

## **Microwave-assisted synthesis of dialkylphosphinic acids and a structure–reactivity study in rare earth metal extraction**

**Ruobing Du,<sup>a</sup> HuaYing An,<sup>a</sup> Suhui Zhang,<sup>a</sup> Donghai Yu,<sup>a</sup> and Ji-Chang Xiao<sup>\* a</sup>**

<sup>a</sup>Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry,  
Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China.

Fax: (+86) 21-6416-6128; Tel: (+86) 21-5492-5340; E-mail: jchxiao@sioc.ac.cn

### Tables of Contents

Experiments.....	S2
Spectrum of dialkyl phosphinic acids.....	S3
Extraction ratio of Ho by di(n-octyl)phosphinic acid in different solvents.....	S4
Computational details.....	S5
Copies of <sup>1</sup> H NMR, <sup>13</sup> C NMR and <sup>31</sup> P NMR.....	S6

## **1. Experiments**

### **1.1 Reagents and instruments**

Octylene, 2,4,4-trimethylpentylene and 2-ethylhexene were purchased from reagent company. Other  $\alpha$ -olefins were synthesized from corresponding ketone using wittig reaction.<sup>1</sup>

A shaker. was adopted for shaking and mixing the aqueous and organic phases. The pH value of aqueous phase was measured by pH meter which was calibrated daily. The concentration of rare earth ions in the aqueous phase was determined by ICP-AES.

### **1.2 Synthesis**

Dialkylphosphinic acids in this article were synthesized with MW-assisted free radical addition method by sodium hypophosphite monohydrate and corresponding  $\alpha$ -olefin under the initiation of peroxide. The temperature of this route was 105°C or higher.

The procedure was modified as the following process. NaH<sub>2</sub>PO<sub>2</sub>·H<sub>2</sub>O (2.12g, 20mmol), acetic acid (1.2g, 20mmol), 2-ethylhexene (4.9g 42mmol) and di-t-butyl peroxide, (1.14g 8mmol), 10ml DMF were added into a 50 mL autoclaves. The mixture was reacted under 105W MW irradiation for a period of suitable time. Solvent was removed under reduced pressure. The residue was dissolved in water, acidified with HCl and then extracted with diethyl ether. The ether layer was washed with water and evaporated. By treating the residue with 1M NaOH to pH=7, the neutral impurities were taken off by ether. After removal of solvent, the residue was treated at 100°C *in vacuo*. Dialkylphosphinic acids were obtained at 70-95 yield.

### **1.3 Extraction procedure**

A stock solution containing 1g/L of each lanthanide element was prepared by dissolving weighed amounts of lanthanide oxide in HCl. Aqueous phase solutions were diluted in extraction study. Extractants diluted with n- dodecane or toluene was used in extraction procedure.

All the extraction and stripping tests were carried out at room temperature with an aqueous to organic phase volume ratio of 1:1. The aqueous phase containing 0.01M of

Ln in chloric acid and the organic phase containing 0.2M extractant. The ionic strength of the aqueous phase was kept at 1M with 1M NaCl. The two phases were placed in separatory funnel and shaken 30 min. This time period was more than sufficient for both temperature and chemical equilibrium to be reached. The equilibrium pH and metal concentrations in the aqueous phase were measured after phase separation. The pH was measured with a pH meter. Ln concentrations in the aqueous phases were determined on an ICP-AES after dilution. Concentrations of Ln in the organic phase were calculated from mass balance using the measured concentrations of Ln in the aqueous solutions before and after extraction.

## 2. Spectrum of dialkyl phosphinic acids

### **Bis(2-ethylhexyl)phosphinic acid (P227)**

ESI-MS:  $m/z = 289.25$  M<sup>-</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  11.63 (s, 1H), 1.85 – 1.66 (m, 4H), 1.26 (bs, 18H), 1.12 (ddd,  $J = 16.7, 7.1, 2.0$  Hz, 6H), 0.86 (t,  $J = 6.5$  Hz, 6H). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  60.77.

### **Bis(2,4,4-trimethylpentyl)phosphinic acid(P272)**

ESI-MS:  $m/z = 289.25$  M<sup>-</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.86 (s, 1H), 2.11 – 2.02 (m, 2H), 1.72 (ddt,  $J = 13.9, 8.5, 4.5$  Hz, 2H), 1.58 – 1.47 (m, 2H), 1.33 (dd,  $J = 14.0, 4.0$  Hz, 2H), 1.17 (dd,  $J = 14.0, 5.8$  Hz, 2H), 1.13 – 1.08 (m, 6H), 0.90 (s, 18H).

### **Bis(2-methylheptyl)phosphinic acid (P218)**

ESI-MS:  $m/z = 289.25$  M<sup>-</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.83 (s, 1H), 1.93 (s, 2H), 1.79 – 1.59 (m, 2H), 1.49 (td,  $J = 15.0, 14.0, 8.5$  Hz, 2H), 1.43 – 1.16 (m, 16H), 1.05 (d,  $J = 8.0$  Hz, 6H), 0.87 (t,  $J = 6.9$  Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  38.74 (dd,  $J = 11.6, 4.1$  Hz, 2C), 37.12 (dd,  $J = 90.8, 6.8$  Hz, 2C), 31.94 (s, 2C), 27.64 (d,  $J = 4.3$  Hz, 2C), 26.40 (s, 2C), 22.64 (s, 2C), 21.25 (d,  $J = 5.7$  Hz, 2C), 14.03 (s, 2C). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  60.12. HRMS (ESI-Negative)  $m/z$ : M<sup>-</sup> calcd for C<sub>16</sub>H<sub>34</sub>O<sub>2</sub>P: 289.2302; found 289.2295.

### **Bis(2-propylpentyl)phosphinic acid (P236)**

ESI-MS:  $m/z = 291.0 [M + H]^+$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  11.54 (s, 1H), 1.87 (tt,  $J = 12.4$ , 6.0 Hz, 2H), 1.59 (dd,  $J = 13.3$ , 6.3 Hz, 4H), 1.33 (dh,  $J = 28.6$ , 7.3, 6.5 Hz, 16H), 0.88 (t,  $J = 7.1$  Hz, 12H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  77.33, 77.02, 76.70, 37.06 (d,  $J = 7.9$  Hz), 34.29 (d,  $J = 90.8$  Hz), 31.70 (d,  $J = 4.3$  Hz), 19.29, 14.29.  $^{31}P$  NMR (162 MHz,  $CDCl_3$ )  $\delta$  60.66. HRMS (LTQ FT)  $m/z$ :  $M^+$  calcd for  $C_{16}H_{36}O_2P$ : 291.2447; found 291.2446.

### Bis(2-isopropylpentyl)phosphinic acid (P2361)

API-MS:  $m/z = 291.0 M^+$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  1.89 (s, 2H), 1.79 – 1.59 (m, 4H), 1.35 (s, 10H), 0.85 (ddd,  $J = 20.6$ , 13.6, 6.9 Hz, 18H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  77.35, 77.03, 76.71, 37.50 (d,  $J = 4.0$  Hz), 34.10 (d,  $J = 6.1$  Hz), 30.72 (d,  $J = 91.8$  Hz), 29.51 (d,  $J = 8.6$  Hz), 20.26, 18.99 (d,  $J = 3.5$  Hz), 18.06 (d,  $J = 2.9$  Hz), 14.28.  $^{31}P$  NMR (162 MHz,  $CDCl_3$ )  $\delta$  61.87. HRMS (LTQ FT)  $m/z$ :  $M^+$  calcd for  $C_{16}H_{36}O_2P$ : 291.2447; found 291.2446.

### Bis(2-t-butylbutyl)phosphinic acid (P247)

ESI-MS:  $m/z = 289.25 M^-$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  11.35 (s, 1H), 1.78 (q,  $J = 14.0$  Hz, 2H), 1.64 - 1.29 (m, , 8H), 1.00 (t,  $J = 7.4$  Hz, 6H), 0.89 (s, 18H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  77.33 (s), 77.01 (s), 76.69 (s), 43.36 (d,  $J = 4.8$  Hz), 34.23 (d,  $J = 9.3$  Hz), 31.90 (s), 30.95 (s), 27.65 (s), 25.08 (s), 13.66 (d,  $J = 2.4$  Hz).  $^{31}P$  NMR (162 MHz,  $CDCl_3$ )  $\delta$  60.56 (d,  $J = 13.1$  Hz). HRMS (ESI-Negative)  $m/z$ :  $M^-$  calcd for  $C_{18}H_{34}O_2P$ : 289.2302; found 289.2307.

## 3. The extraction ratio of di(n-octyl)phosphinic acid in different solvents

In order to contrast the extraction ability in different solvents, Ho was selected to investigate the extraction ratio in n-dodecane and toluene by P208. As illustrated in table 1, the  $K_{ex}$  of Ho in n-dodecane was two orders of magnitude higher than that in toluene.

Table 1 The extraction ratio of Ho by di(n-octyl)phosphinic acid

Solvents	Kex	E%
n-dodecane	2.198	99.78
toluene	0.019	85.05

0.2M di(1-methylheptyl)phosphinic acid in toluene or n-dodecane,  $[HoCl_3]=0.005M$ , Ion strength : 1M

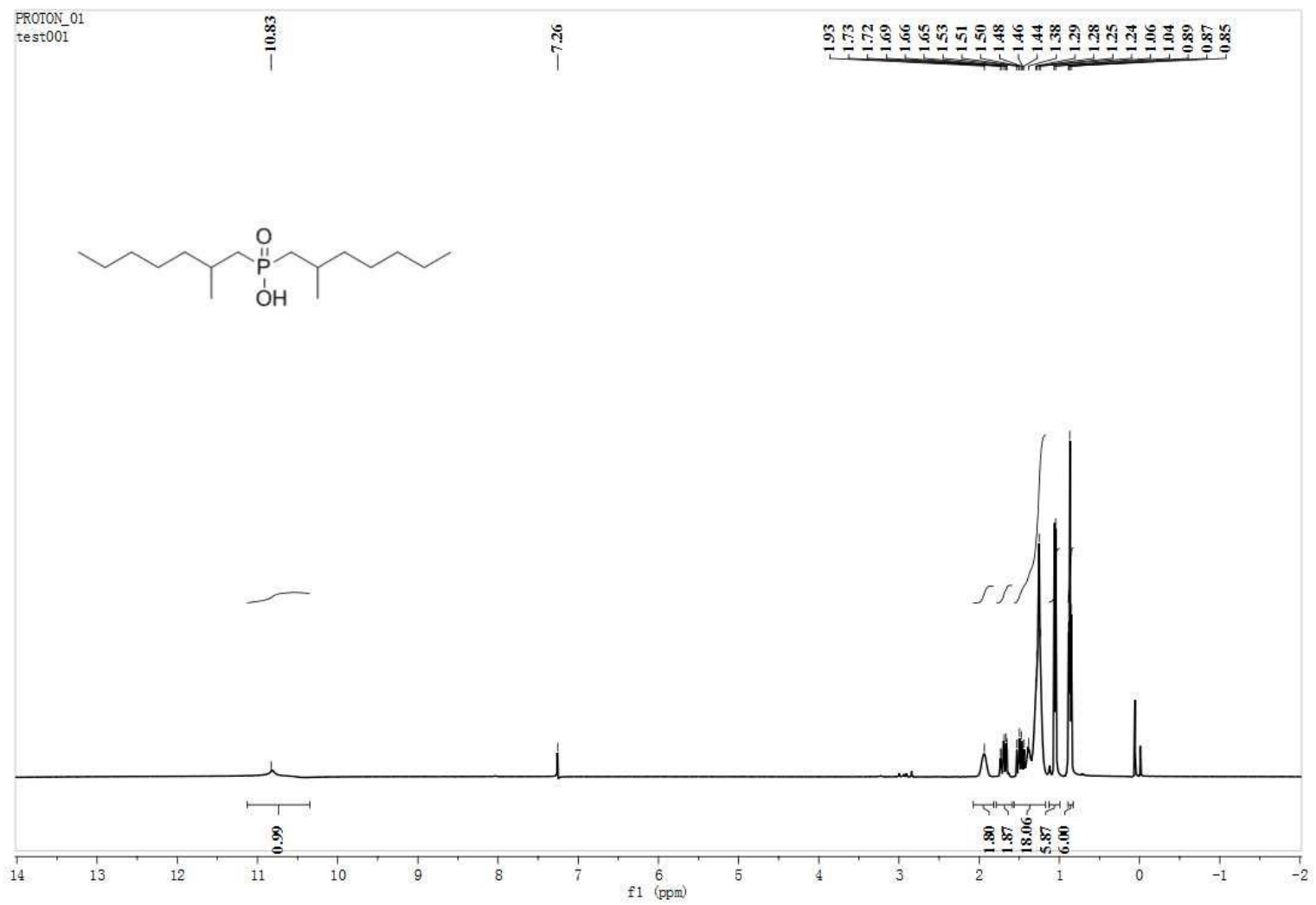
(Na, H)Cl, Initial pH=3, Phase ratio: 1:1

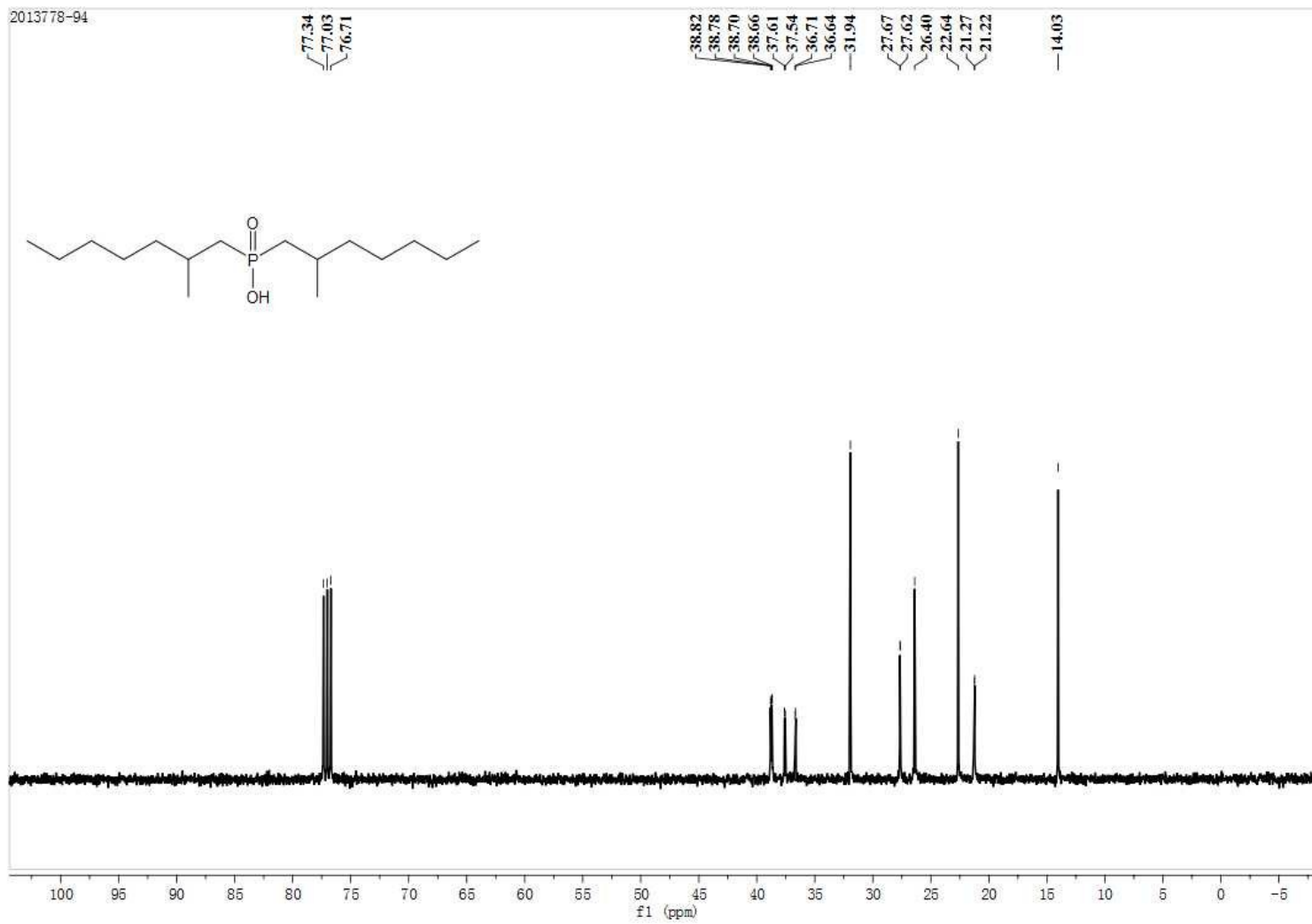
#### 4. Computational details

All geometries were fully optimized at B3PW91 theory level in vacuum. The vibrational frequency was computed for each structures to determine whether it was a minimum point (no imaginary frequency). A single point energy calculation of optimized structures with the SMD solvation model was used for solvent effect to both aqueous phases with water and organic phases with n-dodecane at the same theory level. The 6-311++G\*\* basis set was used for the metal ions connected atoms, oxygen connected atoms and phosphorus connected atoms, and the 6-31+G\* basis set was used for other carbon and hydrogen atoms in alkyl. The large-core relativistic effective core potential developed by Dolg et al. which the electrons in 4f orbital were be patented were used to lanthanides. All calculations were performed using the Gaussian 09, Revision D.01 software package.

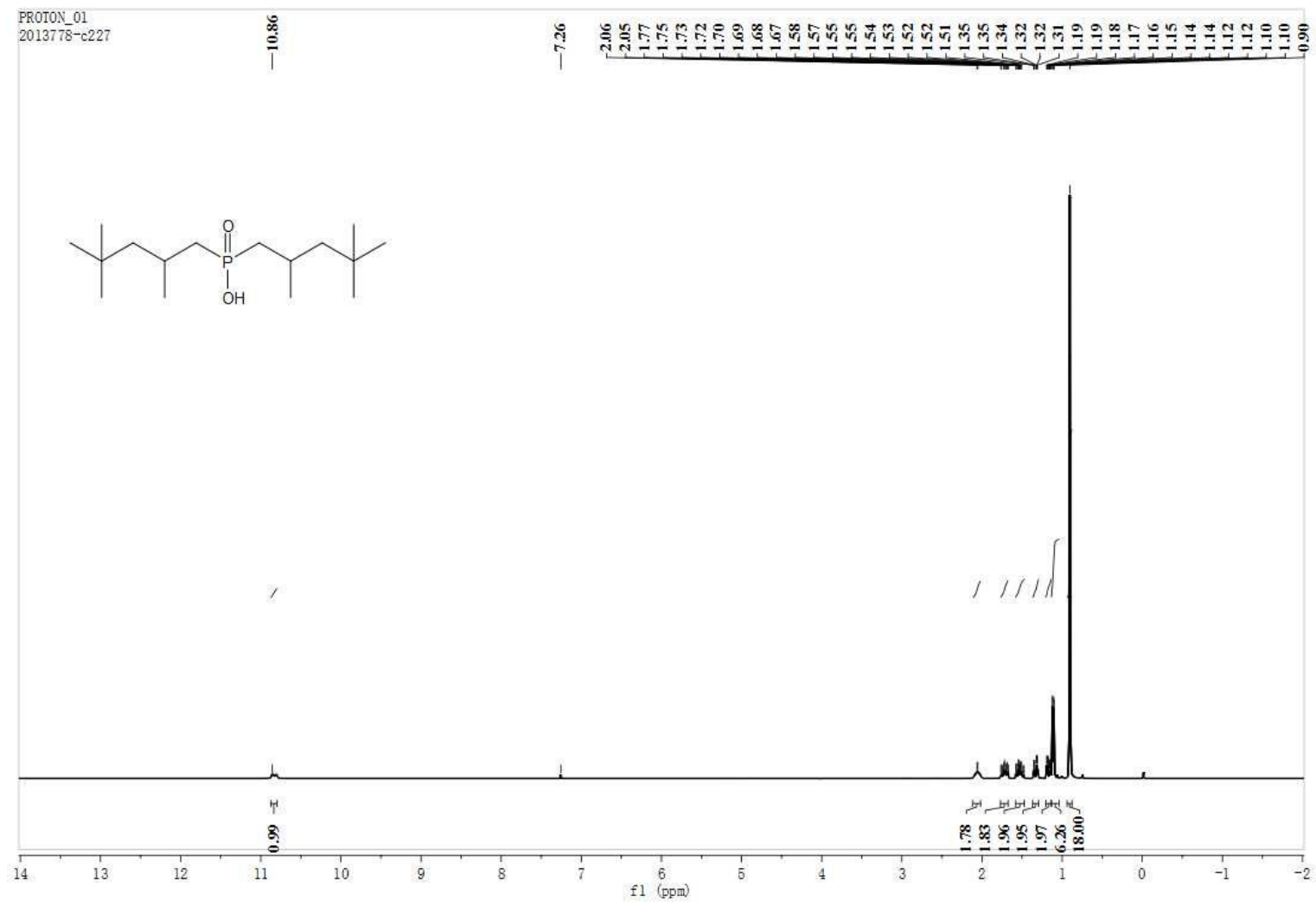
#### Reference:

1. G. J. Abruscato, R. G. Binder, Thomas T. Tidwell, J. Org. Chem., 1972, **37**, 1787–1790



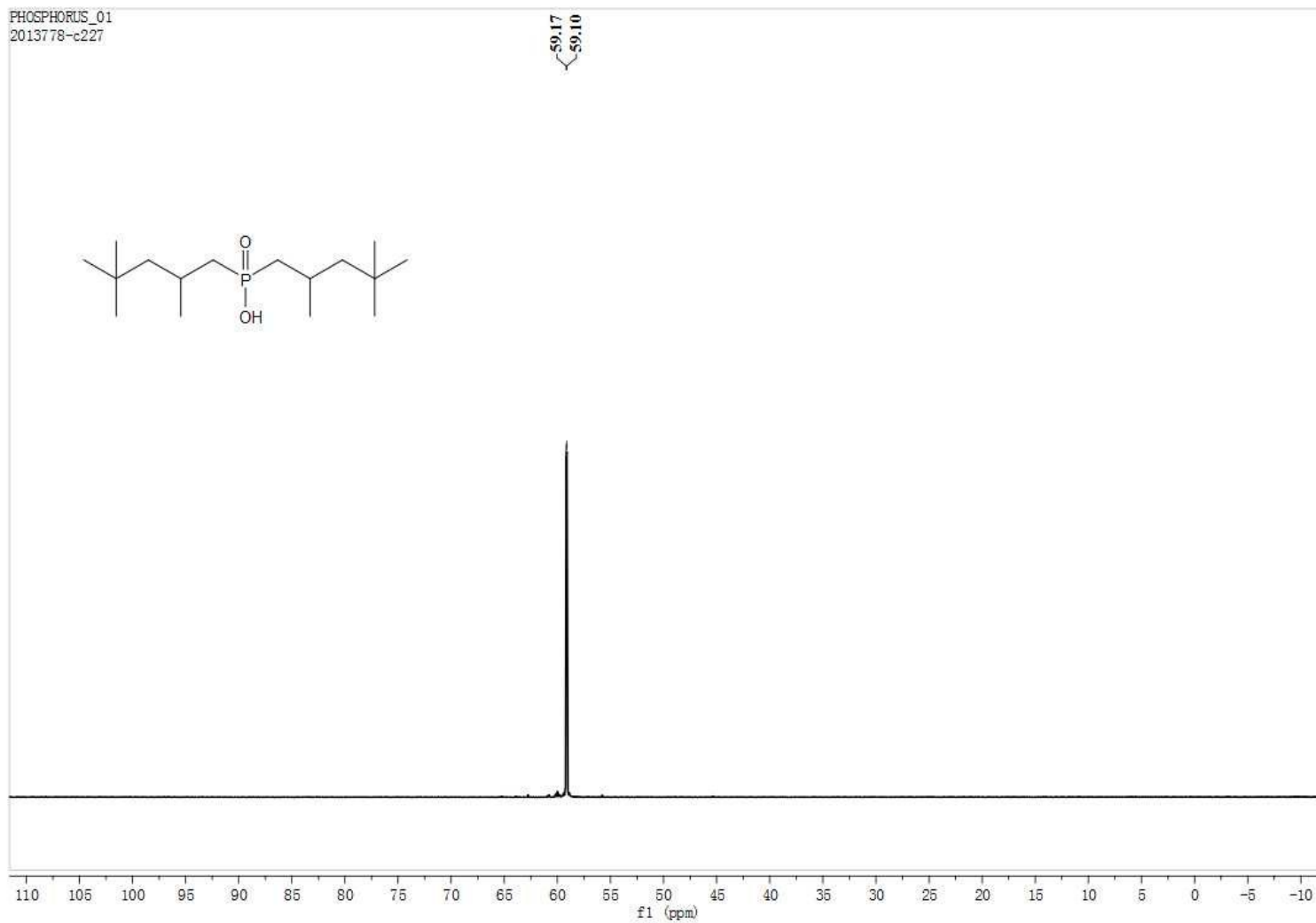


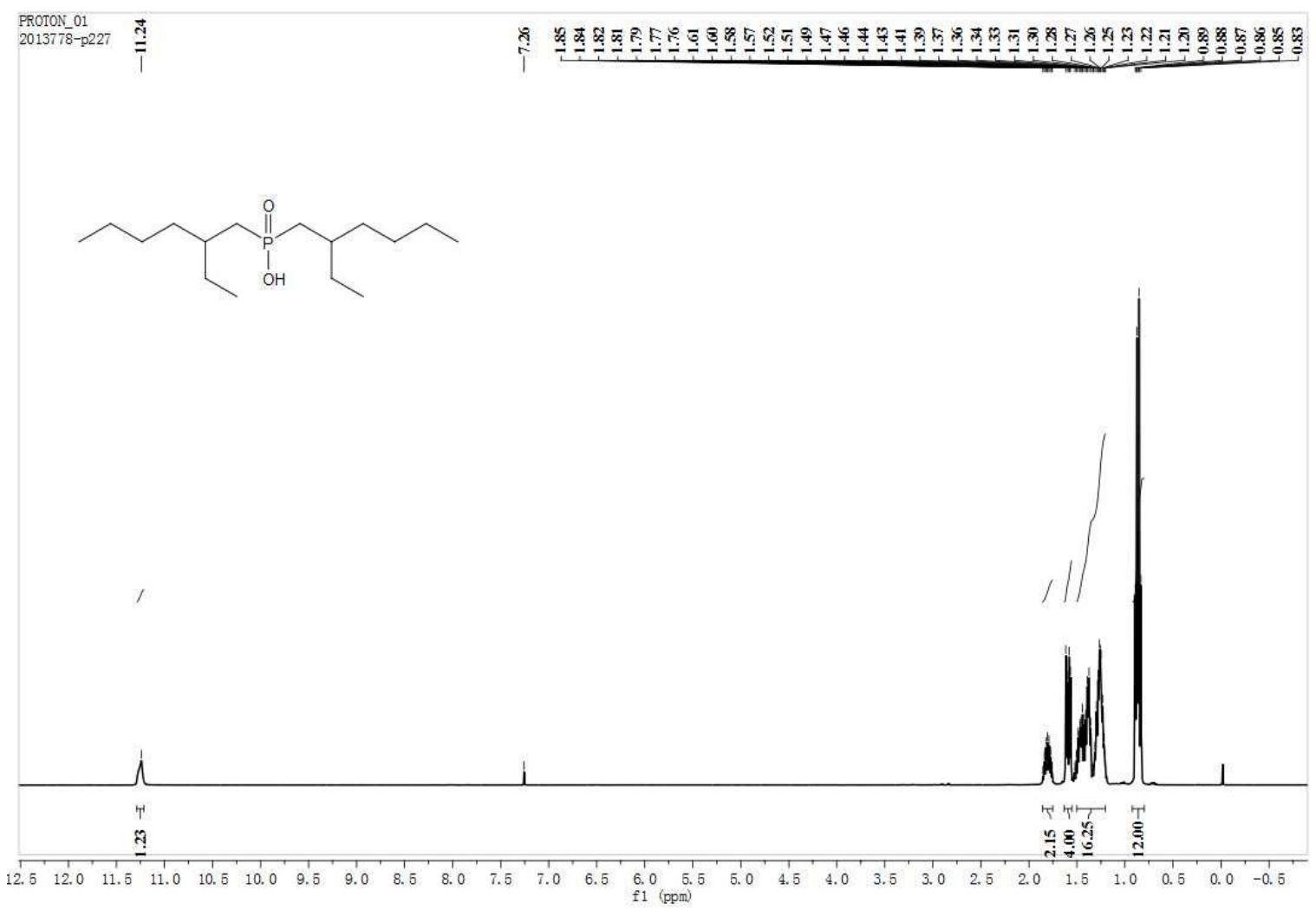
PROTON\_01  
2013778-c227



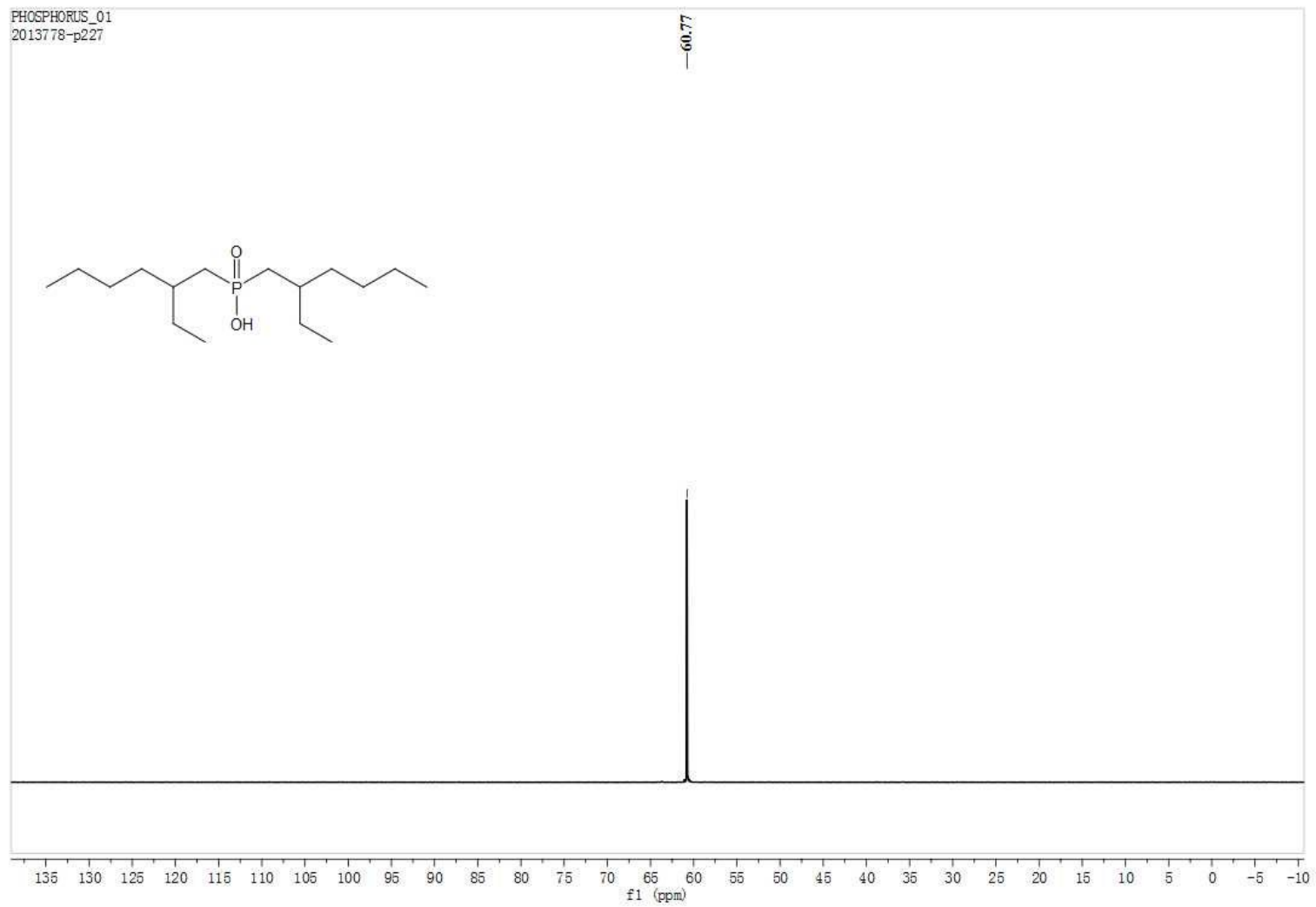


PHOSPHORUS\_01  
2013778-c227

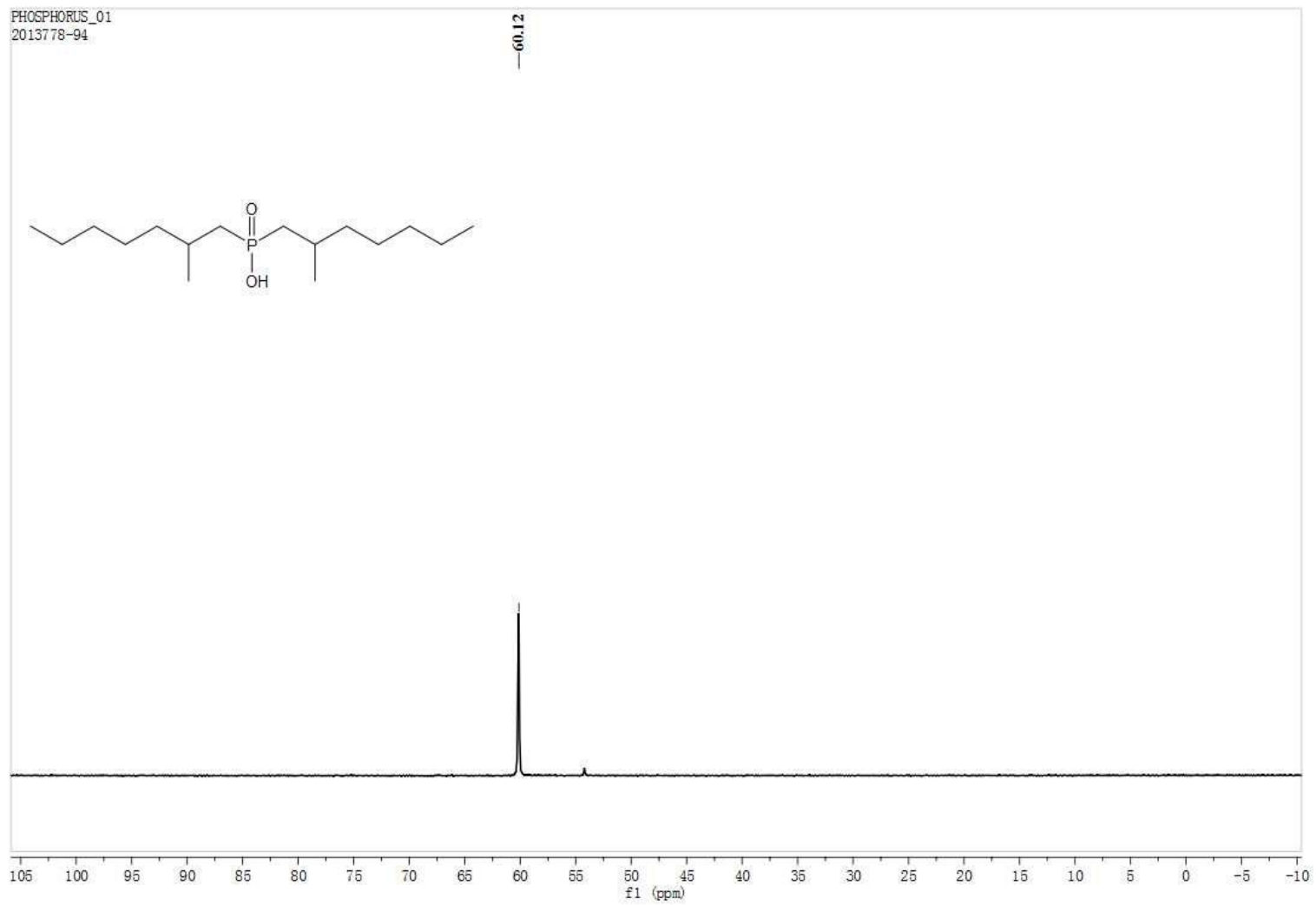


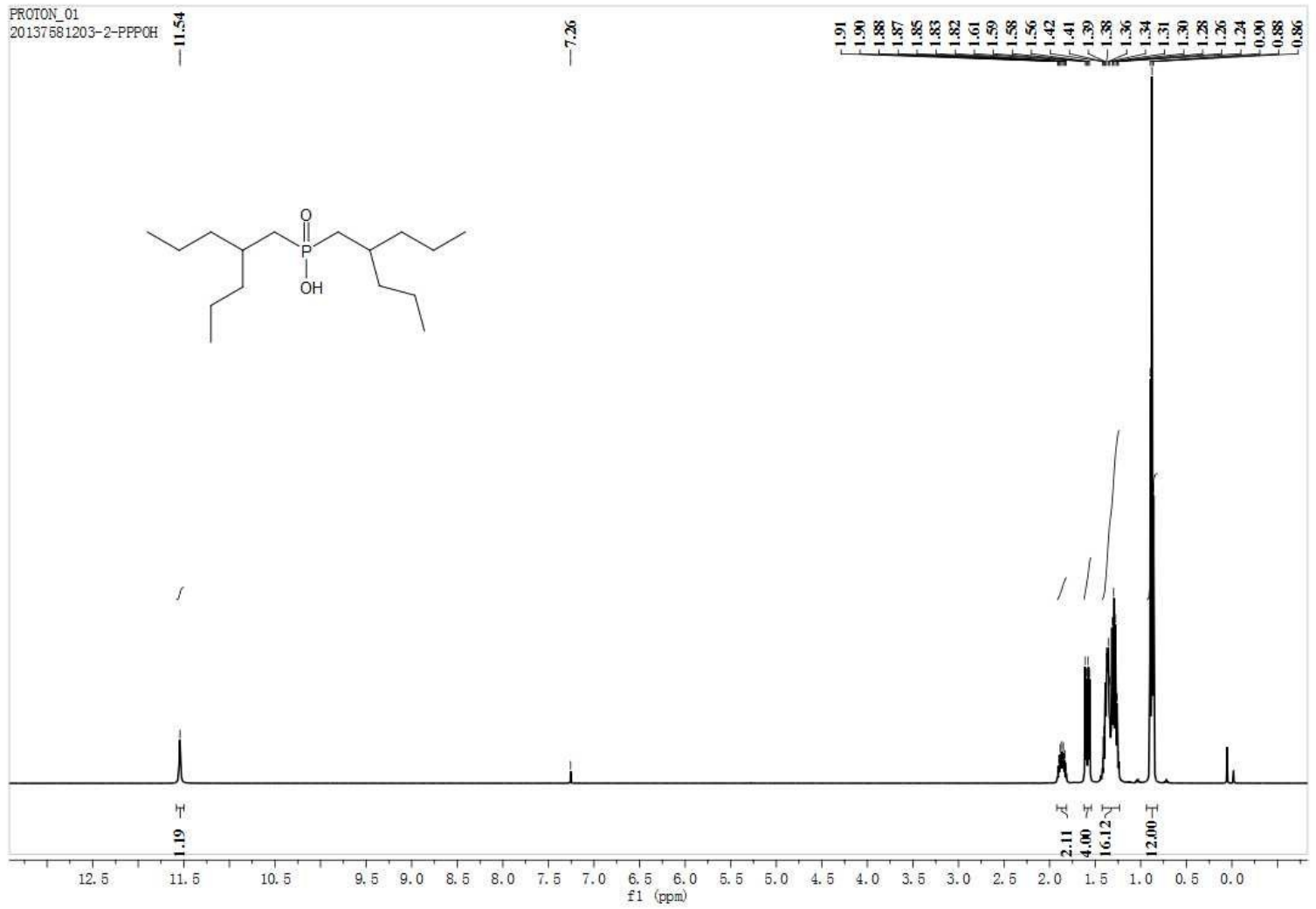


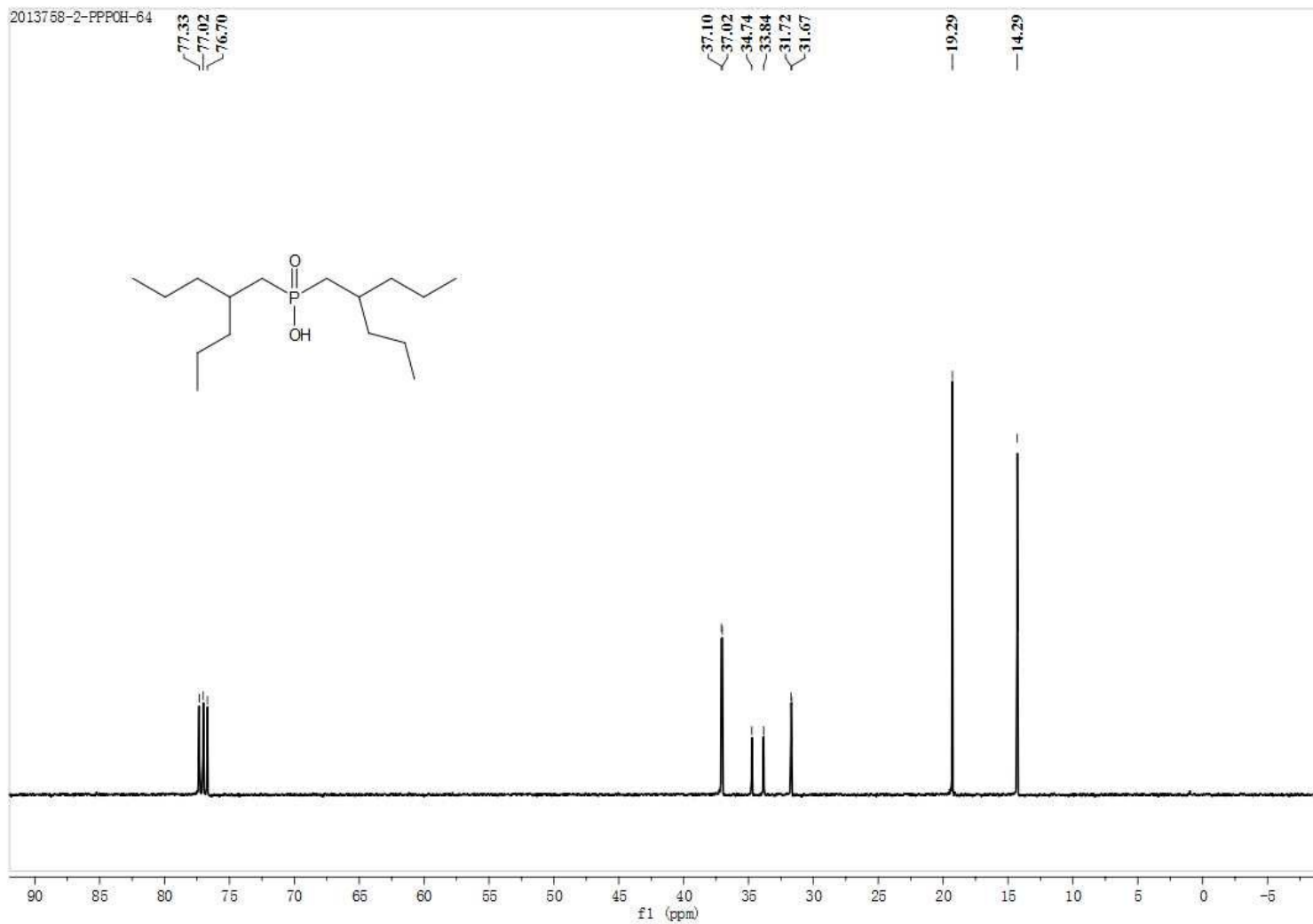
PHOSPHORUS\_01  
2013778-p227



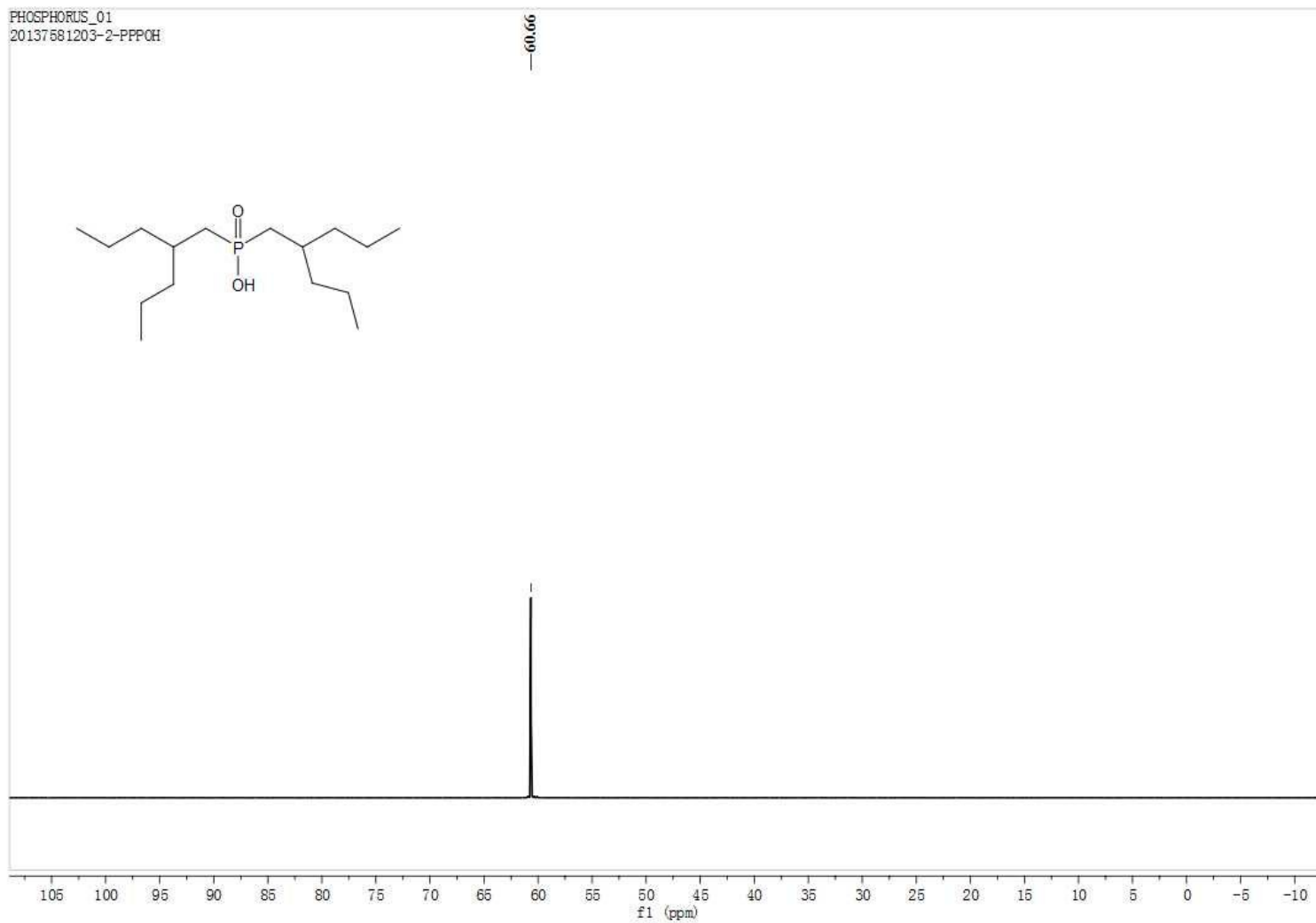
PHOSPHORUS\_01  
2013778-94

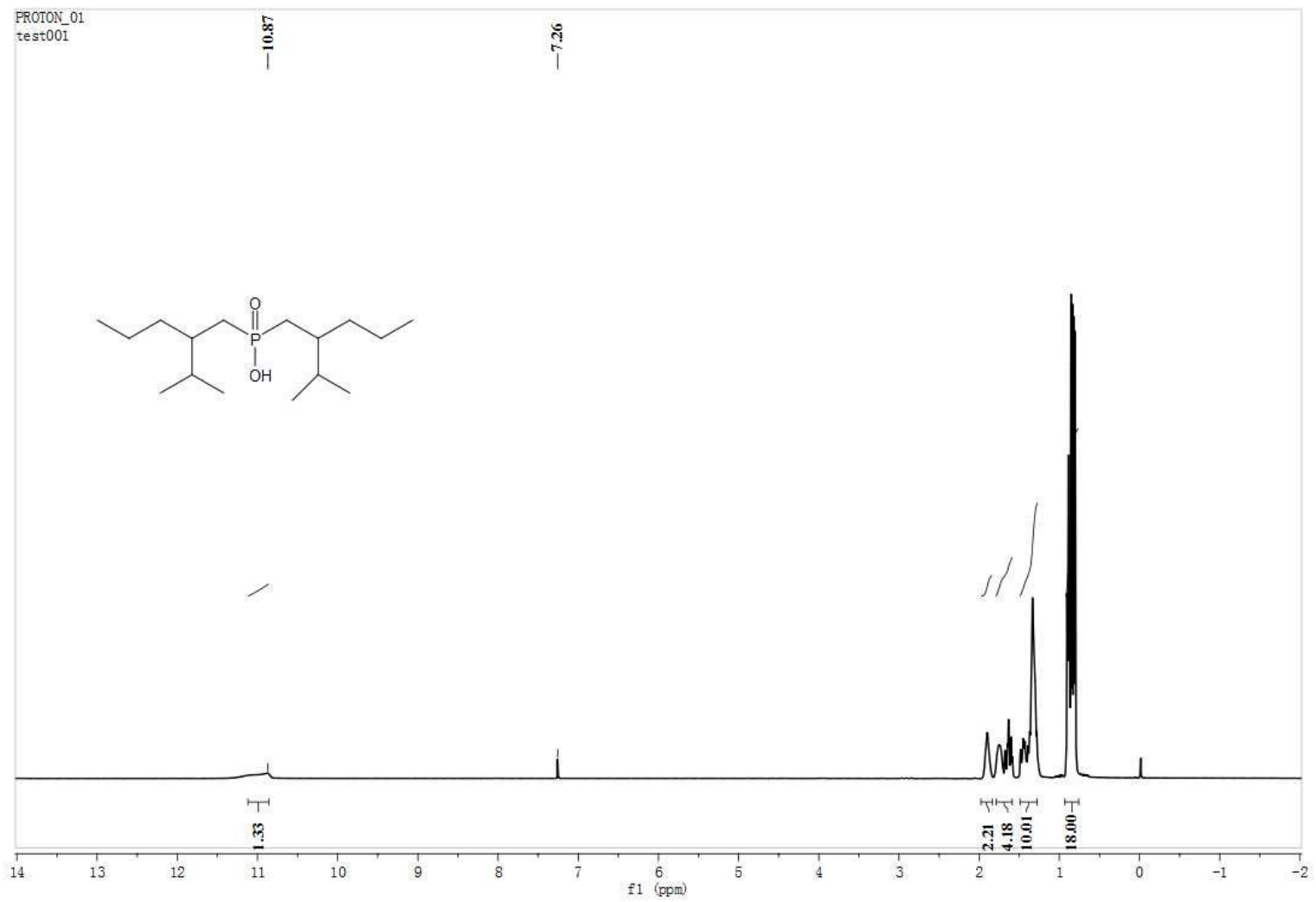






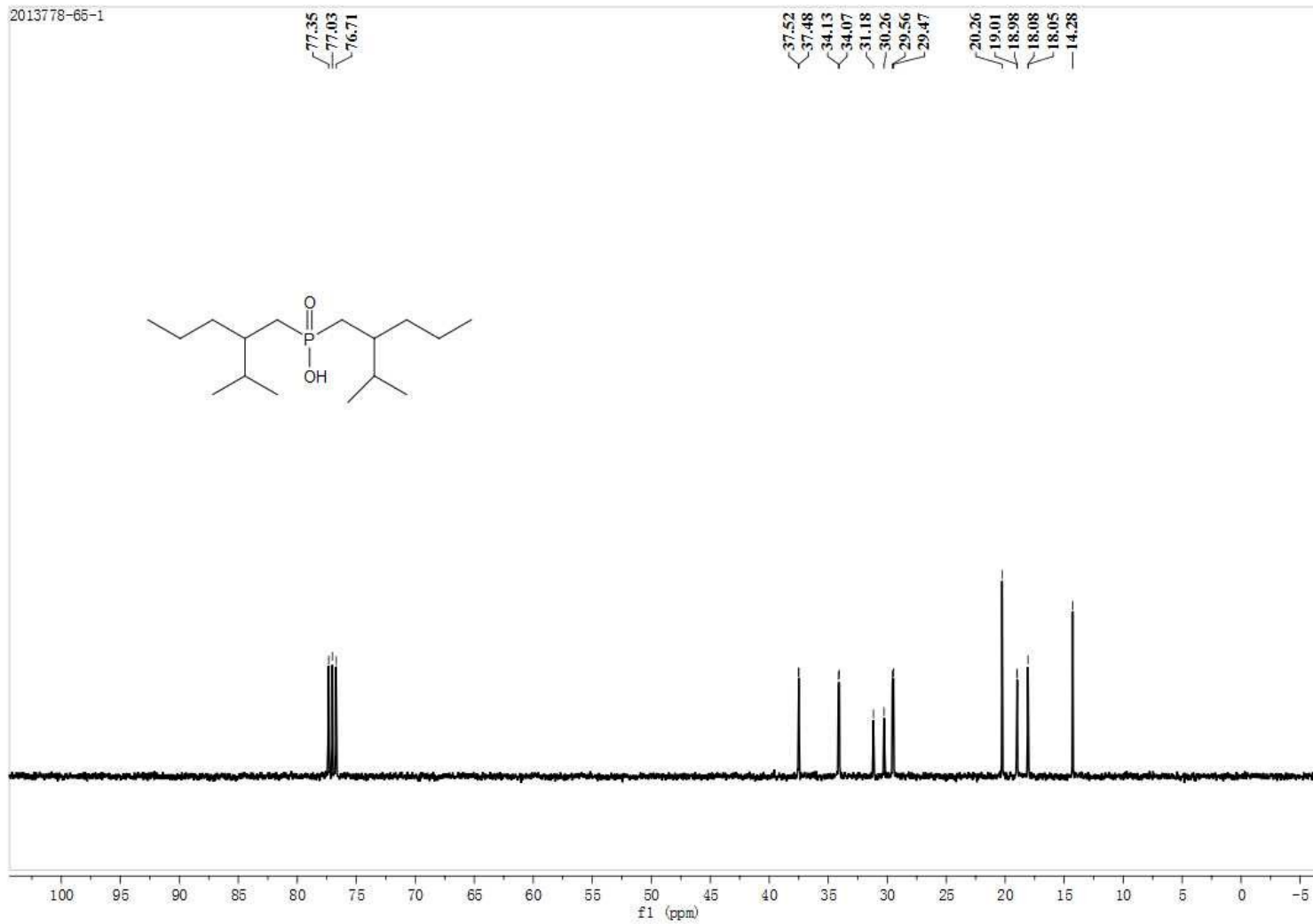
PHOSPHORUS\_01  
20137581203-2-PPPOH



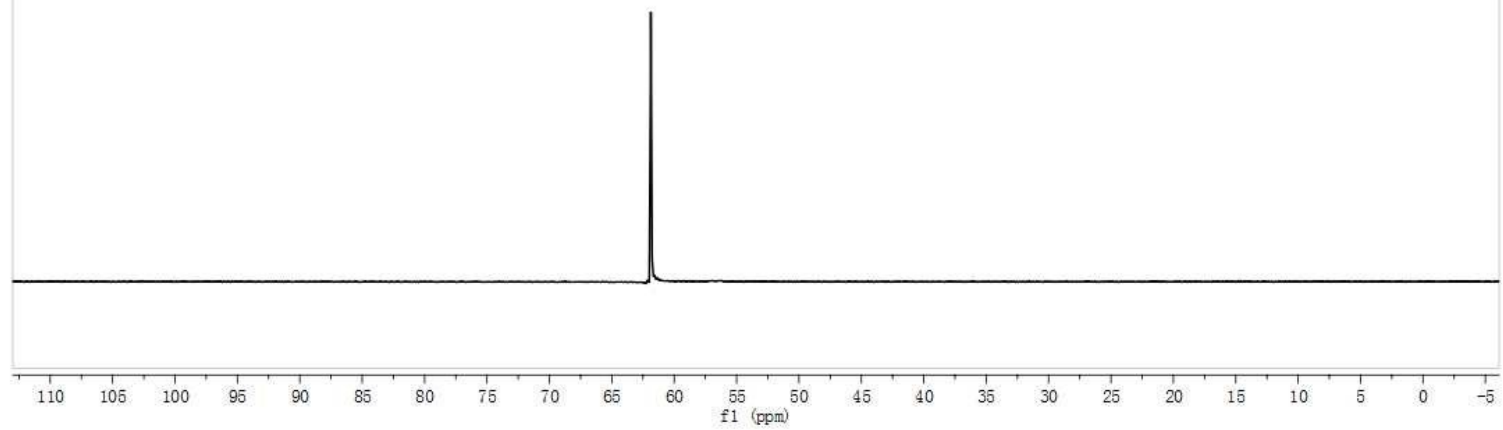
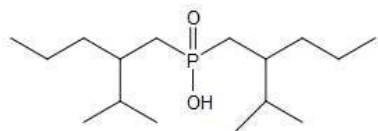


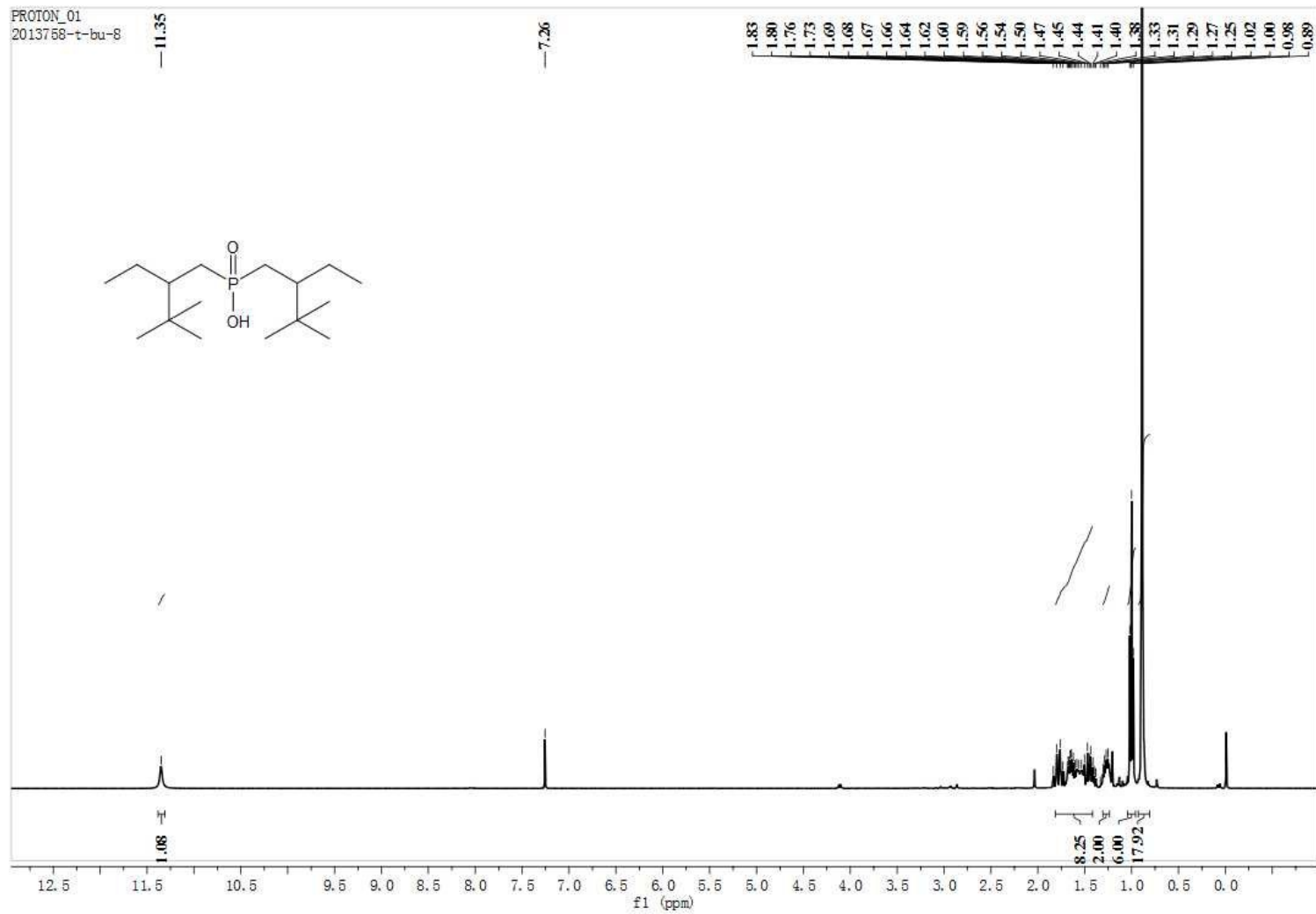


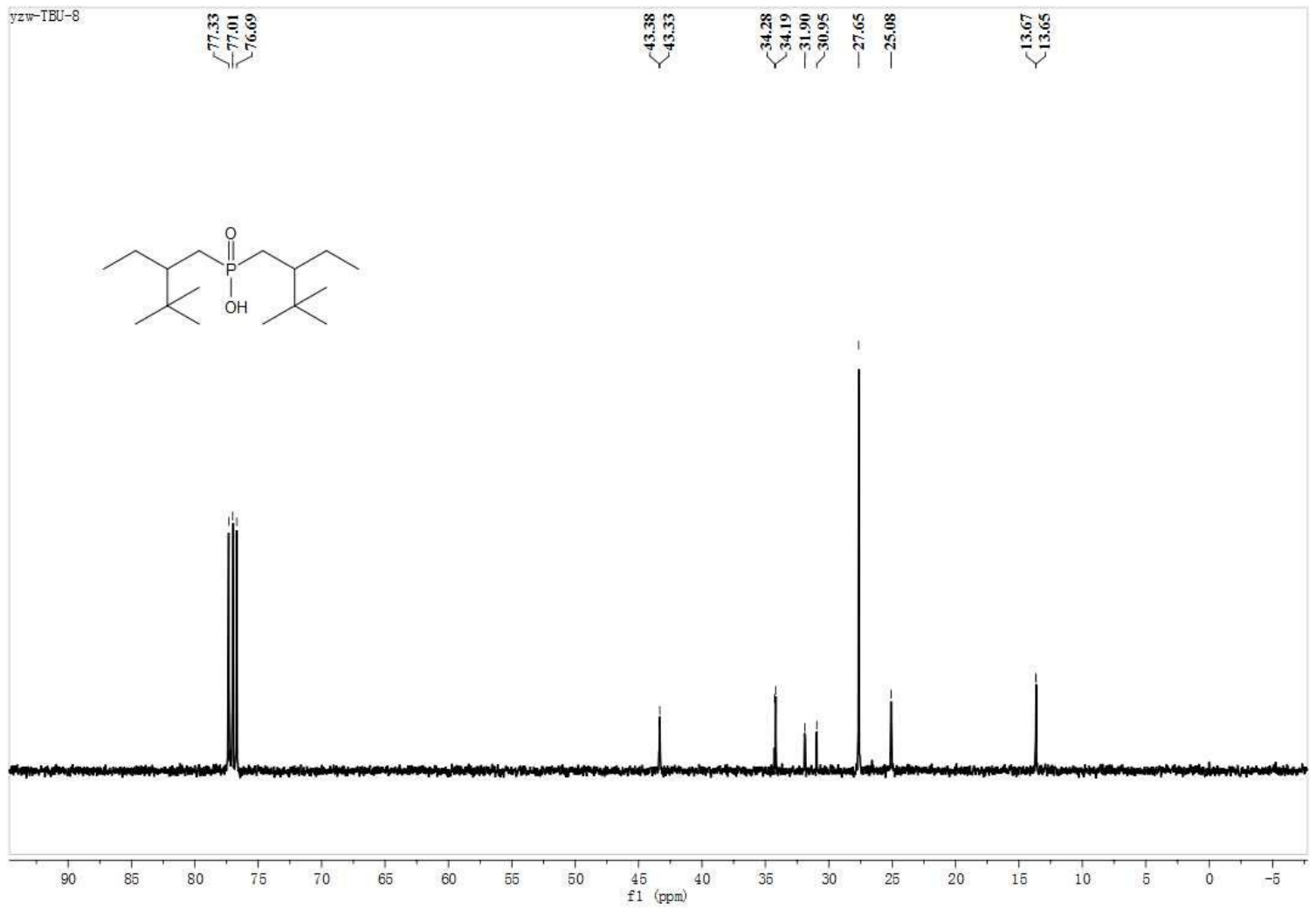
2013778-65-1



PHOSPHORUS\_01  
test001







PHOSPHORUS\_01  
2013758-t-bu-8

