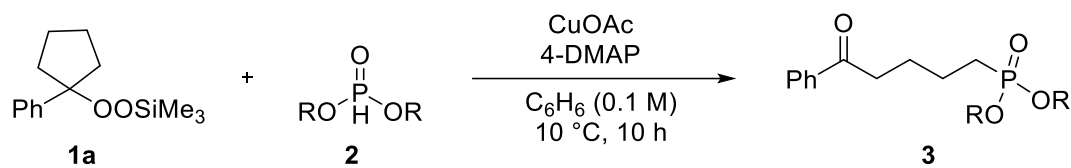
## 1. Reaction optimization

Table S1. The effect of copper catalysts<sup>a</sup>

entry	[Cu]	yield (%) <sup>b</sup>
1	CuI	44
2	CuBr	51
3	CuCl	54
4	CuCN	44
5	CuSCN	46
6	CuOAc	53
7	CuOTf	23
8	Cu <sub>2</sub> O	4
9	Cu(acac) <sub>2</sub>	12
10	Cu(MeCN) <sub>4</sub> BF <sub>4</sub>	45

<sup>a</sup>Reactions were carried out in the presence of diethyl phosphonate **2a** (0.2 mmol), alkylsilyl peroxide **1a** (1.2 equiv), copper salt (5 mol%) and DMAP (1 equiv) in C<sub>6</sub>H<sub>6</sub> (2 mL) at 25 °C for 4 h.

<sup>b</sup> <sup>31</sup>P NMR yield using triphenyl phosphate as an internal standard.

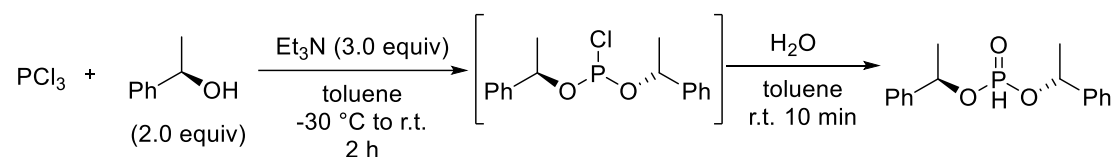
**Table S2.** The effect of amount of reagents<sup>a</sup>

entry	R	CuOAc (mol%)	<b>1a</b> (equiv)	4-DMAP (equiv)	yield (%) <sup>b</sup>
1	Et	10	1.5	1.0	69
2	Et	10	1.5	2.0	96
3	Et	15	1.2	2.0	82
4	Et	15	1.5	1.0	72
5	Et	15	1.5	2.0	99
6	<i>i</i> Pr	10	1.5	2.0	64
7	<i>i</i> Pr	15	1.5	2.0	63

<sup>a</sup>Reactions were carried out in the presence of dialkyl phosphonate **2a** (0.2 mmol), alkylsilyl peroxide **1a** (1.2–1.5 equiv), CuOAc (10–15 mol%) and DMAP (1–2 equiv) in C<sub>6</sub>H<sub>6</sub> (2 mL) at 10°C for 10 h. <sup>b</sup><sup>31</sup>P NMR yield using triphenyl phosphate as an internal standard.

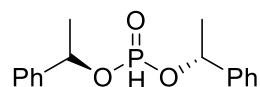
## 2. Synthesis of substrate

### Synthesis of **2g**



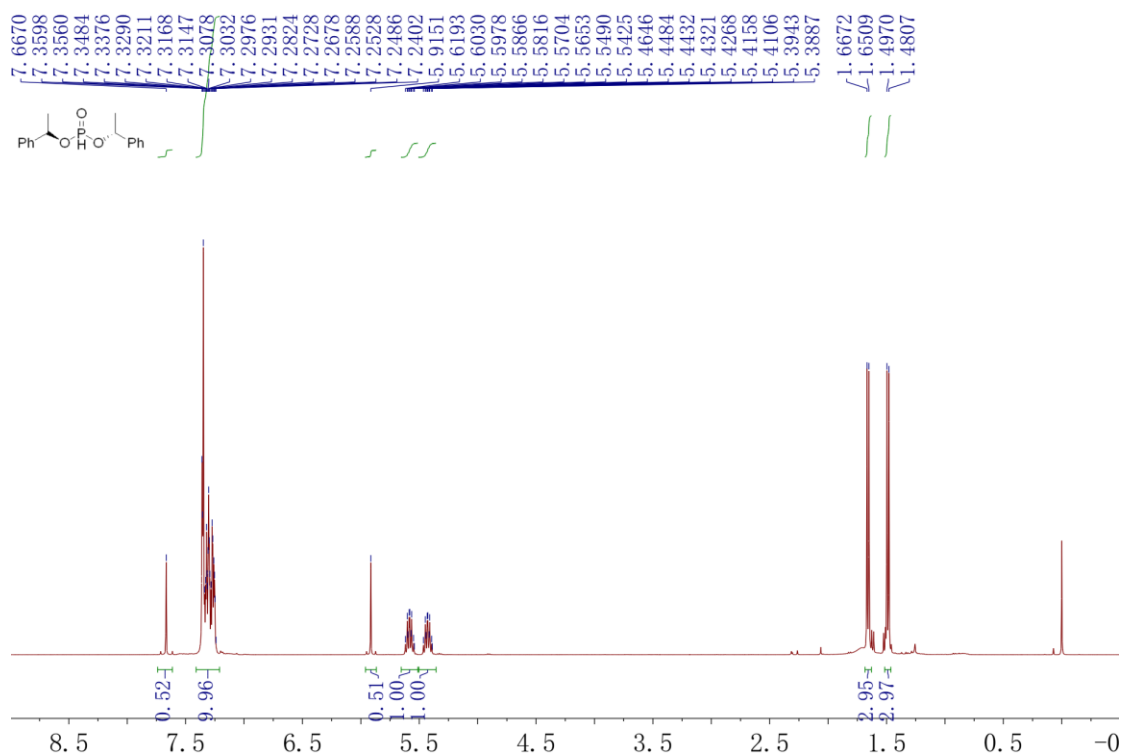
To a solution of (*R*)-(+)-1-phenylethanol (0.85 g, 7.0 mmol) and triethylamine (1.06 g, 10.5 mmol) in dry toluene (10 mL) was added a solution of phosphorus trichloride (0.48 g, 3.5 mmol) in dry toluene (3.5 mL) dropwise at  $-30\text{ }^{\circ}\text{C}$ . The reaction mixture was slowly warmed to room temperature and stirred for 2 h at this temperature. Then,  $\text{H}_2\text{O}$  (1 mL) was added to the mixture. After stirring this mixture for 10 min, the organic layer was dried over  $\text{MgSO}_4$ , filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluted with petroleum ether/ethyl acetate =5:1) to give compound **2g**.

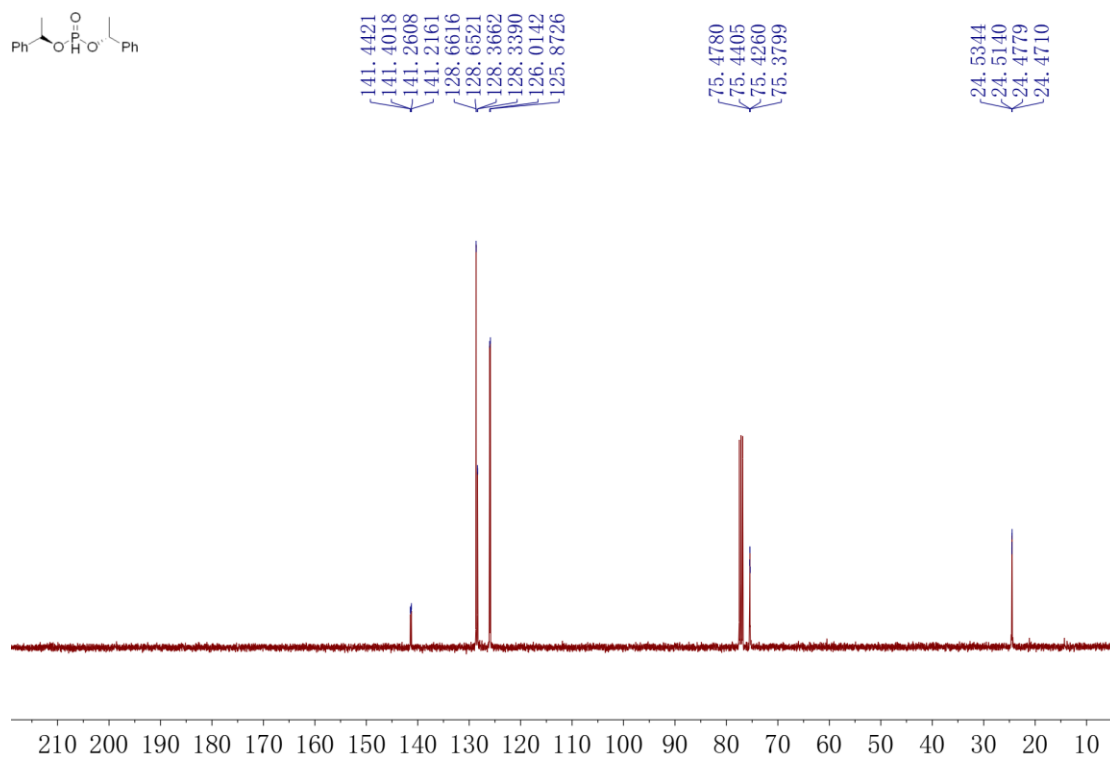
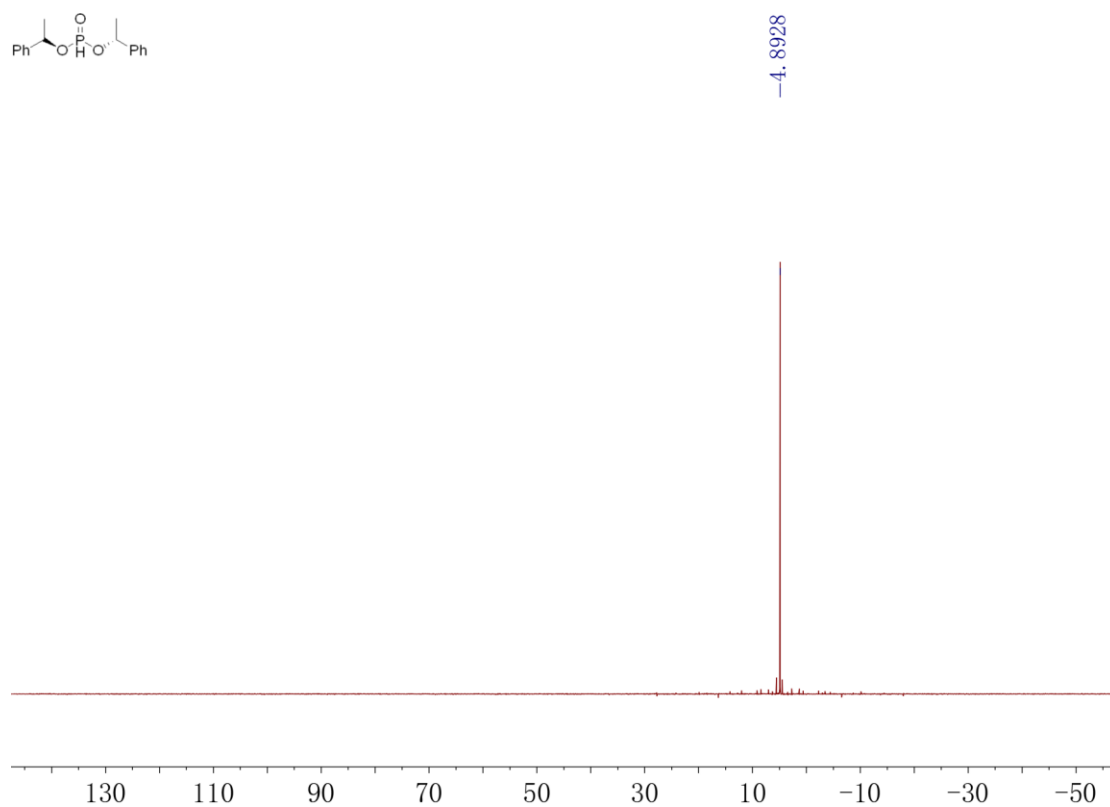
### (*R*)-1-phenylethyl-((*S*)-1-phenylethyl)-phosphonate (**2g**)

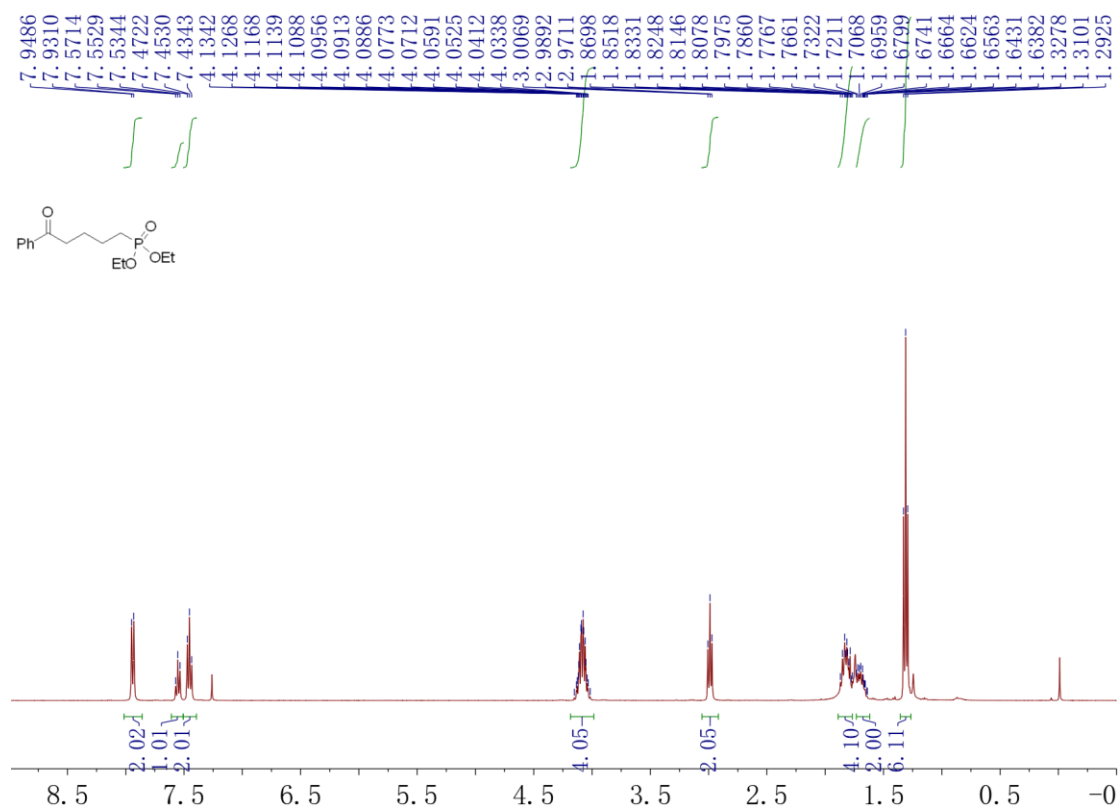


Colorless oil, 40% isolated yield (0.41 g, 1.40 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.40–7.20 (m, 10H), 6.79 (d,  $J$  701.0 Hz, 1H) 5.64–5.52 (m, 1H), 5.49–5.37 (m, 1H), 1.66 (d,  $J$  6.5 Hz, 3H), 1.49 (d,  $J$  6.5 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.4 (d,  $J$  4.0 Hz), 141.2 (d,  $J$  4.5 Hz), 128.6, 128.6, 128.3, 128.3, 125.9, 125.8, 75.4 (d,  $J$  5.1 Hz), 75.3 (d,  $J$  6.0 Hz), 24.4 (d,  $J$  5.5 Hz), 24.4 (d,  $J$  4.3 Hz);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.9; FT-IR (KBr): 2980, 2930, 1632, 1495, 1452, 1377, 1239, 1210, 1070, 962, 758, 699, 545  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{20}\text{O}_3\text{P}^+$  291.1145; Found 291.1142.

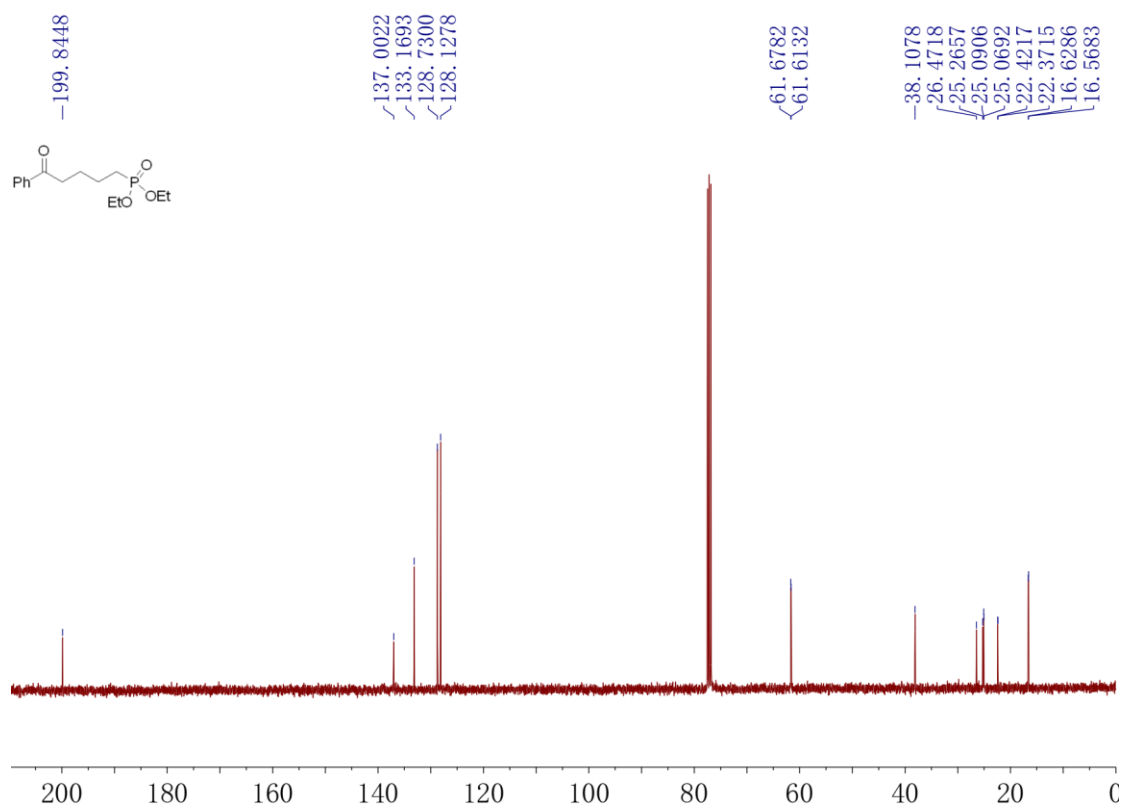
## 3. NMR spectra

 $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **2g**

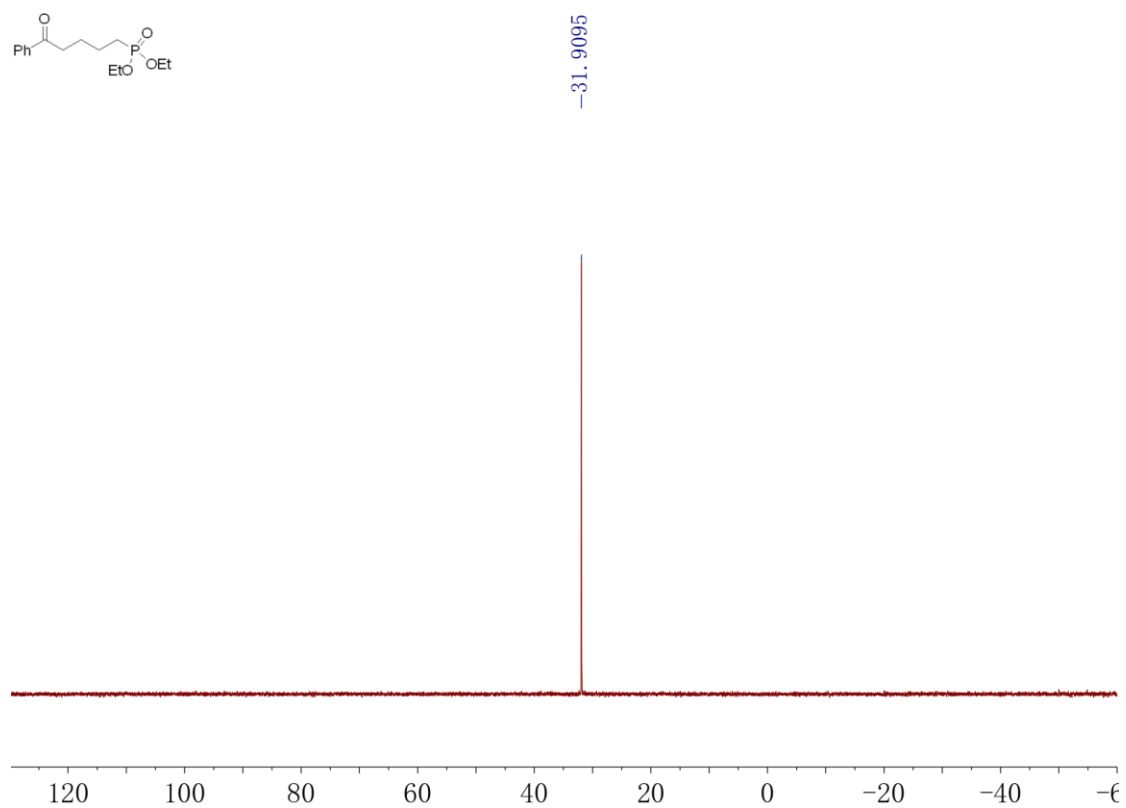
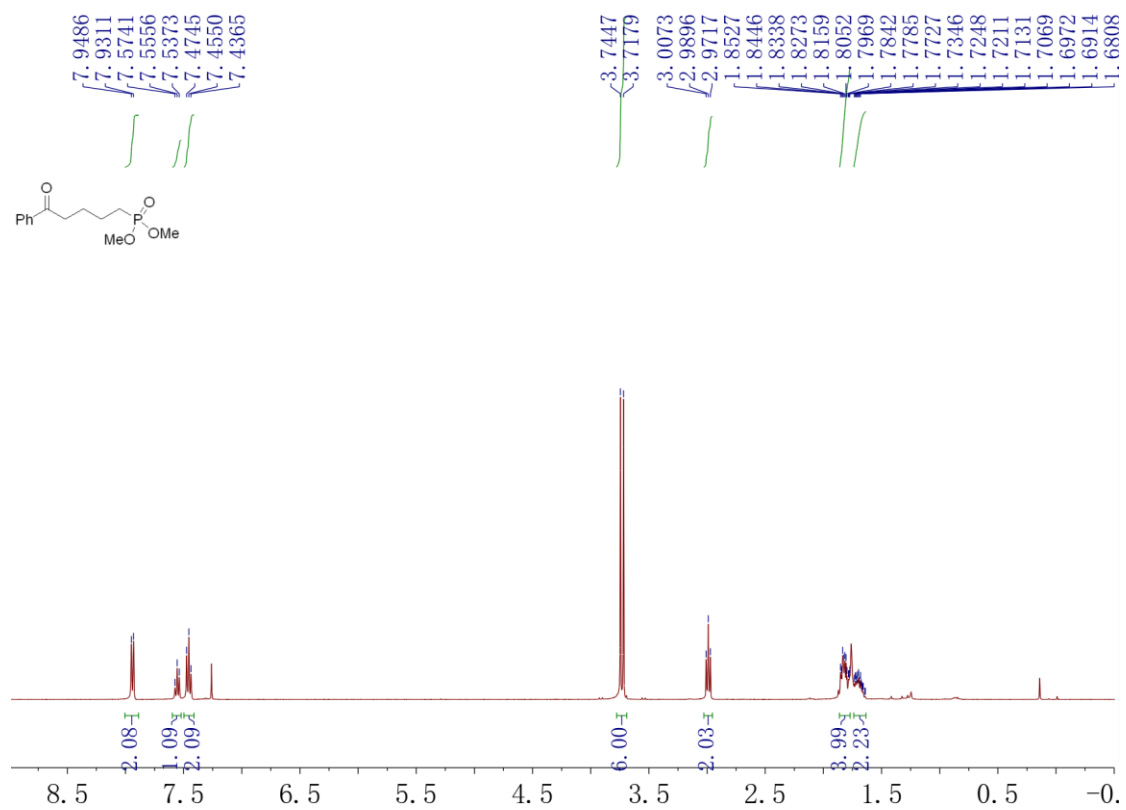
 $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **2g** $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of **2g**



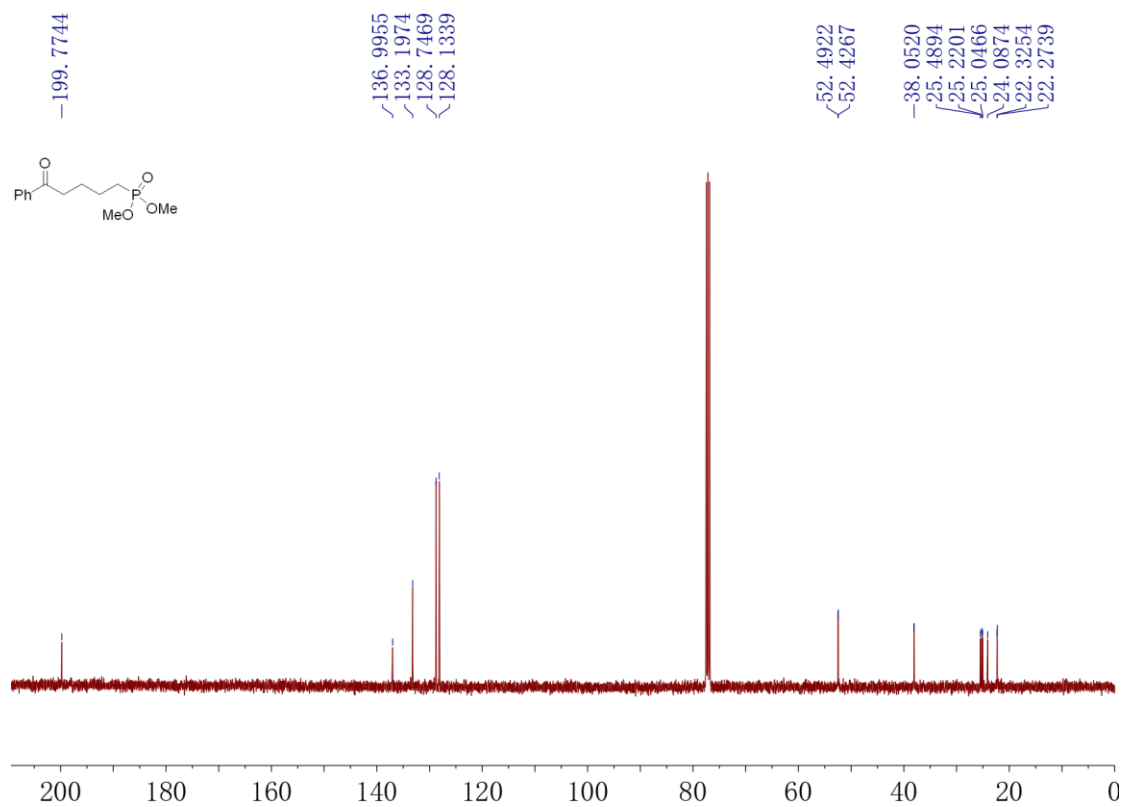
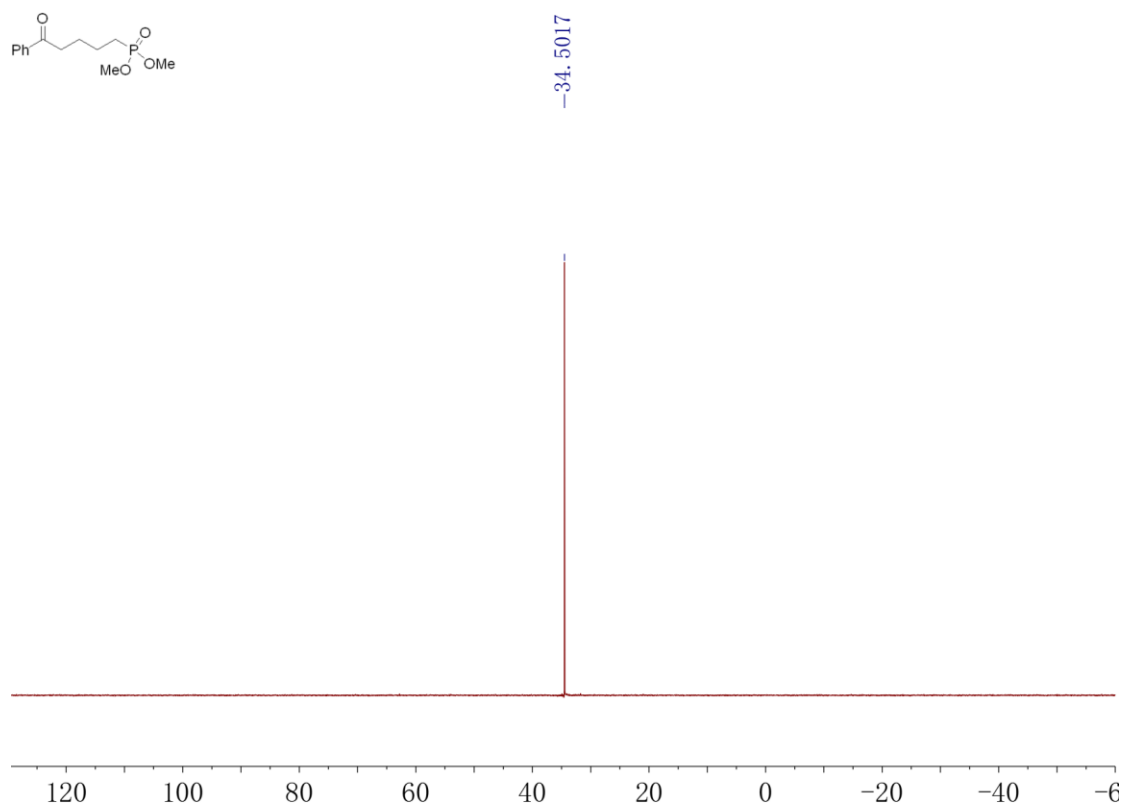
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **3a**

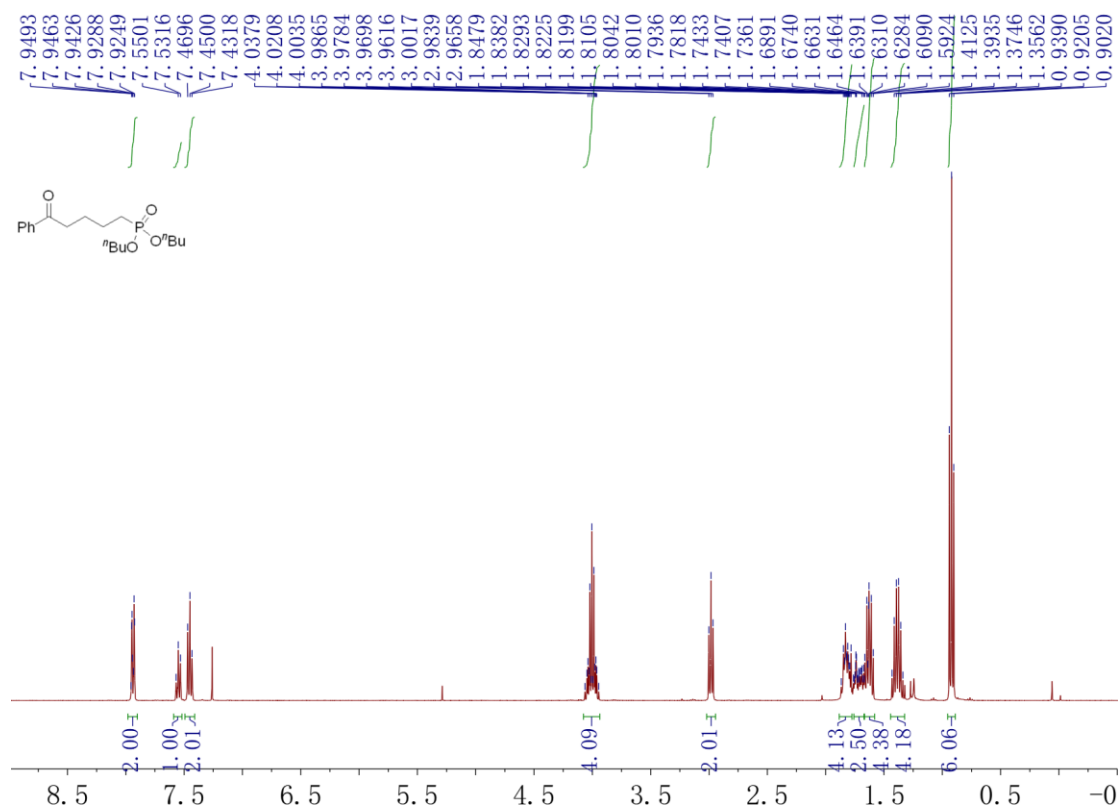
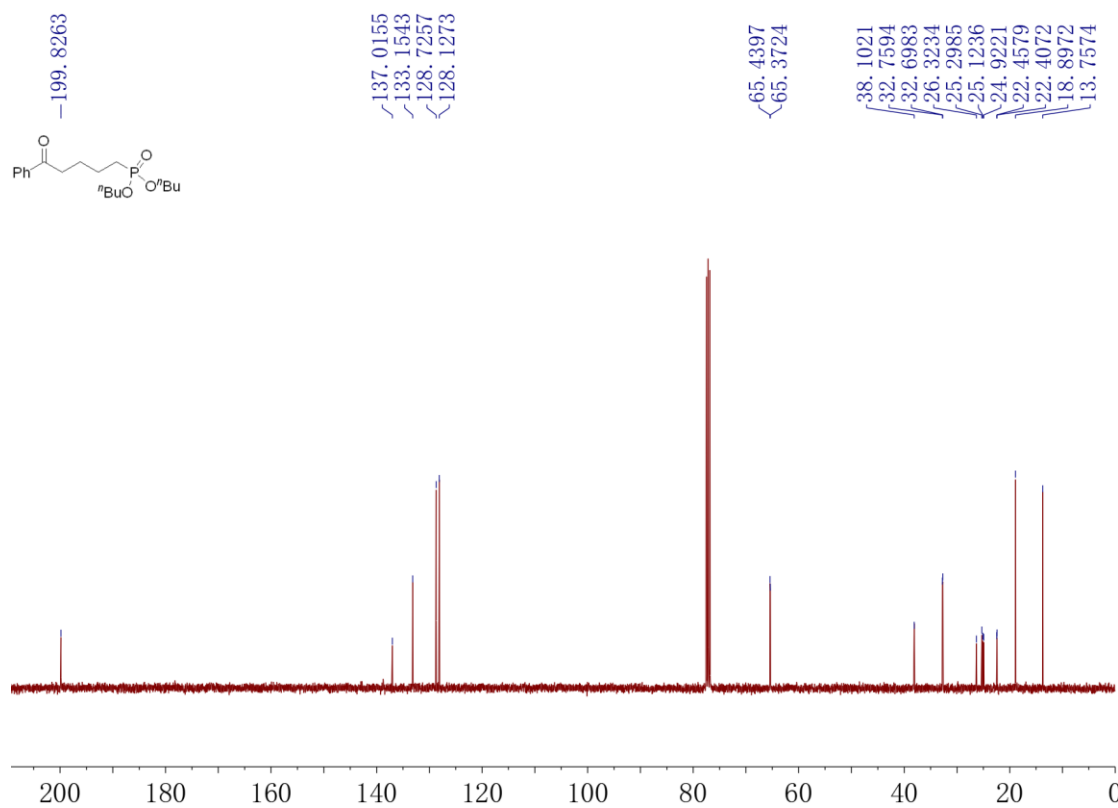


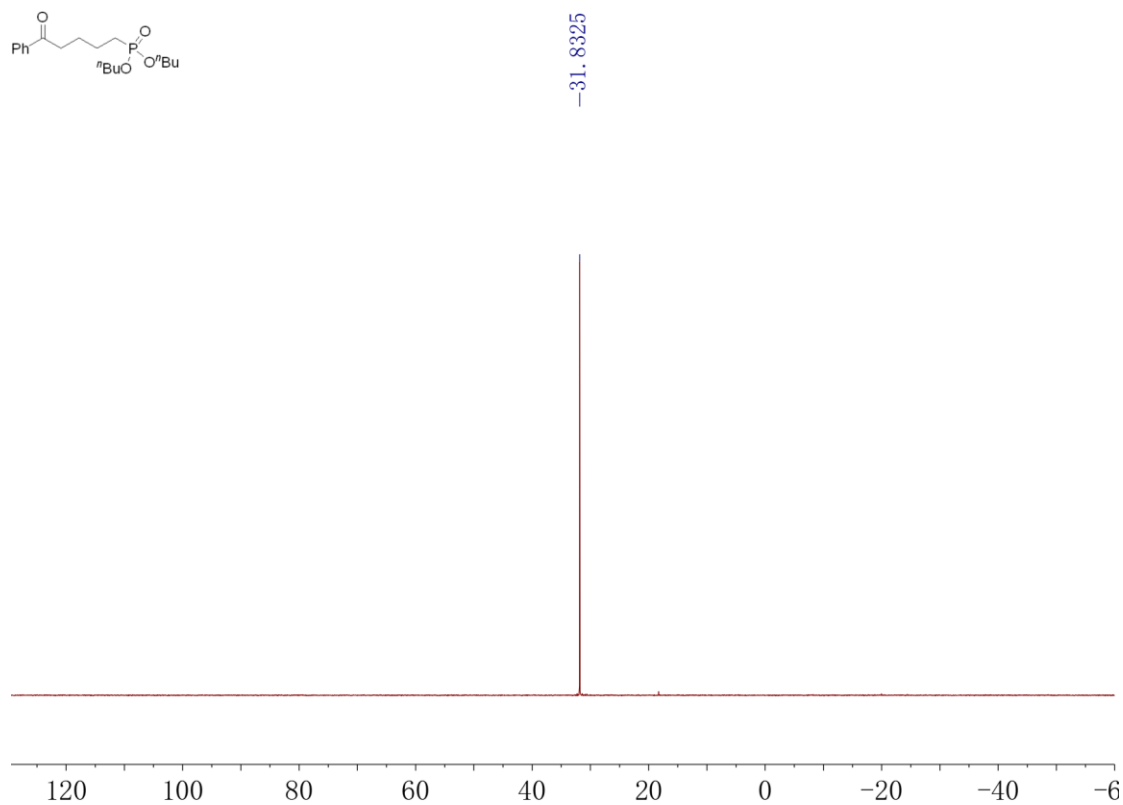
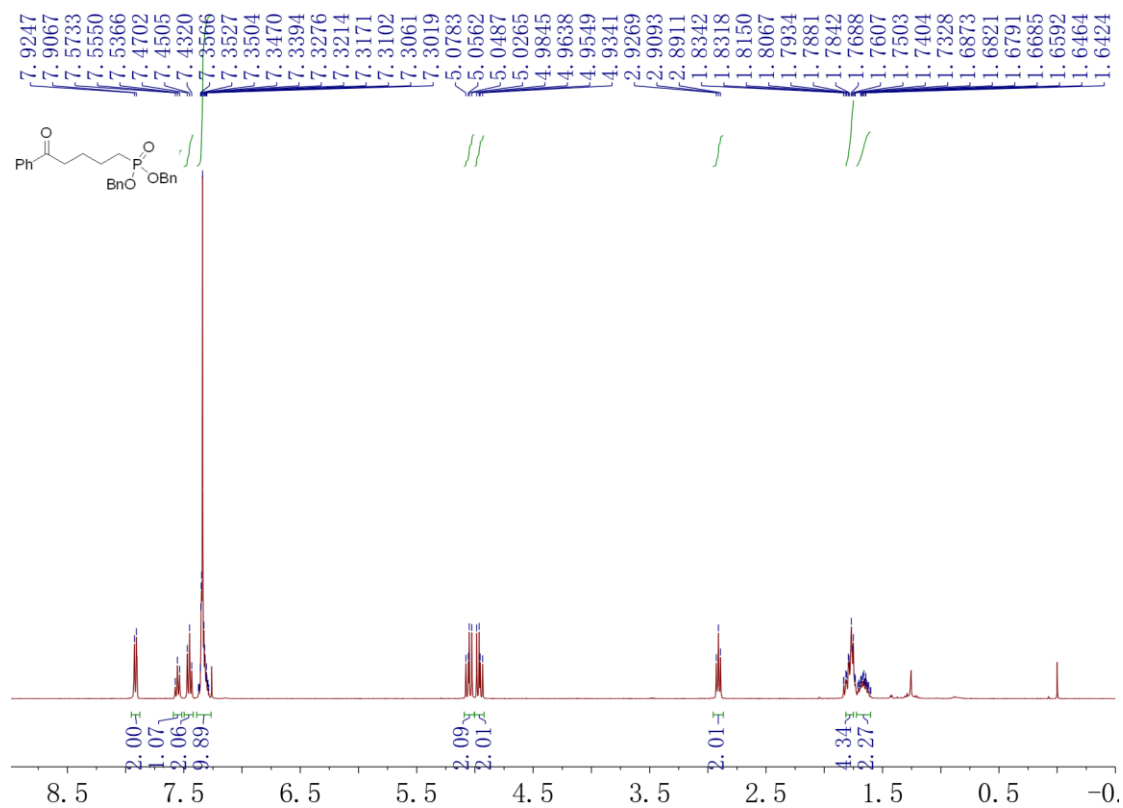
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **3a**

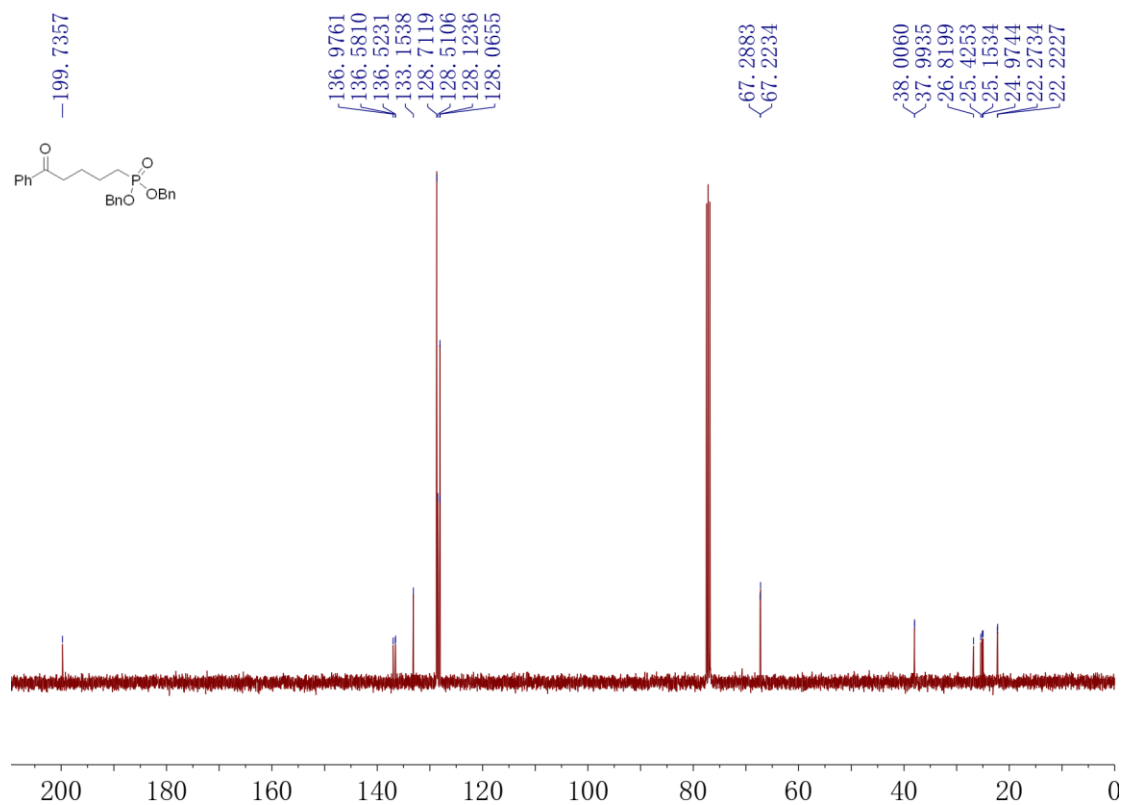
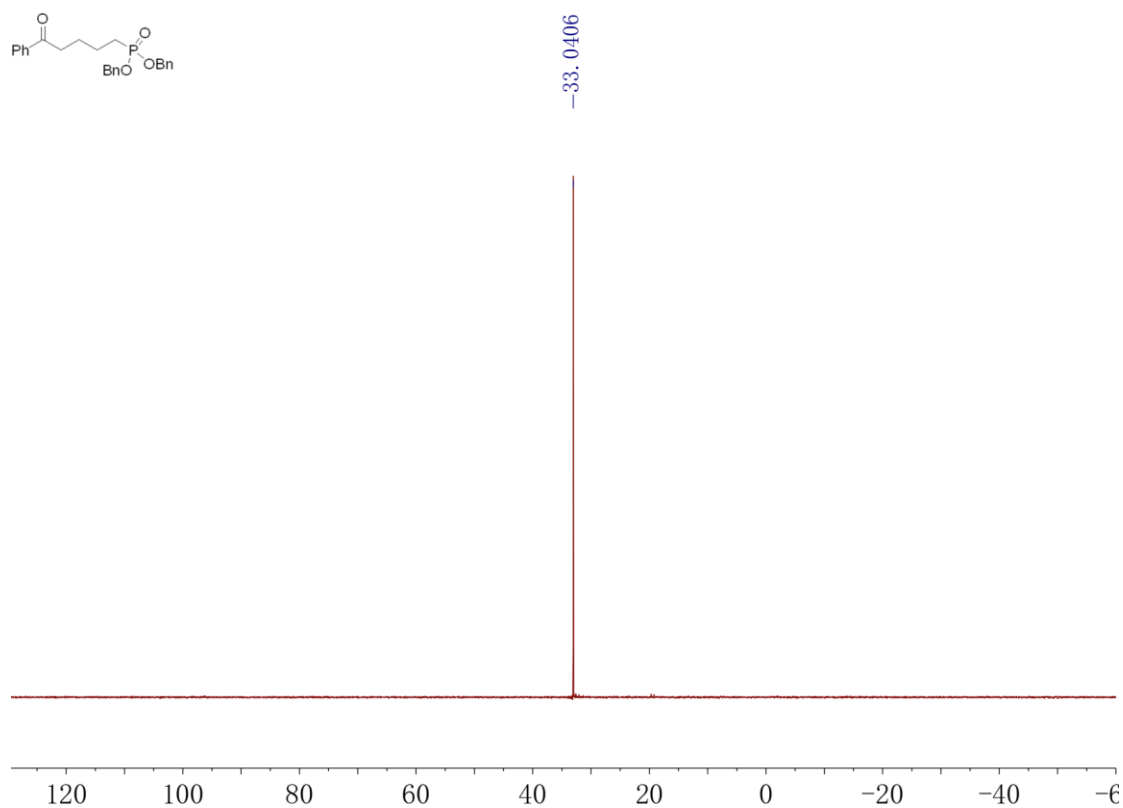
 $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of **3a** $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **3b**

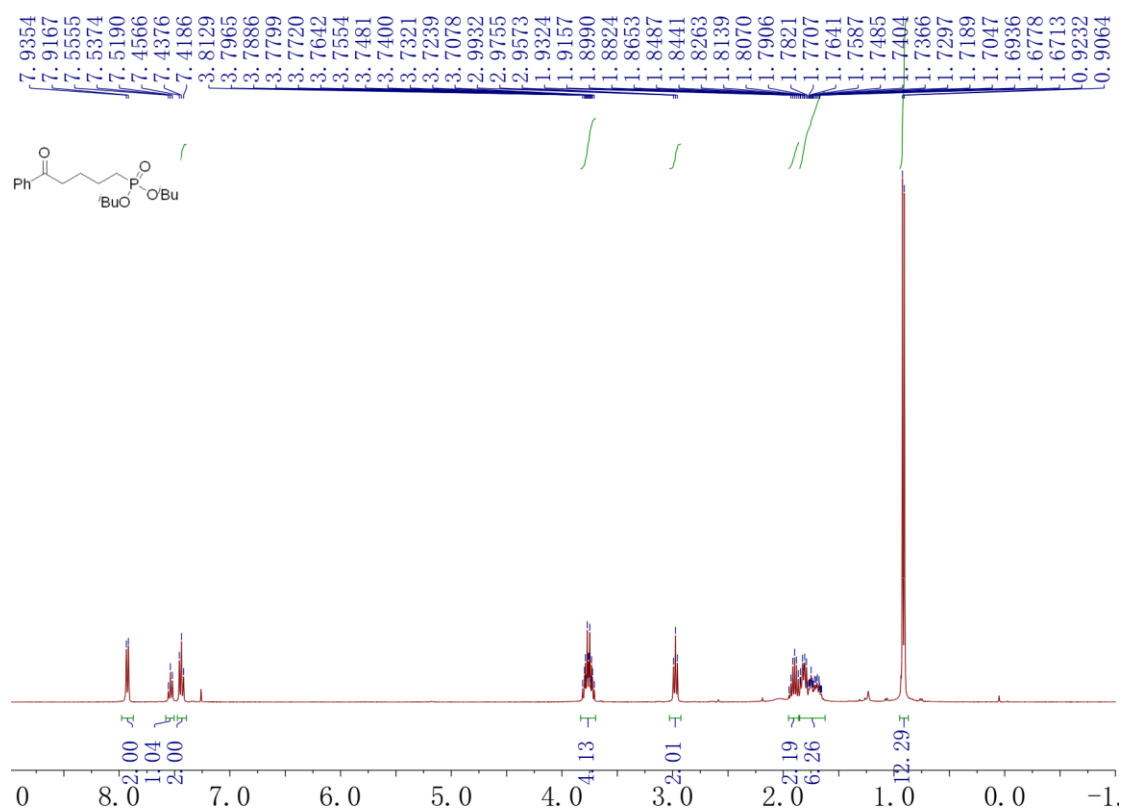


 $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **3b** $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of **3b**

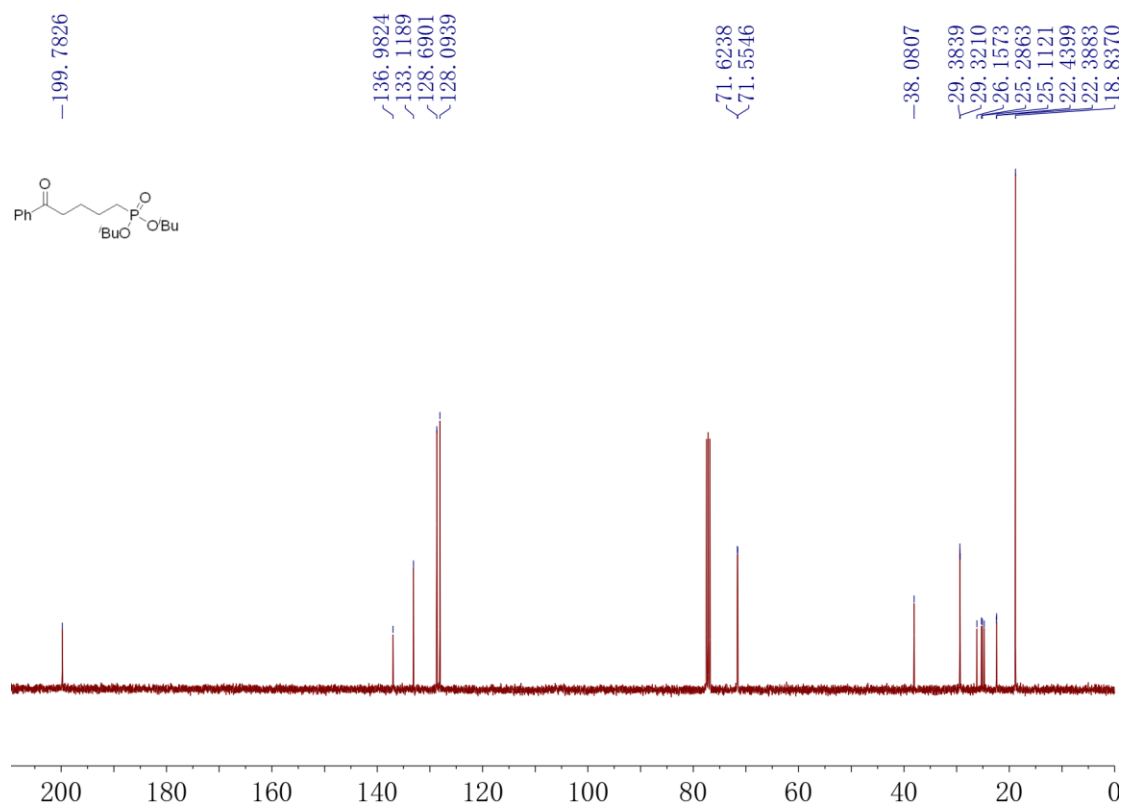
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **3c**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **3c**

 $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of **3c** $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **3d**

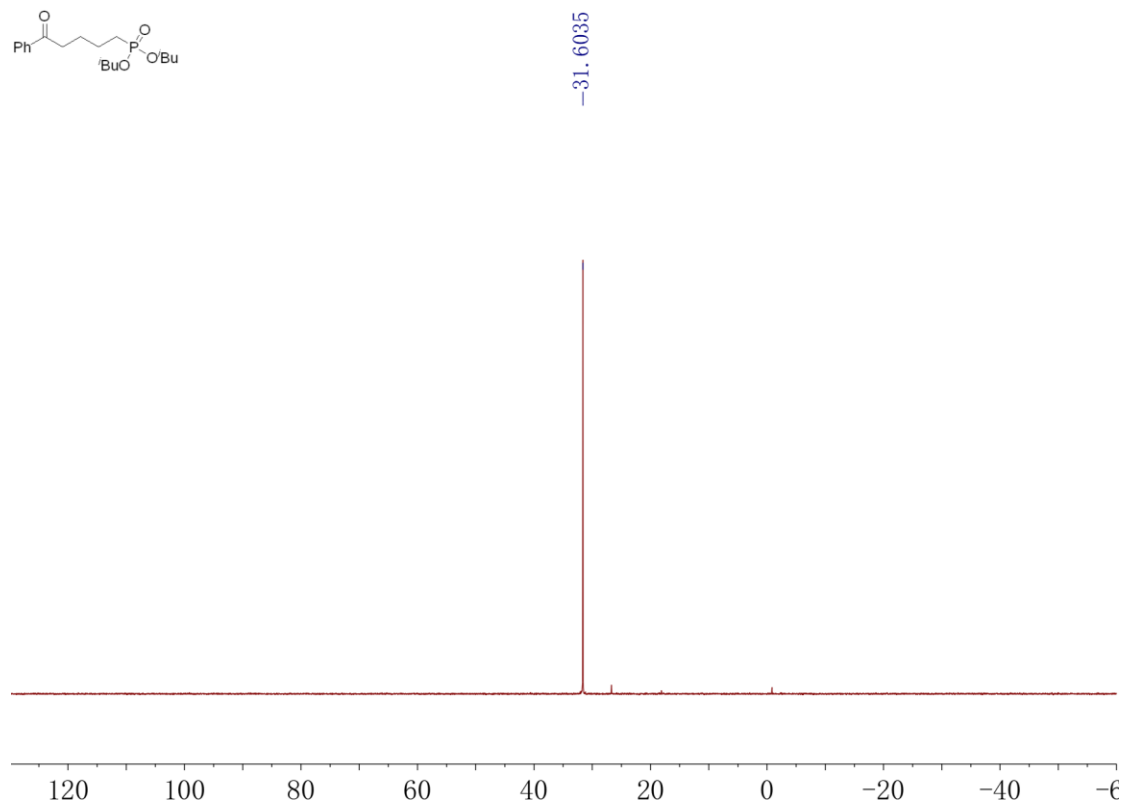
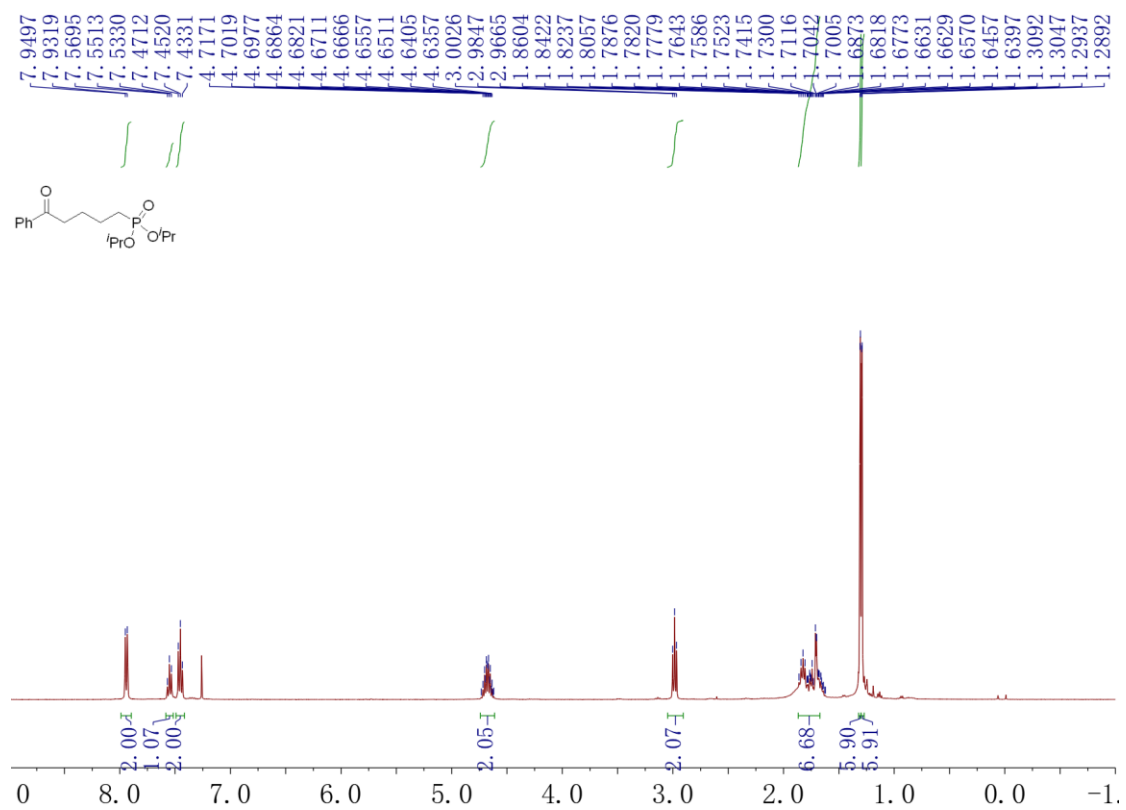
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **3d**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) spectrum of **3d**

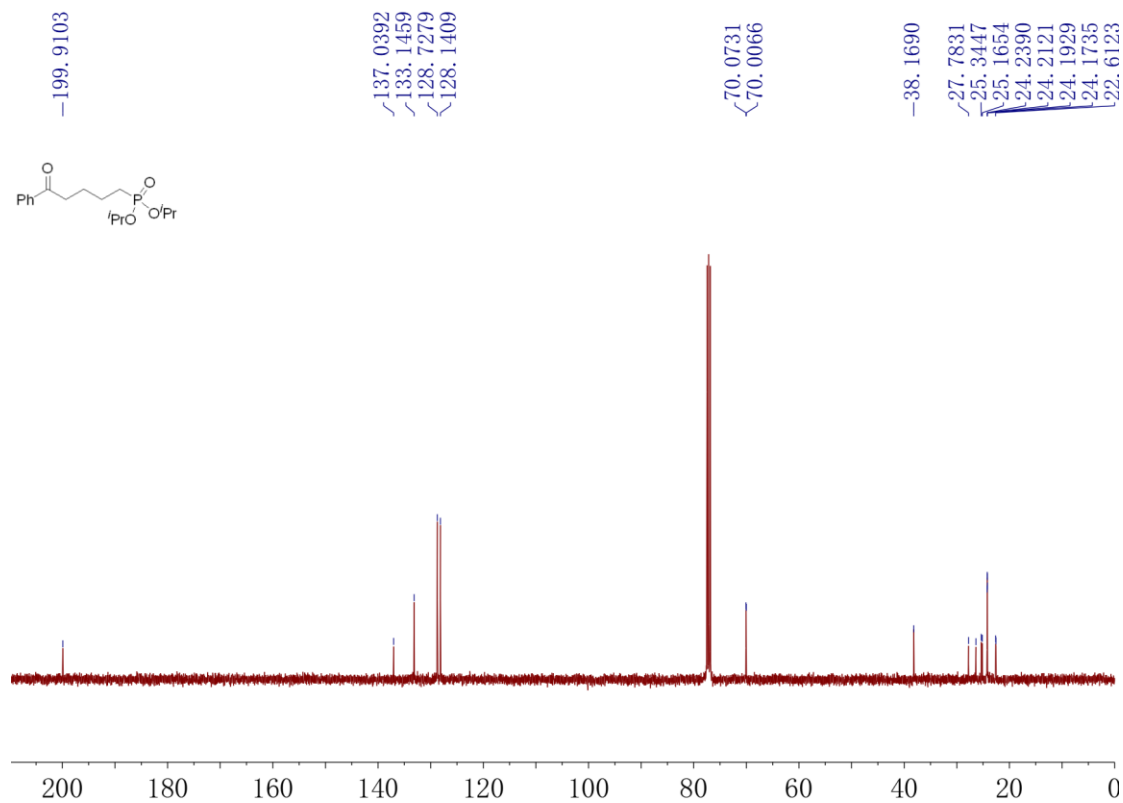


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **3e****

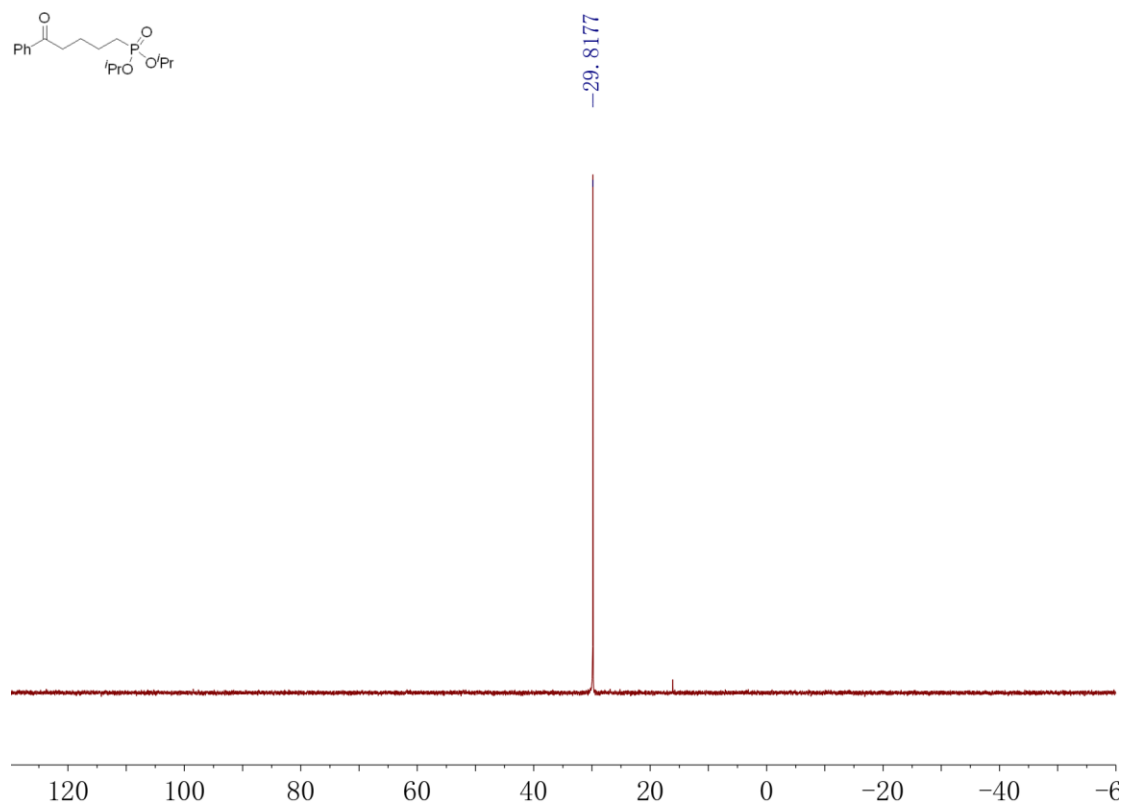


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **3e****

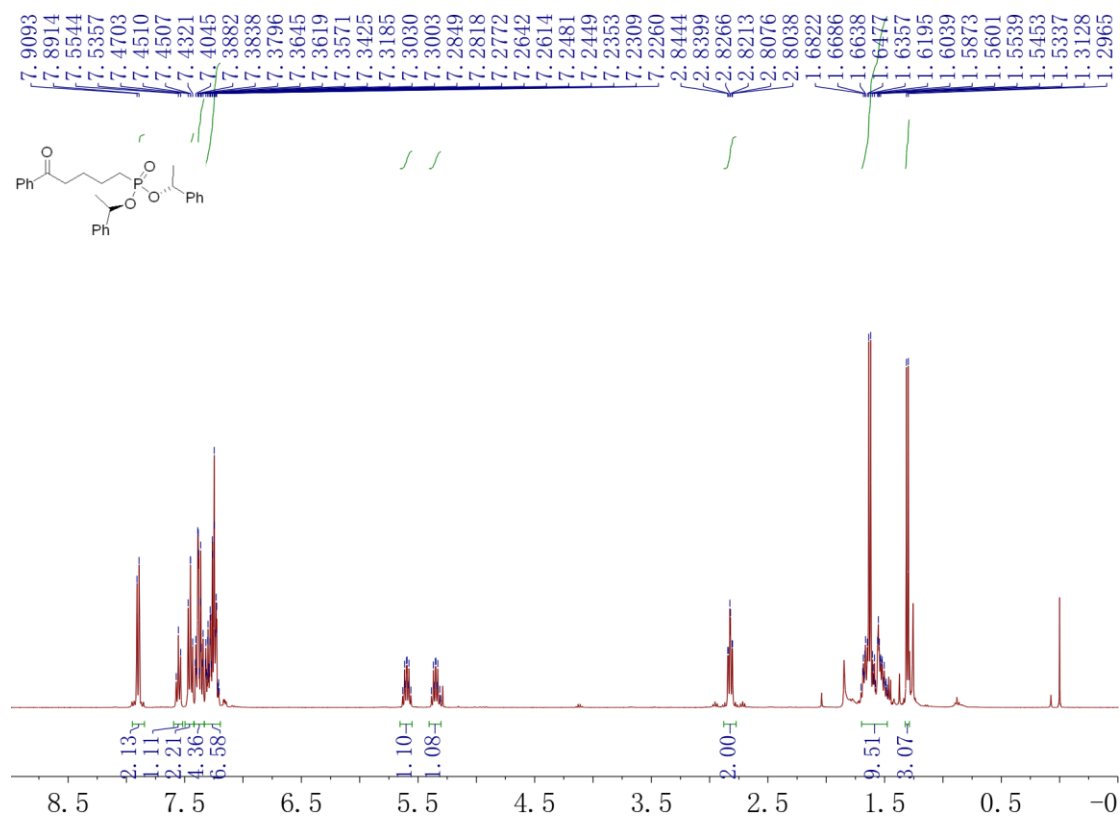
 $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of **3e** $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **3f**



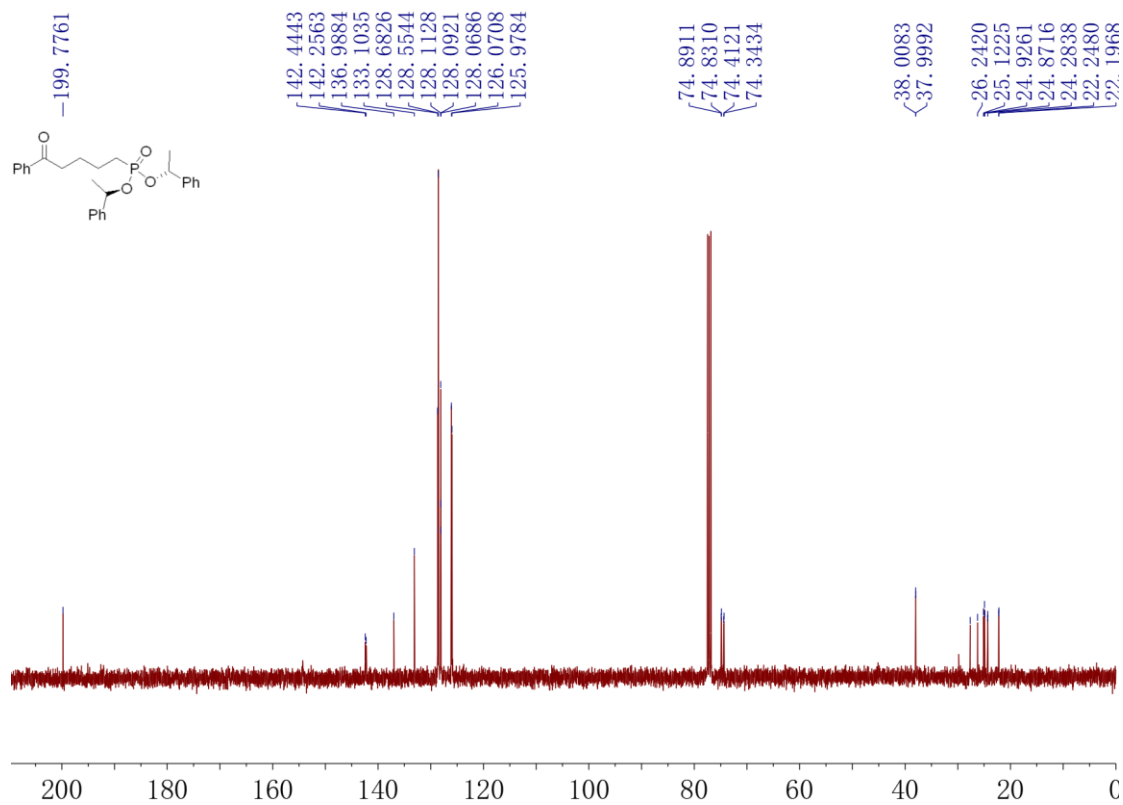
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **3f**



<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) spectrum of **3f**

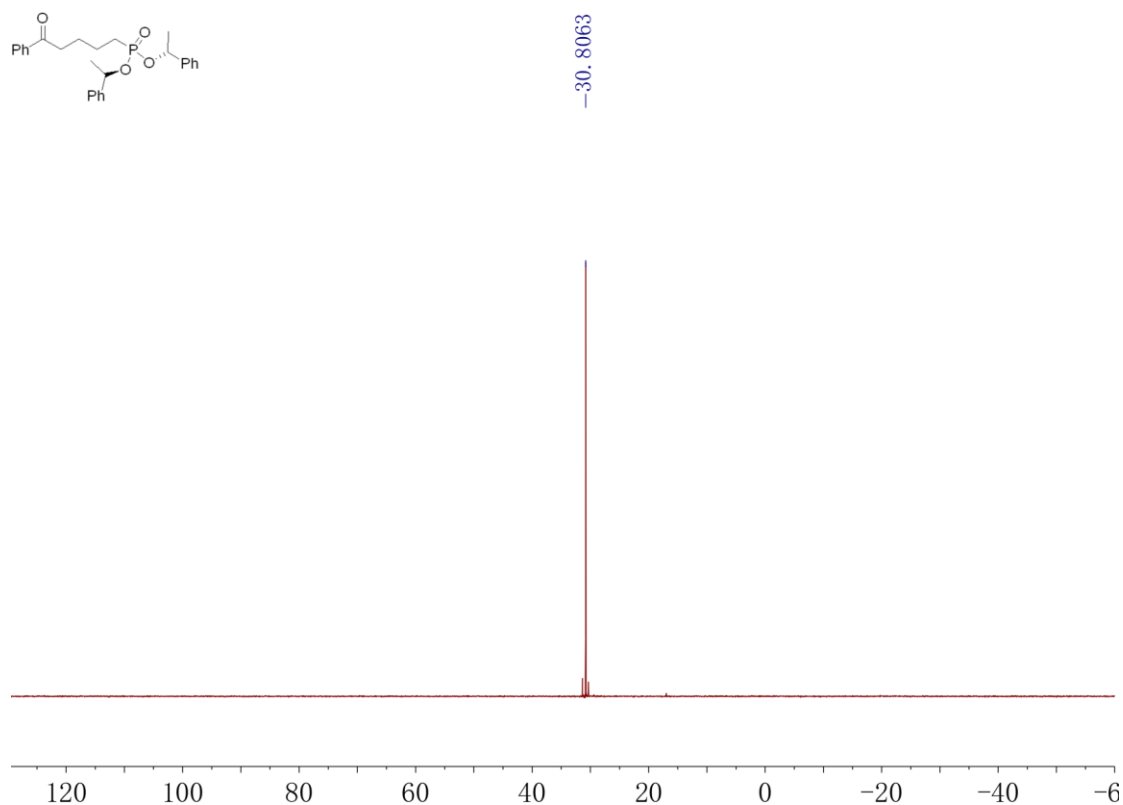
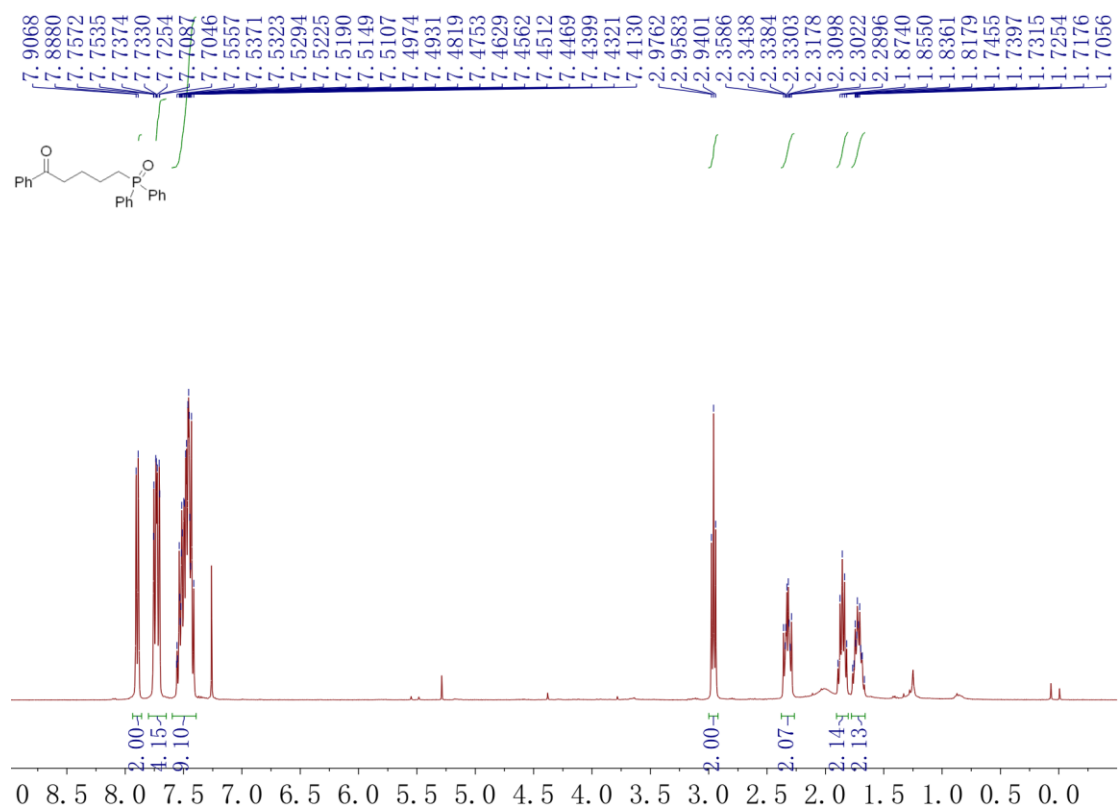


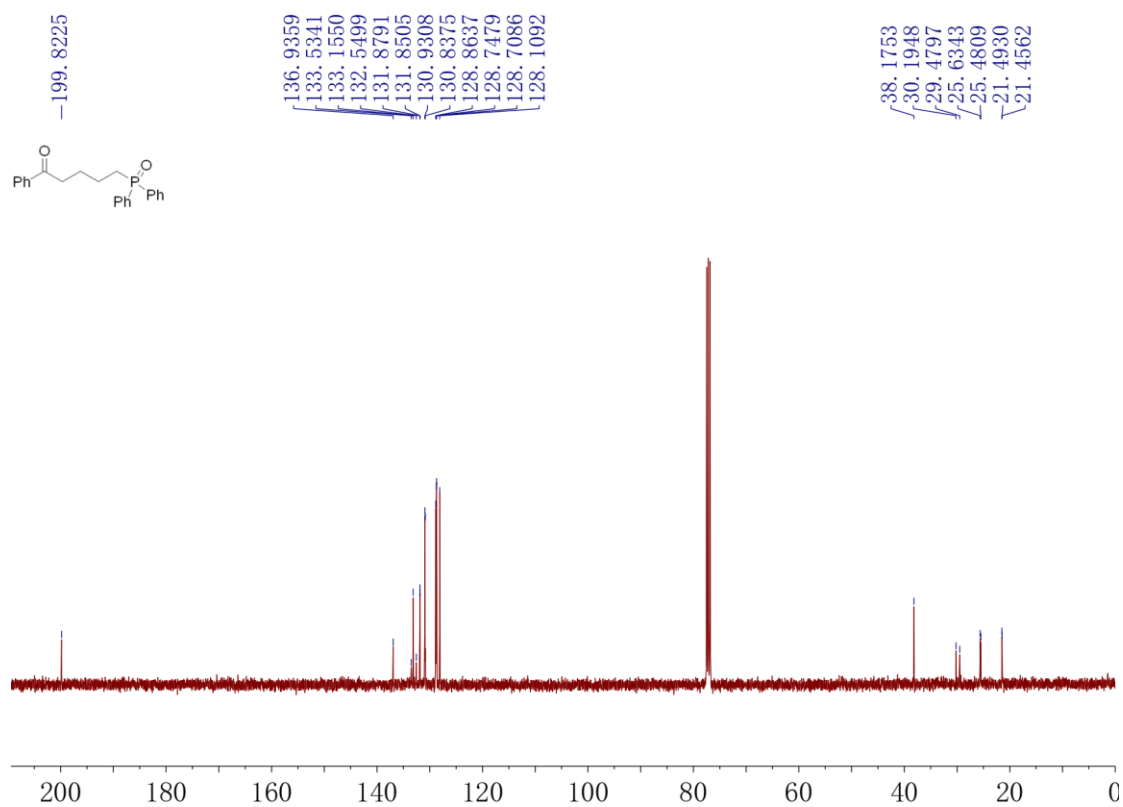
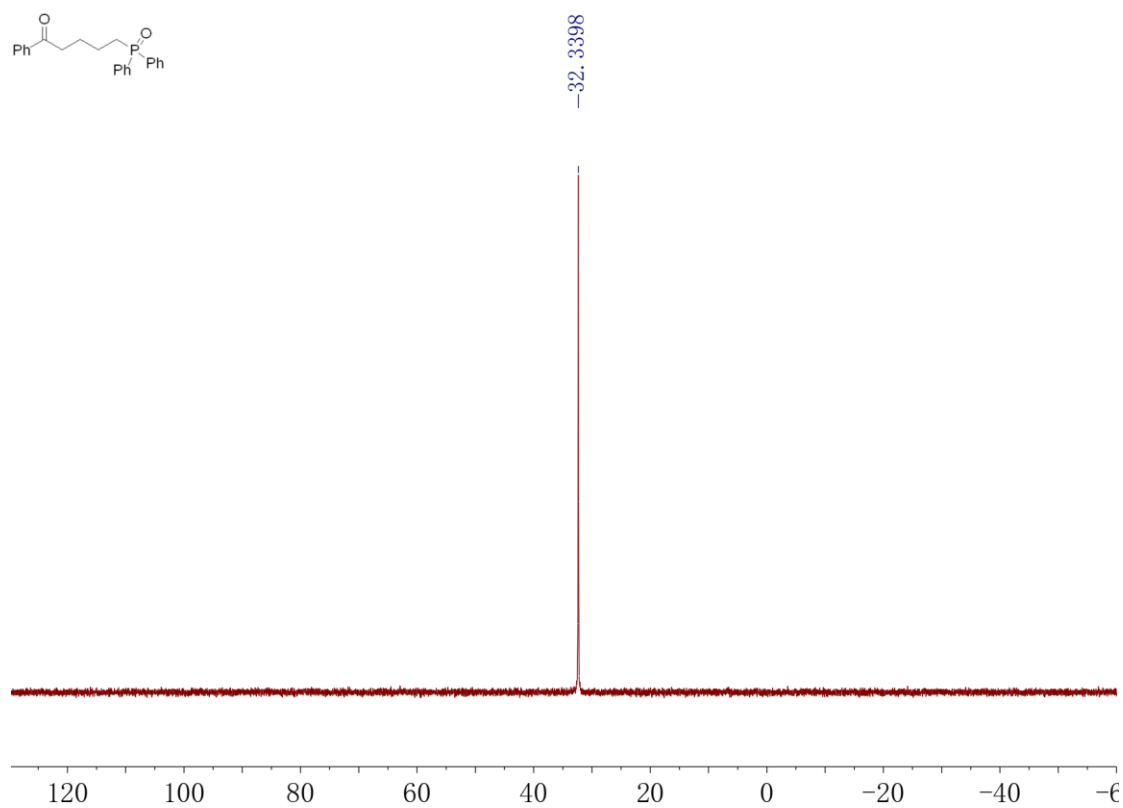
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **3g****

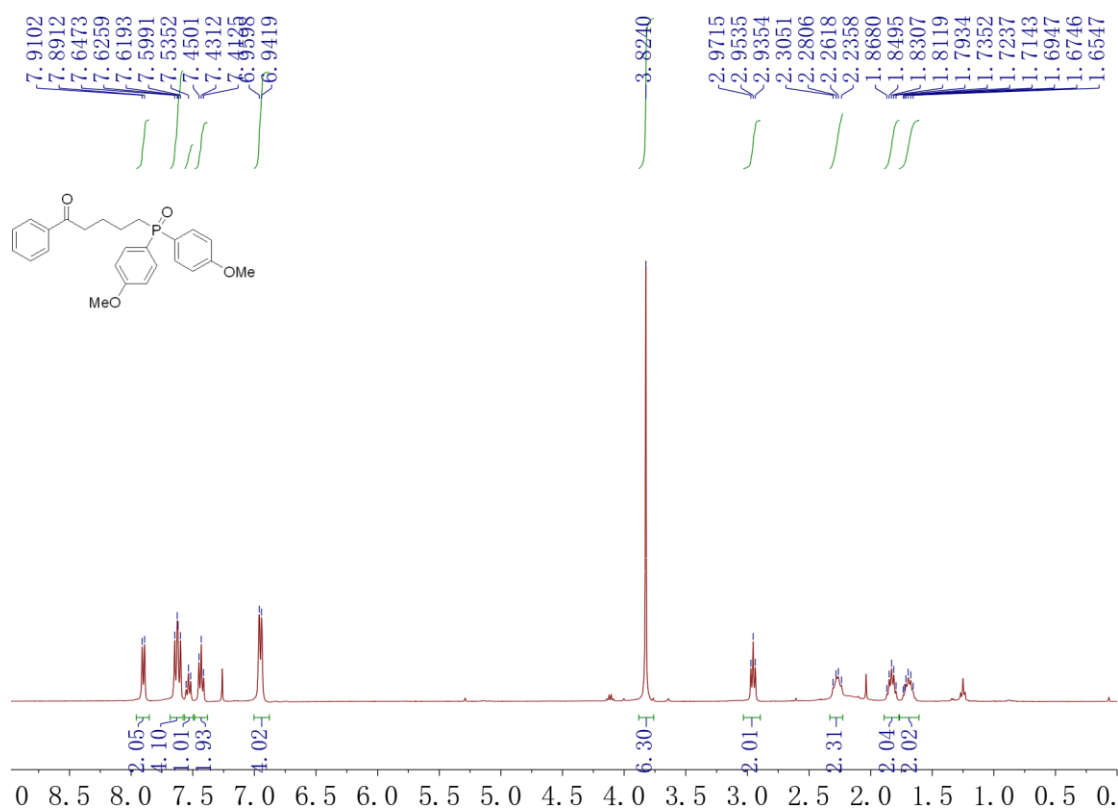
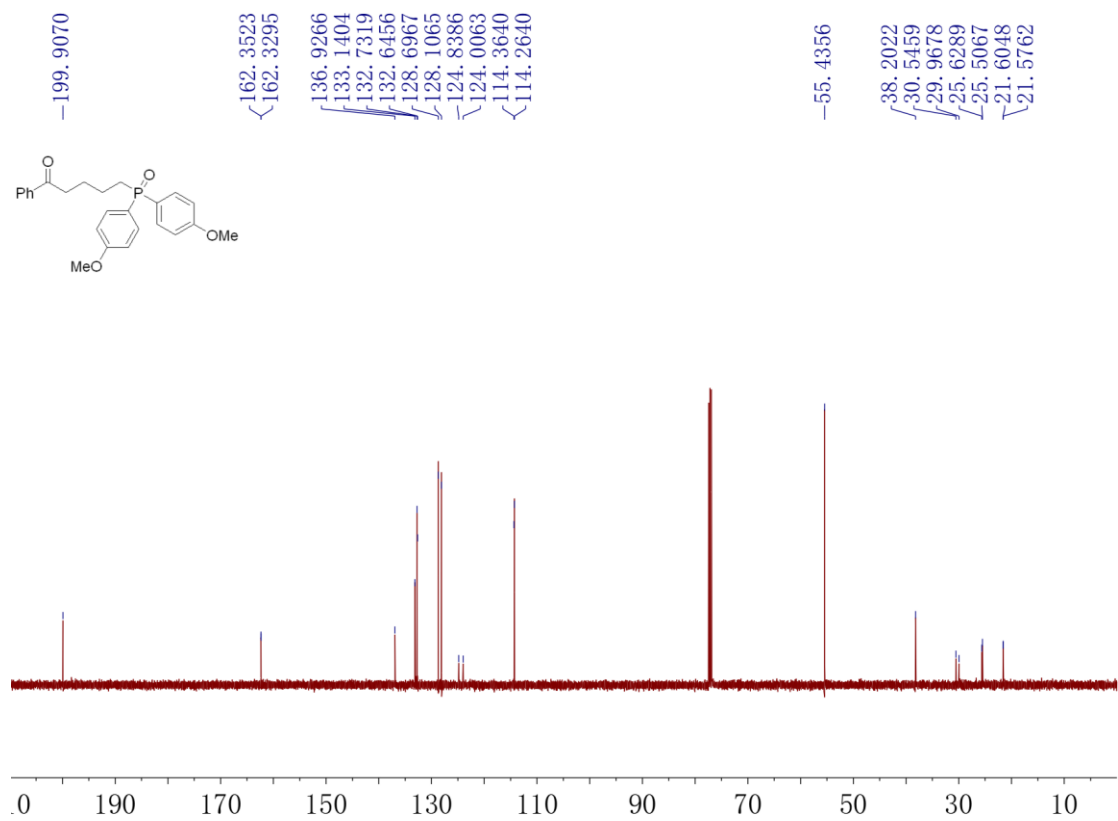


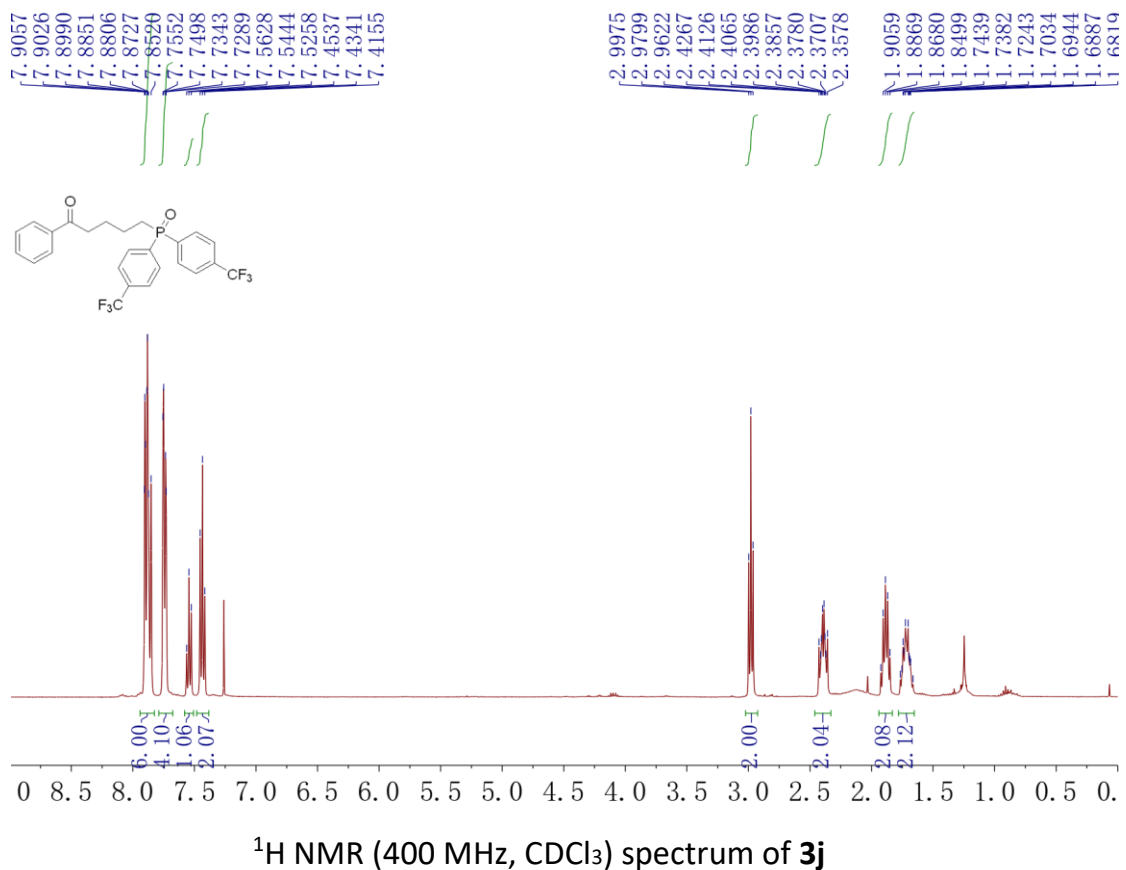
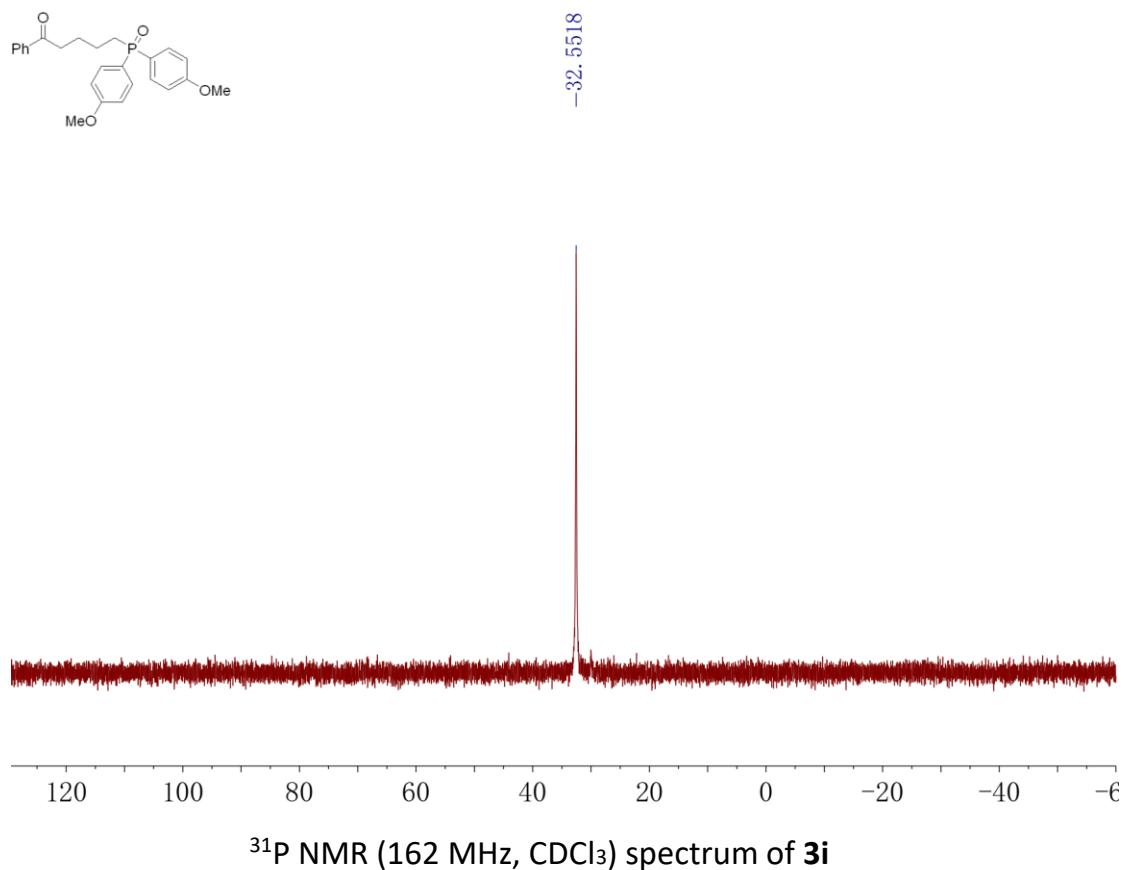
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **3g****

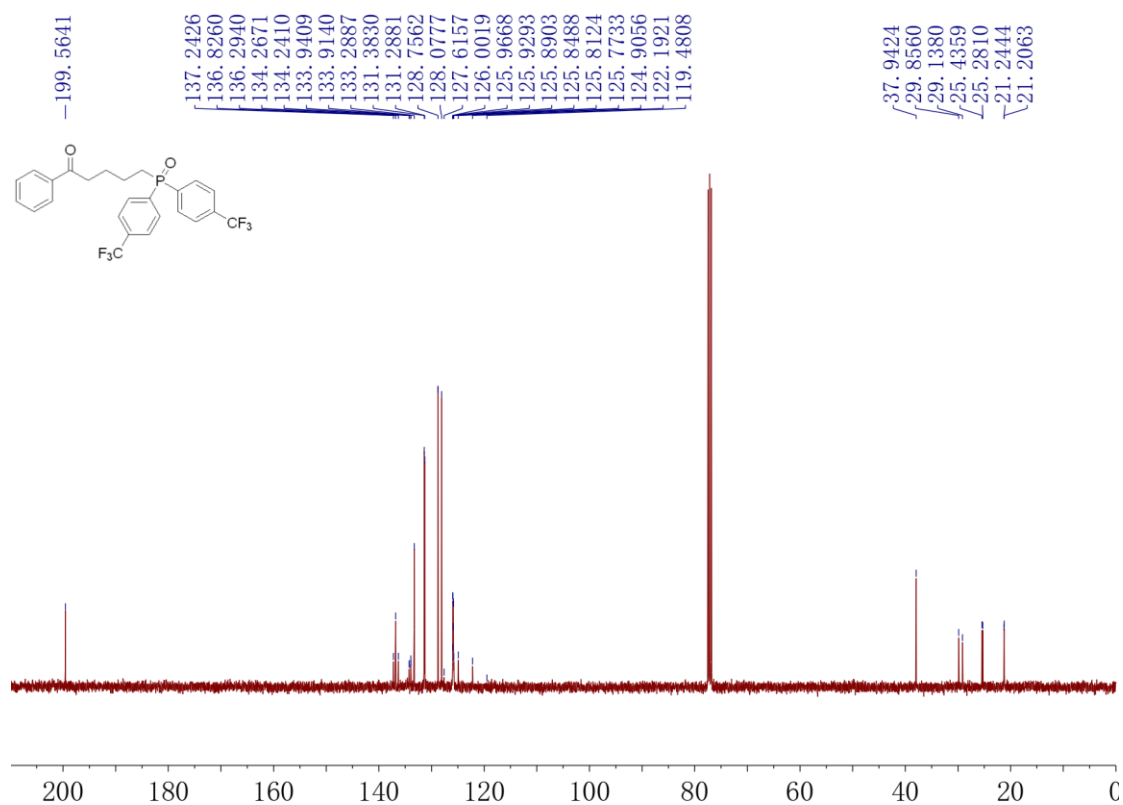
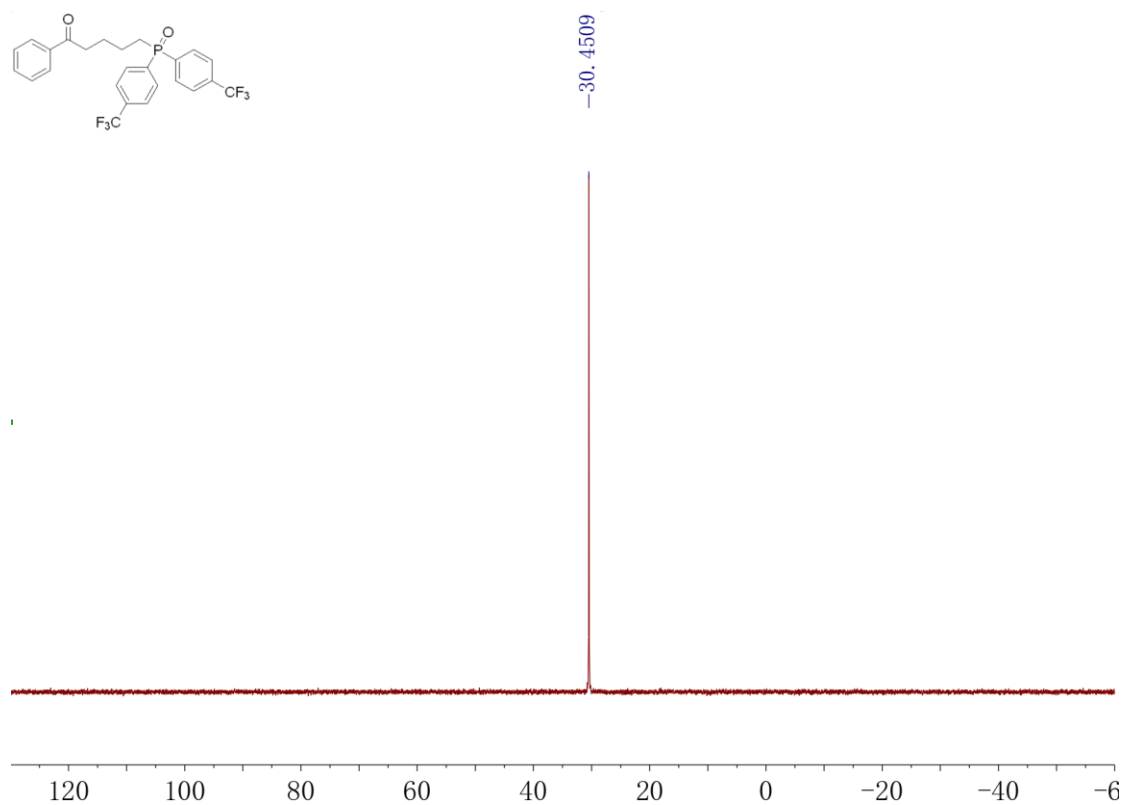


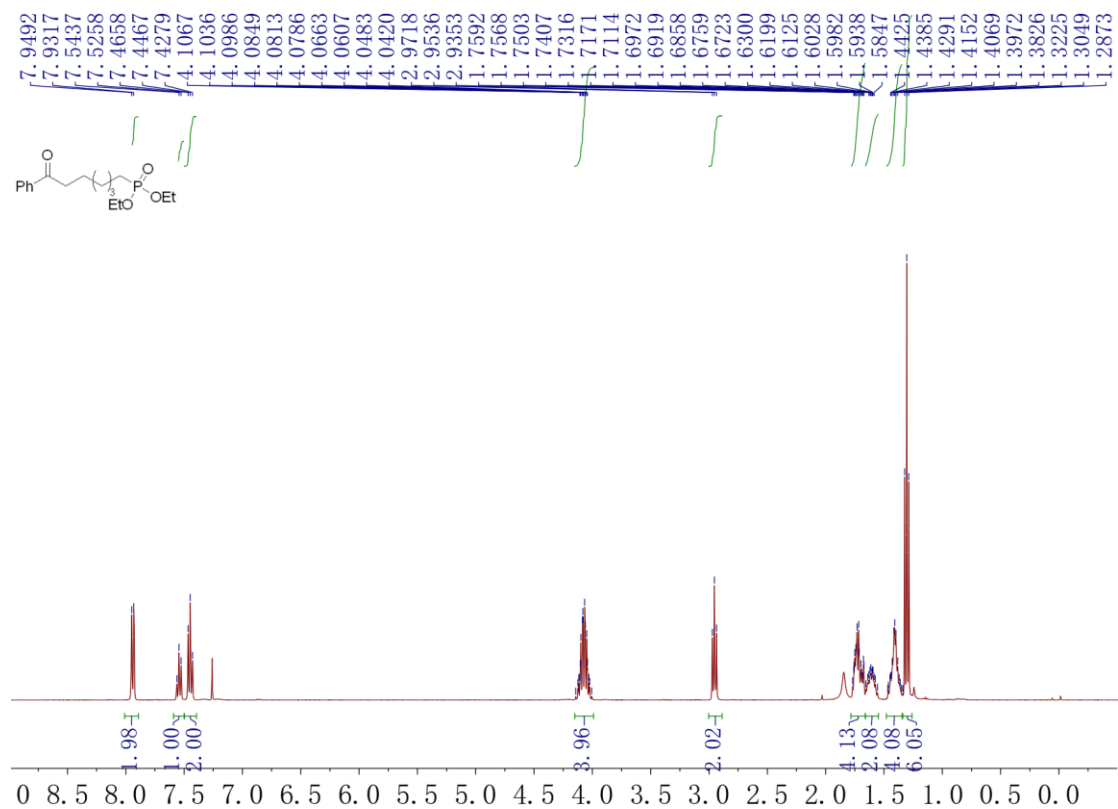
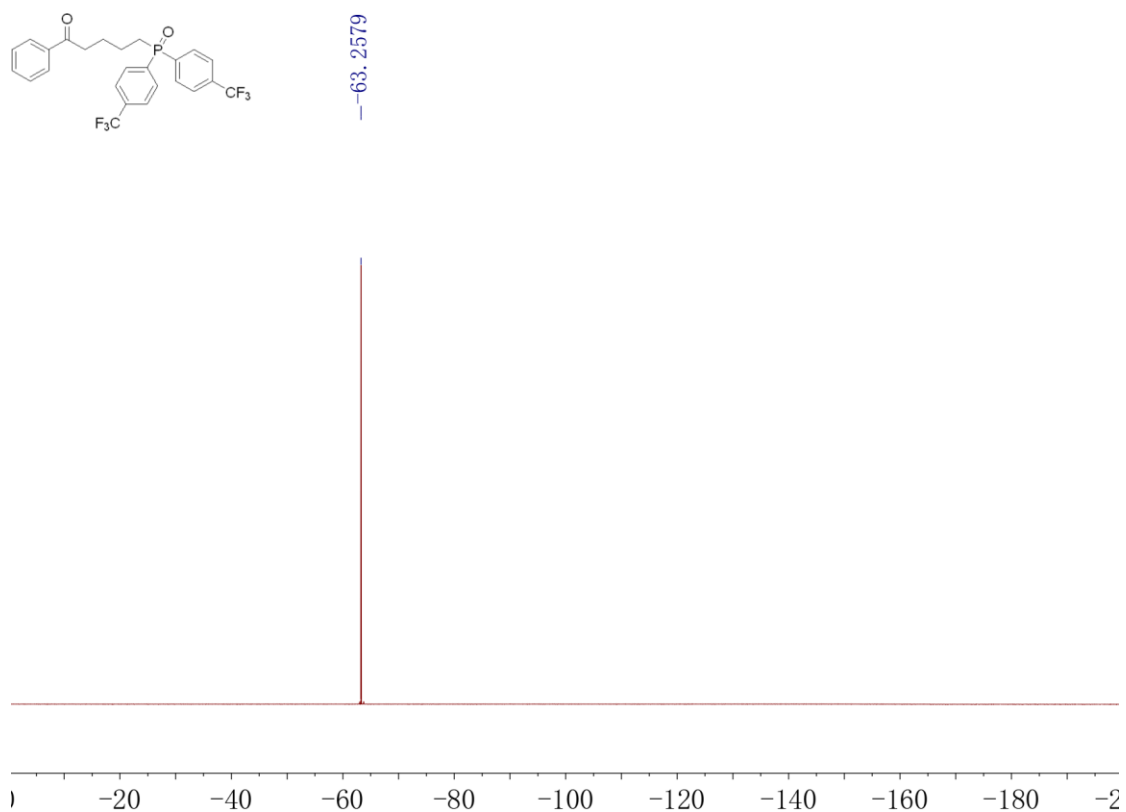
 $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of **3g** $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **3h**

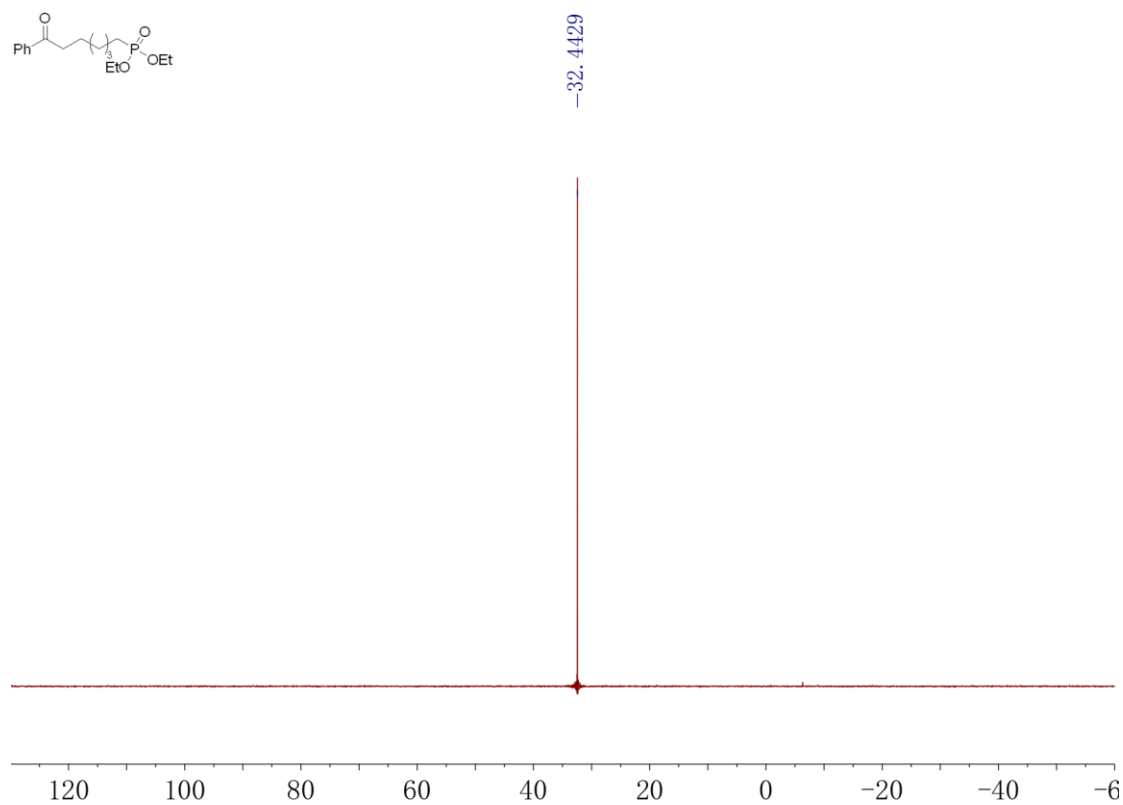
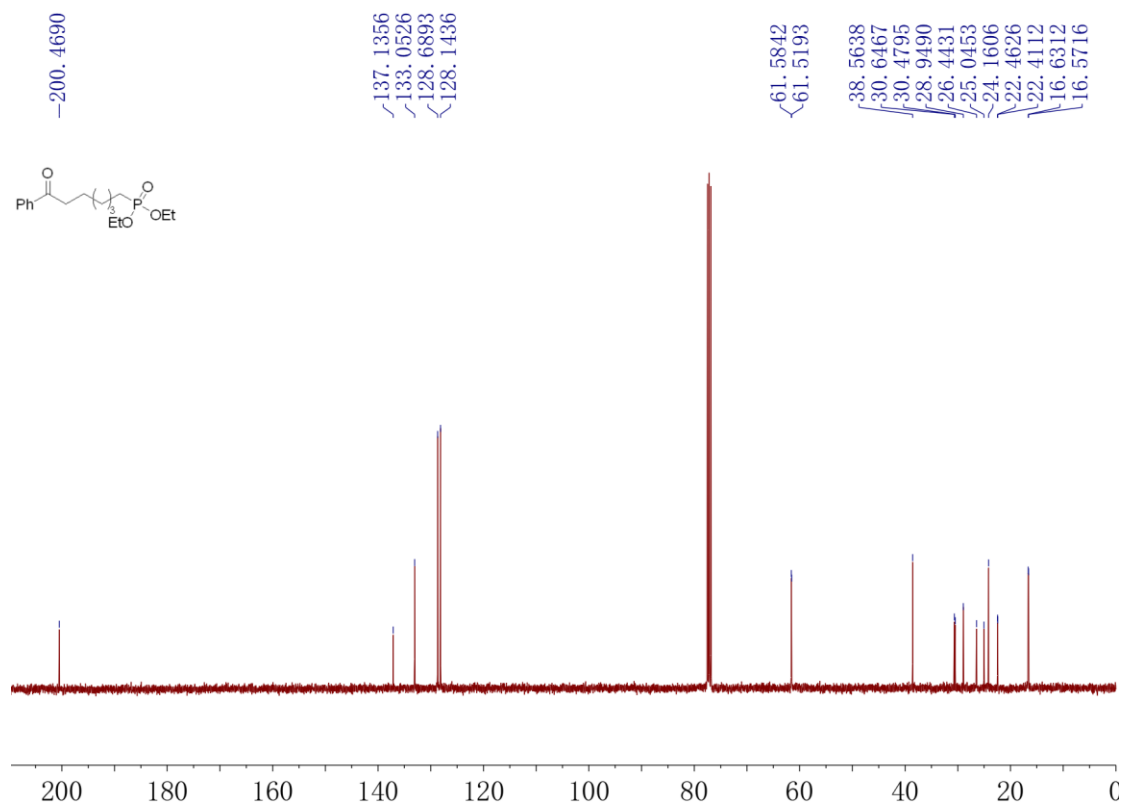
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **3h**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) spectrum of **3h**

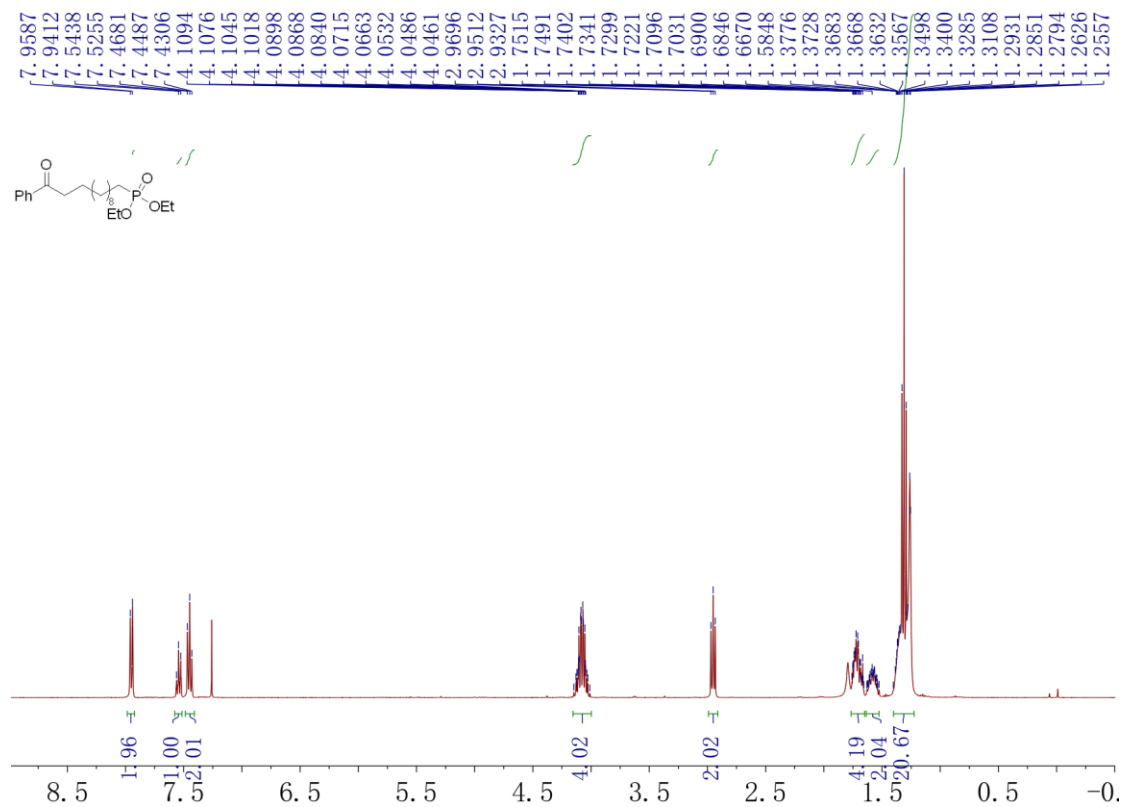
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **3i**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **3i**



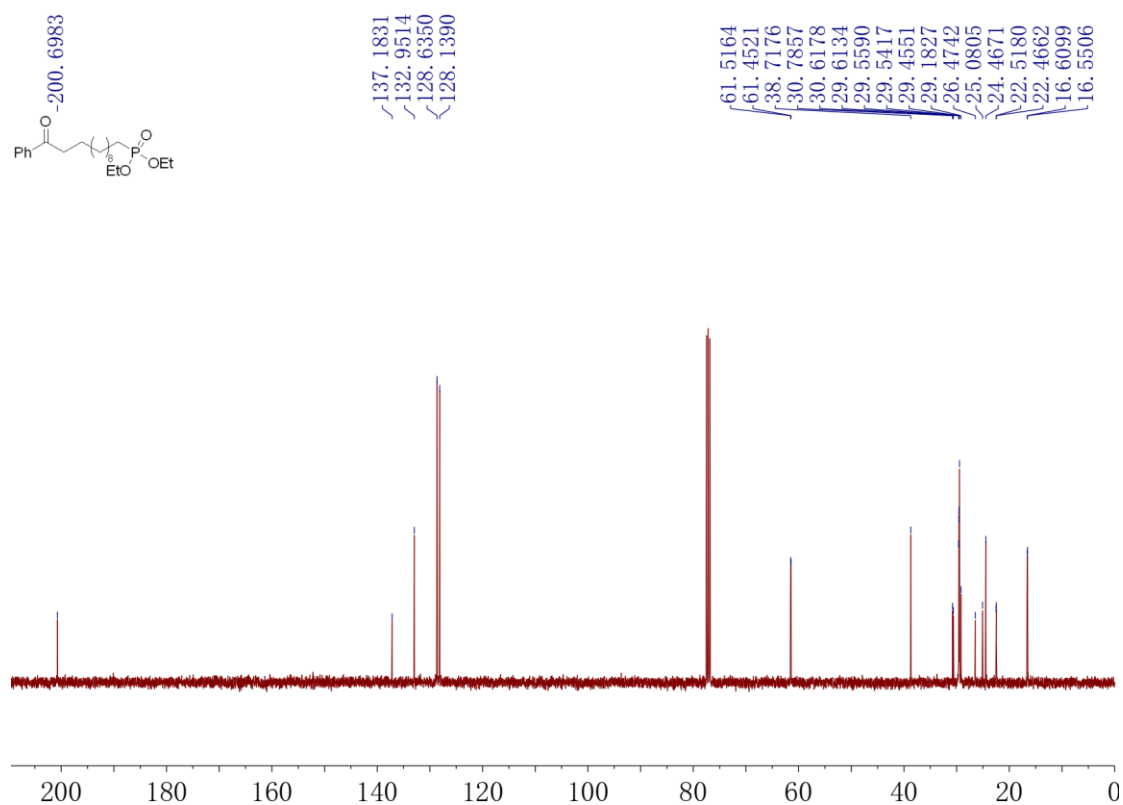
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **3j**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) spectrum of **3j**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **4b****



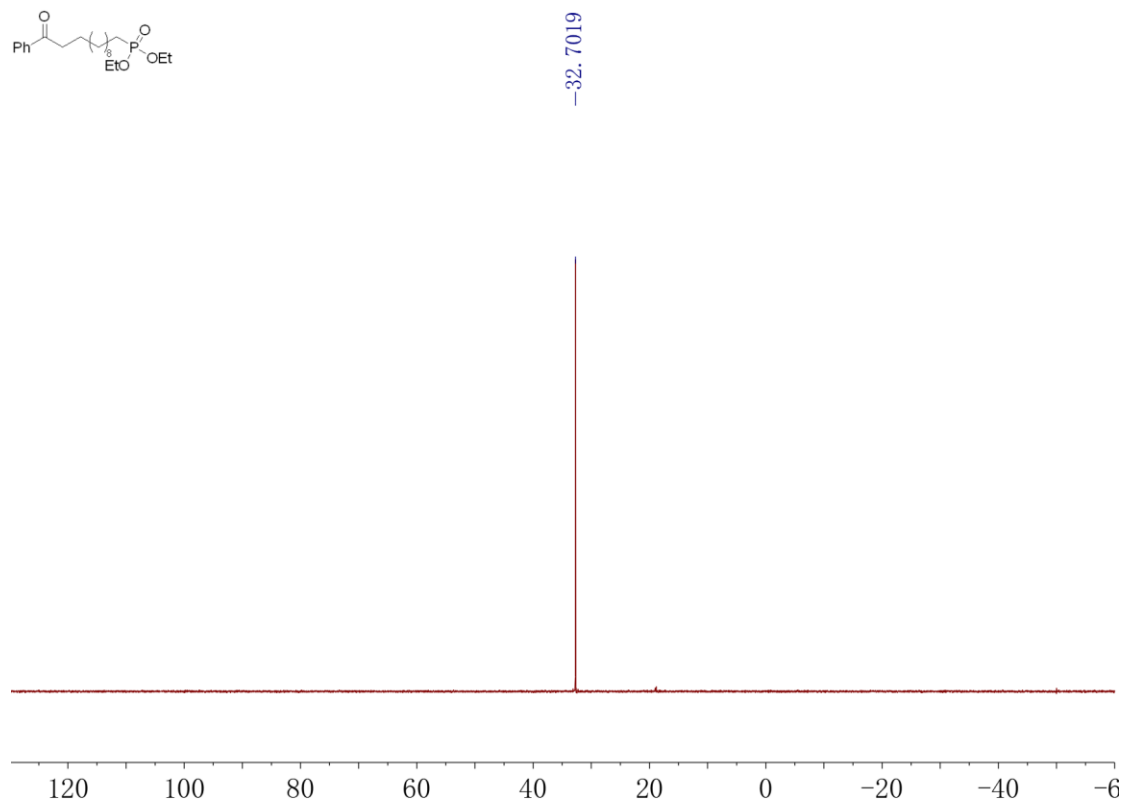
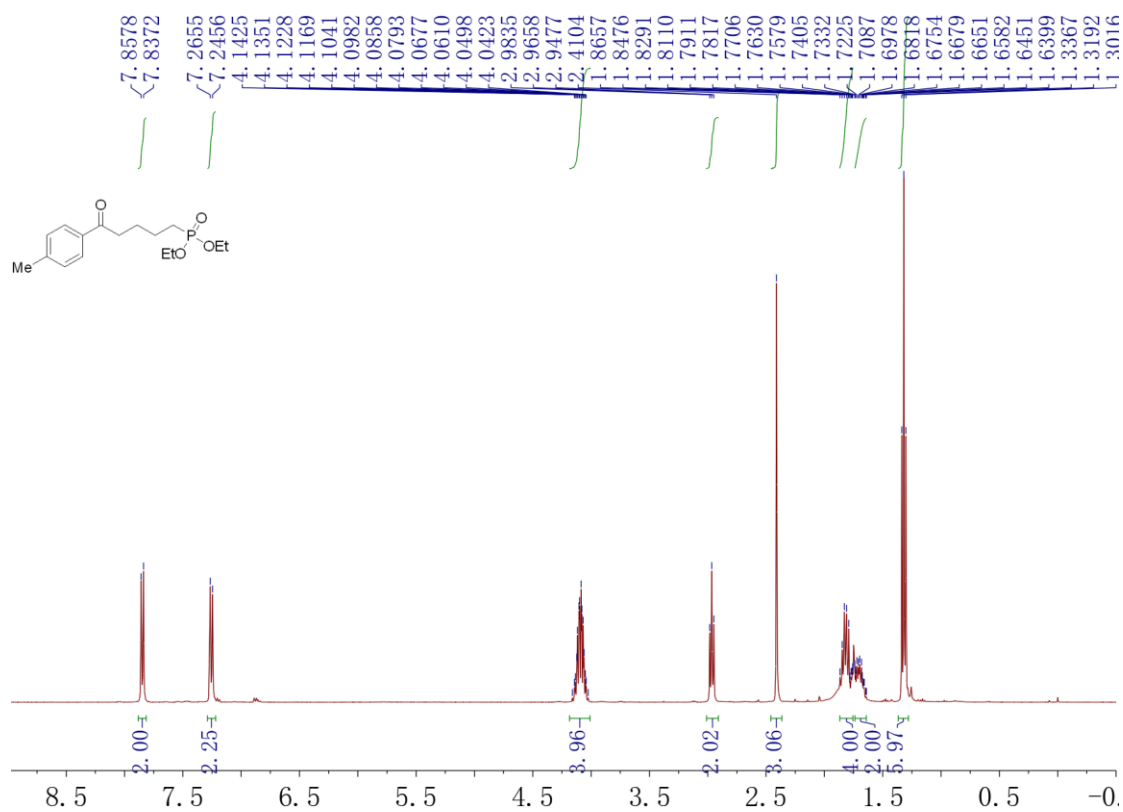


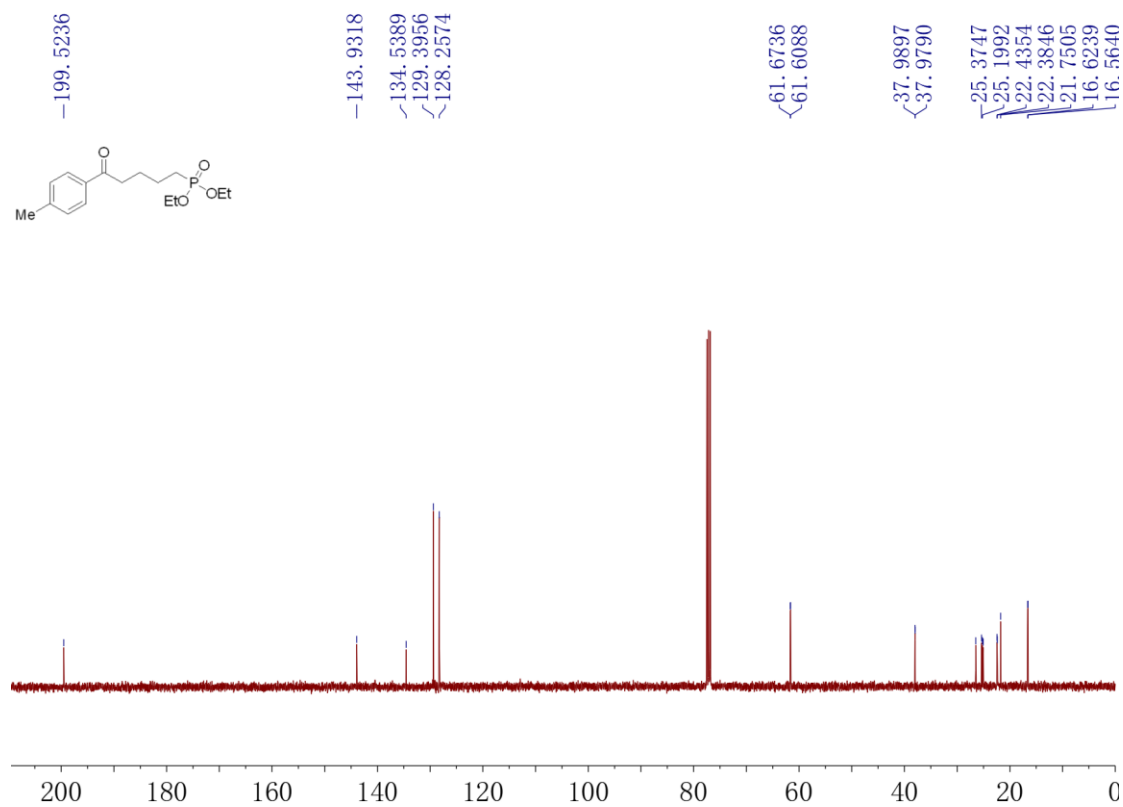
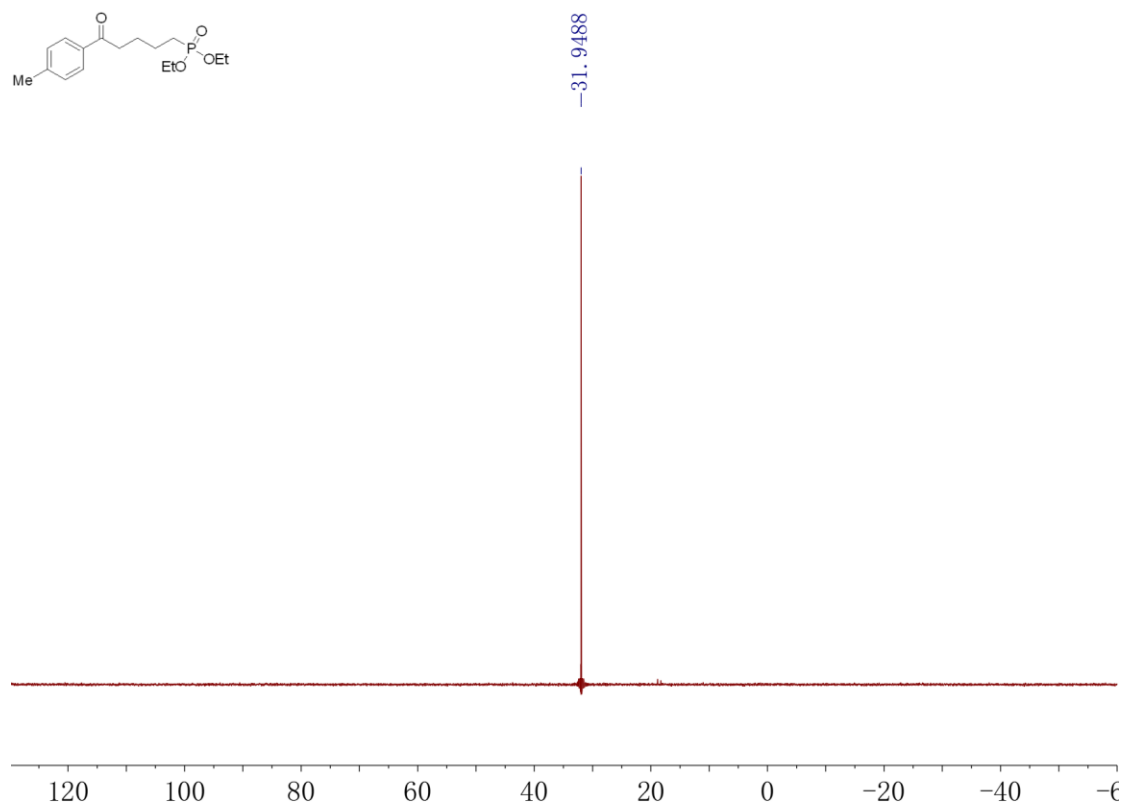
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 4c**

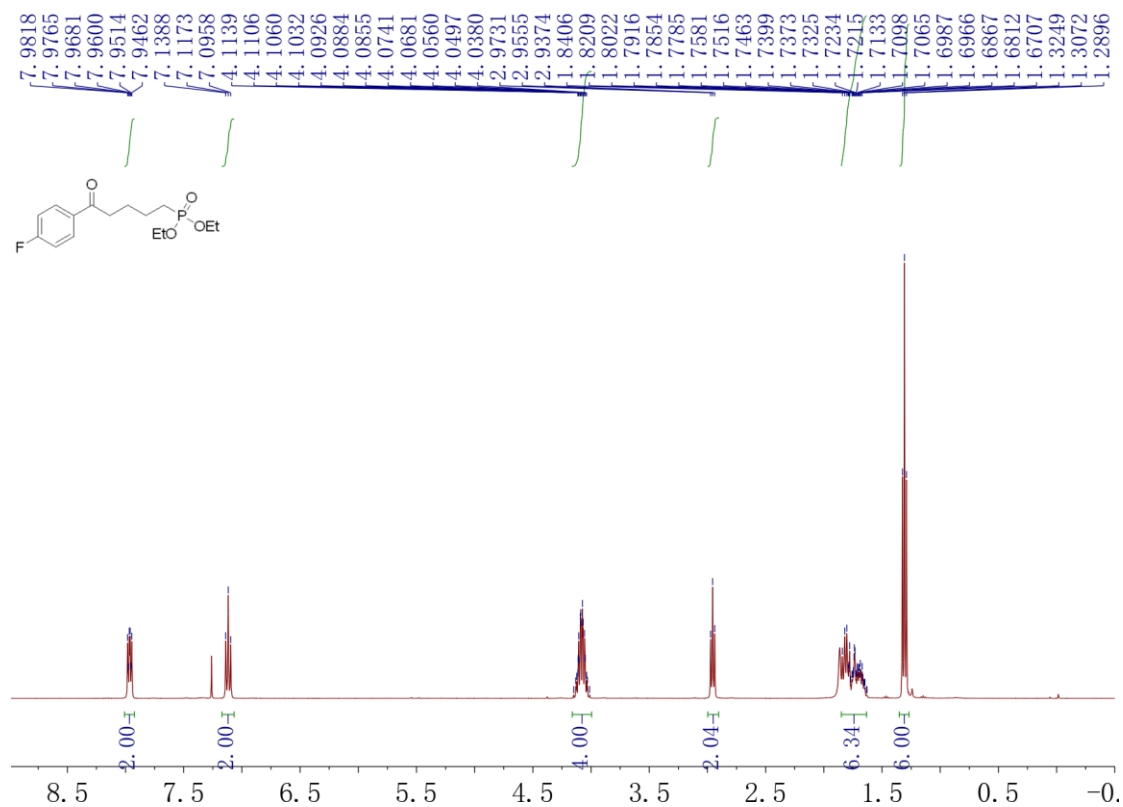


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 4c**

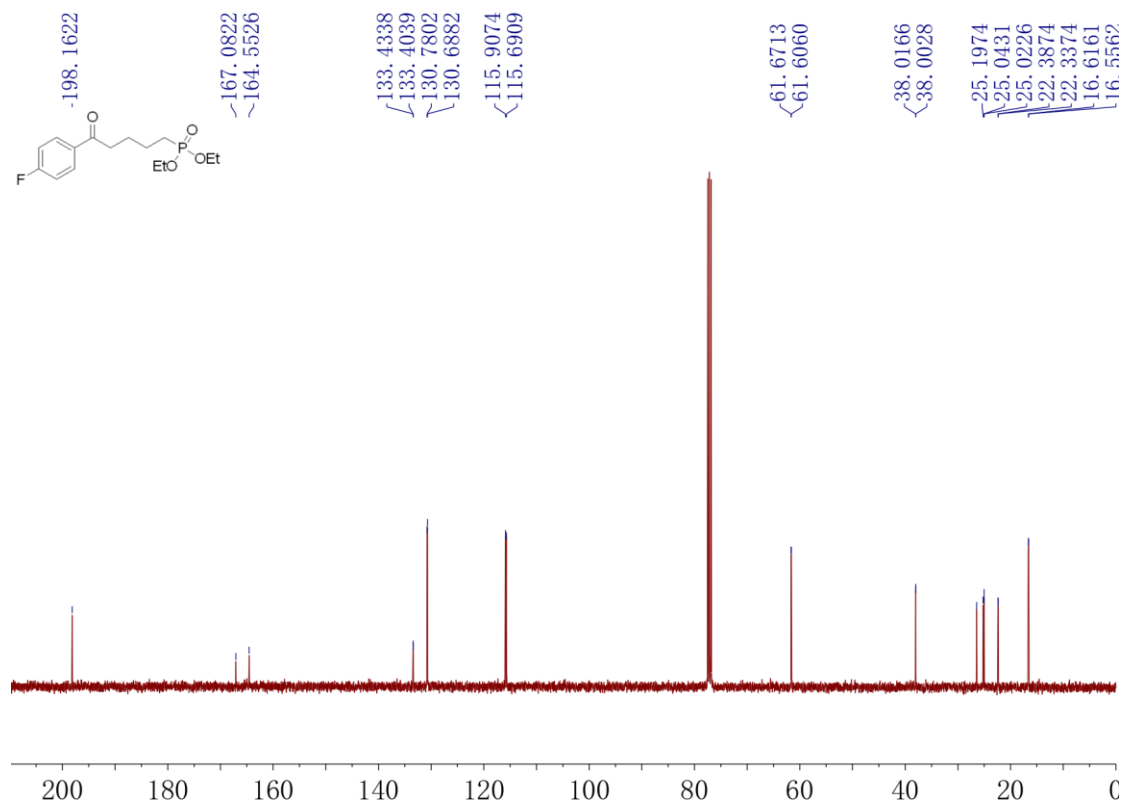


 $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of **4c** $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **4d**

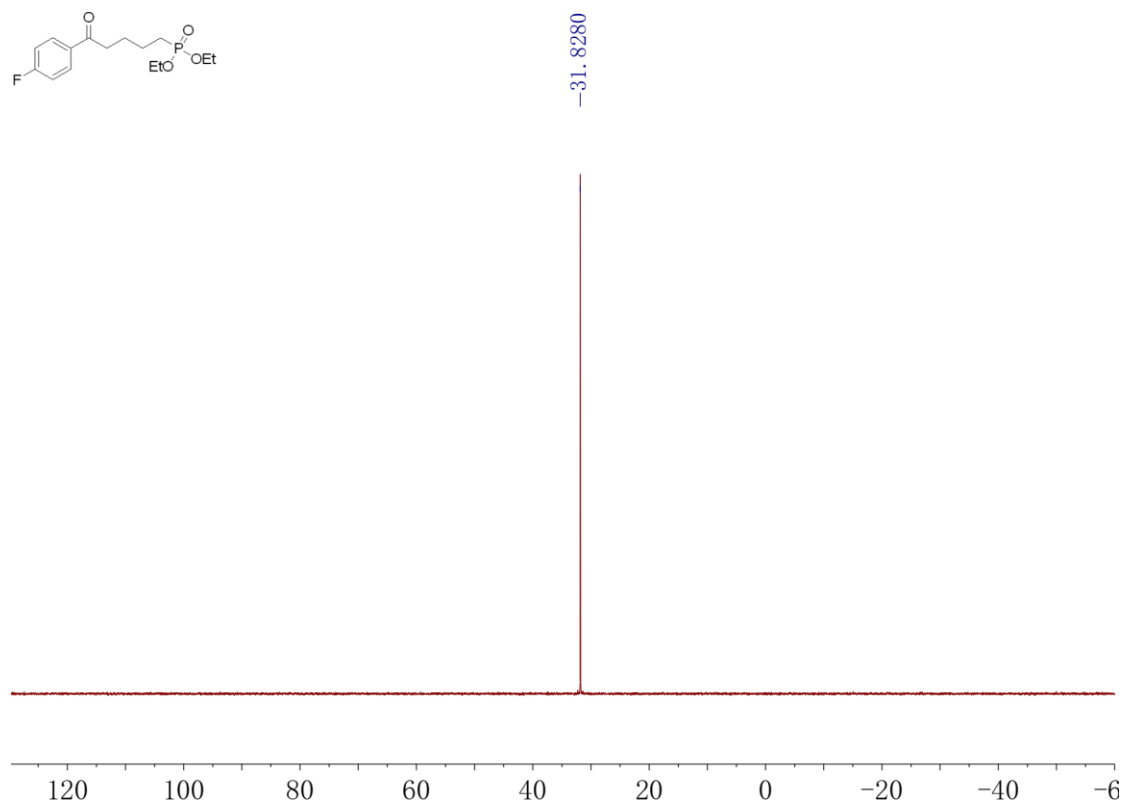
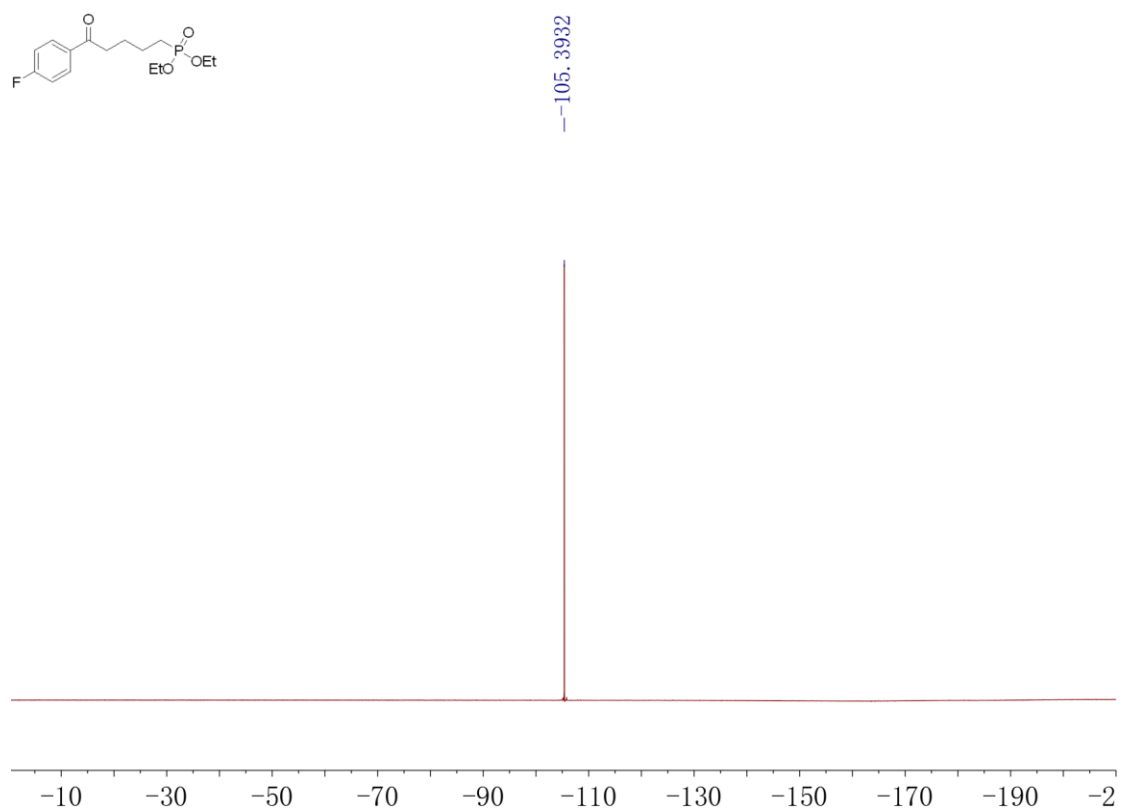
 $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **4d** $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of **4d**

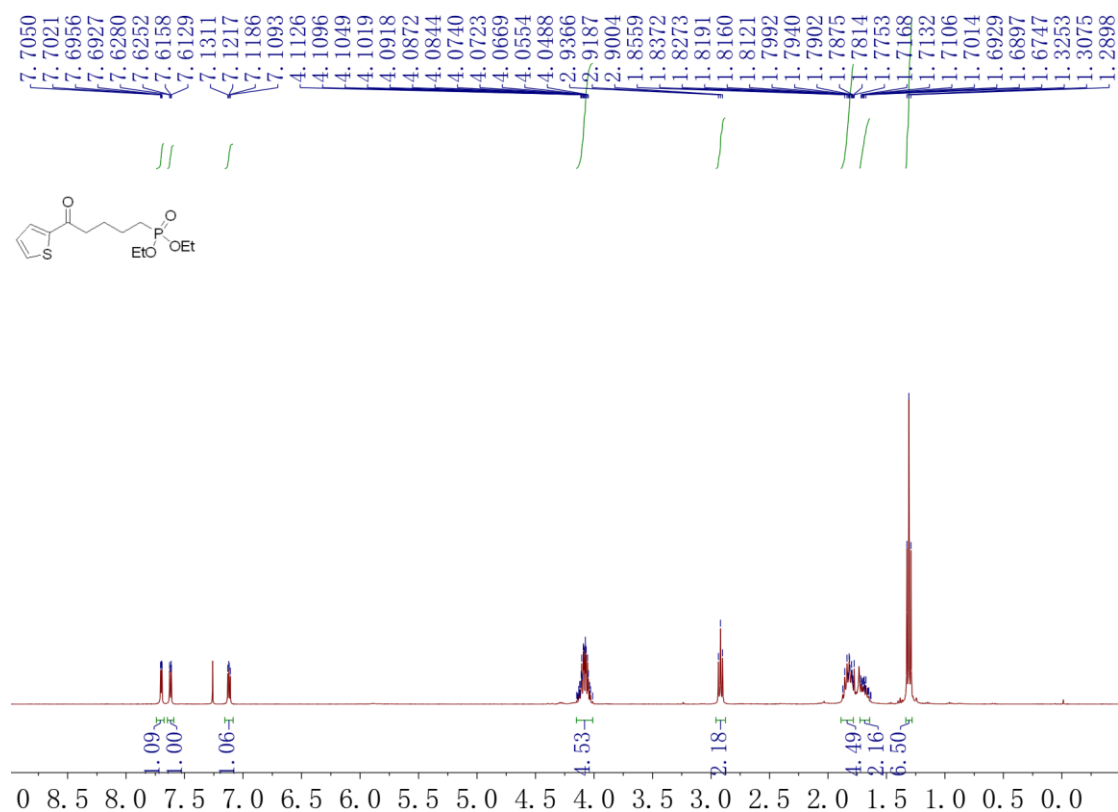
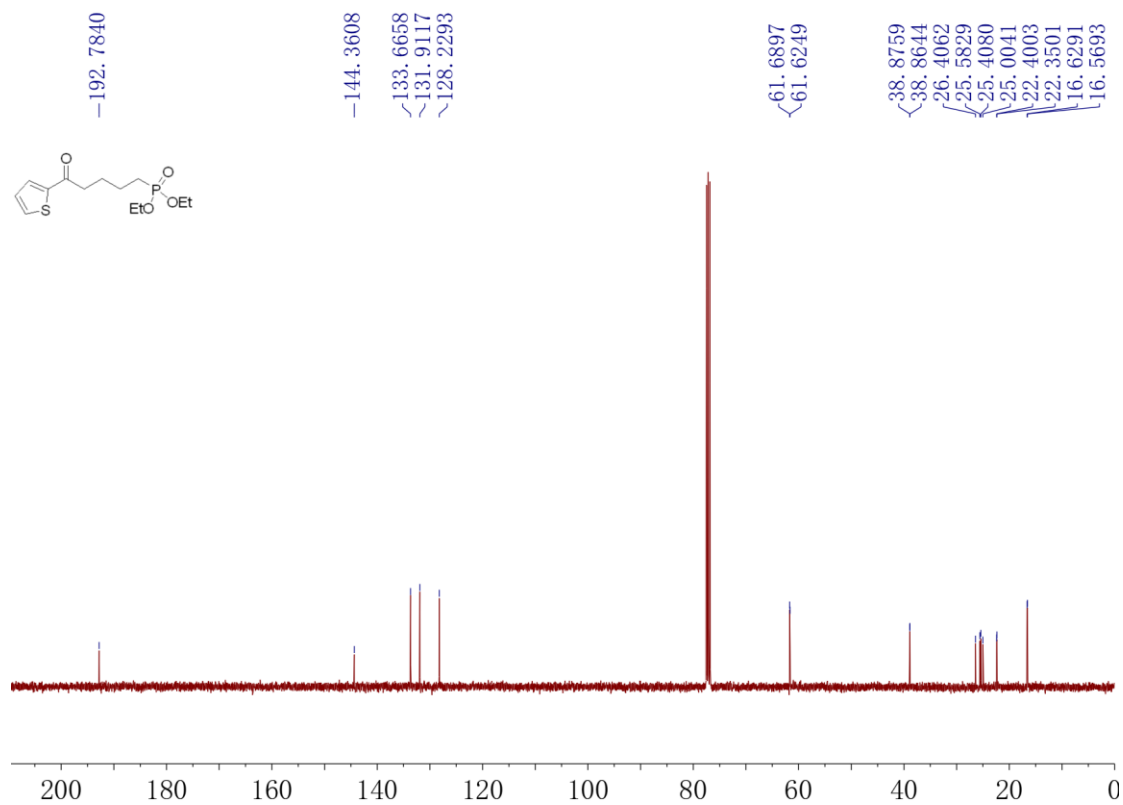


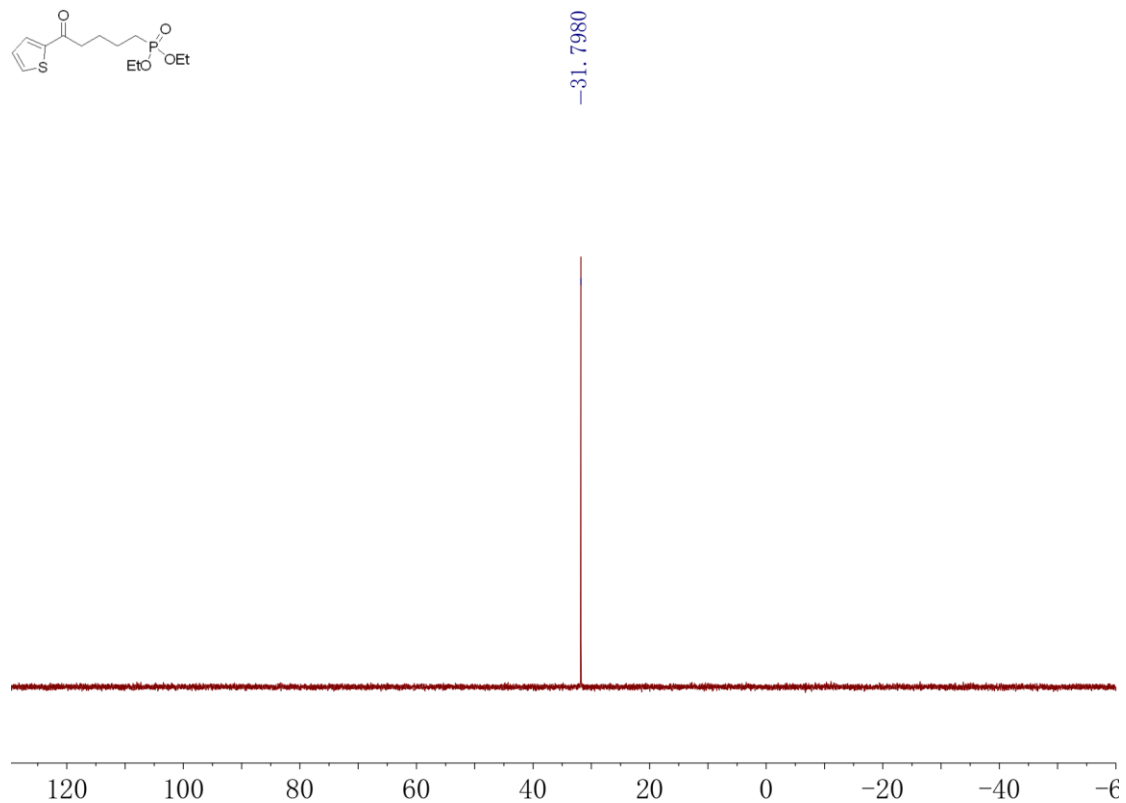
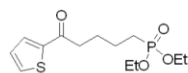
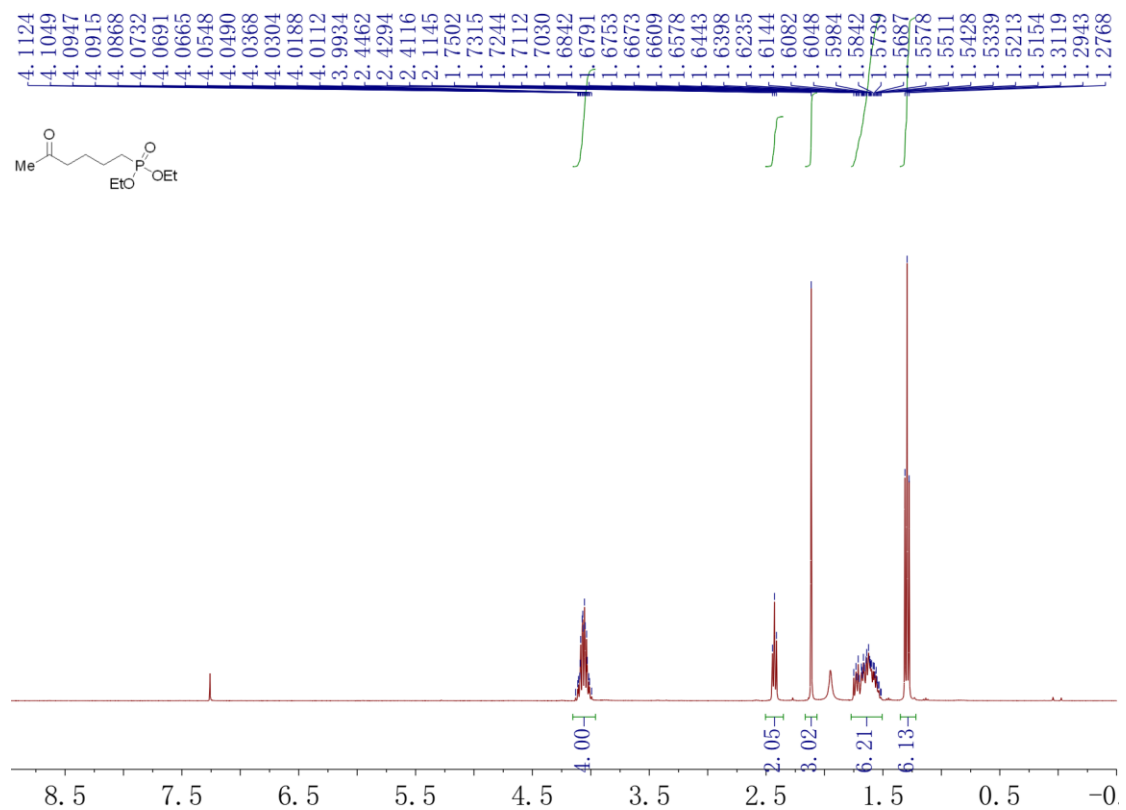
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **4e**

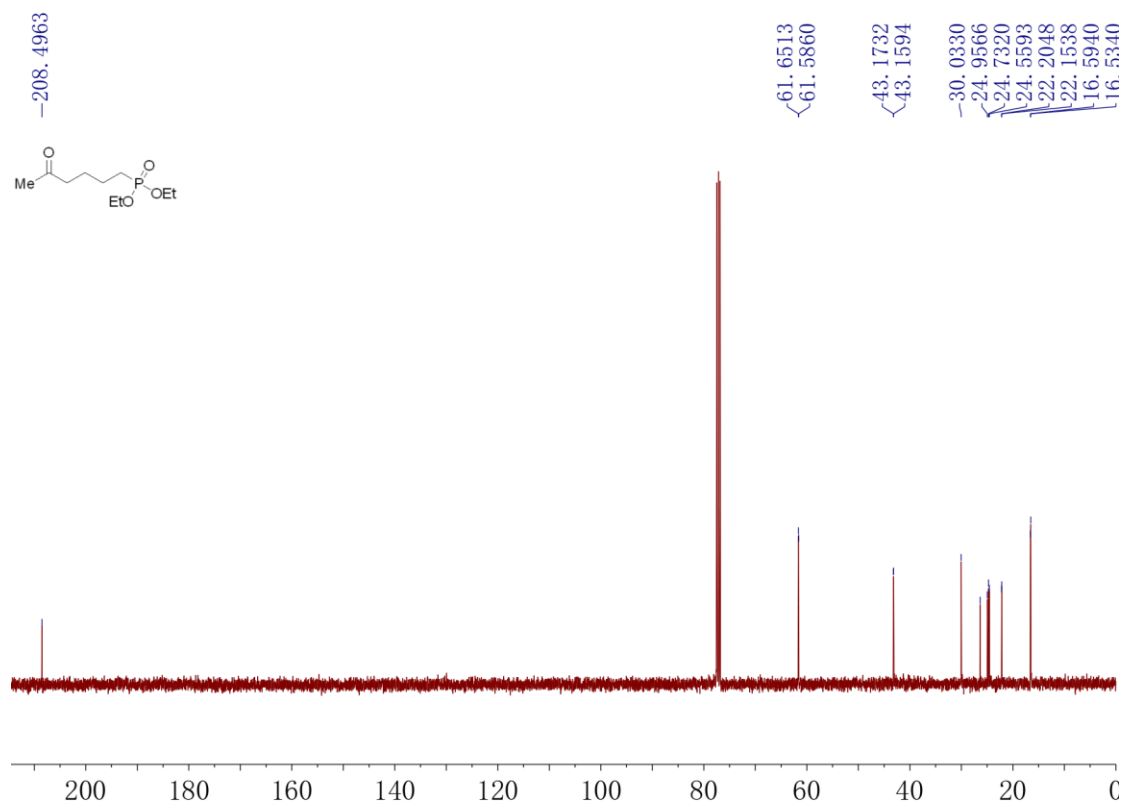
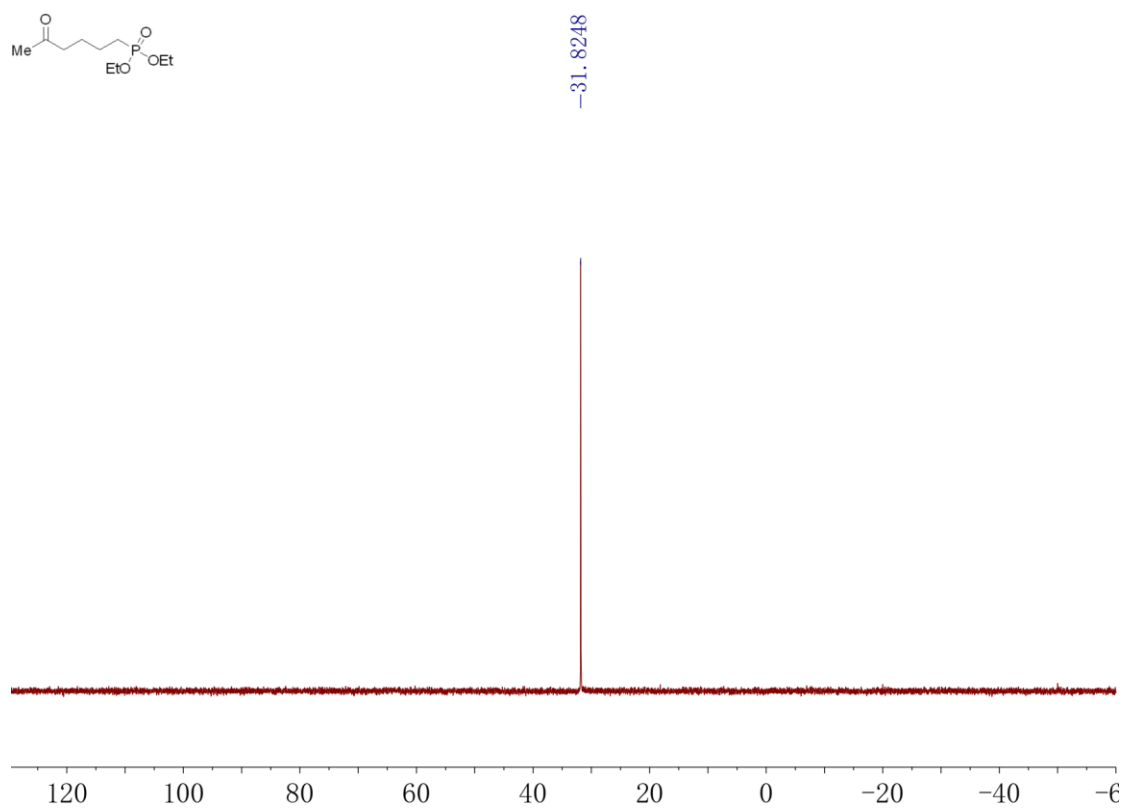


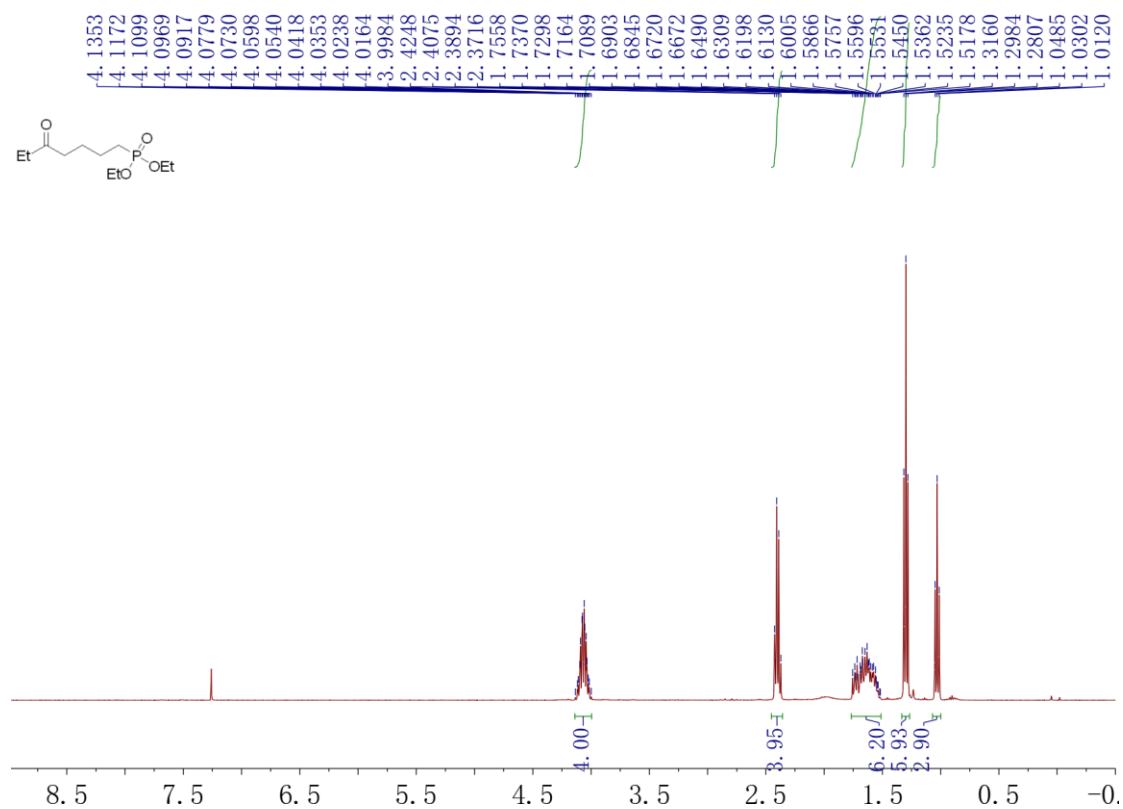
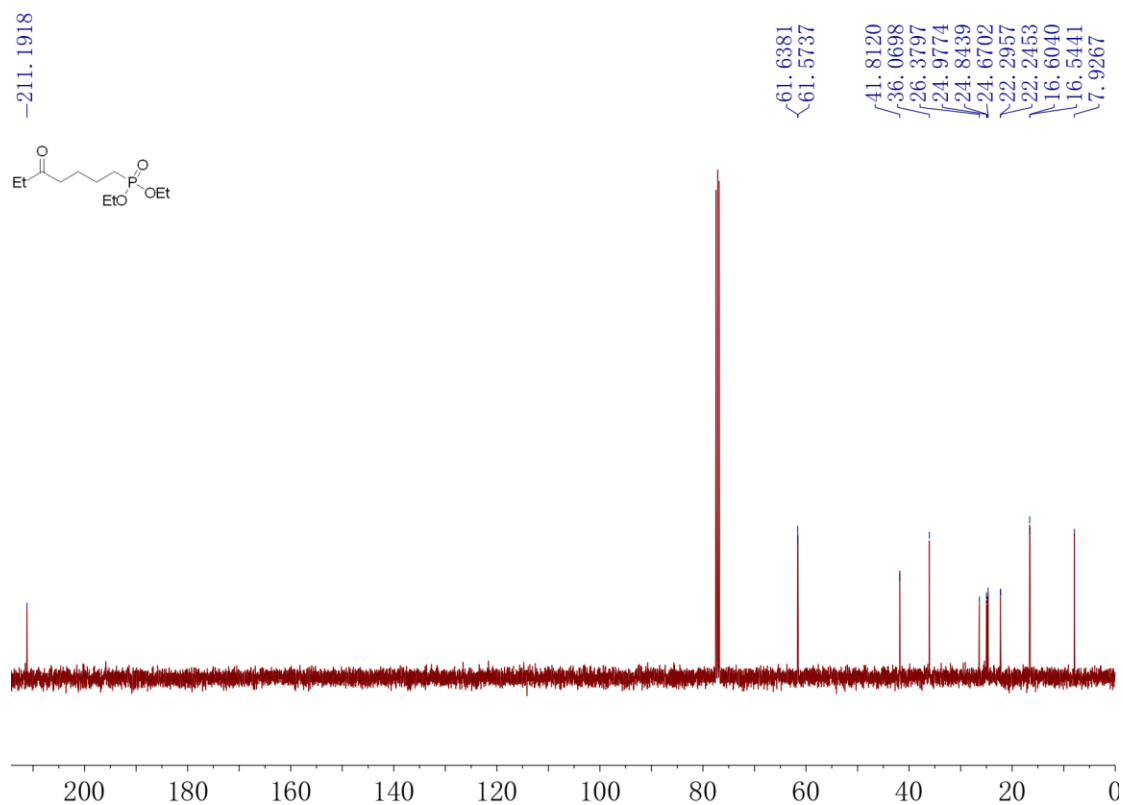
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **4e**

 $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of **4e** $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) spectrum of **4e**

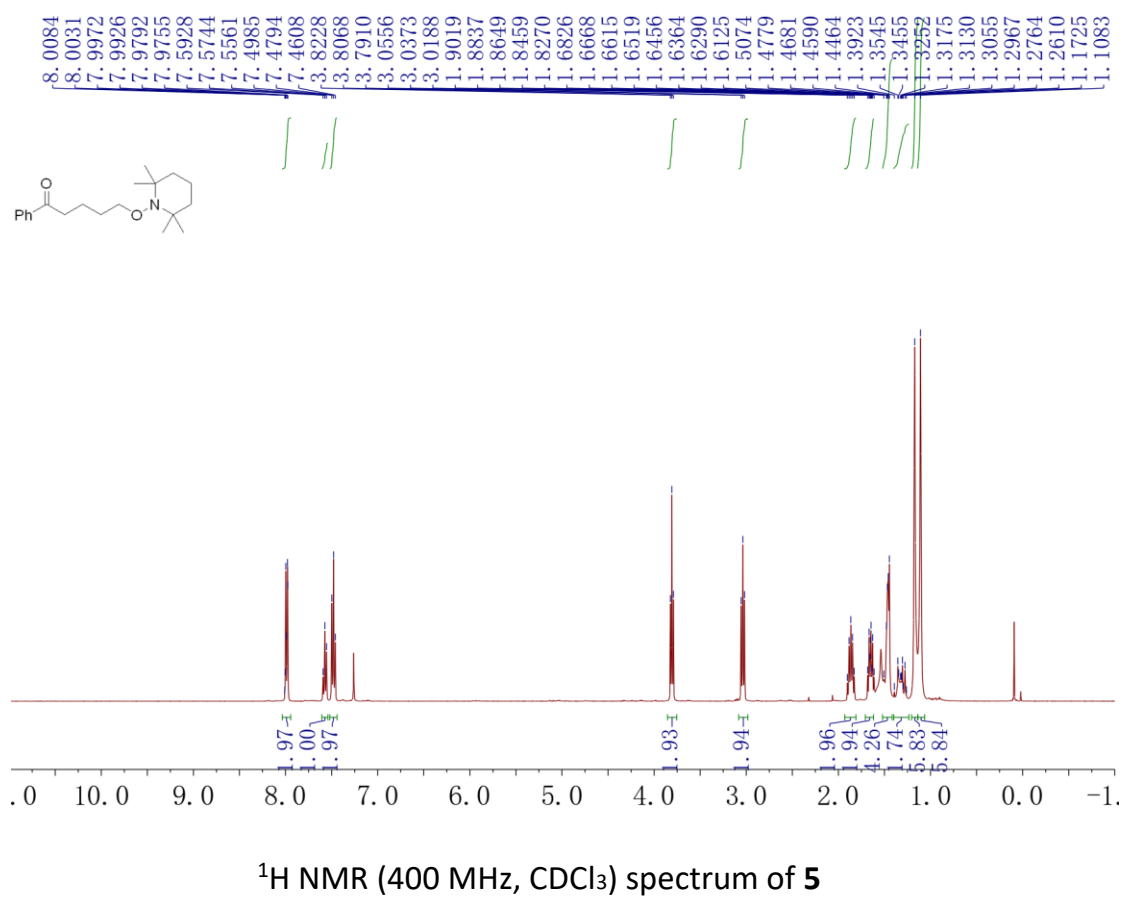
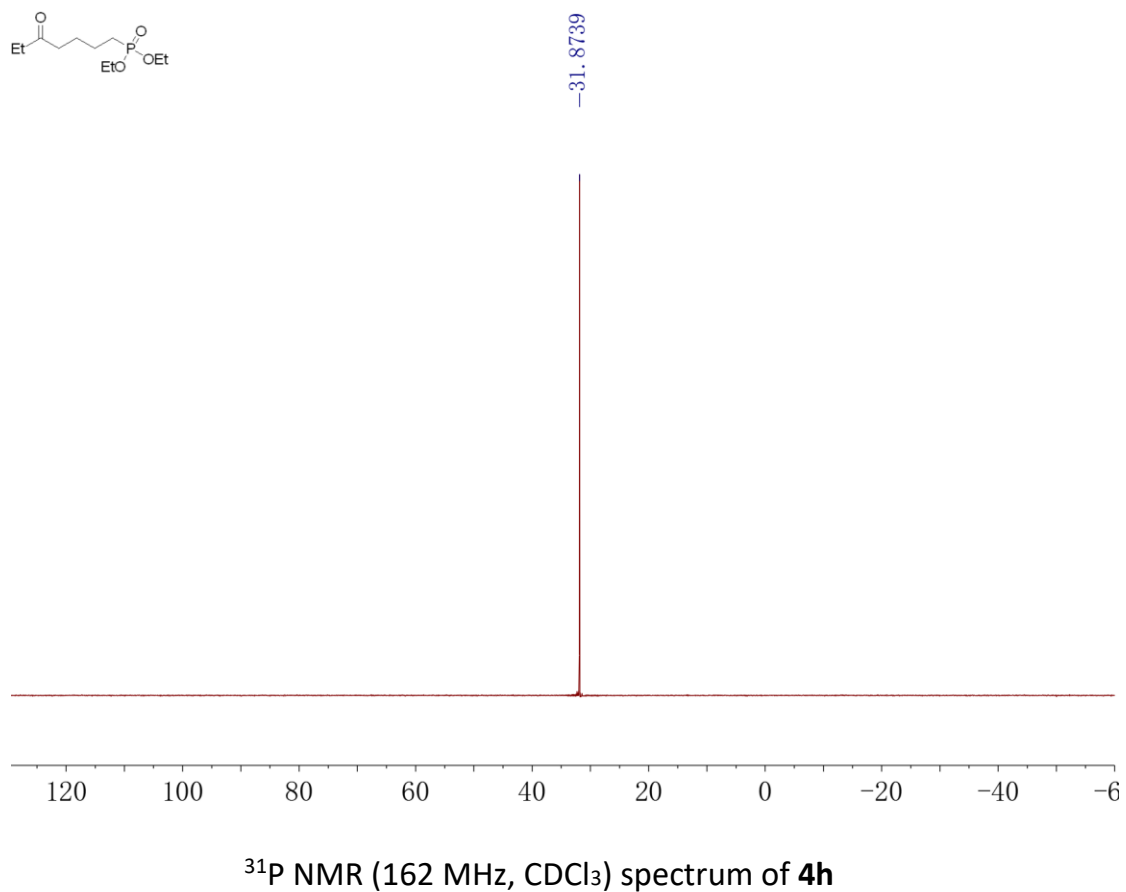
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **4f**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **4f**

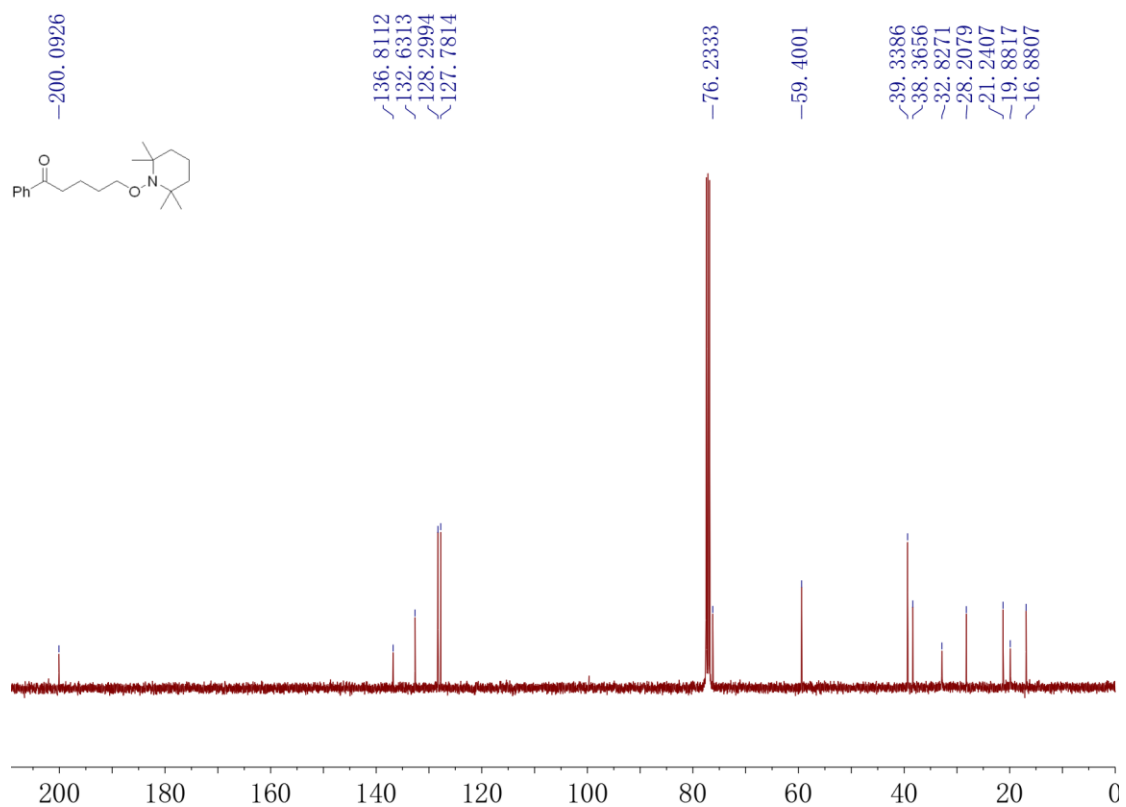
 $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of **4f** $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **4g**

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **4g**<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) spectrum of **4g**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **4h**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **4h**







$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **5**