

Supporting Information

A scalable electrochemical dehydrogenative cross-coupling of P(O)H compounds with RSH/ROH

Yujun Li, Qi Yang, Liquan Yang, Ning Lei and Ke Zheng*

E-mail: kzheng@scu.edu.cn

Contents

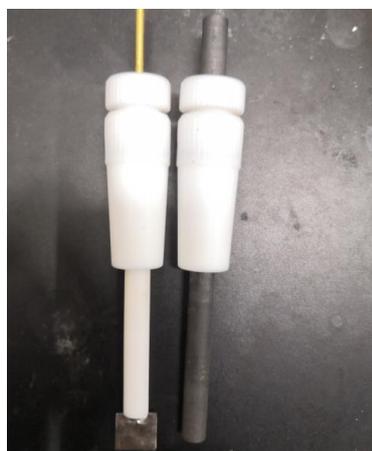
1. General information	1
2. Equipment and experiments pictures	1
3. Experimental procedure	3
4. General procedure for cyclic voltammetry (CV).....	9
5. Detection of H ₂ by GC	10
6. EPR experiments	11
7. X-Ray crystallographic data.....	13
8. Mechanistic studies.....	15
9. Characterization data.....	18
10. References.....	31
11. NMR spectra of product	32

1. General information

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Reactions were monitored by thin layer chromatography (TLC) using silica gel 60 F-254 plates. The instrument for electrolysis was dual display potentiostat (M8801) (made in China) or ElectraSyn 2.0. Cyclic voltammograms were obtained on a CHI 600E potentiostat. Gas chromatographic analyses were performed on SICT GC-2000III gas chromatography instrument with a FID detector. The anode electrode was graphite rod (ϕ 6 mm) and cathodic electrode was platinum plate (15 mm \times 10 mm \times 0.1 mm) or the anode electrode and cathode electrode all were platinum electrodes (15 mm \times 10 mm \times 0.1 mm). Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). NMR spectra were measured on a Bruker avance III HD400 (^1H at 400 MHz, ^{13}C at 101 MHz, ^{31}P at 162 MHz) magnetic resonance spectrometer. Chemical shifts (δ) are reported in ppm using tetramethylsilane as internal standard (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = triplet of doublets, m = multiplet), and coupling constants (J) were reported in Hertz (Hz). ESI-HRMS spectra were recorded on a UPLC of Thermo Q Exactive Focus.

Abbreviations used: GC = graphite rod; RVC = Reticulated Vitreous Carbon; DABCO = 1,4-Diaza[2.2.2]bicyclooctane; NMO = 4-methyl-morpholin-4-oxide; NHPI = *N*-Hydroxyphthalimide; Et_3N = Triethylamine; DMF = *N,N*-Dimethylformamide; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; TEMPO = 2,2,6,6-Tetramethyl-1-piperidyl-1-oxyl.

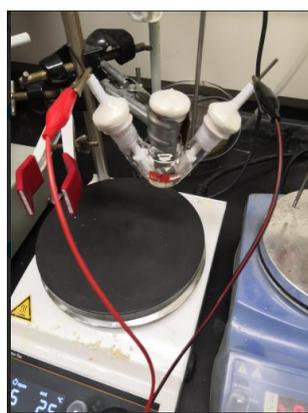
2. Equipment and experiments pictures



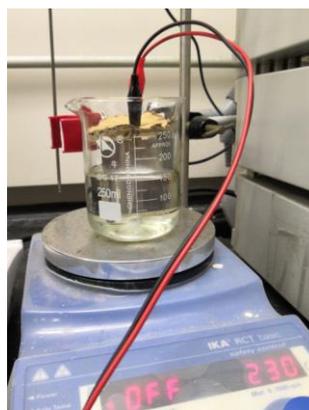
(a) electrodes



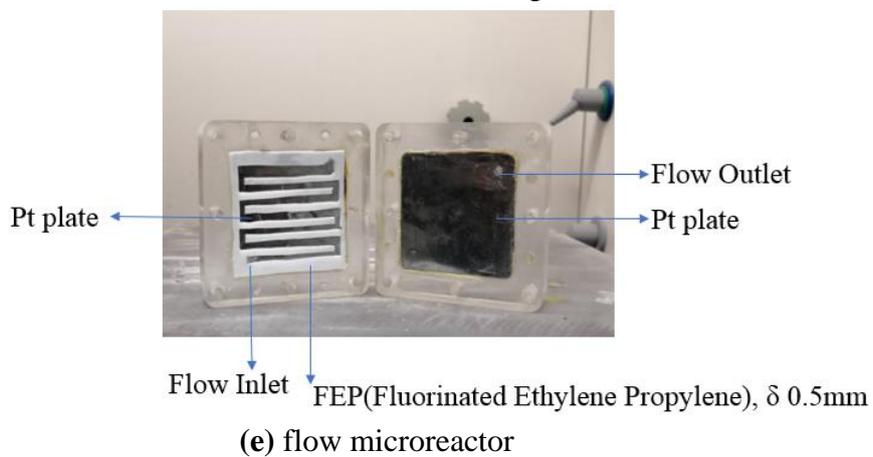
(b) power supply



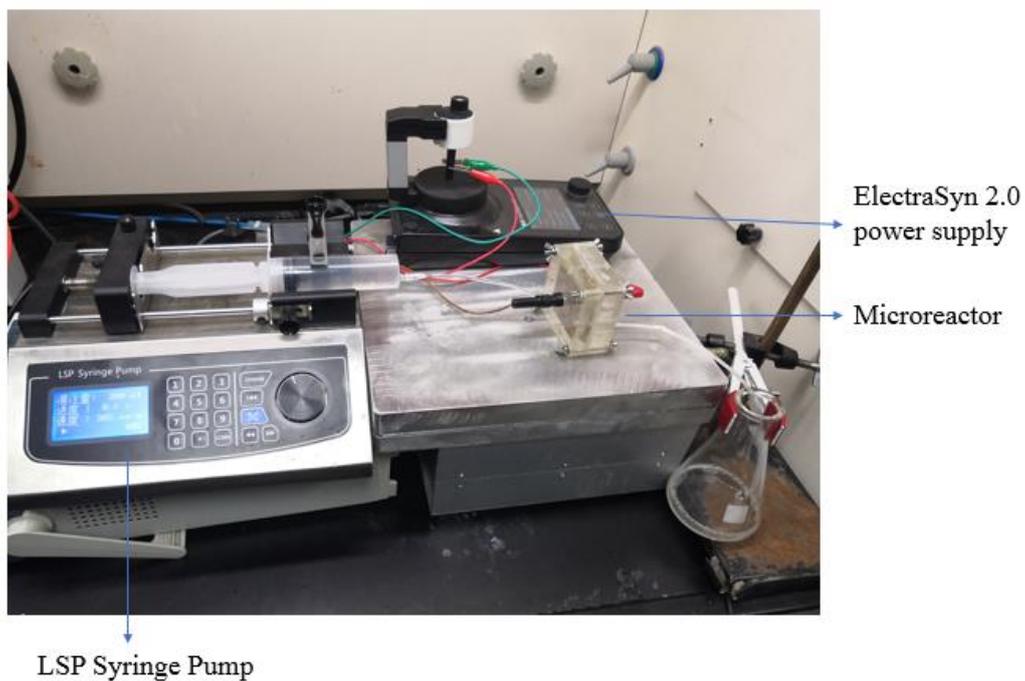
(c) reaction cell



(d) gram scale beaker



(e) flow microreactor

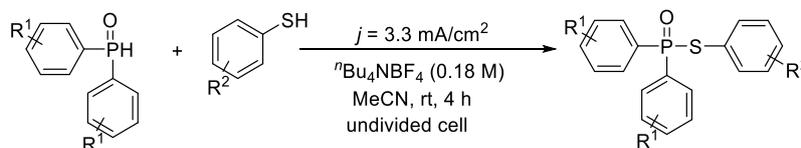


(f) Electrochemical flow setup

Figure S1 Electrolysis setup

3. Experimental procedure

3.1 General procedure for coupling with thiols

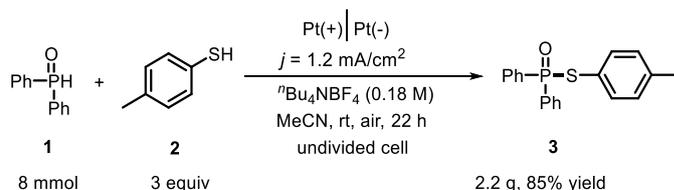


Method A: In an oven-dried undivided three-necked bottle (10 mL) equipped with a stir bar, diphenylphosphine oxide (0.3 mmol), thiol (0.9 mmol), $n\text{Bu}_4\text{BF}_4$ (0.9 mmol) were dissolved in MeCN (5 mL). The bottle was equipped with platinum plate (15 mm×10 mm×0.1 mm) as the anode and cathode. The resulting mixture was electrolyzed at a constant current mode with a constant current density of 3.3 mA/cm² under ambient temperature for corresponding time. When the reaction was finished, the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel (petroleum : ethyl ether = 5 : 1 - 3 : 1) to afford the desired product.

Method B: In an oven-dried undivided three-necked bottle (10 mL) equipped with a stir bar, diphenylphosphine oxide (0.3 mmol), thiol (0.9 mmol), $n\text{Bu}_4\text{BF}_4$ (0.9 mmol) were dissolved in DMF (5 mL). The bottle was equipped with platinum plate (15 mm×10 mm×0.1 mm) as the anode and cathode. The resulting mixture was electrolyzed at a constant current mode with a constant current density of 3.3 mA/cm² under ambient temperature for corresponding time. When the reaction was finished, the solution was extracted with EtOAc (3 × 12 mL) and brine (2 × 12 mL). The combined organic layer was dried with Na_2SO_4 , filtered the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel (petroleum : ethyl ether = 5 : 1 - 3 : 1) to afford the desired product.

Method C: In an exemplary procedure for the electrolysis with an ElectraSyn 2.0, diphenylphosphine oxide (0.3 mmol), thiol (0.9 mmol), $n\text{Bu}_4\text{BF}_4$ (0.9 mmol) were added in sequence to a 5 mL ElectraSyn vial with a stirring bar. The screw thread area of the vial was covered with a piece of Parafilm and screwed to finger-tight with the ElectraSyn vial cap equipped with a Pt electrode (anode) and a Pt electrode (cathode). The undivided cell was adapted to the ElectraSyn 2.0 vial holder and electrolysed under a constant current density of 3.3 mA/cm² for 4 h. When the reaction was finished, the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel (petroleum : ethyl ether = 5 : 1 - 3 : 1) to afford the desired product.

Procedure for gram scale synthesis:

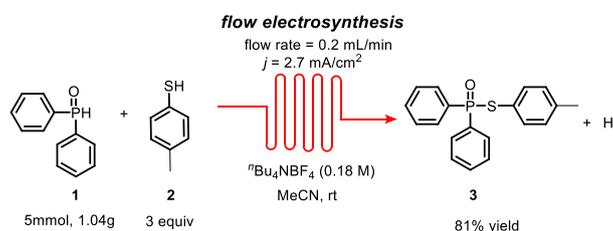


diphenylphosphine oxide (8 mmol, 1.61 g), thiol (24 mmol, 2.98 g), ${}^n\text{Bu}_4\text{BF}_4$ (24 mmol, 7.90 g) were placed in an beaker (250 mL). The beaker was equipped with a stir bar, followed by MeCN (135 mL). Two platinum plate (50 mm×50 mm×0.1 mm) were set up in the beaker. The resulting mixture was electrolyzed at a constant current mode with a constant current density of 1.2 mA/cm² under ambient temperature for 22 h. When the reaction was finished, the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel (petroleum : ethyl ether = 3 : 1) to afford the desired product.

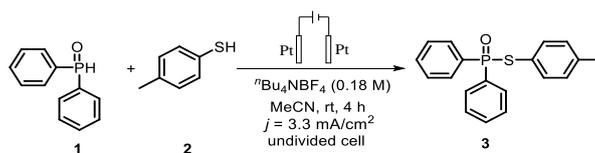
Flow chemistry:

FEP (fluorinated ethylene propylene) with channel 3 mm width; thickness: 0.5 mm; total length of the pipeline of 30.1 cm; volume: 450 μL ; exposed electrode surface: 9.57 cm². (Figure S1e)

The device comprises a micro-flow electrochemical reactor made out of two bodies (75x75x25 mm, Figure S1), which can be polymer. The bodies have a square space in the centre (50x50 mm²), where the two-platinum plate (thickness 0.1 mm) electrodes are placed and FEP was sandwiched between two platinum electrodes. The housing of the reactor has a hole in the middle that allows an easy connection of the electrodes to the power supply by a copper wire. This plate also has 2 holes, one for the inlet and one for the outlet of the reaction solution.



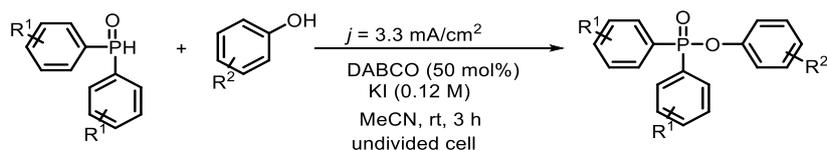
The **1** (5 mmol, 1.04g), **2** (15 mmol, 1.86 g) and ${}^n\text{Bu}_4\text{BF}_4$ (15 mmol, 4.92 g) were dissolved in MeCN (84 mL) and flowed through the electrochemical microreactor (volume = 450 μL) in a flow rate of 0.2 mL/min (Figure S1). A constant current density of 2.7 mA/cm² was employed. The solution was concentrated under reduced pressure on a rotary evaporator. The residue was chromatographed through silica gel eluting with petroleum/ethyl ether to give the product.

Table S1 Optimization of the reaction conditions^[a]

Entry	Deviation from standard conditions	Yield ^[b] (%)
1	None	84
2 ^[c]	1 equiv thiol	49
3 ^[c]	2 equiv thiol	69
4 ^[c]	3 equiv thiol	76
5	LiClO_4 instead of $n\text{Bu}_4\text{NBF}_4$	62
6	$n\text{Bu}_4\text{NPF}_6$ instead of $n\text{Bu}_4\text{NBF}_4$	71
7	MeCN = 4 mL	62
8	MeCN = 7 mL	56
9	DMF instead of MeCN	83
10	MeOH instead of MeCN	49
11	GC (+) Pt (-) instead of Pt (+) Pt (-)	58
12	RVC (+) Pt (-) instead of Pt (+) Pt (-)	68
13	$j = 2.7 \text{ mA/cm}^2$ instead of $j = 3.3 \text{ mA/cm}^2$	64
14	$j = 4.7 \text{ mA/cm}^2$ instead of $j = 3.3 \text{ mA/cm}^2$	56
15	10 mol % Cp_2Fe as additive	58
16	10 mol % $n\text{Bu}_4\text{NBr}$ as additive	81
17	without current	n.d.

[a] Standard conditions: Pt anode, Pt cathode, **1** (0.3 mmol), **2** (0.9 mmol), $n\text{Bu}_4\text{NBF}_4$ (0.18 M), MeCN (5.0 mL), rt, constant current = 5 mA ($j = 3.3 \text{ mA/cm}^2$), 4 h. [b] Isolated yield. [c] 0.12 M $n\text{Bu}_4\text{NBF}_4$

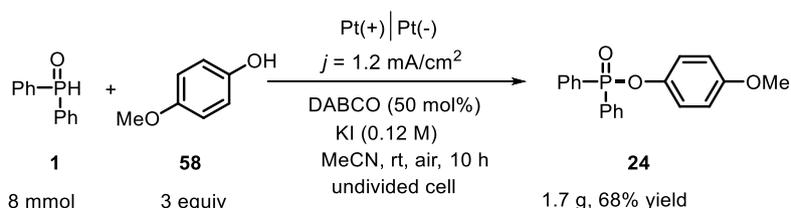
3.2 General procedure for diphenylphosphine oxide with phenol



Method A: In an oven-dried undivided three-necked bottle (10 mL) equipped with a stir bar, diphenylphosphine oxide (0.3 mmol), phenol (0.9 mmol), KI (0.6 mmol), DABCO (0.15 mmol) were dissolved in MeCN (5 mL) and stir for 10 minutes. The bottle was equipped with graphite rod (ϕ 6 mm, about 8 mm immersion depth in solution) as the anode and platinum plate (15 mm \times 10 mm \times 0.1 mm) as the cathode. The resulting mixture was electrolyzed at a constant current mode with a constant current density of 3.3 mA/cm² under ambient temperature for corresponding time. When the reaction was finished, the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel (petroleum : ethyl ether = 5 : 1 - 1 : 1) to afford the desired product.

Method B: In an exemplary procedure for the electrolysis with an ElectraSyn 2.0, diphenylphosphine oxide (0.3 mmol), phenol (0.9 mmol), KI (0.6 mmol), DABCO (0.15 mmol) were added in sequence to a 5 mL ElectraSyn vial with a stirring bar. The screw thread area of the vial was covered with a piece of Parafilm and screwed to finger-tight with the ElectraSyn vial cap equipped with a graphite electrode (anode) and a Pt electrode (cathode). The undivided cell was adapted to the ElectraSyn 2.0 vial holder and electrolysed under a constant current density of 3.3 mA/cm² for 3.5 h. When the reaction was finished, the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel (petroleum : ethyl ether = 5 : 1 - 1 : 1) to afford the desired product.

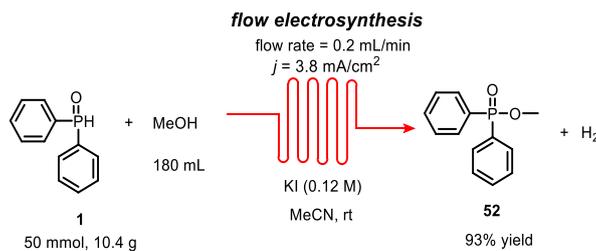
Procedure for gram scale synthesis:



Diphenylphosphine oxide (8 mmol, 1.61g), phenol (24 mmol, 2.98 g), KI (16 mmol, 2.66 g), DABCO (4 mmol, 450 mg) were placed in an beaker (250 mL). The beaker was equipped with a stir bar, followed by MeCN (135 mL) and stir for 20 minutes. Two platinum plate (50 mm \times 50 mm \times 0.1 mm) were set up in the beaker. The resulting mixture was electrolyzed at a constant current mode with a constant current density of 1.2 mA/cm² under ambient temperature for 10 h. When the reaction was finished, the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel (petroleum : ethyl ether = 3 : 1) to afford the desired product.

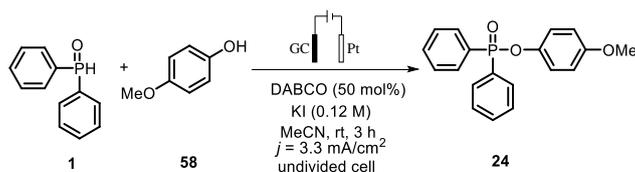
Flow chemistry:

FEP (fluorinated ethylene propylene) with channel 3 mm width; thickness: 0.5 mm.; total length of the pipeline of 30.1 cm; volume: 450 μ L; exposed electrode surface: 9.57 cm². (Figure S1e) The device comprises a micro-flow electrochemical reactor made out of two bodies (75x75x25 mm, Figure S1), which can be polymer. The bodies have a square space in the centre (50x50 mm²), where the two-platinum plate (thickness 0.1 mm) electrodes are placed and FEP was sandwiched between two platinum electrodes. The housing of the reactor has a hole in the middle that allows an easy connection of the electrodes to the power supply by a copper wire. This plate also has 2 holes, one for the inlet and one for the outlet of the reaction solution.



The **1** (50 mmol, 10.4 g) and KI (100 mmol, 16.7 g) was dissolved in MeCN/MeOH (4:1, 0.84 L) and flowed through the electrochemical microreactor (volume = 450 μ L) in a flow rate of 0.2 mL/min (Figure S1). A constant current density of 3.8 mA/cm² was employed. The solution was concentrated under reduced pressure on a rotary evaporator. The residue was chromatographed through silica gel eluting with petroleum/ethyl ether to give the product.

Table S2 Optimization of the reaction conditions^[a]



Entry	Deviation from standard conditions	Yield ^[b] (%)
1	None	78
2 ^[c]	No DABCO	25
3	0.25 equiv DABCO	72
4	1.0 equiv DABCO	68
5	1.5 equiv DABCO	69
6	quinoline instead of DABCO	65
7	NMO instead of DABCO	47
8	NHPI instead of DABCO	n.d.
9 ^[c]	Et ₃ N instead of DABCO	n.d.
10 ^[c]	DBU instead of DABCO	n.d.
11	ⁿ Bu ₄ NI instead of KI	68
12	NaI instead of KI	77
13	NH ₄ I instead of KI	n.d.
14	LiBr instead of KI	n.d.
15	ⁿ Bu ₄ NBF ₄ instead of KI	trace
16	Pt (+) Pt (-) instead of GC (+) Pt (-)	77
17	C (+) Pt (-) instead of GC (+) Pt (-)	71
18	GC (+) GC (-) instead of GC (+) Pt (-)	57
19	$j = 2.0 \text{ mA/cm}^2$ instead of $j = 3.3 \text{ mA/cm}^2$, 4 h	50
20	$j = 4.7 \text{ mA/cm}^2$ instead of $j = 3.3 \text{ mA/cm}^2$, 2 h 30 min	67
21	2.5 V instead of $j = 3.3 \text{ mA/cm}^2$, 2 h 10 min	66
22	without current	n.d.

[a] Standard conditions: GC anode, Pt cathode, **1** (0.3 mmol), **58** (0.9 mmol), DABCO (50 mol%), KI (0.12 M), MeCN (5.0 mL), rt, constant current = 5 mA ($j = 3.3 \text{ mA/cm}^2$), 3 h. [b] Isolated yield.

[c] 5 equiv **58**. n.d. = not detected

4. General procedure for cyclic voltammetry (CV)

Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line at room temperature. The working electrode was a platinum disk electrode, the counter electrode a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution, and separated from reaction by a salt bridge. 10 mL of MeCN containing 0.1 M $n\text{Bu}_4\text{NBF}_4$ were poured into the electrochemical cell in all experiments. Concentration: 0.03 M. The scan rate is 0.1 V/s, ranging from 0 V to 2.5 V. The peak potentials vs. Ag/AgCl for used. The obvious oxidation peaks of 4-methylbenzenethiol and 4-methoxyphenol were observed 1.859V , 1.511V respectively.

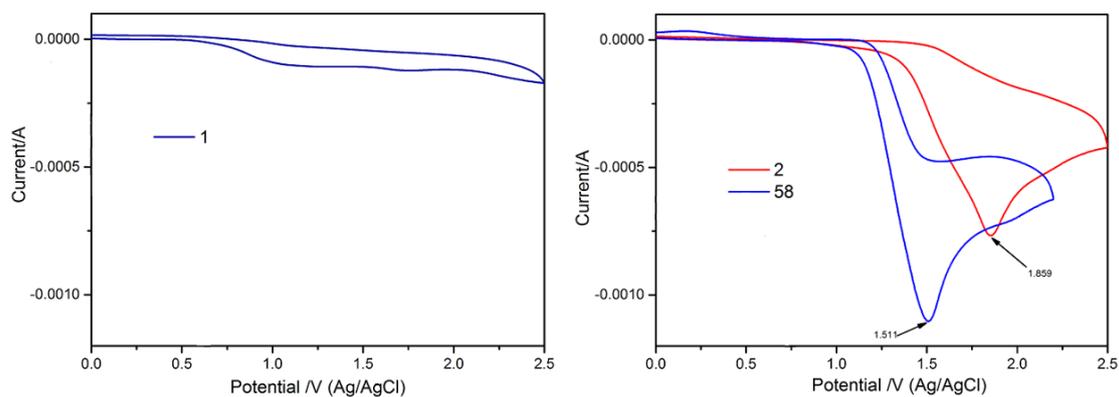
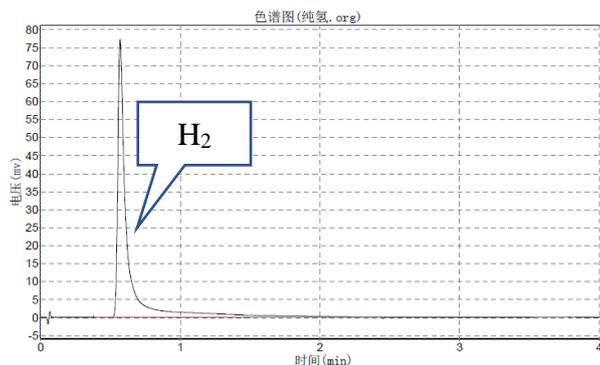


Figure S2 Cyclic voltammetry experiment of reactants

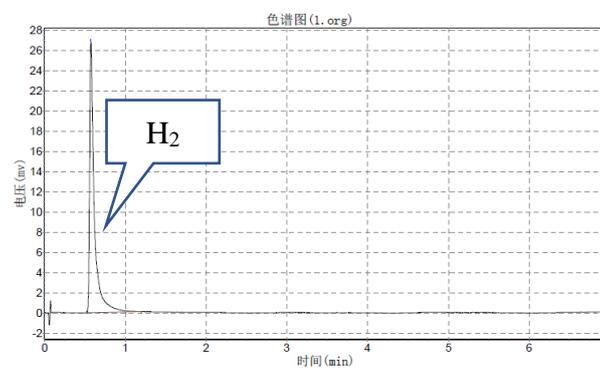
5. Detection of H₂ by GC



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		0.573	76291.617	354313.906	100.0000
总计			76291.617	354313.906	100.0000

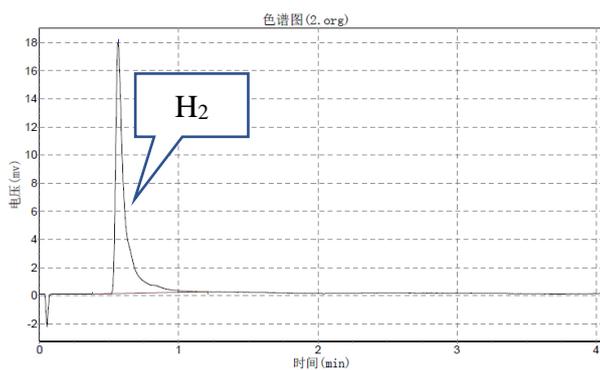
(a) standard hydrogen sample



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		0.573	26812.145	108501.555	100.0000
总计			26812.145	108501.555	100.0000

(b) P(O)H-SH



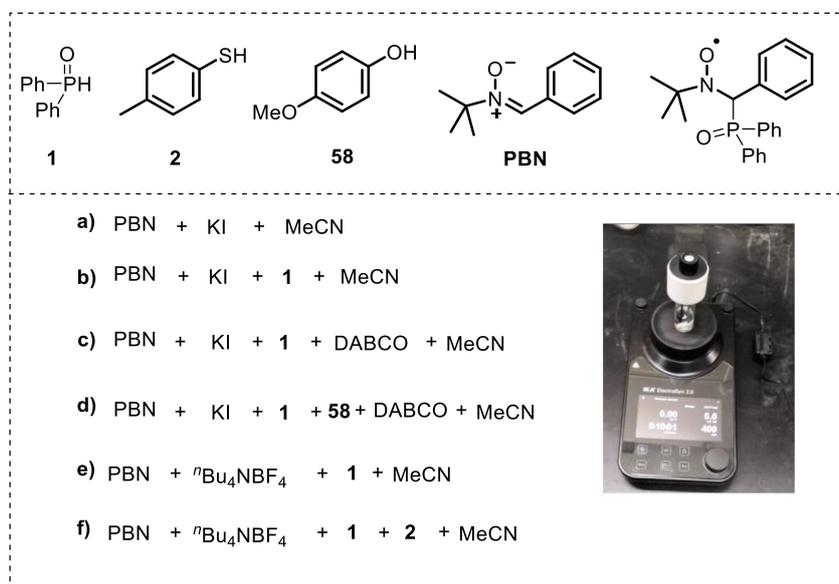
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		0.563	17893.477	80247.000	100.0000
总计			17893.477	80247.000	100.0000

(c) P(O)H-OH

6. EPR experiments

EPR spectra were recorded at room temperature on a Bruker ESP-300E: Receiver Gain = 1.78×10^4 ; Phase = 0 deg; Harmoni = 1; Mod. Frequency = 100.000 KHz; Mod. Amplitude = 6.00 G; Center Field = 3360.00 G; Sweep width 90.000 G; Resolution = 2048 points; Conversion Time = 40.00 ms; Time const. = 20.48 ms; Sweep time = 81.92 s; Power = 60.39 mw.



EPR study of reaction a:

Under constant current conditions, a ElectraSyn 2.0 equipped with a stir bar was loaded with KI (0.6 mmol) and PBN (0.30 mmol) in 5.0 mL MeCN was stirred at rt. After 10 mins, the solution sample was taken out into a small tube and analyzed by EPR.

EPR study of reaction b:

Under constant current conditions, a ElectraSyn 2.0 equipped with a stir bar was loaded with **1** (0.30 mmol), KI (0.6 mmol) and PBN (0.30 mmol) in 5.0 mL MeCN was stirred at rt. After 10 mins, the solution sample was taken out into a small tube and analyzed by EPR.

EPR study of reaction c:

Under constant current conditions, a ElectraSyn 2.0 equipped with a stir bar was loaded with **1** (0.30 mmol), DABCO (0.15 mmol), KI (0.6 mmol) and PBN (0.30 mmol) in 5.0 mL MeCN was stirred at rt. After 10 mins, the solution sample was taken out into a small tube and analyzed by EPR.

EPR study of reaction d:

Under constant current conditions, a ElectraSyn 2.0 equipped with a stir bar was loaded with **1** (0.30 mmol), **58** (0.90 mmol), DABCO (0.15 mmol), KI (0.6 mmol) and PBN (0.30 mmol) in 5.0 mL MeCN was stirred at rt. After 10 mins, the solution sample was taken out into a small tube and analyzed by EPR.

EPR study of reaction e:

Under constant current conditions, a ElectraSyn 2.0 equipped with a stir bar was loaded with **1** (0.30 mmol), $n\text{Bu}_4\text{NBF}_4$ (0.9 mmol) and PBN (0.30 mmol) in 5.0 mL MeCN was stirred at rt. After 10 mins, the solution sample was taken out into a small tube and analyzed by EPR.

EPR study of reaction f:

Under constant current conditions, a ElectraSyn 2.0 equipped with a stir bar was loaded with **1** (0.30 mmol), **2** (0.90 mmol), $n\text{Bu}_4\text{NBF}_4$ (0.9 mmol) and PBN (0.30 mmol) in 5.0 mL MeCN was stirred at rt. After 10 mins, the solution sample was taken out into a small tube and analyzed by EPR.

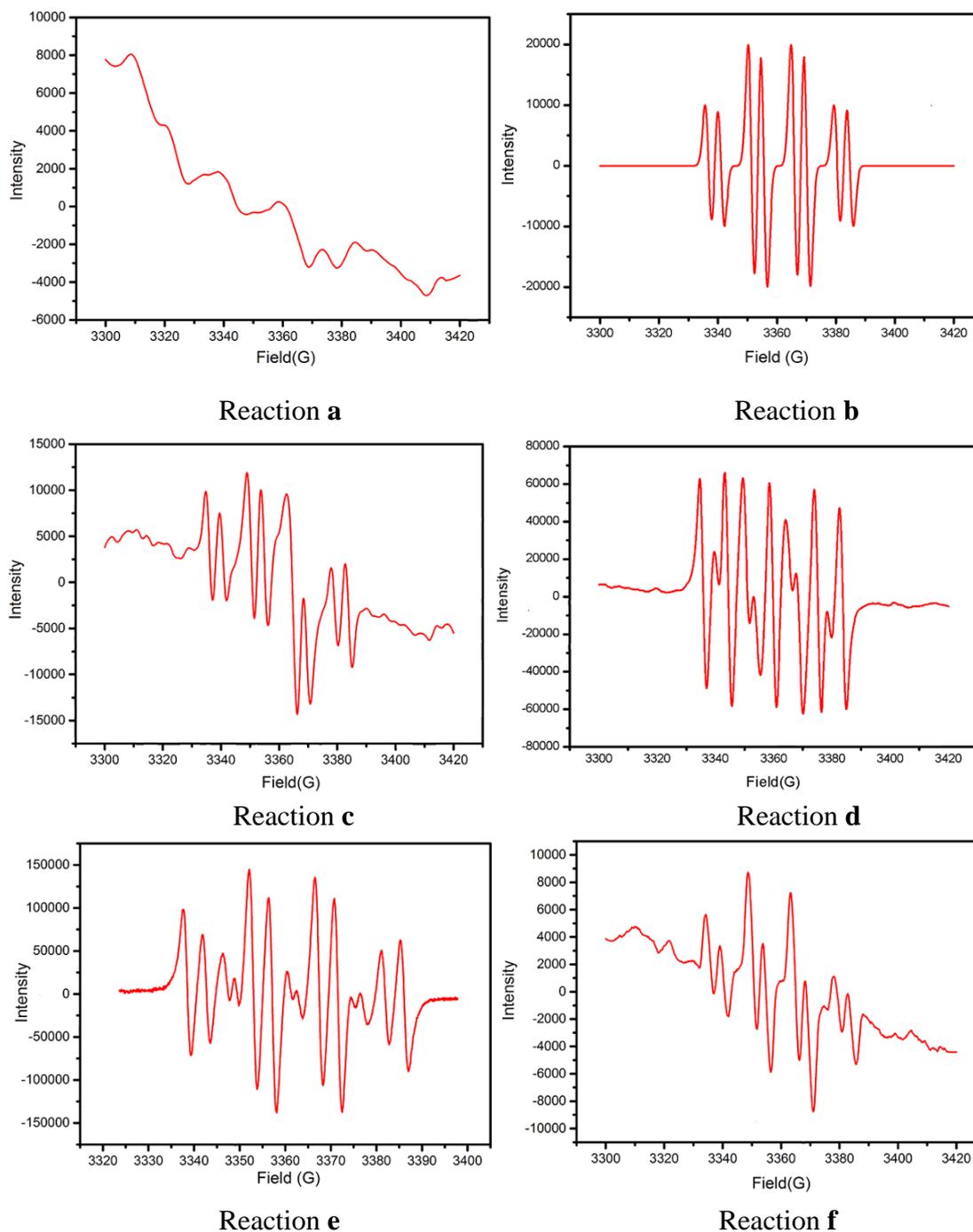
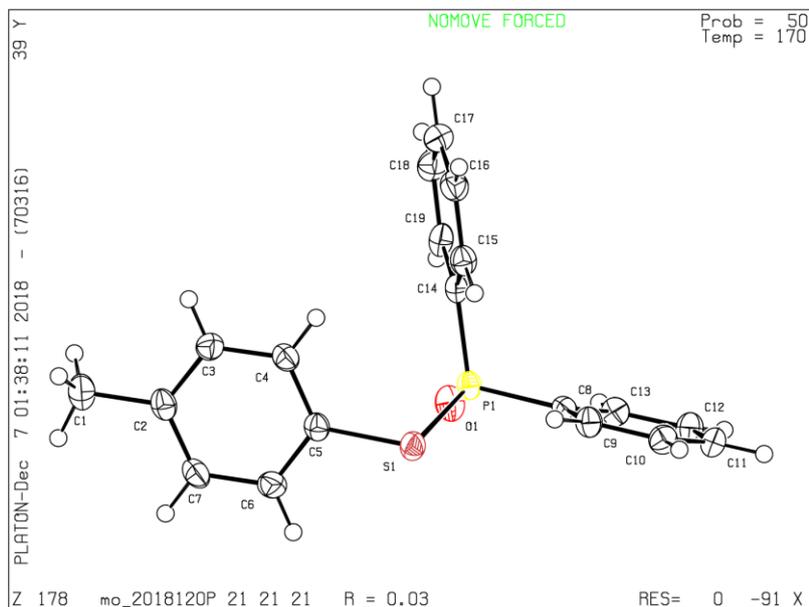
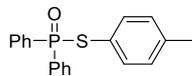


Figure S3 EPR experiments pictures

7. X-Ray crystallographic data

X-Ray crystallographic data of 3:



Bond precision: C-C = 0.0036 Å

Wavelength=0.71073

Cell: a=8.5391(4) b=11.0667(5) c=16.9456(9)
 alpha=90 beta=90 gamma=90
 Temperature: 170 K

	Calculated	Reported
Volume	1601.35(13)	1601.35(13)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C19 H17 O P S	?
Sum formula	C19 H17 O P S	C19 H17 O P S
Mr	324.36	324.35
Dx, g cm ⁻³	1.345	1.345
Z	4	4
Mu (mm ⁻¹)	0.301	0.301
F000	680.0	680.0
F000'	681.13	
h, k, lmax	11, 14, 22	11, 14, 22
Nref	3980 [2276]	3962
Tmin, Tmax	0.897, 0.973	0.588, 0.746
Tmin'	0.887	

Correction method= # Reported T Limits: Tmin=0.588 Tmax=0.746
 AbsCorr = MULTI-SCAN

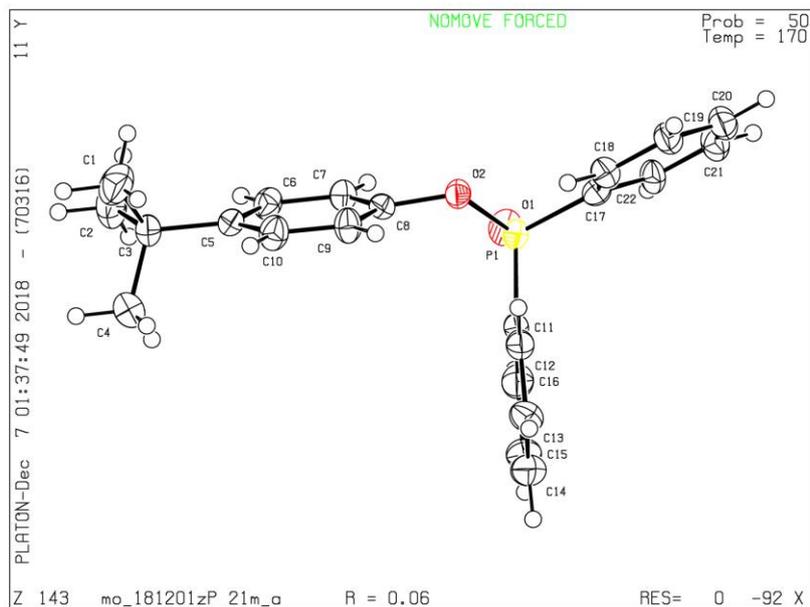
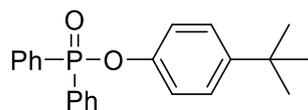
Data completeness= 1.74/1.00 Theta(max)= 28.296

R(reflections)= 0.0332(3457) wR2(reflections)= 0.0885(3962)

S = 1.008

Npar= 200

X-Ray crystallographic data of 28:



Bond precision: C-C = 0.0075 Å

Wavelength=0.71073

Cell: a=8.9390 (15) b=11.3093 (18) c=9.5031 (17)
 alpha=90 beta=100.362 (5) gamma=90
 Temperature: 170 K

	Calculated	Reported
Volume	945.0 (3)	945.0 (3)
Space group	P 21	P 21
Hall group	P 2yb	P 2yb
Moiety formula	C22 H23 O2 P	?
Sum formula	C22 H23 O2 P	C22 H23 O2 P
Mr	350.37	350.37
Dx, g cm ⁻³	1.231	1.231
Z	2	2
Mu (mm ⁻¹)	0.157	0.157
F000	372.0	372.0
F000'	372.35	
h,k,lmax	11,15,12	11,15,12
Nref	4716 [2473]	4654
Tmin,Tmax	0.910,0.954	0.510,0.746
Tmin'	0.910	

Correction method= # Reported T Limits: Tmin=0.510 Tmax=0.746
 AbsCorr = MULTI-SCAN

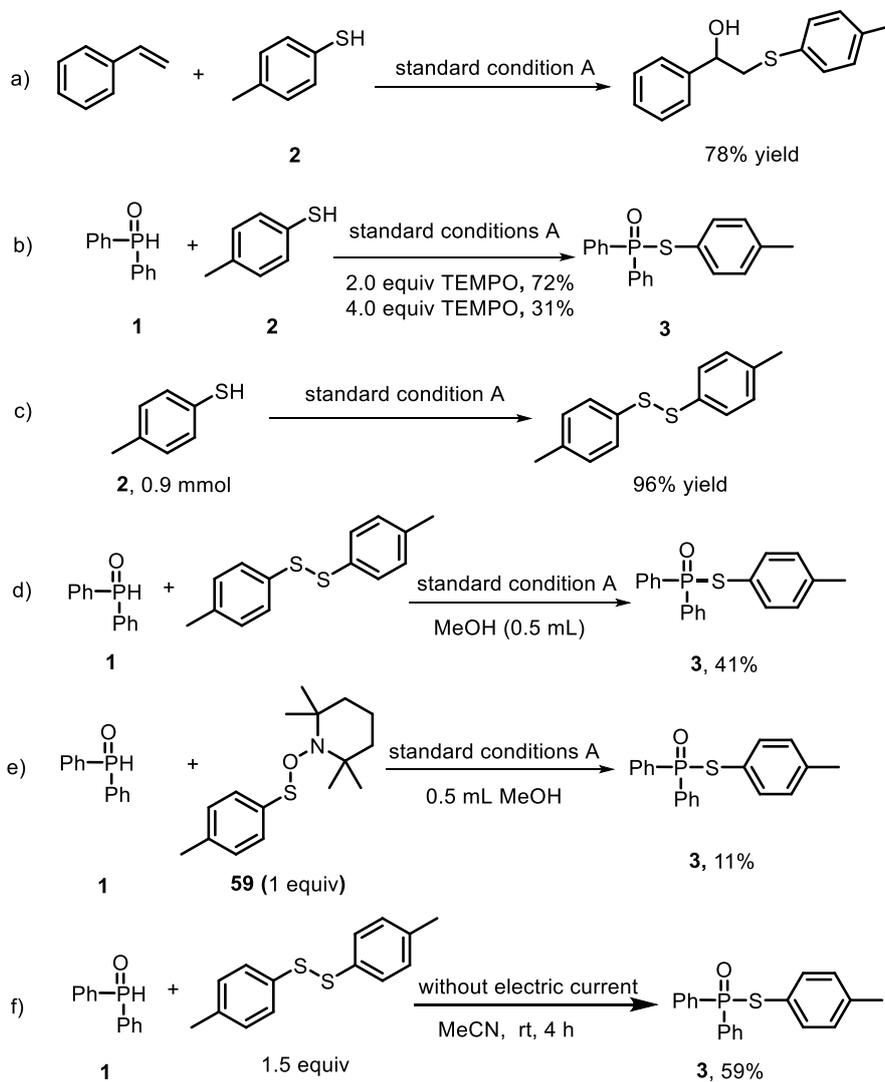
Data completeness= 1.88/0.99 Theta(max)= 28.382

R(reflections)= 0.0572 (3416) wR2(reflections)= 0.1624 (4654)

S = 1.003

Npar= 229

8. Mechanistic studies



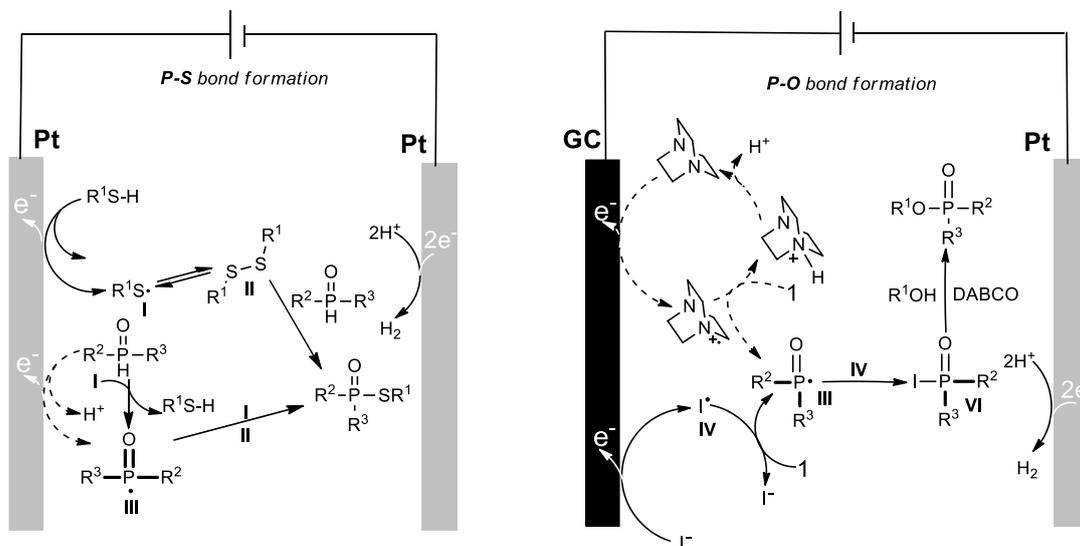
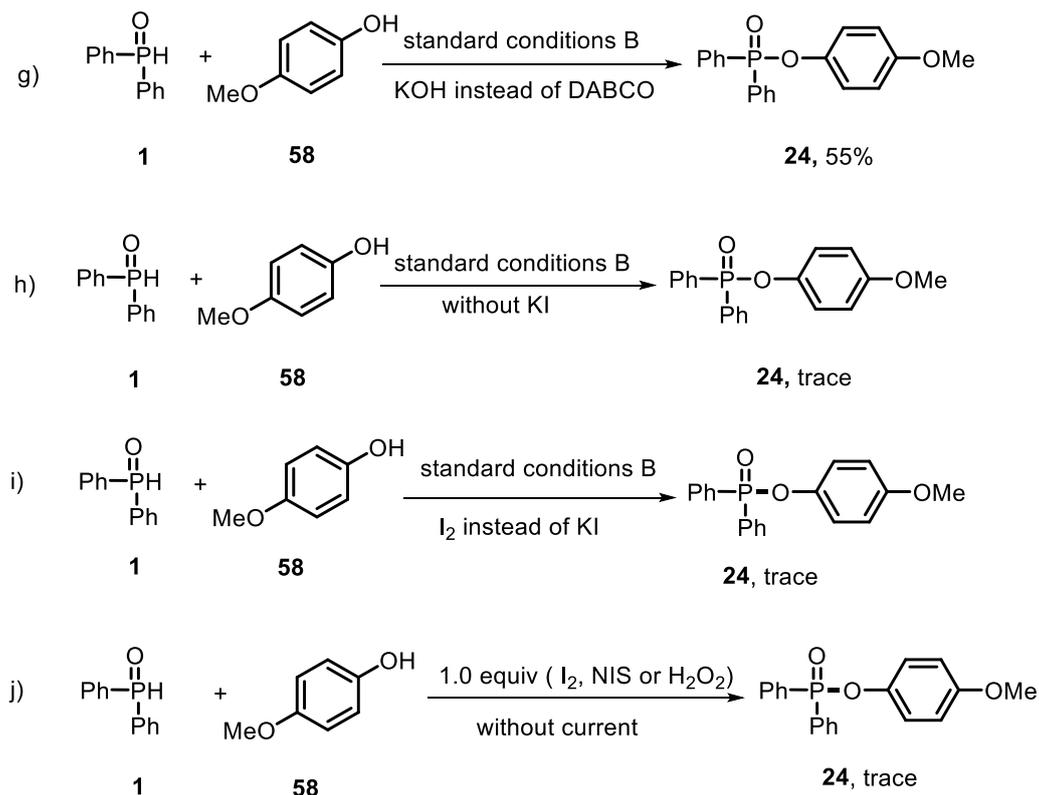
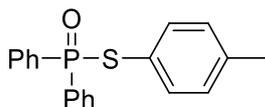


Figure S4 Mechanistic studies experiments

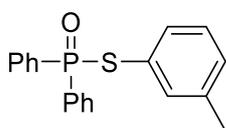
To shine light on the mechanism of this electrochemical dehydrogenative cross-coupling reaction, several control experiments were conducted. For the P-O bond formation, lower yields of the P-S coupling product **3** were obtained by adding 2.0 equiv. or 4.0 equiv. of TEMPO under the standard condition A (72% and 31% yields were obtained, respectively; equation b). The disulfide was obtained in 96% yield without substrate **1** under the standard conditions (equation c). These results suggested that thiyl radical intermediates were involved in the catalytic cycle. When disulphide was subjected to the standard conditions with adding methanol as a proton source, the coupling product

3 was obtained in 41% yield (equation d), suggesting that the disulphide was one of the intermediates of this transformation. Furthermore, the radical trapping product **59** could react with **1** under the standard condition to afford the product **3** in 11% yield (equation e), indicating that the sulfur radical could be regenerated by the homolytic cleavage of the S-O bond of **59**. To our surprise, we found that the diphenylphosphine oxide **1** could react with disulfide to give 59% yield of the product **3** without an electric current (equation f). For the P-O bond formation, the reaction worked well and the coupling product **24** was obtained in 55% yield, when using KOH instead of DABCO as base. Moreover, only trace product was obtained in absence of KI under the standard condition, indicating that the KI was essential for this reaction. Different from the previous report, only trace amount of product was obtained, when using I₂ instead of KI, suggesting that the I₂ was not involved in the catalytic cycle. No desired product was obtained, when the chemical oxidants such as I₂, NIS, H₂O₂ were adding to the reaction without electricity. Based on the EPR results we have observed, we considered that the phosphorus radicals could generated from the P(O)H compounds by anode oxidation directly or by a HAT process with sulfur radicals (SI-6; experiments **a-f**). The signal of phosphorus radicals was observed without 4-methylbenzenethiol **2** under the standard condition, which suggested that the phosphorus radicals could generated by anode oxidation directly under electric current (SI-6; experiment **e**). So, according to the results we observed and previous literature reports, several alternative mechanisms were also proposed (Figure S4), such as the mechanisms including the phosphorus radicals generated from the P(O)H compounds by anode oxidation directly or DABCO working as a hydrogen atom transfer (HAT) reagent in the reaction.

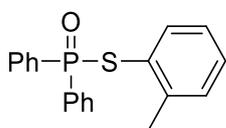
9. Characterization data



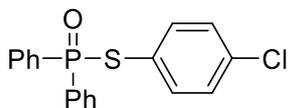
S-(p-tolyl) diphenylphosphinothioate (3)¹. Yield = 84%; white solid; Mp: 117-119 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.79 (m, 4H), 7.54 – 7.47 (m, 2H), 7.47 – 7.39 (m, 4H), 7.32 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 2.24 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 142.92, 142.80, 139.22, 139.20, 135.40, 135.37, 133.19, 132.29, 132.26, 132.13, 131.71, 131.61, 130.00, 129.98, 128.60, 128.47, 122.27, 122.22, 21.18. ³¹P NMR (162 MHz, CDCl₃) δ = 41.39. HRMS (ESI) calcd for C₁₉H₁₈OPS (M+H)⁺: 325.0810, found: 325.0808



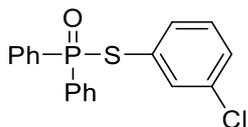
S-(m-tolyl) diphenylphosphinothioate (4)¹. Yield = 66%; white solid; Mp: 96-98 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.89 – 7.80 (m, 4H), 7.52-7.48(m, 2H), 7.48 – 7.37 (m, 4H), 7.23 (dd, *J* = 8.3, 0.9 Hz, 2H), 7.12 – 7.00 (m, 2H), 2.21 (s, 3H). ³¹P NMR (162 MHz, CDCl₃) δ = 41.33. HRMS (ESI) calcd for C₁₉H₁₈OPS (M+H)⁺: 325.0810, found: 325.0812



S-(o-tolyl) diphenylphosphinothioate (5)¹. Yield = 73%; white solid; Mp: 72-74 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.76 (m, 4H), 7.53 – 7.39 (m, 7H), 7.19 – 7.09 (m, 2H), 7.04 – 6.97 (m, 1H), 2.34 (s, 3H). ³¹P NMR (162 MHz, CDCl₃) δ = 41.01. HRMS (ESI) calcd for C₁₉H₁₈OPS (M+H)⁺: 325.0810, found: 325.0815

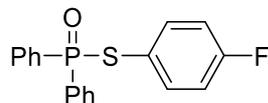


S-(4-chlorophenyl) diphenylphosphinothioate (6)¹. Yield = 80%; white solid; Mp: 108-110 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.79 (m, 4H), 7.57 – 7.50 (m, 2H), 7.49 – 7.42 (m, 4H), 7.38 (dd, *J* = 8.5, 1.6 Hz, 2H), 7.21 – 7.14 (m, 2H). ³¹P NMR (162 MHz, CDCl₃) δ = 41.55. HRMS (ESI) calcd for C₁₈H₁₅ClOPS (M+H)⁺: 345.0264, found: 345.0262

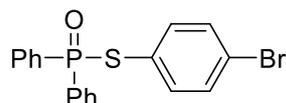


S-(3-chlorophenyl) diphenylphosphinothioate (7)². Yield = 78%; white solid; 185-187 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.80 (m, 4H), 7.58 – 7.51 (m, 2H), 7.48-7.44 (m, 4H), 7.39 (d, *J*

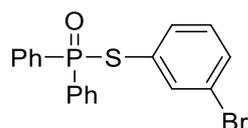
= 6.8 Hz, 2H), 7.26 – 7.19 (m, 1H), 7.14 (t, $J = 8.2$ Hz, 1H). ^{31}P NMR (162 MHz, CDCl_3) $\delta = 41.69$. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{15}\text{ClOPS}$ ($\text{M}+\text{H}$) $^+$: 325.0264, found: 325.0269



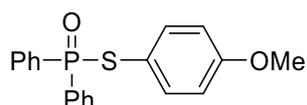
S-(4-fluorophenyl) diphenylphosphinothioate (8)¹. Yield = 66%; white solid; Mp: 109-111 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.88 – 7.79 (m, 4H), 7.56 – 7.49 (m, 2H), 7.49 – 7.37 (m, 6H), 6.90 (t, $J = 8.6$ Hz, 2H). ^{31}P NMR (162 MHz, CDCl_3) $\delta = 41.56$. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{15}\text{FOPS}$ ($\text{M}+\text{H}$) $^+$: 329.0560, found: 329.0557



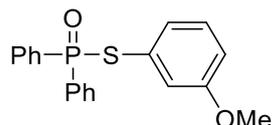
S-(4-bromophenyl) diphenylphosphinothioate (9)¹. Yield = 86%; white solid; Mp: 107-109 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.88 – 7.79 (m, 4H), 7.57 – 7.50 (m, 2H), 7.50 – 7.42 (m, 4H), 7.36 – 7.28 (m, 4H). ^{31}P NMR (162 MHz, CDCl_3) $\delta = 41.48$. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{15}\text{BrOPS}$ ($\text{M}+\text{H}$) $^+$: 388.9759, found: 388.9765



S-(3-bromophenyl) diphenylphosphinothioate (10)³. Yield = 66%; white solid; Mp: 190-192 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.89 – 7.79 (m, 4H), 7.52 -7.51(m, 3H), 7.49-7.43 (m, 5H), 7.37 (d, $J = 7.8$ Hz, 1H), 7.08 (t, $J = 7.9$ Hz, 1H). ^{31}P NMR (162 MHz, CDCl_3) $\delta = 41.75$. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{15}\text{BrOPS}$ ($\text{M}+\text{H}$) $^+$: 388.9759, found: 388.9759

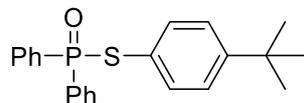


S-(4-methoxyphenyl) diphenylphosphinothioate (11)¹. Yield = 70%; white solid; Mp: 137-139 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.90 – 7.79 (m, 4H), 7.54 – 7.47 (m, 2H), 7.47 – 7.38 (m, 4H), 7.37 – 7.30 (m, 2H), 6.72 (d, $J = 8.8$ Hz, 2H), 3.71 (s, 3H). ^{31}P NMR (162 MHz, CDCl_3) $\delta = 41.38$. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{18}\text{O}_2\text{PS}$ ($\text{M}+\text{H}$) $^+$: 341.0760, found: 341.0762

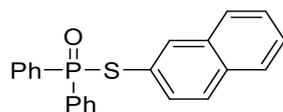


S-(3-methoxyphenyl) diphenylphosphinothioate (12)¹. Yield = 75%; colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.92 – 7.79 (m, 4H), 7.56 – 7.47 (m, 2H), 7.48 – 7.36 (m, 4H), 7.10 (t, $J = 7.9$ Hz, 1H), 7.04 (dd, $J = 7.7, 1.2$ Hz, 1H), 7.00 – 6.94 (m, 1H), 6.82 – 6.75 (m, 1H), 3.66 (s, 3H). ^{31}P NMR

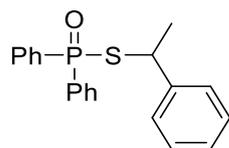
(162 MHz, CDCl₃) δ = 41.41. **HRMS** (ESI) calcd for C₁₉H₁₈O₂PS (M+H)⁺: 341.0760, found: 341.0762



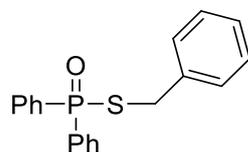
S-(4-(tert-butyl)phenyl) diphenylphosphinothioate (13)¹. Yield = 75%; white solid; Mp: 124-126 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.87-7.81 (m, 4H), 7.54 – 7.47 (m, 2H), 7.43-7.41 (m, 4H), 7.35 (dd, *J* = 8.5, 1.7 Hz, 2H), 7.24 – 7.18 (m, 2H), 1.23 (s, 9H). ³¹P NMR (162 MHz, CDCl₃) δ = 41.58. **HRMS** (ESI) calcd for C₂₂H₂₄OPS (M+H)⁺: 367.1280, found: 367.1281



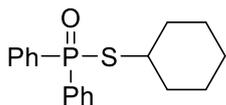
S-(naphthalen-2-yl) diphenylphosphinothioate (14)¹. Yield = 47%; white solid; Mp: 106-108 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.99 (s, 1H), 7.92 – 7.84 (m, 4H), 7.76 – 7.67 (m, 2H), 7.66 (d, *J* = 8.6 Hz, 1H), 7.52 – 7.47 (m, 3H), 7.43 (m, *J* = 9.8, 4.9, 1.7 Hz, 6H). ³¹P NMR (162 MHz, CDCl₃) δ = 41.49. **HRMS** (ESI) calcd for C₂₂H₁₈OPS (M+H)⁺: 361.0810, found: 361.0813



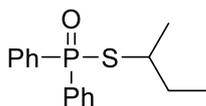
S-(1-phenylethyl) diphenylphosphinothioate (15). Yield = 67%; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.71 (m, 4H), 7.53 – 7.47 (m, 1H), 7.47 – 7.40 (m, 3H), 7.36-7.33 (m, 2H), 7.21 – 7.10 (m, 5H), 4.50-4.46 (m, 1H), 1.73 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 143.08, 143.04, 134.55, 133.49, 133.28, 132.29, 132.26, 132.22, 132.08, 132.05, 131.94, 131.83, 131.22, 131.12, 128.68, 128.55, 128.51, 128.42, 127.39, 127.02, 77.43, 77.11, 76.80, 44.49, 44.47, 24.95, 24.91. ³¹P NMR (162 MHz, CDCl₃) δ = 41.82. **HRMS** (ESI) calcd for C₂₀H₂₀OPS (M+H)⁺: 339.0967, found: 339.0966



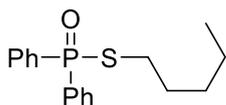
S-benzyl diphenylphosphinothioate (16)¹. Yield = 62%; white solid; Mp: 88-90 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.83 (m, 4H), 7.56 – 7.49 (m, 2H), 7.49 – 7.41 (m, 4H), 7.25 – 7.13 (m, 5H), 4.02 (d, *J* = 9.2 Hz, 2H). ³¹P NMR (162 MHz, CDCl₃) δ = 42.81. **HRMS** (ESI) calcd for C₁₉H₁₈OPS (M+H)⁺: 325.0810, found: 325.0815



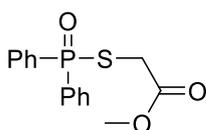
S-cyclohexyl diphenylphosphinothioate (17)¹. Yield = 90%; white solid; Mp: 87–89 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.83 (m, 4H), 7.57 – 7.39 (m, 6H), 3.33–3.25 (m, 1H), 1.94 (dd, *J* = 9.7, 4.1 Hz, 2H), 1.71 – 1.58 (m, 2H), 1.60 – 1.40 (m, 3H), 1.33 – 1.20 (m, 3H). ³¹P NMR (162 MHz, CDCl₃) δ = 42.02. **HRMS** (ESI) calcd for C₁₈H₂₂OPS (M+H)⁺: 317.1123, found: 317.1122



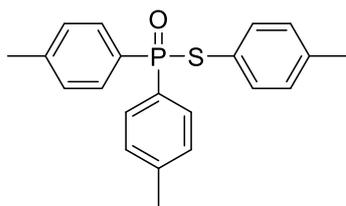
S-(sec-butyl) diphenylphosphinothioate (18). Yield = 80%; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.84 (m, 4H), 7.55 – 7.42 (m, 6H), 3.29–3.22 (m, 1H), 1.76 – 1.54 (m, 2H), 1.34 (d, *J* = 6.9 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 134.66, 134.41, 133.59, 133.35, 132.14, 132.12, 131.58, 131.48, 131.37, 128.63, 128.50, 77.42, 77.10, 76.79, 43.24, 43.22, 31.67, 31.62, 23.23, 23.19, 11.06. ³¹P NMR (162 MHz, CDCl₃) δ = 41.90. **HRMS** (ESI) calcd for C₁₆H₂₀OPS (M+H)⁺: 291.0967, found: 291.0972



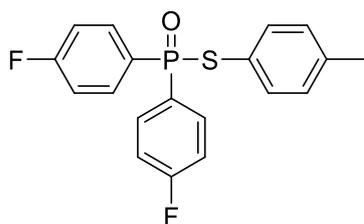
S-pentyl diphenylphosphinothioate (19). Yield = 84%; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.84 (m, 4H), 7.57 – 7.51 (m, 2H), 7.51 – 7.44 (m, 4H), 2.82–2.76 (m, 2H), 1.68 – 1.55 (m, 2H), 1.31 – 1.22 (m, 4H), 0.83 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 134.02, 132.95, 132.25, 132.22, 131.54, 131.43, 128.71, 128.58, 30.73, 30.27, 30.22, 29.28, 29.26, 22.04, 13.87. ³¹P NMR (162 MHz, CDCl₃) δ = 43.11. **HRMS** (ESI) calcd for C₁₇H₂₂OPS (M+H)⁺: 305.1123, found: 305.1123



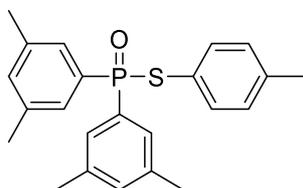
methyl 2-((diphenylphosphoryl)thio)acetate (20). Yield = 84%; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.84 (m, 4H), 7.60 – 7.54 (m, 2H), 7.53 – 7.46 (m, 4H), 3.62 (d, *J* = 10.9 Hz, 2H), 3.54 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 169.12, 169.07, 132.80, 132.72, 132.69, 131.73, 131.64, 131.54, 128.85, 128.72, 77.44, 77.13, 76.81, 52.68, 30.09. ³¹P NMR (162 MHz, CDCl₃) δ = 42.98. **HRMS** (ESI) calcd for C₁₅H₁₆O₃PS (M+H)⁺: 307.0552, found: 307.0547



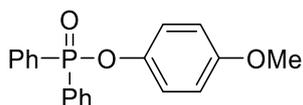
S-(p-tolyl) di-p-tolylphosphinothioate (21)¹. Yield = 53%; white solid; Mp: 88-90 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.72 (dd, *J* = 12.7, 8.1 Hz, 4H), 7.32 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.25 – 7.17 (m, 4H), 7.00 (d, *J* = 8.2 Hz, 2H), 2.37 (s, 6H), 2.25 (s, 3H). ³¹P NMR (162 MHz, CDCl₃) δ = 41.88. **HRMS** (ESI) calcd for C₂₁H₂₂OPS (M+H)⁺: 353.1123, found: 353.1121



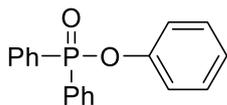
S-(p-tolyl) bis(4-fluorophenyl)phosphinothioate (22)¹. Yield = 84%; white solid; Mp: 97-99 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.77 (m, 4H), 7.30 (dd, *J* = 8.1, 1.7 Hz, 2H), 7.18 – 7.10 (m, 4H), 7.03 (d, *J* = 8.2 Hz, 2H), 2.27 (s, 3H). ³¹P NMR (162 MHz, CDCl₃) δ = 39.23. **HRMS** (ESI) calcd for C₁₉H₁₆F₂OPS (M+H)⁺: 361.0622, found: 361.0623



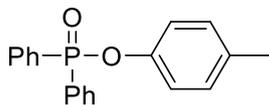
S-(p-tolyl) bis(3,5-dimethylphenyl)phosphinothioate(23)¹. Yield = 80%; white solid; Mp: 141-143 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, *J* = 13.2 Hz, 4H), 7.33 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.10 (s, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 2.31 (s, 12H), 2.24 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 139.00, 138.98, 138.25, 138.12, 135.41, 135.37, 133.01, 131.96, 129.92, 129.90, 129.23, 129.12, 122.79, 122.74, 77.48, 77.16, 76.84, 21.29, 21.14. ³¹P NMR (162 MHz, CDCl₃) δ = 42.56. **HRMS** (ESI) calcd for C₂₃H₂₆OPS (M+H)⁺: 381.1436, found: 381.1635



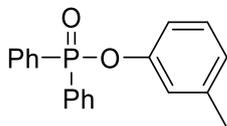
4-methoxyphenyl diphenylphosphinate(24)⁴. Yield = 78%; white solid; Mp: 100-102 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.81 (m, 4H), 7.57 – 7.48 (m, 2H), 7.50 – 7.39 (m, 4H), 7.14 – 7.05 (m, 2H), 6.78 – 6.69 (m, 2H), 3.72 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 156.37, 144.35, 144.26, 132.43, 132.40, 131.90, 131.80, 131.68, 130.31, 128.64, 128.51, 121.68, 121.63, 114.60, 77.38, 77.06, 76.74, 55.53. ³¹P NMR (162 MHz, CDCl₃) δ = 30.55. **HRMS** (ESI) calcd for C₁₉H₁₈O₃P (M+H)⁺: 325.0988, found: 325.0995



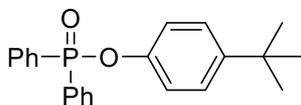
phenyl diphenylphosphinate (25)⁴. Yield = 54%; white solid; Mp: 134-136 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.84 (m, 4H), 7.55-7.51 (m, 2H), 7.48-7.43 (m, 4H), 7.27 – 7.17 (m, 4H), 7.07 (t, *J* = 6.9 Hz, 1H). ³¹P NMR (162 MHz, CDCl₃) δ = 30.40. HRMS (ESI) calcd for C₁₈H₁₆O₂P (M+H)⁺ : 295.0882, found:295.0882



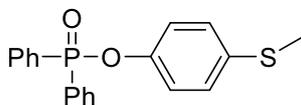
p-tolyl diphenylphosphinate(26)⁴. Yield = 64%; white solid; Mp: 113-115 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.82 (m, 4H), 7.51 (dd, *J* = 10.5, 4.3 Hz, 2H), 7.46-7.41(m, 4H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 2.23 (s, 3H). ³¹P NMR (162 MHz, CDCl₃) δ = 30.27. HRMS (ESI) calcd for C₁₉H₁₈O₂P (M+H)⁺ : 309.1039, found: 309.1044



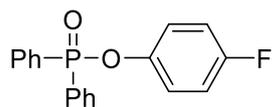
m-tolyl diphenylphosphinate(27)⁴. Yield = 69%; white solid; Mp: 108-110 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.84 (m, 4H), 7.55 – 7.48 (m, 2H), 7.49 – 7.41 (m, 4H), 7.08 (dd, *J* = 15.6, 7.8 Hz, 2H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 2.25 (s, 3H). ³¹P NMR (162 MHz, CDCl₃) δ = 30.17. HRMS (ESI) calcd for C₁₉H₁₈O₂P (M+H)⁺ : 309.1039, found: 309.1035



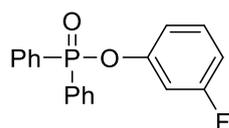
4-(tert-butyl)phenyl diphenylphosphinate(28)⁴. Yield = 63%; white solid; Mp: 170-172 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.95 – 7.84 (m, 4H), 7.57 – 7.48 (m, 2H), 7.50 – 7.42 (m, 4H), 7.27 – 7.20 (m, 2H), 7.09 (dd, *J* = 8.8, 1.1 Hz, 2H), 1.24 (s, 9H). ³¹P NMR (162 MHz, CDCl₃) δ = 30.22. HRMS (ESI) calcd for C₂₂H₂₄O₂P (M+H)⁺ : 351.1508, found: 351.1502



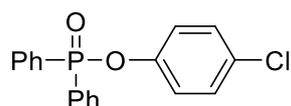
4-(methylthio)phenyl diphenylphosphinate(29). Yield = 65%; white solid; Mp: 106-108 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.84 (m, 4H), 7.57 – 7.50 (m, 2H), 7.51 – 7.41 (m, 4H), 7.13 (s, 4H), 2.40 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 148.73, 148.65, 134.17, 134.16, 132.56, 132.53, 131.86, 131.76, 131.48, 130.11, 128.71, 128.58, 128.39, 121.33, 121.29, 16.56. ³¹P NMR (162 MHz, CDCl₃) δ = 30.85. HRMS (ESI) calcd for C₁₉H₁₈O₂PS (M+H)⁺ : 341.0760, found: 341.0764



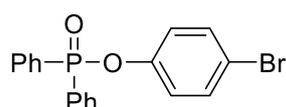
4-fluorophenyl diphenylphosphinate(30)⁴. Yield = 77%; white solid; Mp: 131-133 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.83 (m, 4H), 7.59 – 7.51 (m, 2H), 7.51 – 7.42 (m, 4H), 7.21-7.15 (m, 1H), 7.02 (d, *J* = 8.9 Hz, 1H), 7.00 – 6.94 (m, 1H), 6.81-6.76 (m, 1H). ³¹P NMR (162 MHz, CDCl₃) δ = 31.27. **HRMS** (ESI) calcd for C₁₈H₁₅FO₂P (M+H)⁺ : 313.0788, found: 313.0786



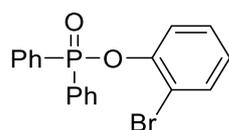
3-fluorophenyl diphenylphosphinate(31). Yield = 81%; white solid; Mp: 130-132 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.80 (m, 4H), 7.59 – 7.51 (m, 2H), 7.51 – 7.42 (m, 4H), 7.21-7.16 (m, 1H), 7.05 – 6.99 (m, 1H), 6.99 – 6.93 (m, 1H), 6.81-6.77(m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ = 164.17, 161.71, 157.82, 151.82, 151.74, 151.71, 151.63, 138.00, 132.70, 132.67, 131.81, 131.71, 131.23, 130.45, 130.35, 129.86, 128.78, 128.65, 116.57, 116.54, 116.52, 116.49, 111.83, 111.63, 108.94, 108.89, 108.69, 108.64, 77.40, 77.09, 76.77. ³¹P NMR (162 MHz, CDCl₃) δ = 31.28. **HRMS** (ESI) calcd for C₁₈H₁₅FO₂P (M+H)⁺ : 313.0788, found: 313.0783



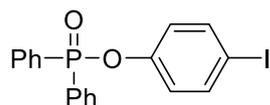
4-chlorophenyl diphenylphosphinate(32)⁴. Yield = 76%; white solid; Mp: 117-119 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.81 (m, 4H), 7.58 – 7.50 (m, 2H), 7.48-7.44 (m, 4H), 7.23 – 7.11 (m, 4H). ³¹P NMR (162 MHz, CDCl₃) δ = 31.31. **HRMS** (ESI) calcd for C₁₈H₁₅ClO₂P (M+H)⁺ : 329.0493, found: 329.0486



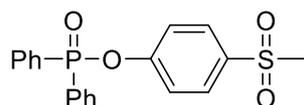
4-bromophenyl diphenylphosphinate(33)⁴. Yield = 73%; white solid; Mp: 115-117 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.81 (m, 4H), 7.58 – 7.50 (m, 2H), 7.50 – 7.43 (m, 4H), 7.36 – 7.30 (m, 2H), 7.09 (dd, *J* = 9.0, 1.2 Hz, 2H). ³¹P NMR (162 MHz, CDCl₃) δ = 31.33. **HRMS** (ESI) calcd for C₁₈H₁₅BrO₂P (M+H)⁺ : 372.9988, found: 372.9979



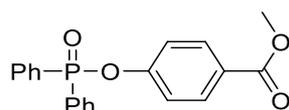
2-bromophenyl diphenylphosphinate(34)⁵. Yield = 71%; white solid; Mp: 102-104 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.05 – 7.94 (m, 4H), 7.62-7.60 (m, 1H), 7.55 – 7.48 (m, 3H), 7.48 – 7.41 (m, 4H), 7.15 (ddd, *J* = 8.3, 7.6, 1.6 Hz, 1H), 6.92 (ddd, *J* = 8.2, 7.5, 1.0 Hz, 1H). ³¹P NMR (162 MHz, CDCl₃) δ = 31.73. **HRMS** (ESI) calcd for C₁₈H₁₅BrO₂P (M+H)⁺ : 372.9988, found: 372.9994



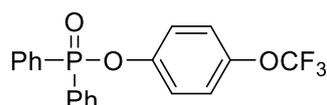
4-iodophenyl diphenylphosphinate(35)⁴. Yield = 75%; white solid; Mp: 140-142 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.82 (m, 4H), 7.58 – 7.50 (m, 4H), 7.50 – 7.42 (m, 4H), 7.01 – 6.94 (m, 2H). ³¹P NMR (162 MHz, CDCl₃) δ = 31.25. HRMS (ESI) calcd for C₁₈H₁₅IO₂P (M+H)⁺ : 420.9849, found: 420.9846



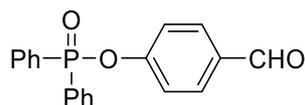
4-(methylsulfonyl)phenyl diphenylphosphinate(36). Yield = 64%; white solid; Mp: 111-113 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.95 – 7.80 (m, 6H), 7.62 – 7.55 (m, 2H), 7.54 – 7.46 (m, 4H), 7.42 (dd, *J* = 8.8, 0.9 Hz, 2H), 3.00 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 155.22, 155.14, 136.53, 133.04, 133.01, 131.75, 131.64, 130.69, 129.57, 129.32, 128.96, 128.82, 121.58, 121.53, 77.43, 77.11, 76.79, 44.60. ³¹P NMR (162 MHz, CDCl₃) δ = 32.55. HRMS (ESI) calcd for C₁₉H₁₈O₄PS (M+H)⁺ : 373.0658, found: 373.0663



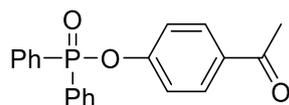
methyl 4-((diphenylphosphoryl)oxy)benzoate(37). Yield = 77%; white solid; Mp: 126-128 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.84 (m, 6H), 7.58 – 7.51 (m, 2H), 7.49-7.45 (m, 4H), 7.29 (dd, *J* = 8.8, 1.0 Hz, 2H), 3.85 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 166.30, 154.79, 154.71, 132.76, 132.73, 131.80, 131.69, 131.52, 131.11, 129.74, 128.81, 128.67, 126.49, 120.56, 120.51, 77.42, 77.10, 76.78, 52.11. ³¹P NMR (162 MHz, CDCl₃) δ = 31.36. HRMS (ESI) calcd for C₂₀H₁₈O₄P (M+H)⁺ : 353.0937, found: 353.0939



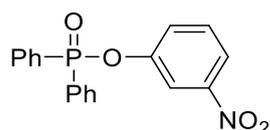
4-(trifluoromethoxy)phenyl diphenylphosphinate(38)⁴. Yield = 70%; white solid; Mp: 58-60 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.95 – 7.81 (m, 4H), 7.59 – 7.51 (m, 2H), 7.51 – 7.43 (m, 4H), 7.25 – 7.17 (m, 2H), 7.09 (d, *J* = 8.9 Hz, 2H). ³¹P NMR (162 MHz, CDCl₃) δ = 31.59. HRMS (ESI) calcd for C₁₉H₁₅F₃O₃P (M+H)⁺ : 379.0705, found: 379.0711



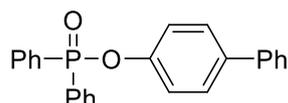
4-formylphenyl diphenylphosphinate(39)⁶. Yield = 46%; white solid; Mp: 98-100 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.89 (s, 1H), 7.94 – 7.86 (m, 4H), 7.79 (d, *J* = 8.6 Hz, 2H), 7.57-7.54 (m, 2H), 7.52 – 7.46 (m, 4H), 7.39 (d, *J* = 8.0 Hz, 2H). ³¹P NMR (162 MHz, CDCl₃) δ = 31.77. HRMS (ESI) calcd for C₁₉H₁₆O₃P (M+H)⁺ : 323.0832, found: 323.0829



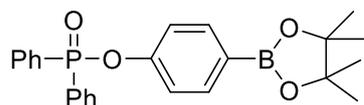
4-acetylphenyl diphenylphosphinate(40)⁶. Yield = 79%; white solid; Mp: 111-113 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.95 – 7.81 (m, 6H), 7.60 – 7.53 (m, 2H), 7.54 – 7.44 (m, 4H), 7.30 (dd, *J* = 8.7, 0.9 Hz, 2H), 2.53 (s, 3H). ³¹P NMR (162 MHz, CDCl₃) δ = 31.42. HRMS (ESI) calcd for C₂₀H₁₈O₃P (M+H)⁺ : 337.0988, found: 337.0985



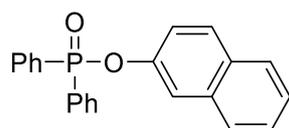
3-nitrophenyl diphenylphosphinate(41)⁷. Yield = 61%; white solid; Mp: 122-124 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.01 (dd, *J* = 3.3, 2.2 Hz, 1H), 7.99 – 7.94 (m, 1H), 7.94 – 7.87 (m, 4H), 7.64 – 7.62 (m, 1H), 7.58-7.56 (m, 2H), 7.54 – 7.47 (m, 4H), 7.43 (t, *J* = 8.2 Hz, 1H). ³¹P NMR (162 MHz, CDCl₃) δ = 32.90. HRMS (ESI) calcd for C₁₈H₁₅NO₄P (M+H)⁺ : 340.0733, found: 340.0726



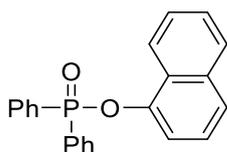
[1,1'-biphenyl]-4-yl diphenylphosphinate(42)⁴. Yield = 62%; white solid; Mp: 152-154 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.92-7.89 (m, 4H), 7.52 (dd, *J* = 7.3, 1.4 Hz, 2H), 7.49 – 7.42 (m, 8H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.24 (m, 3H). ³¹P NMR (162 MHz, CDCl₃) δ = 30.79. HRMS (ESI) calcd for C₂₄H₂₀O₂P (M+H)⁺ : 371.1195, found: 371.1200



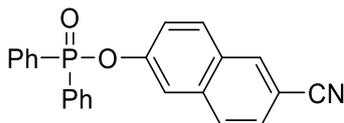
4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl diphenylphosphinate(43). Yield = 41%; white solid; Mp: 117-119 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.83 (m, 4H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.55 – 7.49 (m, 2H), 7.48 – 7.41 (m, 4H), 7.23 (dd, *J* = 8.6, 1.1 Hz, 2H), 1.30 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ = 153.60, 153.52, 136.50, 132.54, 132.51, 131.87, 131.77, 131.43, 130.05, 128.70, 128.57, 120.02, 119.97, 83.84, 24.86. ³¹P NMR (162 MHz, CDCl₃) δ = 30.42. HRMS (ESI) calcd for C₂₄H₂₇BO₄P (M+H)⁺ : 421.1735, found: 421.1728



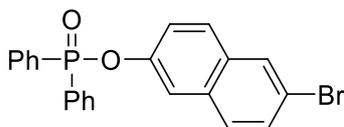
naphthalen-2-yl diphenylphosphinate(44)⁴. Yield = 72%; white solid; Mp: 120-122 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.97 – 7.89 (m, 4H), 7.72 (dd, *J* = 14.3, 6.3 Hz, 4H), 7.55 – 7.48 (m, 2H), 7.48 – 7.41 (m, 5H), 7.40 – 7.34 (m, 2H). ³¹P NMR (162 MHz, CDCl₃) δ = 30.75. HRMS (ESI) calcd for C₂₂H₁₈O₂P (M+H)⁺ : 345.1039, found: 345.1036



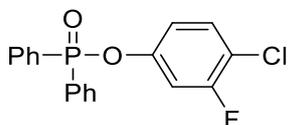
naphthalen-1-yl diphenylphosphinate(45)⁴. Yield = 47%; white solid; Mp: 110-112 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.26 – 8.18 (m, 1H), 8.02 – 7.89 (m, 4H), 7.79 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.58 – 7.42 (m, 10H), 7.25 (dd, *J* = 9.0, 7.0 Hz, 1H). ³¹P NMR (162 MHz, CDCl₃) δ = 30.86. HRMS (ESI) calcd for C₂₂H₁₈O₂P (M+H)⁺ : 345.1039, found: 345.1046



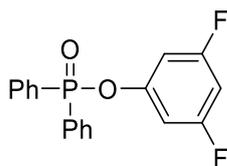
6-cyanonaphthalen-2-yl diphenylphosphinate(46). Yield = 68%; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 8.12 (s, 1H), 7.99 – 7.88 (m, 4H), 7.78 (dd, *J* = 10.5, 6.2 Hz, 3H), 7.59 – 7.52 (m, 3H), 7.50-7.46 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ = 151.16, 151.07, 135.50, 133.80, 132.84, 132.81, 131.82, 131.72, 131.13, 130.49, 129.76, 129.41, 128.87, 128.77, 128.74, 127.10, 122.68, 122.63, 119.10, 117.38, 117.33, 108.72, 77.42, 77.10, 76.78. ³¹P NMR (162 MHz, CDCl₃) δ = 31.83. HRMS (ESI) calcd for C₂₃H₁₇NO₂P (M+H)⁺ : 370.0991, found: 370.0991



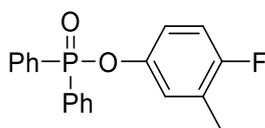
6-bromonaphthalen-2-yl diphenylphosphinate(47). Yield = 63%; white solid; Mp: 119-121 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.85 (m, 5H), 7.66 (s, 1H), 7.61 (d, *J* = 8.9 Hz, 1H), 7.57 – 7.50 (m, 3H), 7.50 – 7.42 (m, 5H), 7.36 (dd, *J* = 8.9, 1.8 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ = 148.91, 148.83, 132.69, 132.66, 132.35, 131.87, 131.77, 131.68, 131.34, 129.96, 129.66, 129.15, 128.90, 128.80, 128.66, 121.84, 121.79, 119.13, 117.31, 117.26, 77.41, 77.10, 76.78. ³¹P NMR (162 MHz, CDCl₃) δ = 31.28. HRMS (ESI) calcd for C₂₂H₁₇BrO₂P (M+H)⁺ : 423.0144, found: 423.0135



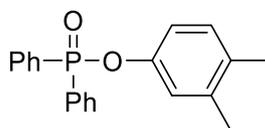
4-chloro-3-fluorophenyl diphenylphosphinate(48). Yield = 81%; white solid; Mp: 99-101 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.79 (m, 4H), 7.60 – 7.52 (m, 2H), 7.53 – 7.43 (m, 4H), 7.25 (dd, *J* = 13.6, 5.0 Hz, 1H), 7.08-7.07 (m, 1H), 7.00-6.97 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ = 159.20, 156.71, 150.09, 149.99, 149.91, 132.95, 132.92, 131.78, 131.68, 130.83, 130.71, 129.33, 128.89, 128.76, 117.48, 117.43, 117.39, 117.18, 117.01, 112.42, 110.19, 110.14, 109.95, 109.90, 104.60, 104.37, 77.43, 77.11, 76.79. ³¹P NMR (162 MHz, CDCl₃) δ = 32.31. HRMS (ESI) calcd for C₁₈H₁₅ClFO₂P (M+H)⁺ : 347.0398, found: 347.0440



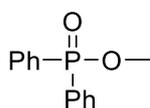
3,5-difluorophenyl diphenylphosphinate(49). Yield = 72%; white solid; Mp: 135-137 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.94 – 7.81 (m, 4H), 7.59-7.54 (m, 2H), 7.53 – 7.45 (m, 4H), 6.82-6.80 (m, 2H), 6.58-6.52 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ = 164.36, 164.21, 161.89, 161.74, 152.27, 152.19, 132.92, 132.89, 131.77, 131.66, 130.79, 129.42, 128.88, 128.75, 105.07, 105.02, 104.93, 104.86, 104.78, 104.73, 100.82, 100.57, 100.32, 77.39, 77.08, 76.76. ^{31}P NMR (162 MHz, CDCl_3) δ = 32.24. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{14}\text{F}_2\text{O}_2\text{P}$ ($\text{M}+\text{H}$) $^+$: 331.0694, found: 331.0692



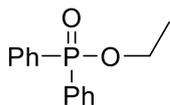
4-fluoro-3-methylphenyl diphenylphosphinate(50). Yield = 57%; white solid; Mp: 102-105 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.88-7.84 (m, 4H), 7.58 – 7.50 (m, 2H), 7.50 – 7.42 (m, 4H), 7.05 (dd, J = 6.2, 2.7 Hz, 1H), 6.96 – 6.89 (m, 1H), 6.83 (t, J = 8.9 Hz, 1H), 2.17 (d, J = 1.9 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ = 159.28, 156.89, 146.26, 146.18, 132.57, 132.54, 131.85, 131.75, 131.46, 130.08, 128.71, 128.57, 126.31, 126.11, 123.52, 123.47, 123.42, 119.20, 119.16, 119.12, 119.08, 115.72, 115.48, 14.65, 14.62. ^{31}P NMR (162 MHz, CDCl_3) δ = 30.91. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{17}\text{FO}_2\text{P}$ ($\text{M}+\text{H}$) $^+$: 327.0945, found: 327.0942



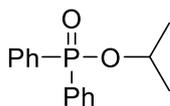
3,4-dimethylphenyl diphenylphosphinate(51). Yield = 41%; white solid; Mp: 112-114 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.89-7.85 (m, 4H), 7.56 – 7.49 (m, 2H), 7.49 – 7.41 (m, 4H), 7.01 (s, 1H), 6.95 (d, J = 8.3 Hz, 1H), 6.89 (d, J = 8.3 Hz, 1H), 2.15 (d, J = 7.4 Hz, 6H). ^{31}P NMR (162 MHz, CDCl_3) δ = 29.95. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{20}\text{O}_2\text{P}$ ($\text{M}+\text{H}$) $^+$: 323.1195, found: 323.1200



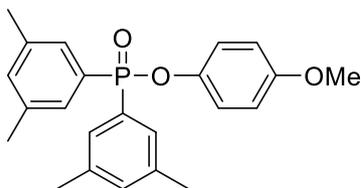
methyl diphenylphosphinate(52)⁴. Yield = 91%; colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.86 – 7.77 (m, 4H), 7.57 – 7.50 (m, 2H), 7.50 – 7.42 (m, 4H), 3.77 (d, J = 11.1 Hz, 3H). ^{31}P NMR (162 MHz, CDCl_3) δ = 33.26. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{14}\text{O}_2\text{P}$ ($\text{M}+\text{H}$) $^+$: 233.0726, found: 233.0723



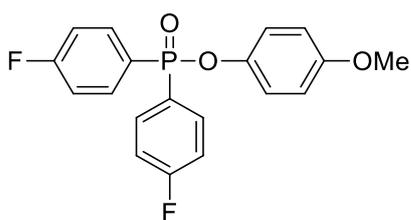
ethyl diphenylphosphinate(53)⁴. Yield = 79%; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.82-7.79 (m, 4H), 7.55 – 7.48 (m, 2H), 7.45 -7.42(m, 4H), 4.11-4.07 (m, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ³¹P NMR (162 MHz, CDCl₃) δ = 31.39. HRMS (ESI) calcd for C₁₄H₁₆O₂P (M+H)⁺ : 247.0882, found: 247.0889



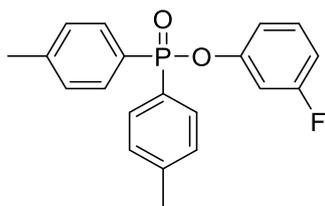
isopropyl diphenylphosphinate(54)⁴. Yield = 40%; white solid; Mp: 101-103 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.86 – 7.77 (m, 4H), 7.50 (m, *J* = 6.4, 2.9, 1.4 Hz, 2H), 7.44-7.41 (m, 4H), 4.71-4.63 (m, 1H), 1.35 (d, *J* = 6.2 Hz, 6H). ³¹P NMR (162 MHz, CDCl₃) δ = 29.81. HRMS (ESI) calcd for C₁₅H₁₈O₂P (M+H)⁺ : 261.1039, found: 261.1039



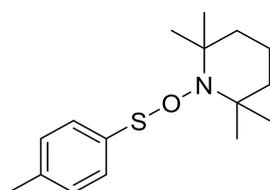
4-methoxyphenyl bis(3,5-dimethylphenyl)phosphinate(55). Yield = 54%; white solid; Mp: 100-103 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.49 (d, *J* = 12.7 Hz, 4H), 7.19 – 7.03 (m, 4H), 6.74 (d, *J* = 8.9 Hz, 2H), 3.71 (s, 3H), 2.33 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ = 156.26, 144.51, 144.43, 138.30, 138.16, 134.08, 131.62, 130.19, 129.42, 129.32, 121.75, 121.70, 114.55, 77.40, 77.08, 76.76, 55.53, 21.29 ³¹P NMR (162 MHz, CDCl₃) δ = 31.86. HRMS (ESI) calcd for C₂₃H₂₆O₃P (M+H)⁺ : 381.1614, found: 381.1611



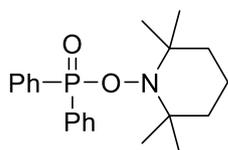
4-methoxyphenyl bis(4-fluorophenyl)phosphinate(56). Yield = 69%; colorless oil ; ¹H NMR (400 MHz, CDCl₃) δ 7.90-7.83 (m, 4H), 7.17-7.12 (m, 4H), 7.10 – 7.05 (m, 2H), 6.75 (d, *J* = 9.0 Hz, 2H), 3.72 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 166.66, 166.62, 164.13, 164.09, 156.56, 144.01, 143.93, 134.51, 134.42, 134.39, 134.30, 127.51, 127.48, 126.09, 126.06, 121.59, 121.55, 116.28, 116.13, 116.06, 115.92, 114.69, 77.41, 77.09, 76.78, 55.52. ³¹P NMR (162 MHz, CDCl₃) δ = 28.62. HRMS (ESI) calcd for C₁₉H₁₆F₂O₃P (M+H)⁺ : 361.0800, found: 361.0795



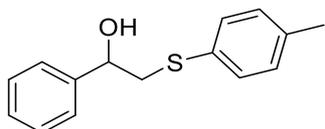
3-fluorophenyl di-p-tolylphosphinate(57). Yield = 30%; colorless oil ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.75 (dd, $J = 12.4, 8.1$ Hz, 4H), 7.31 – 7.24 (m, 4H), 7.18 -7.15(m, 1H), 7.01 (dd, $J = 8.3, 0.8$ Hz, 1H), 6.96- 6.92(m, 1H), 6.78 -6.75(m, 1H), 2.38 (s, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) $\delta = 164.16, 161.70, 143.24, 143.21, 131.80, 131.69, 130.37, 130.28, 129.49, 129.35, 128.19, 126.79, 77.37, 77.05, 76.74, 21.69$ $^{31}\text{P NMR}$ (162 MHz, CDCl_3) $\delta = 32.40$ **HRMS** (ESI) calcd for $\text{C}_{20}\text{H}_{19}\text{FO}_2\text{P}$ ($\text{M}+\text{H}$) $^+$: 341.1101, found: 341.1096



2,2,6,6-tetramethyl-1-(p-tolylthio)oxy)piperidine(59). Yield = 24%; colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.58 – 7.52 (m, 2H), 7.25 (d, $J = 7.9$ Hz, 2H), 2.39 (s, 3H), 1.75 – 1.34 (m, 15H), 0.92 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) $\delta = 147.09, 139.46, 129.27, 125.94, 77.38, 77.07, 76.75, 61.19, 58.75, 43.52, 41.41, 35.35, 32.60, 28.74, 27.96, 26.99, 21.23, 17.30$. **HRMS** (ESI) calcd for $\text{C}_{16}\text{H}_{26}\text{NOS}$ ($\text{M}+\text{H}$) $^+$: 280.1730, found: 280.1730



2,2,6,6-tetramethylpiperidin-1-yl diphenylphosphinate(60). Yield = 26%; colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.91 – 7.80 (m, 4H), 7.53 – 7.37 (m, 6H), 1.31 – 0.88 (m, 18H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) $\delta = 134.51, 133.16, 131.68, 131.58, 131.55, 128.35, 128.23, 61.62, 61.60, 40.11, 16.89$. $^{31}\text{P NMR}$ (162 MHz, CDCl_3) $\delta = 33.66$. **HRMS** (ESI) calcd for $\text{C}_{21}\text{H}_{29}\text{NO}_2\text{P}$ ($\text{M}+\text{H}$) $^+$: 358.1930, found: 358.1927

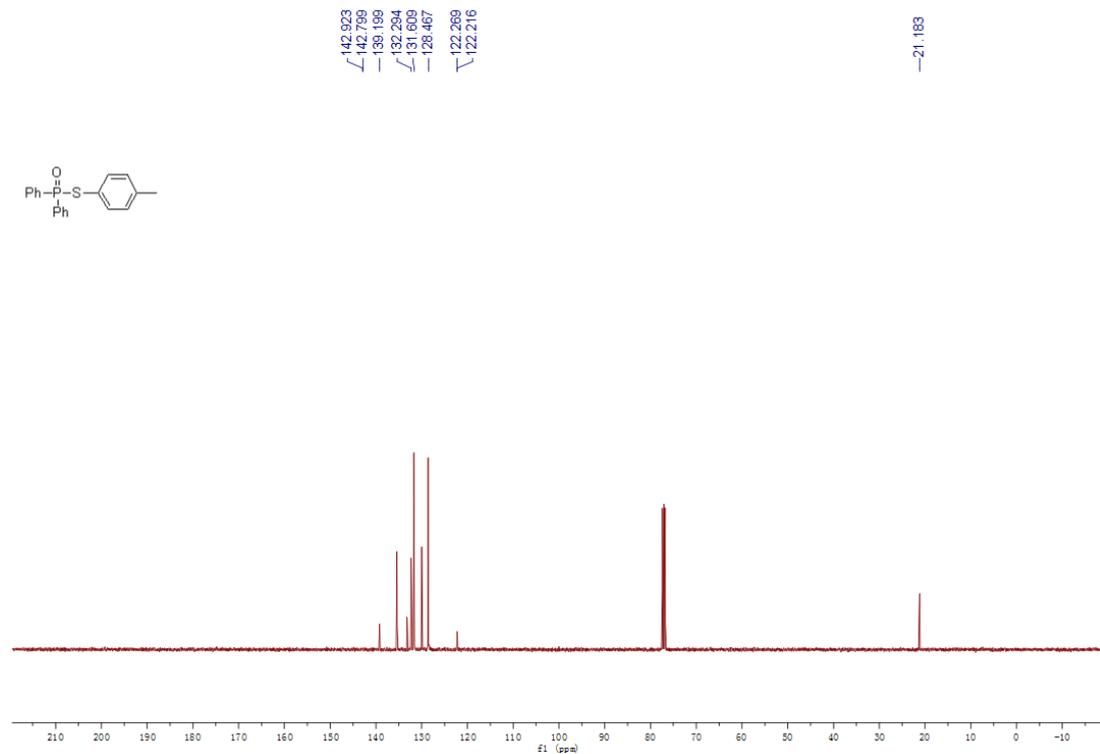
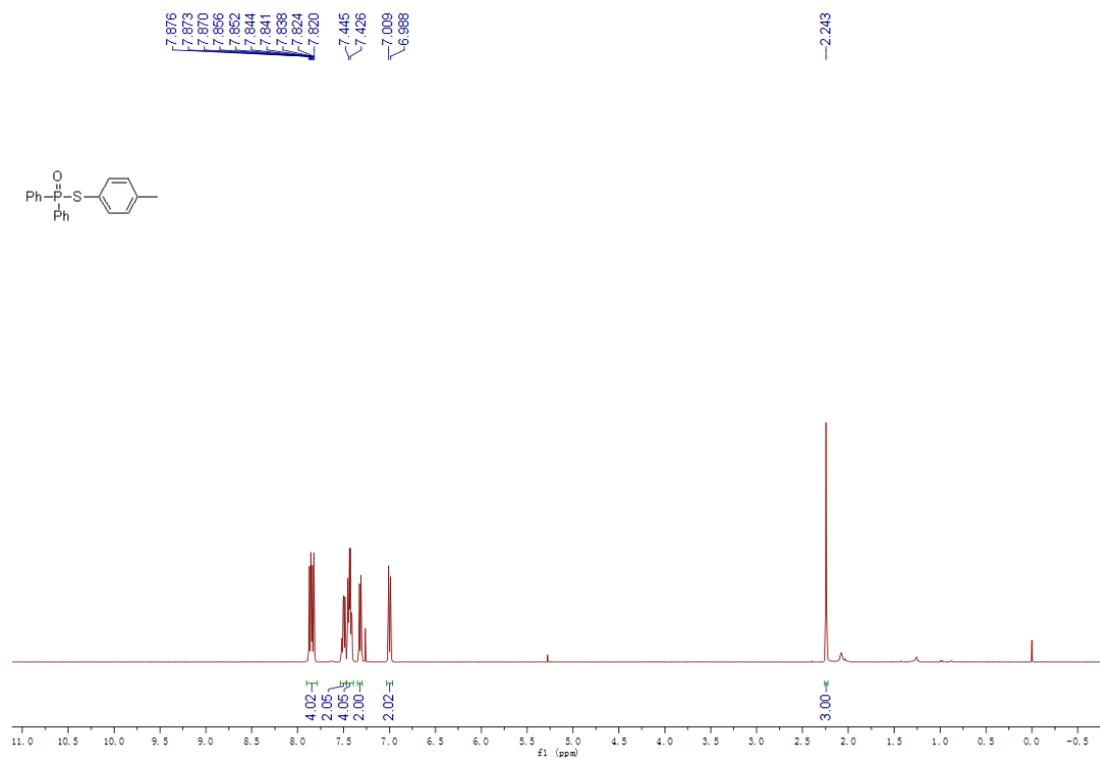


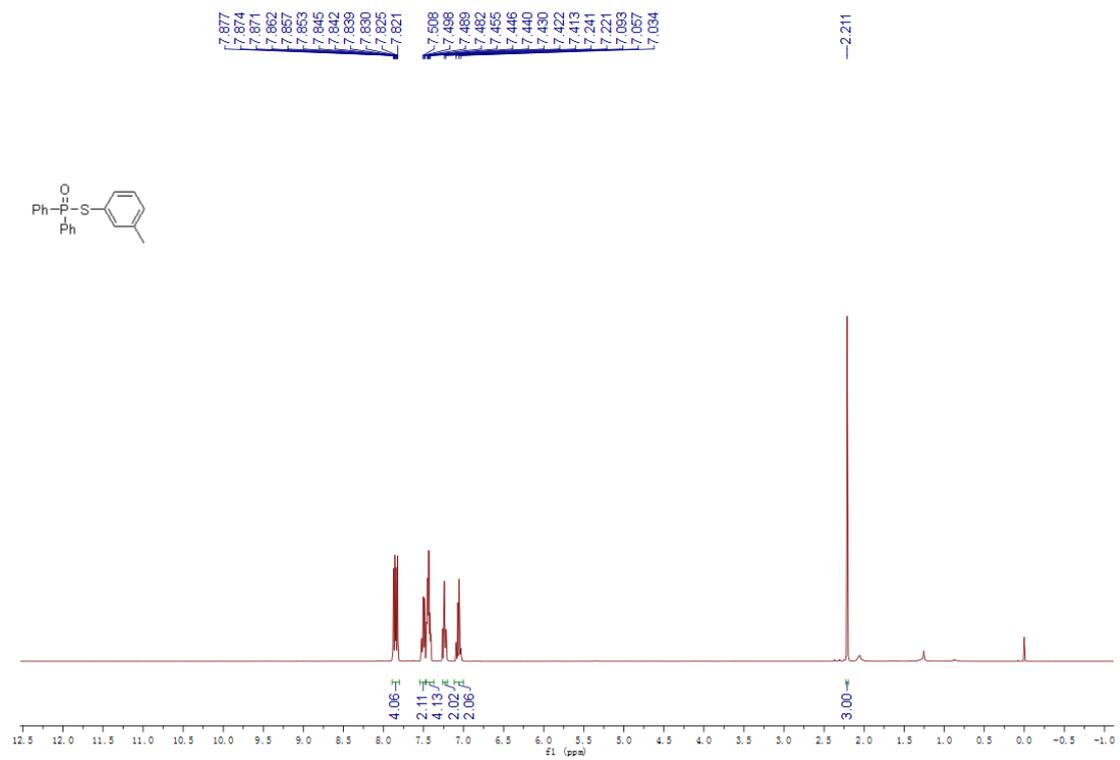
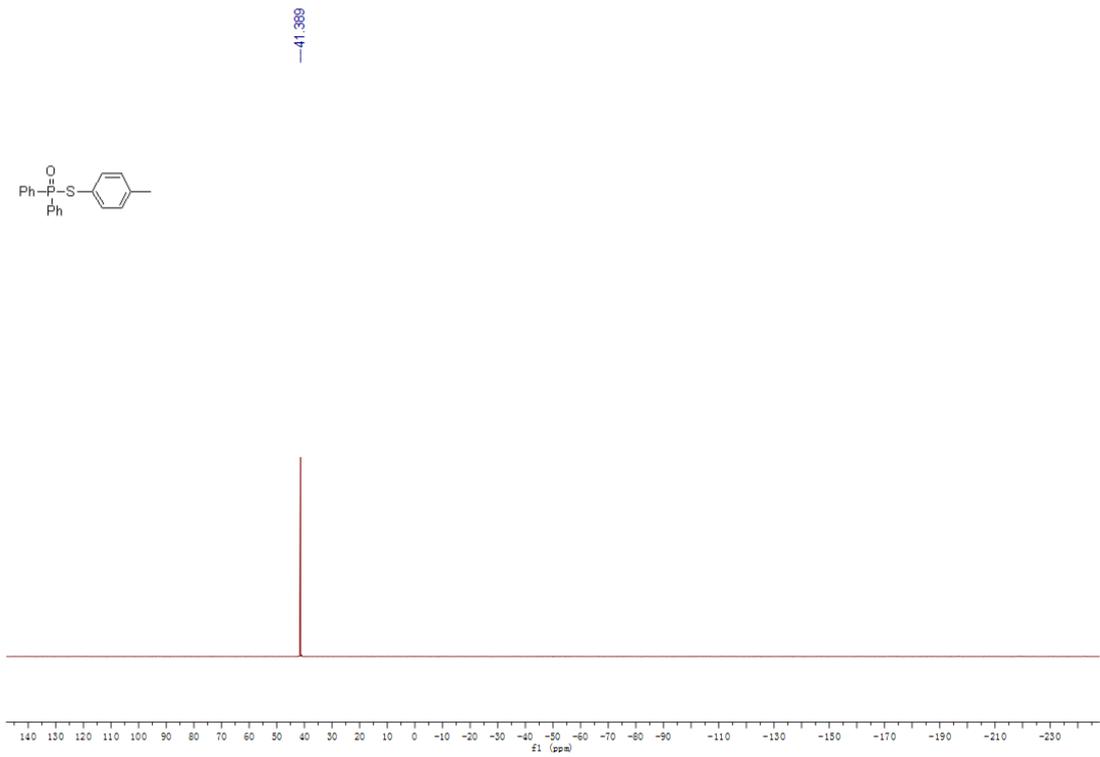
1-phenyl-2-(p-tolylthio)ethan-1-ol. Yield = 78%; colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36 – 7.23 (m, 7H), 7.13 (d, $J = 7.9$ Hz, 2H), 4.66 (dd, $J = 9.6, 3.3$ Hz, 1H), 3.26 (dd, $J = 13.8, 3.4$ Hz, 1H), 3.02 (dd, $J = 13.8, 9.7$ Hz, 1H), 2.96 (s, 1H), 2.33 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) $\delta = 142.18, 137.18, 131.10, 130.90, 130.00, 128.57, 127.96, 125.90, 71.47, 44.85, 21.12$. **HRMS** (ESI) calcd for $\text{C}_{15}\text{H}_{17}\text{OS}$ ($\text{M}+\text{H}$) $^+$: 245.0995, found: 245.0998

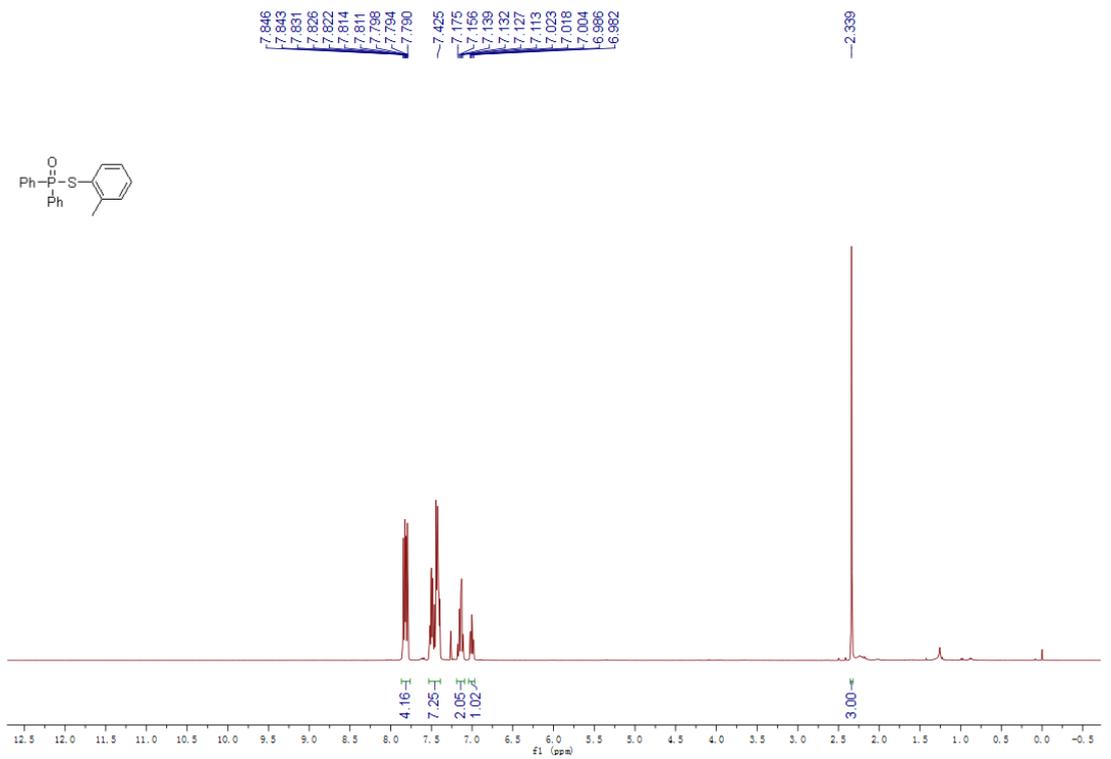
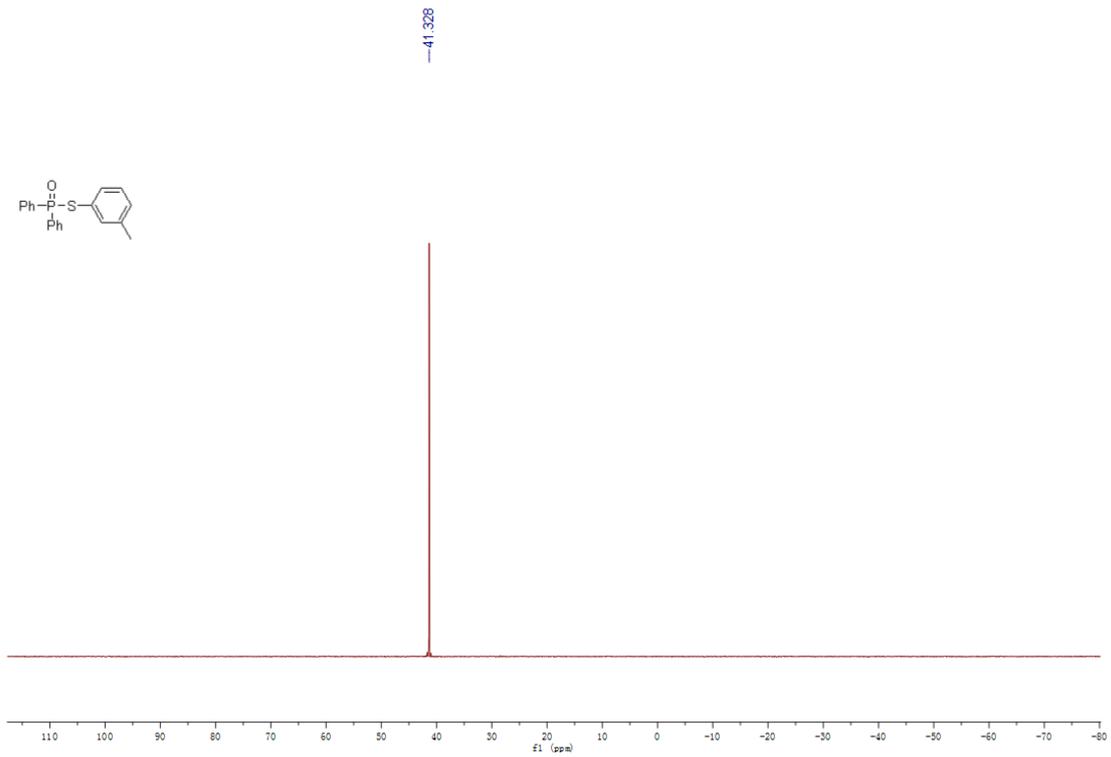
10. References

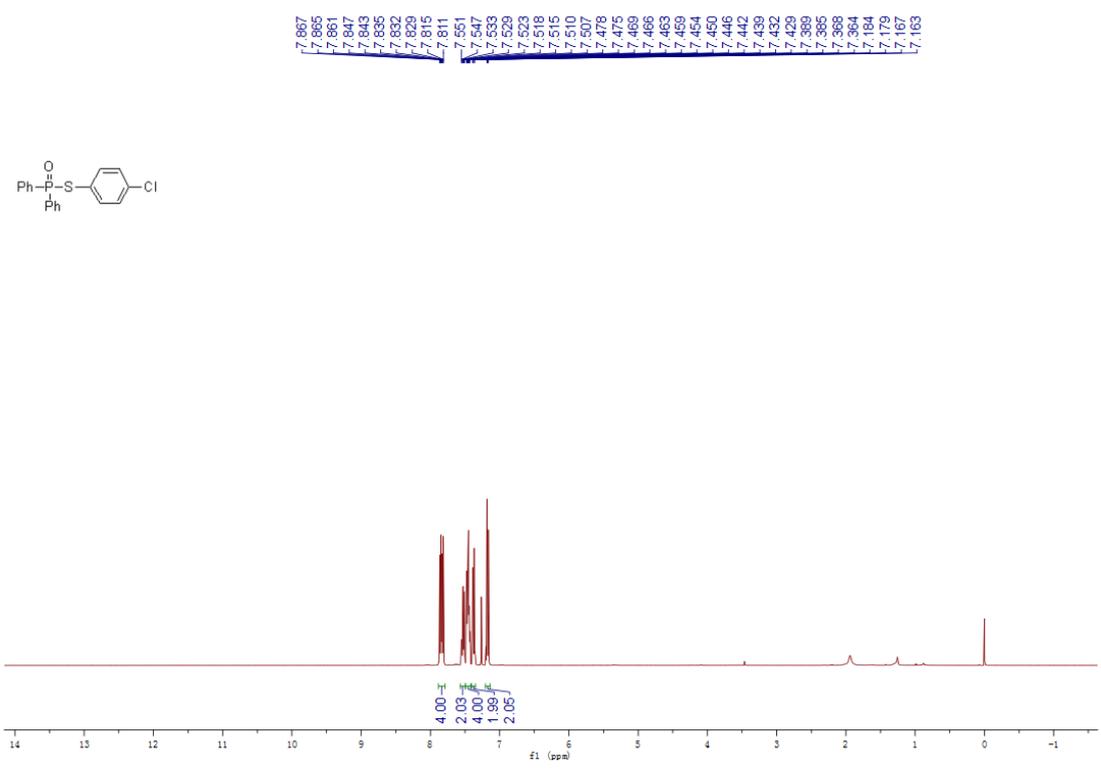
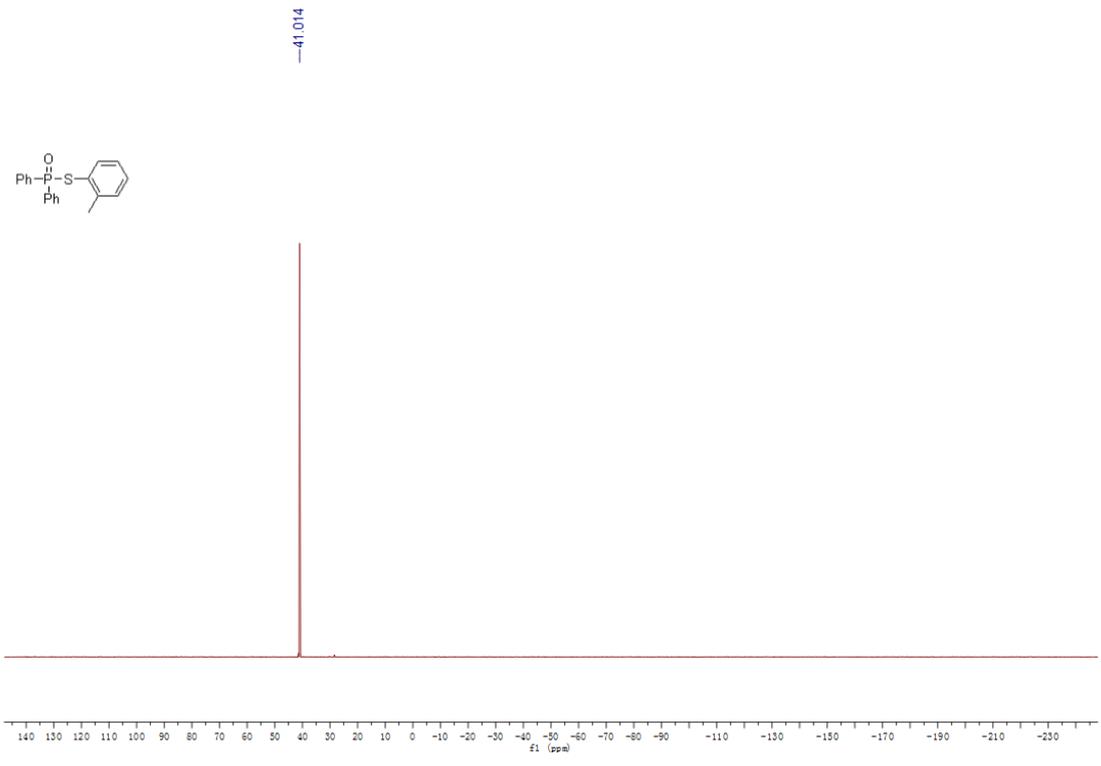
1. J. G. Sun, H. Yang, P. Li, B. Zhang, *Org. Lett.* **2016**, *18*, 5114-5117.
2. M. Xia, J. Cheng, *Tetrahedron Lett.* **2016**, *57*, 4702-4704.
3. J. Wang, X. Huang, Z. Ni, S. Wang, J. Wu, Y. Pan, *Green Chem.* **2015**, *17*, 314-319.
4. B. Xiong, G. Wang, C. Zhou, Y. Liu, J. Li, P. Zhang, K. Tang, *Phosphorus, Sulfur, and Silicon and the Related Elements* **2017**, *193*, 239-244.
5. T. Yuan, S. Huang, C. Cai, G. P. Lu, *Org. Biomol. Chem.* **2017**, *16*, 30-33.
6. H.-J. Hong, J. Lee, A. R. Bae, I.-H. Um, *Bull. Korean. Chem. Soc.* **2013**, *34*, 2001-2005.
7. B. Xiong, K. Zeng, S. Zhang, Y. Zhou, C.-T. Au, S.-F. Yin, *Tetrahedron* **2015**, *71*, 9293-9298.

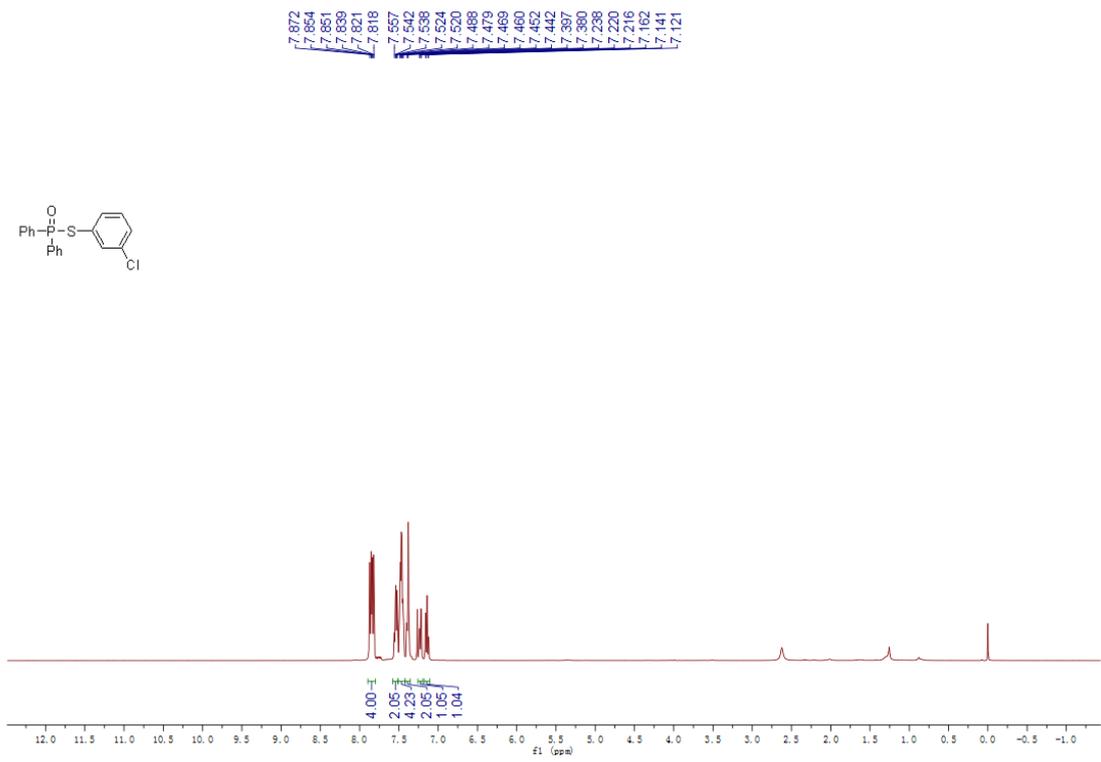
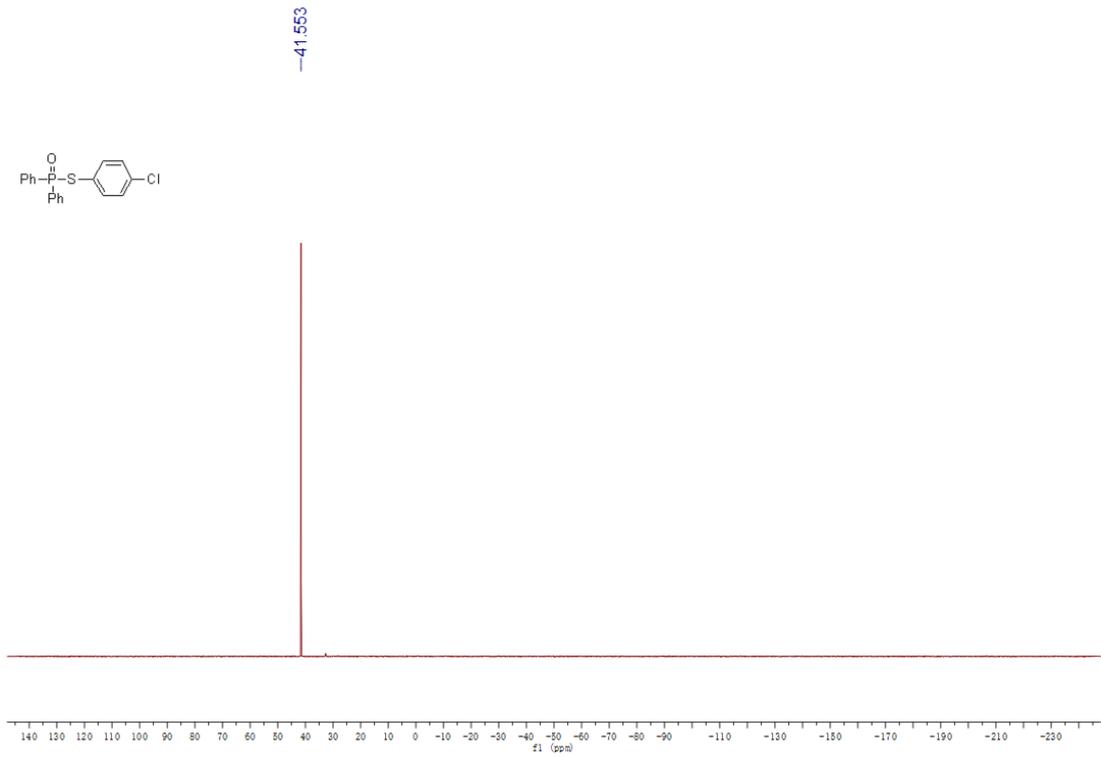
11. NMR spectra of product

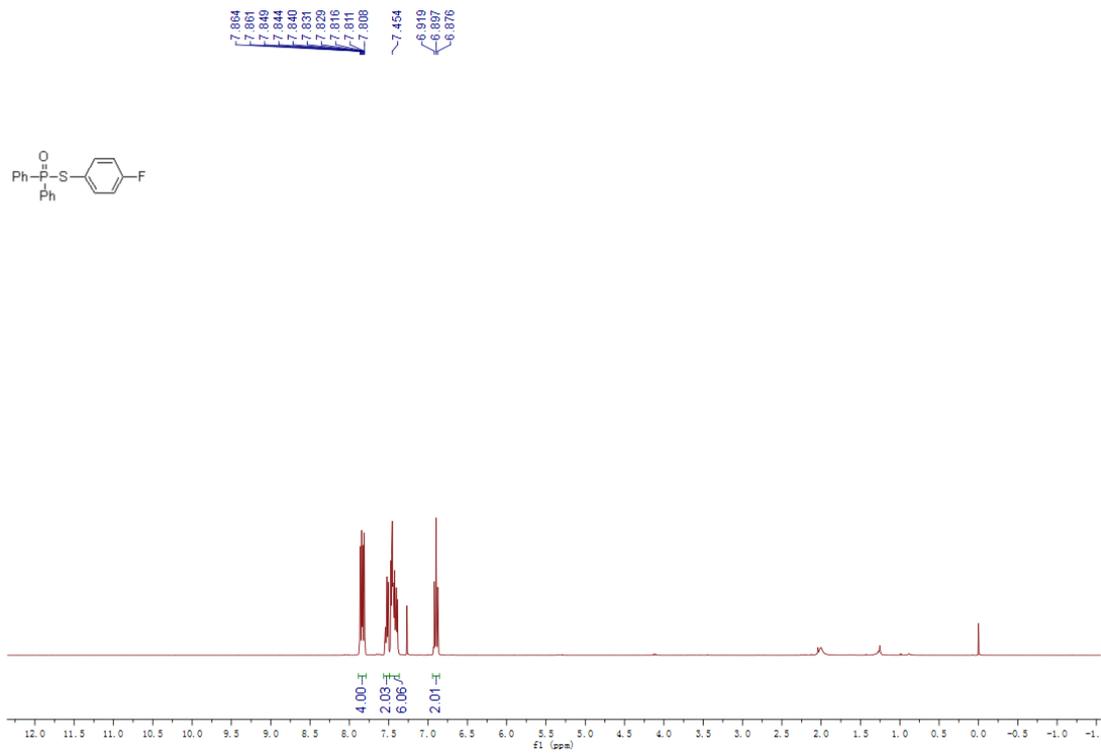
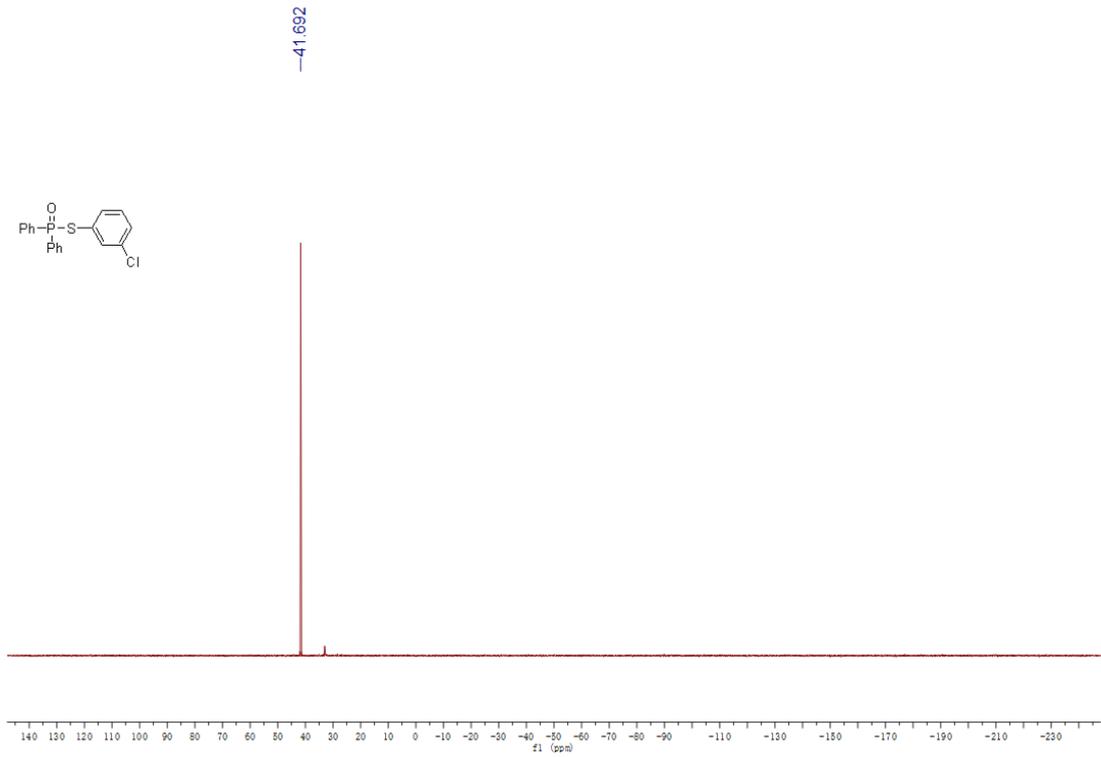


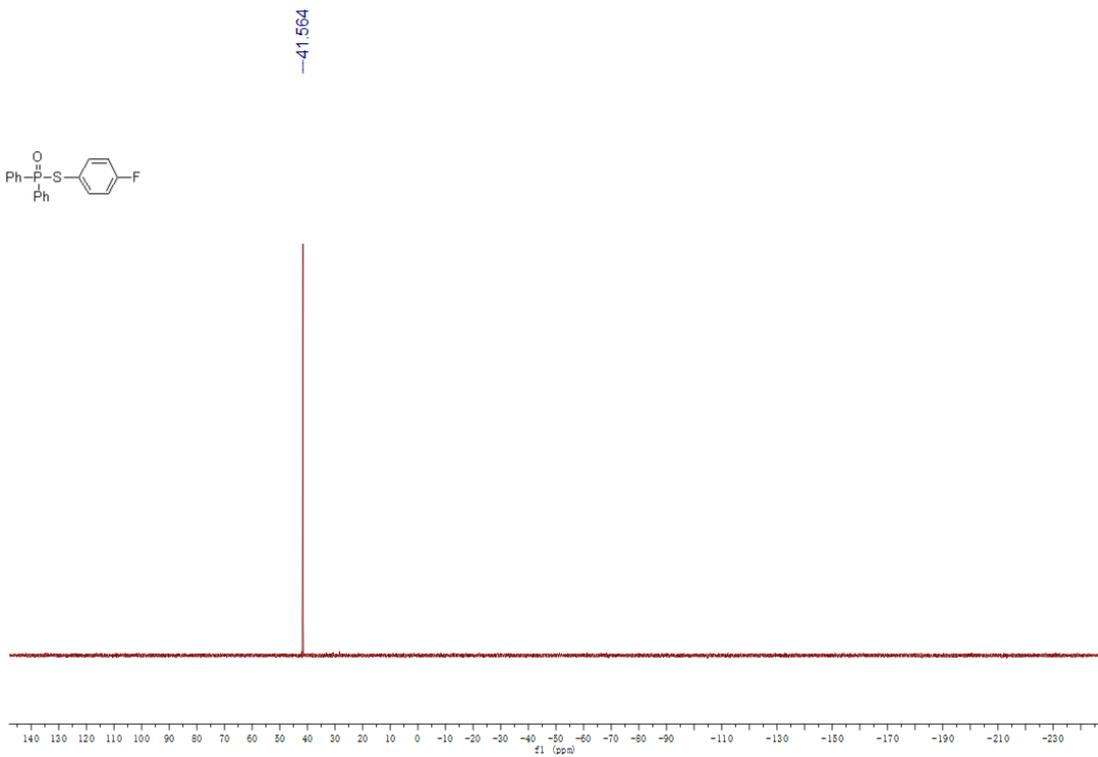
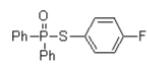




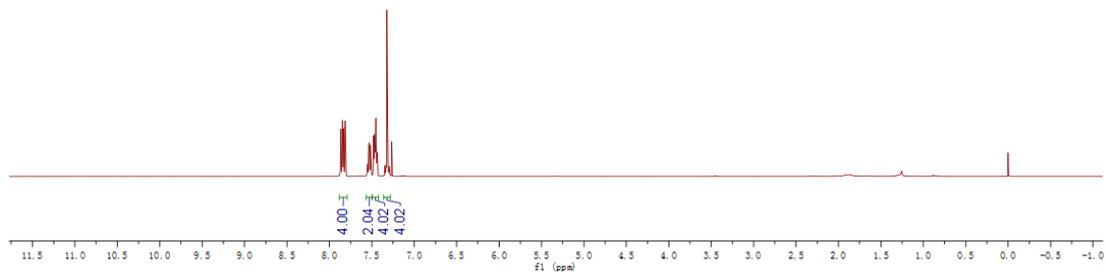
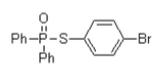


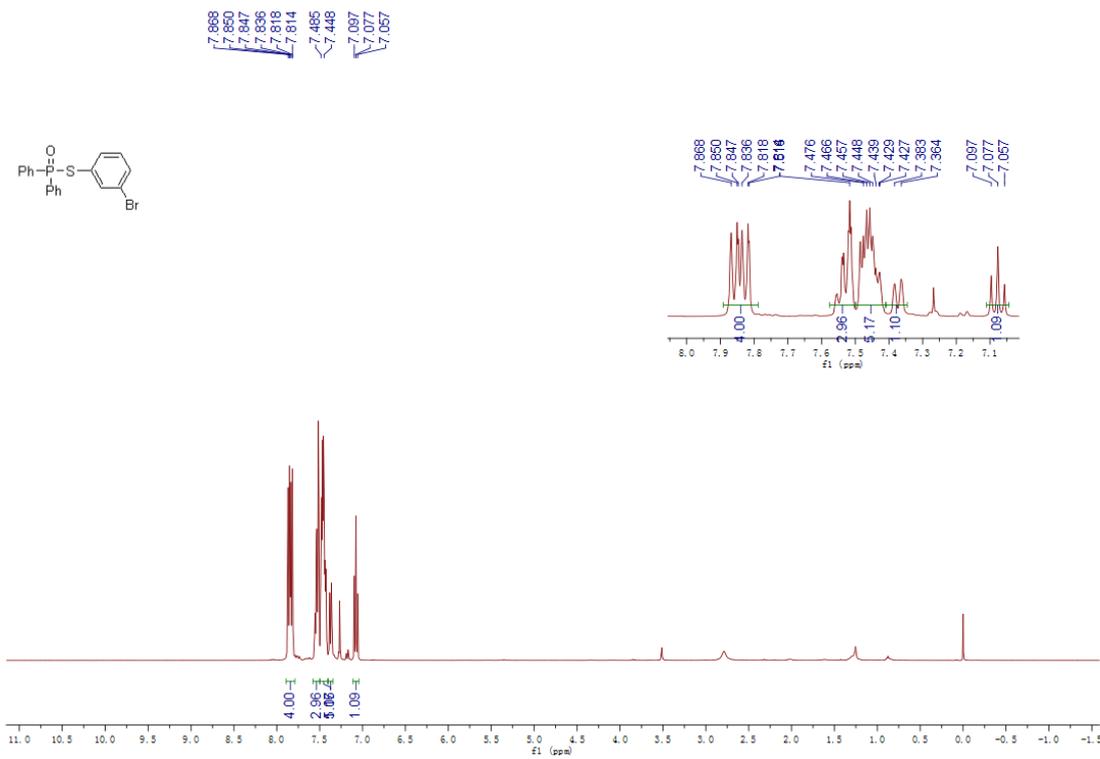
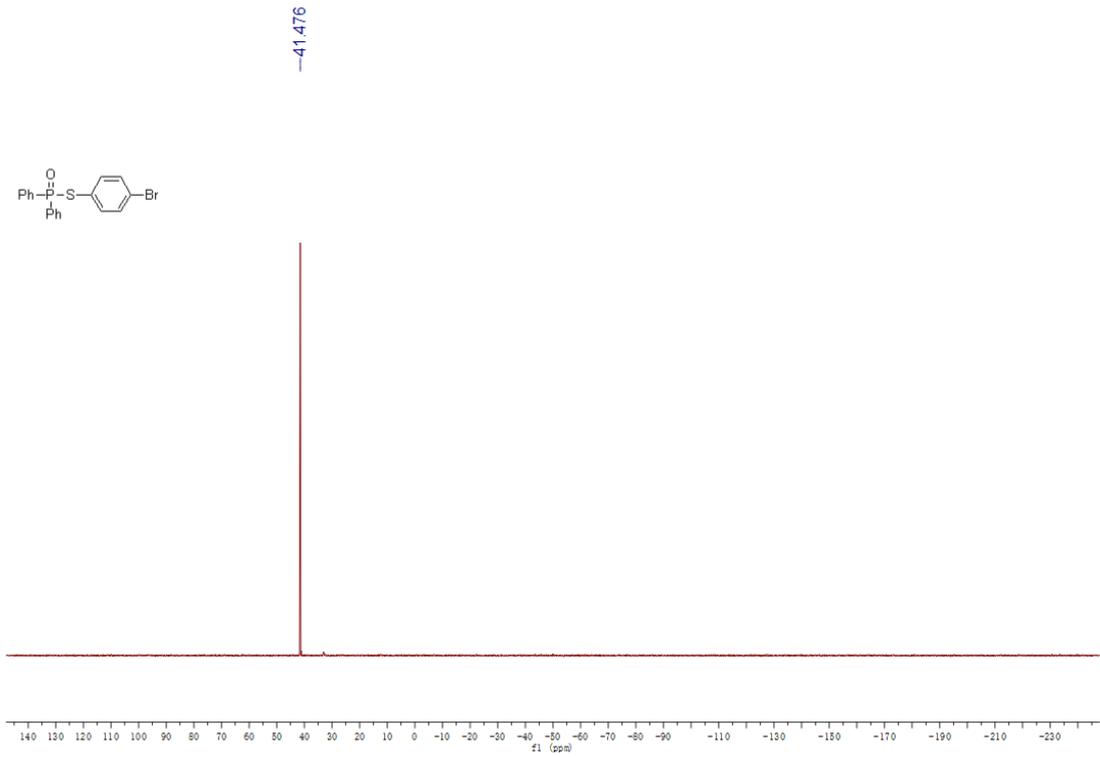


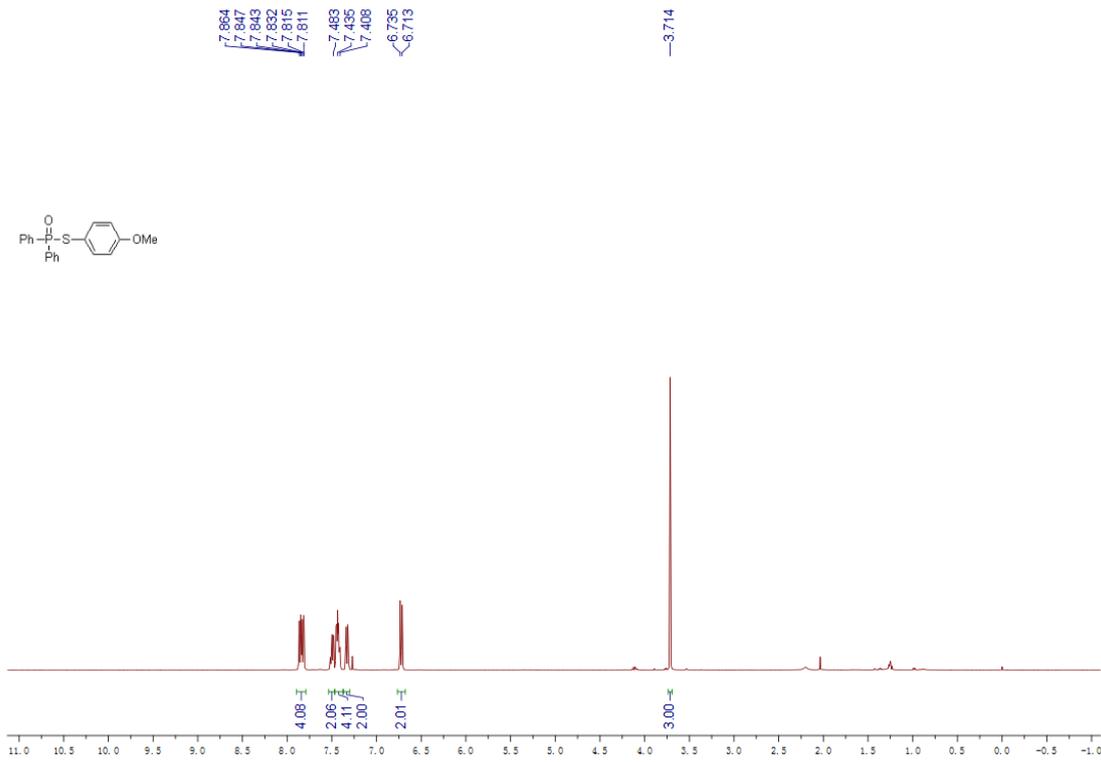
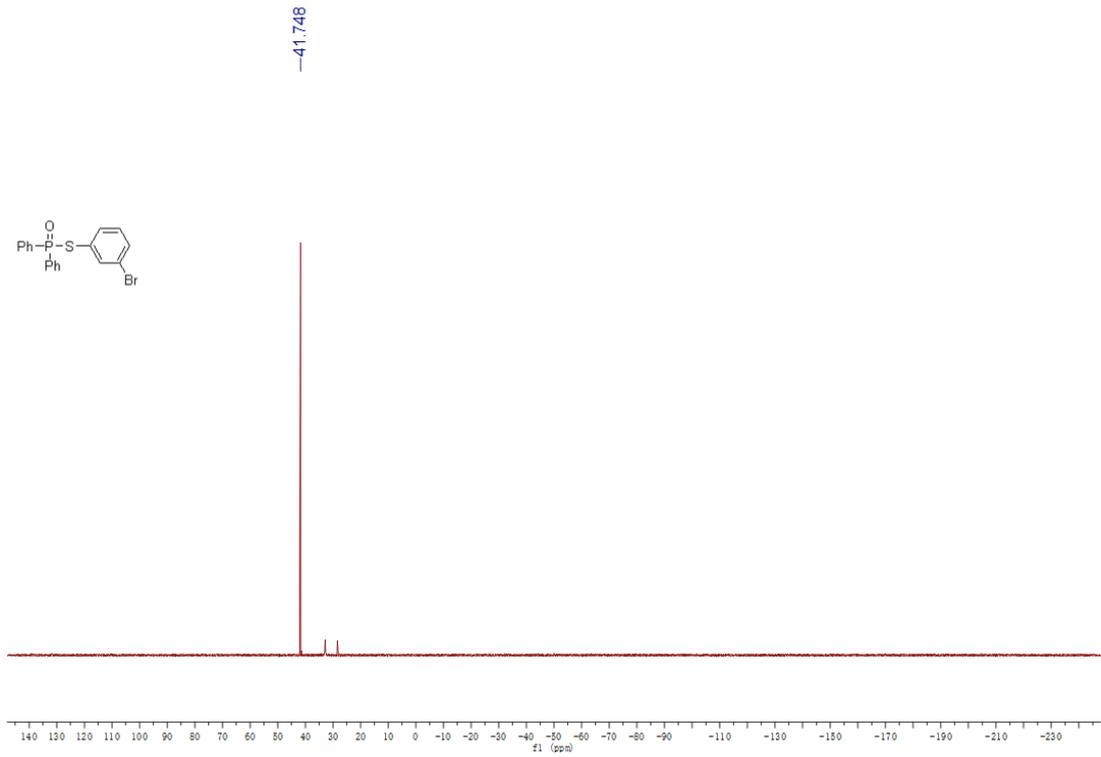


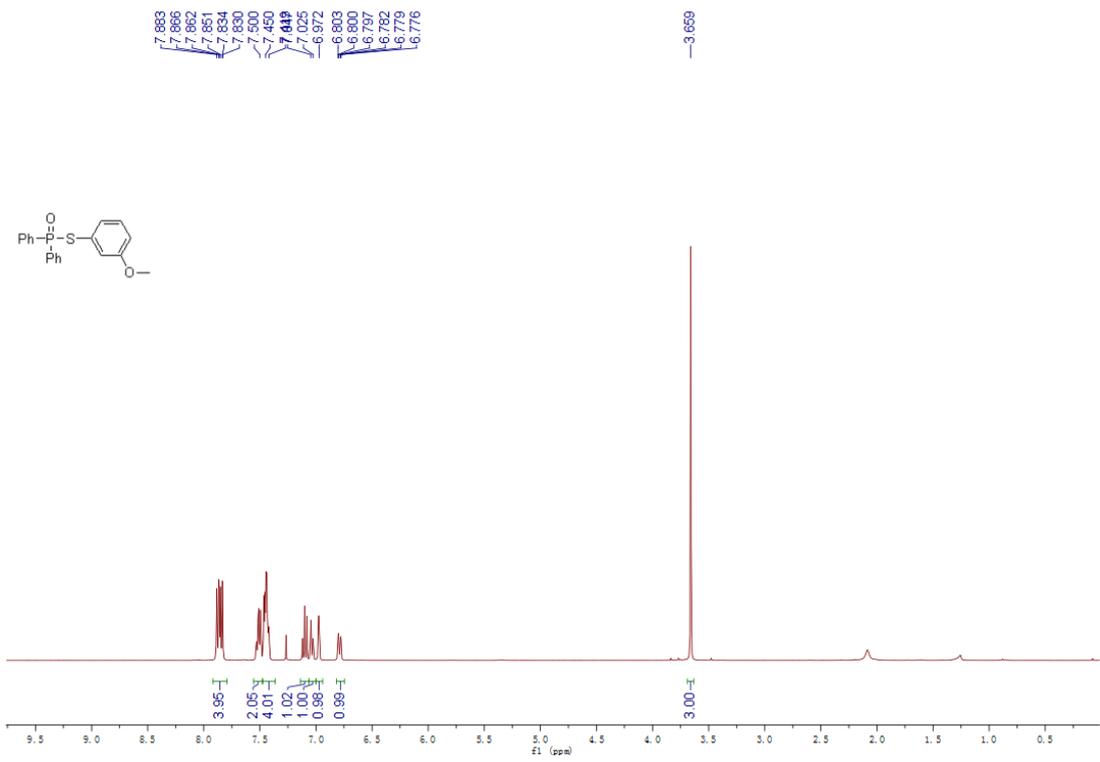
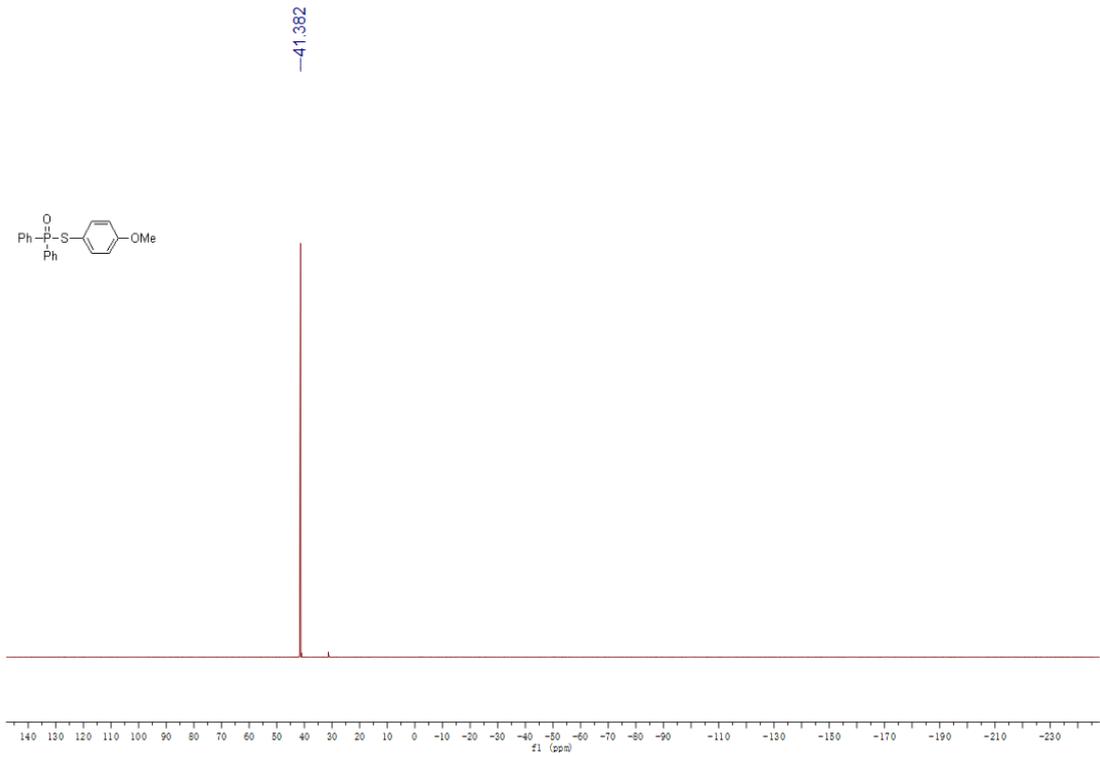


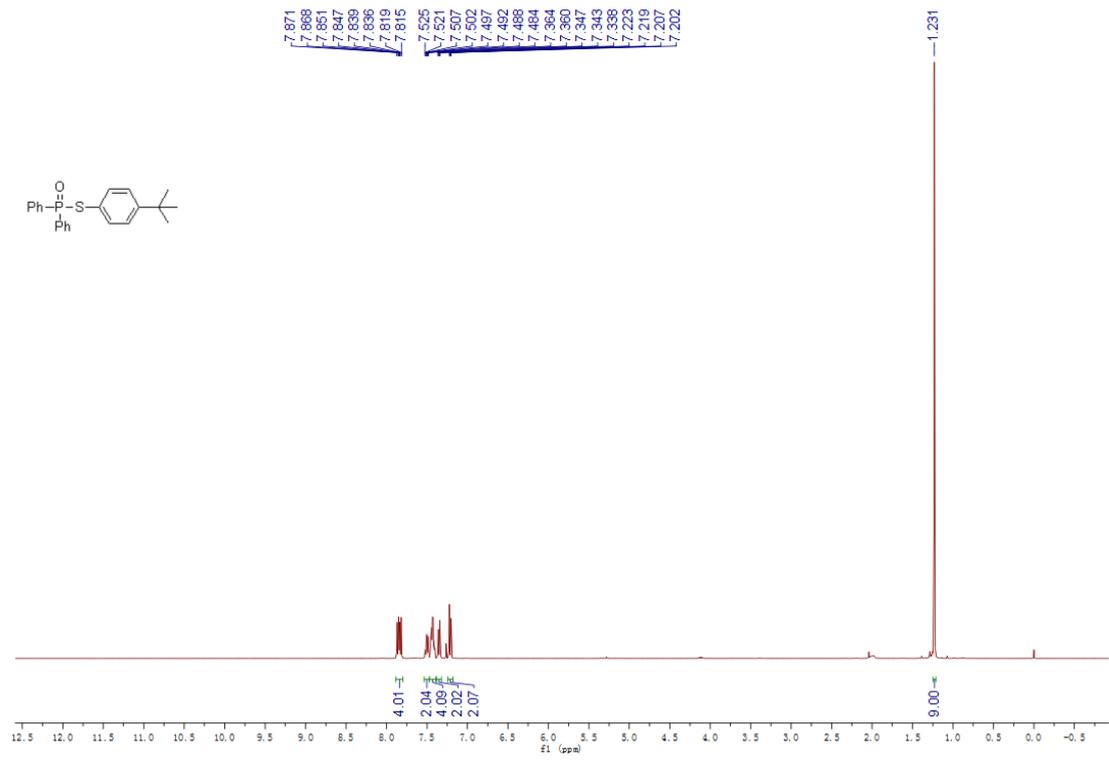
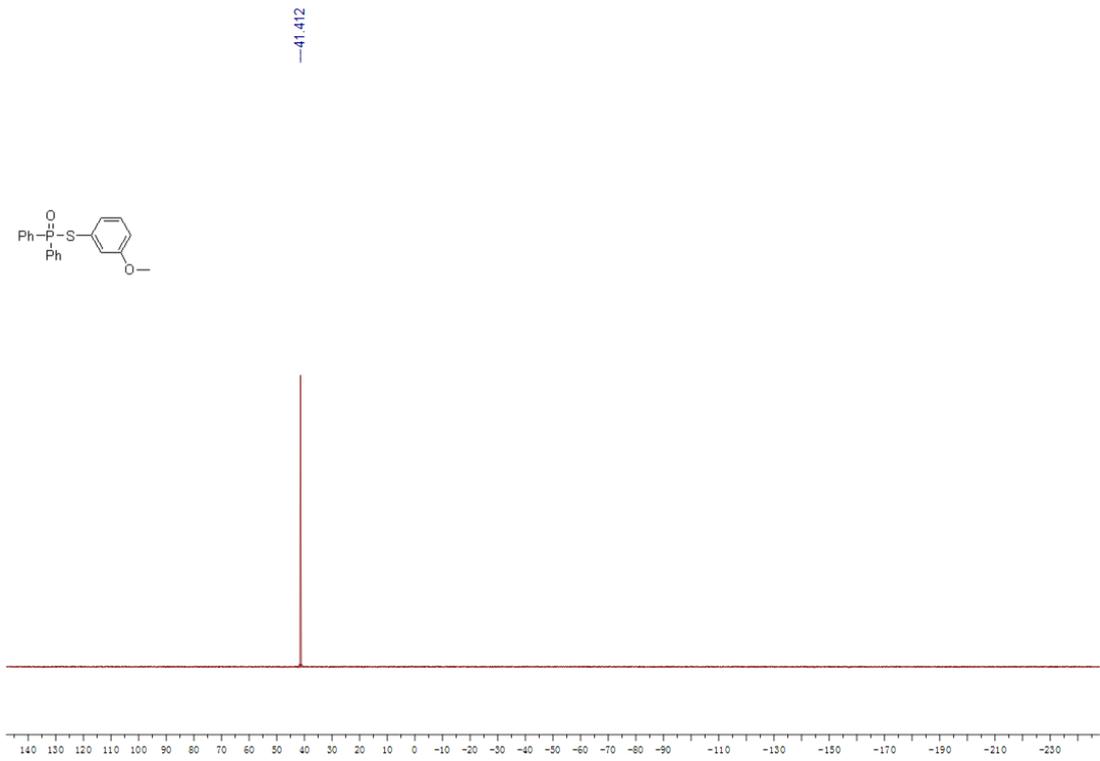
7.968
7.965
7.961
7.947
7.844
7.835
7.832
7.829
7.815
7.811
7.745
7.743
7.738
7.730
7.723
7.719
7.717
7.710
7.705
7.701
7.296

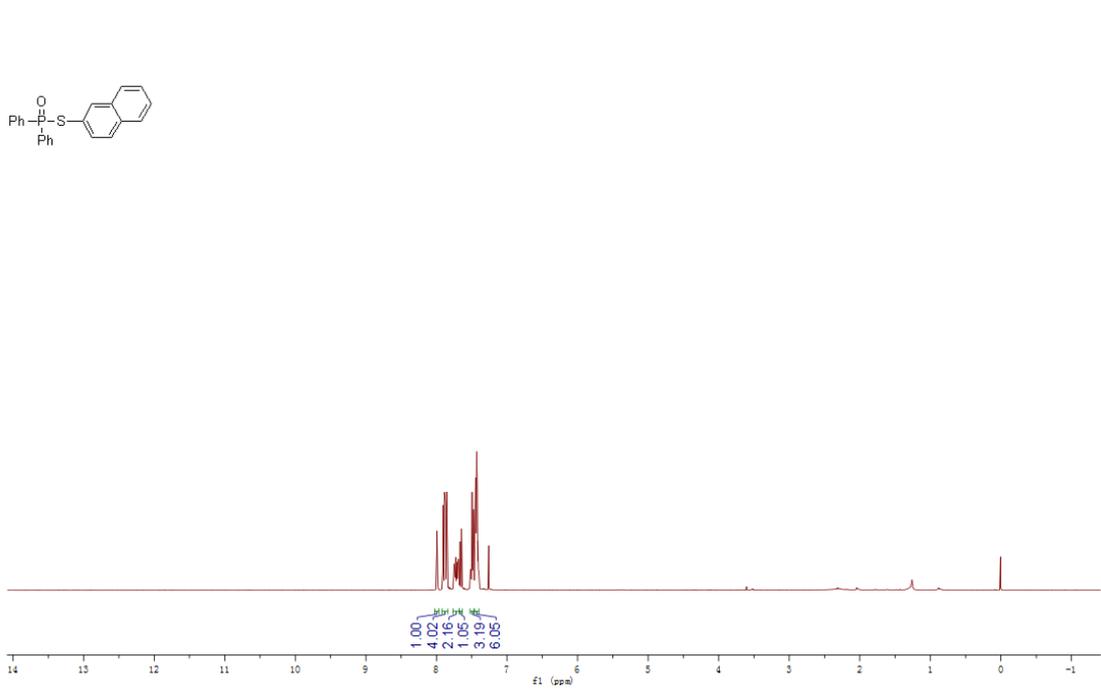
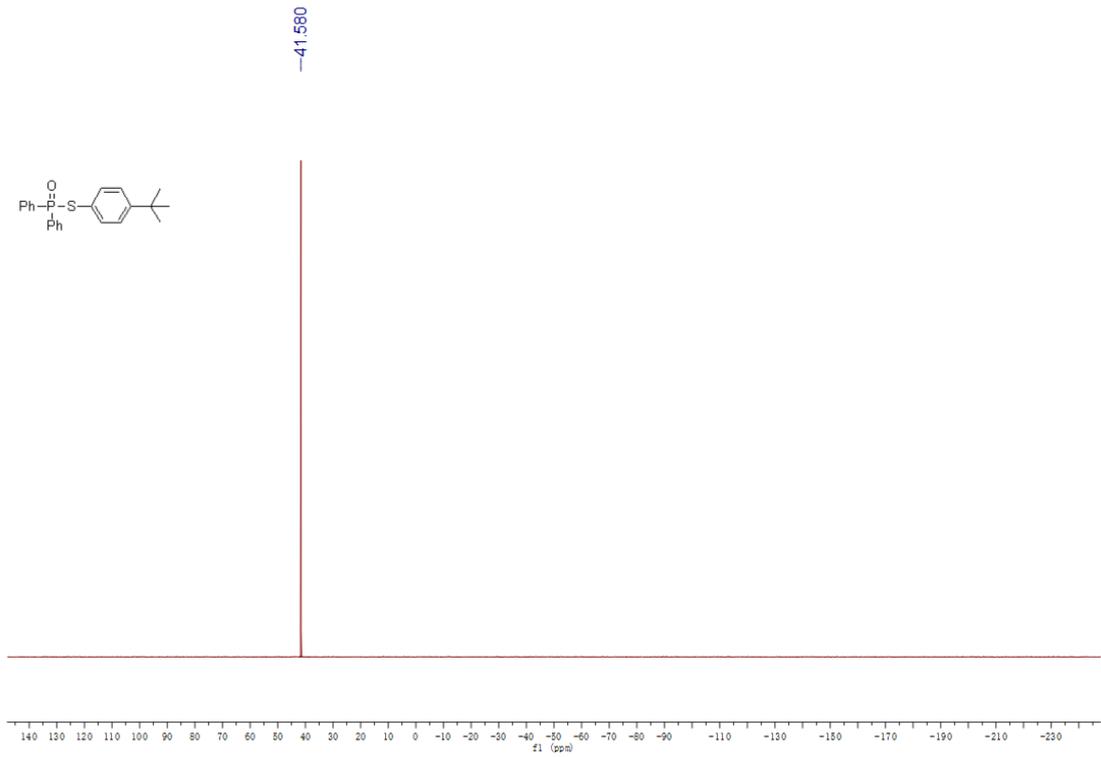


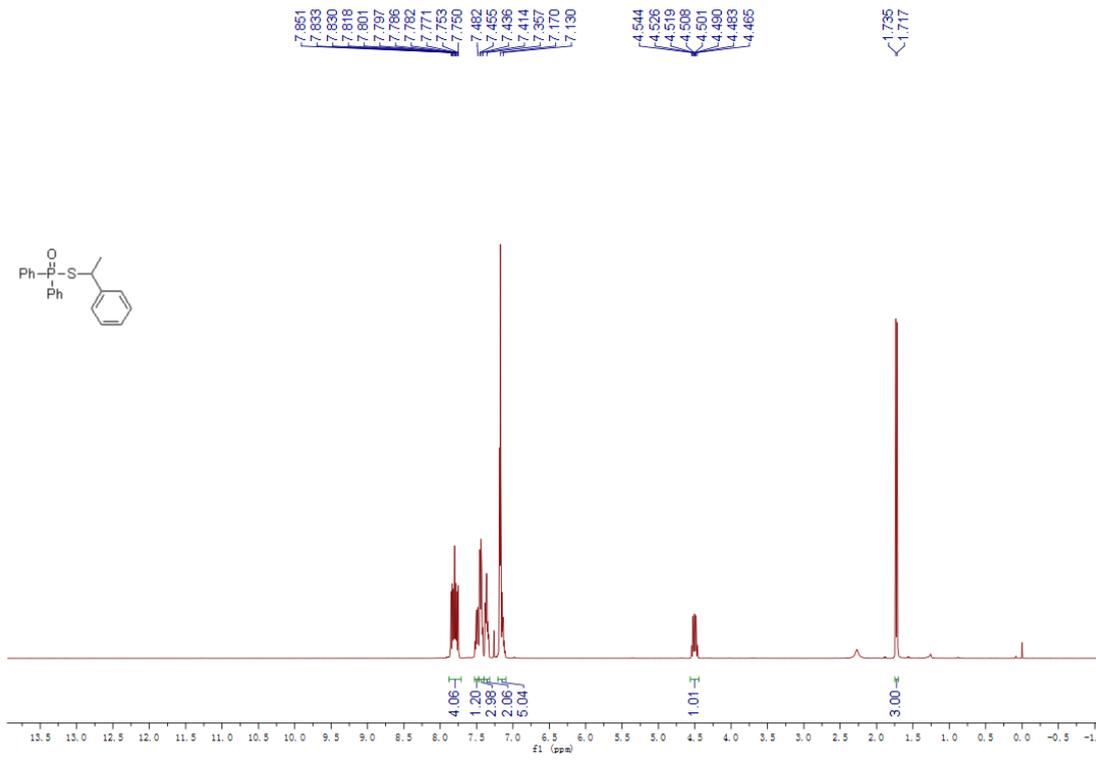
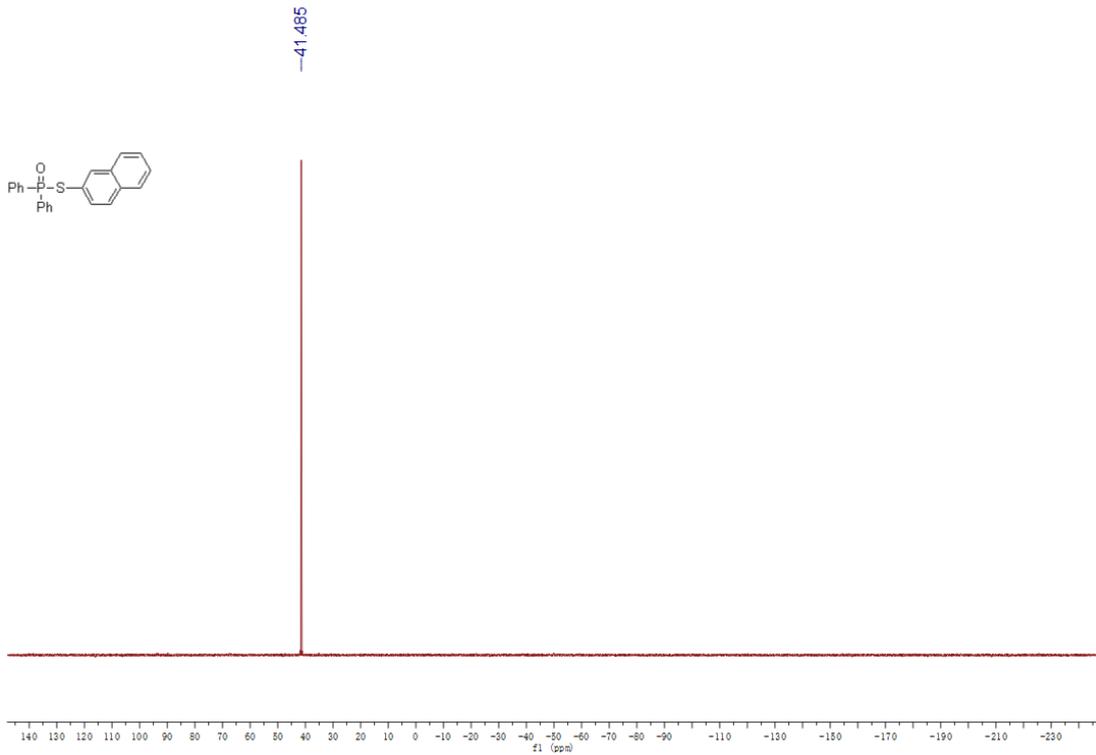


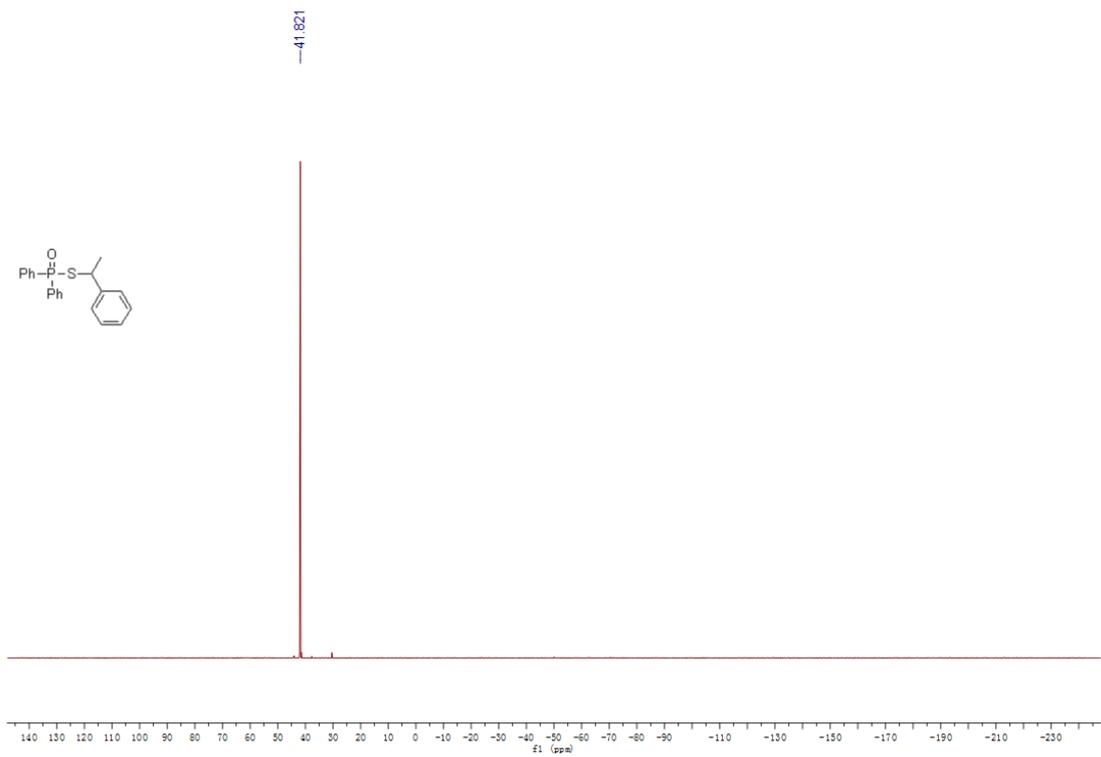
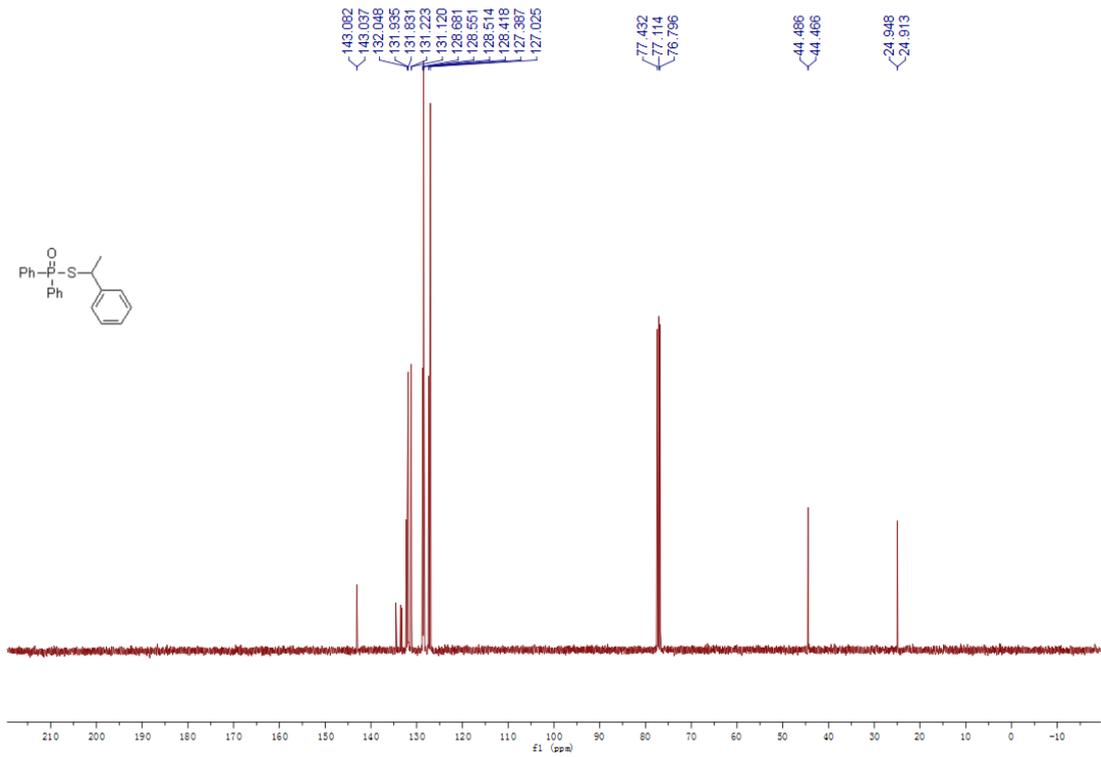


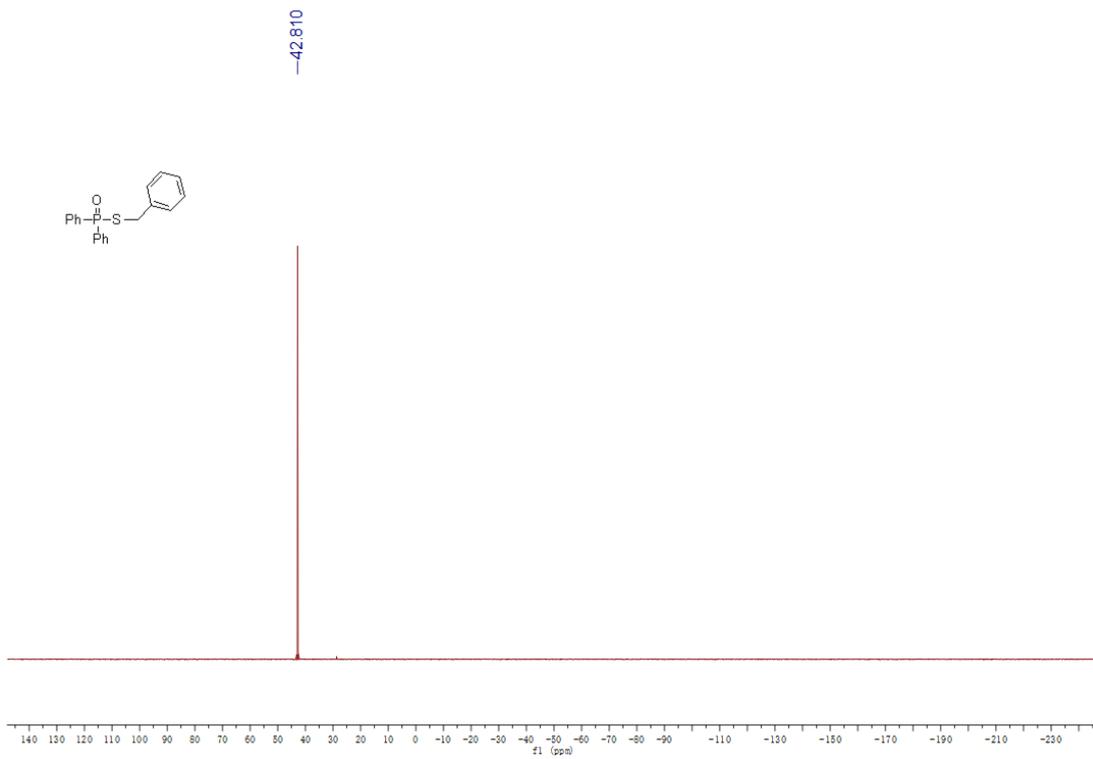
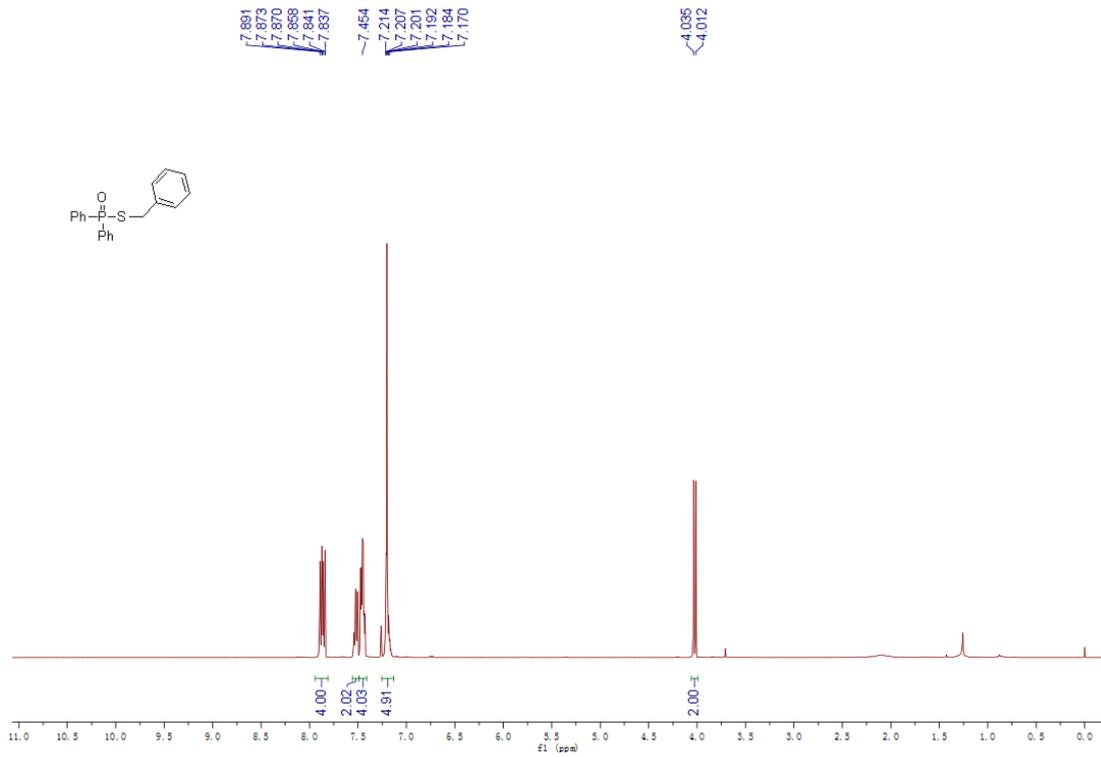


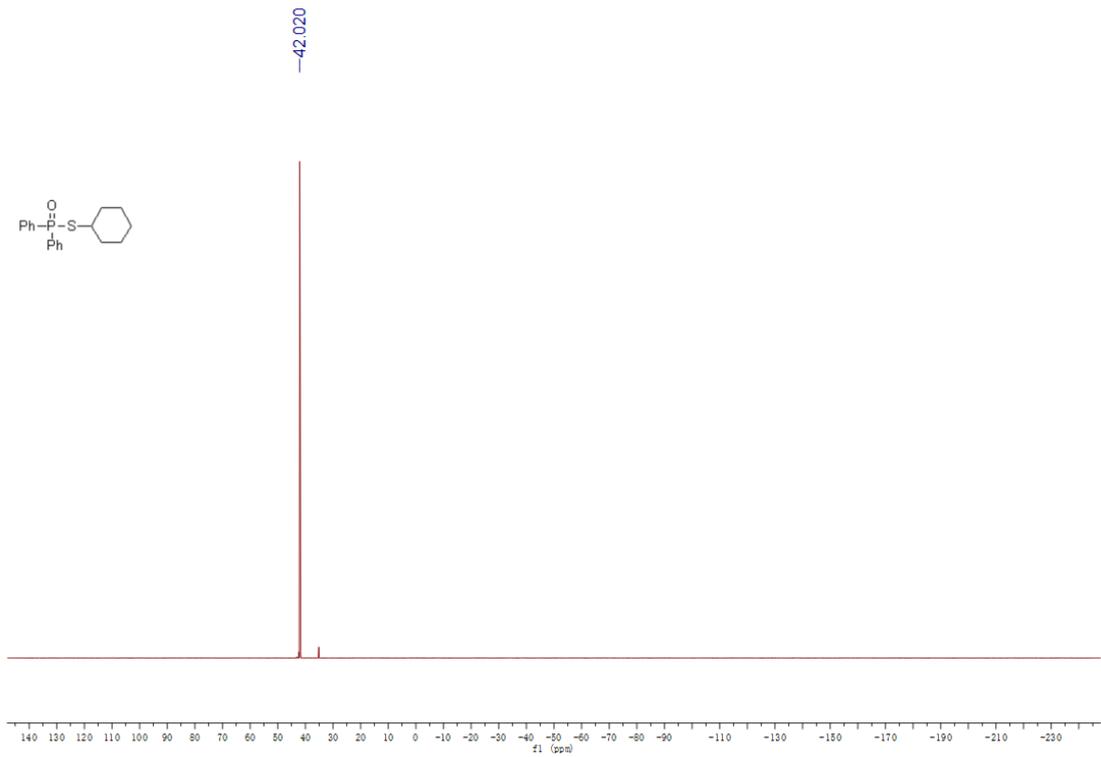
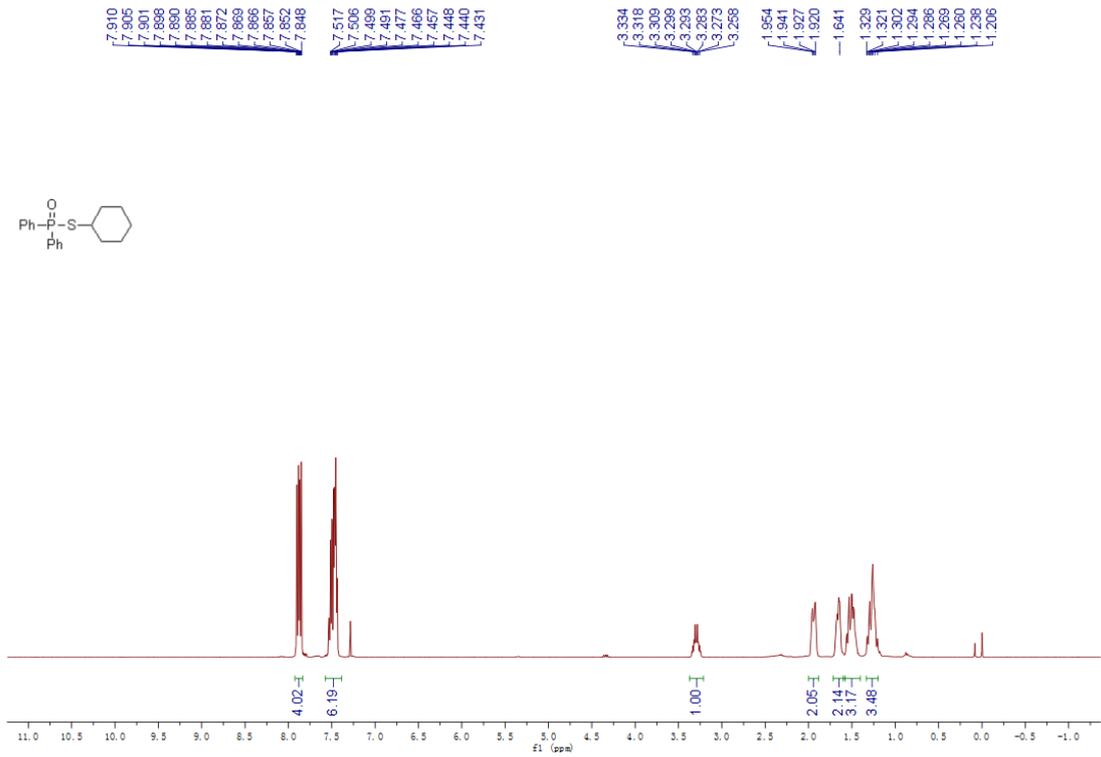


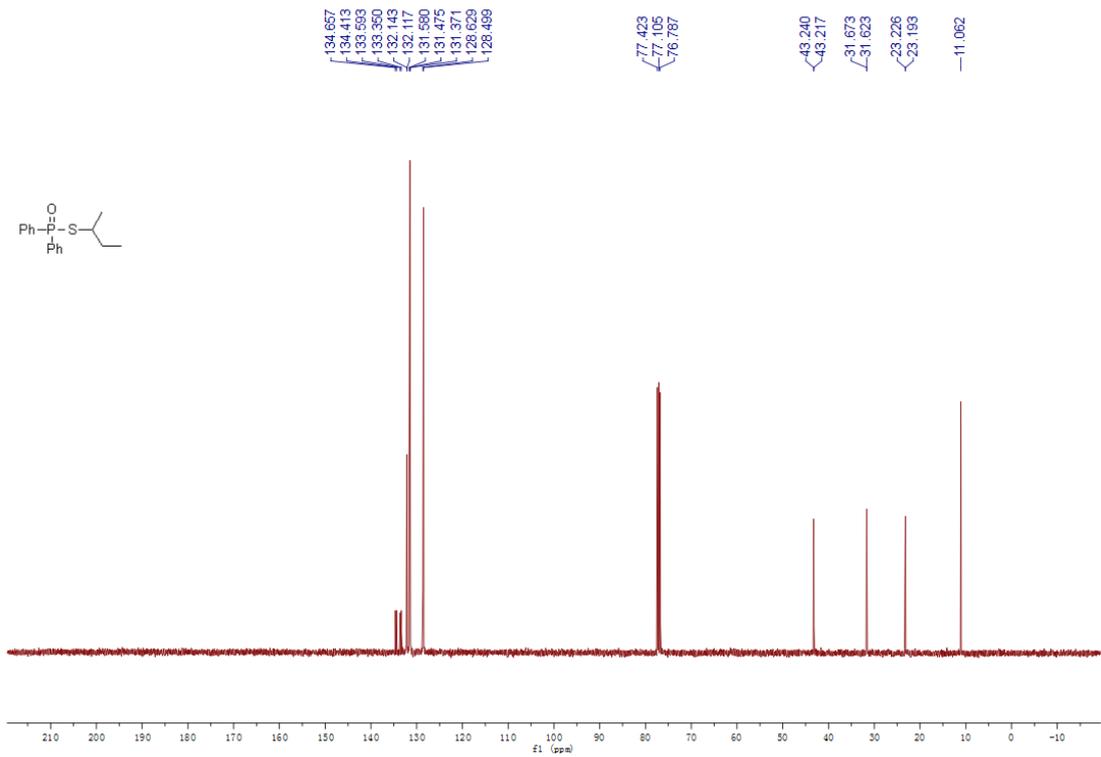
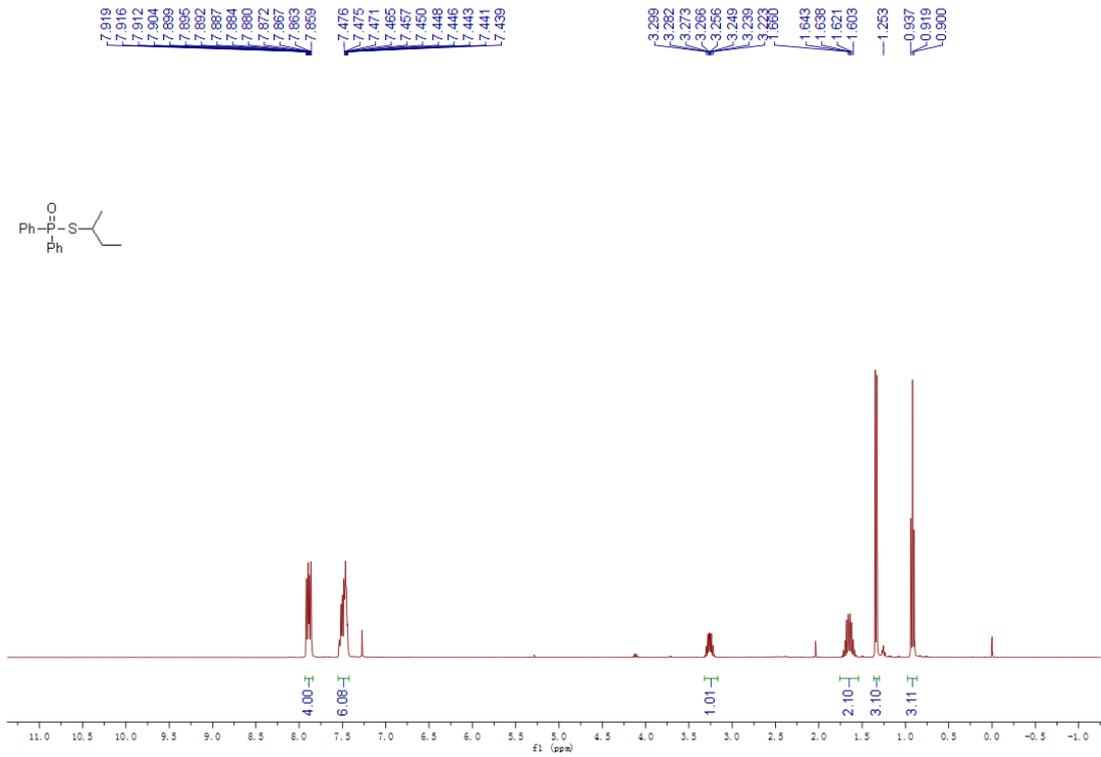


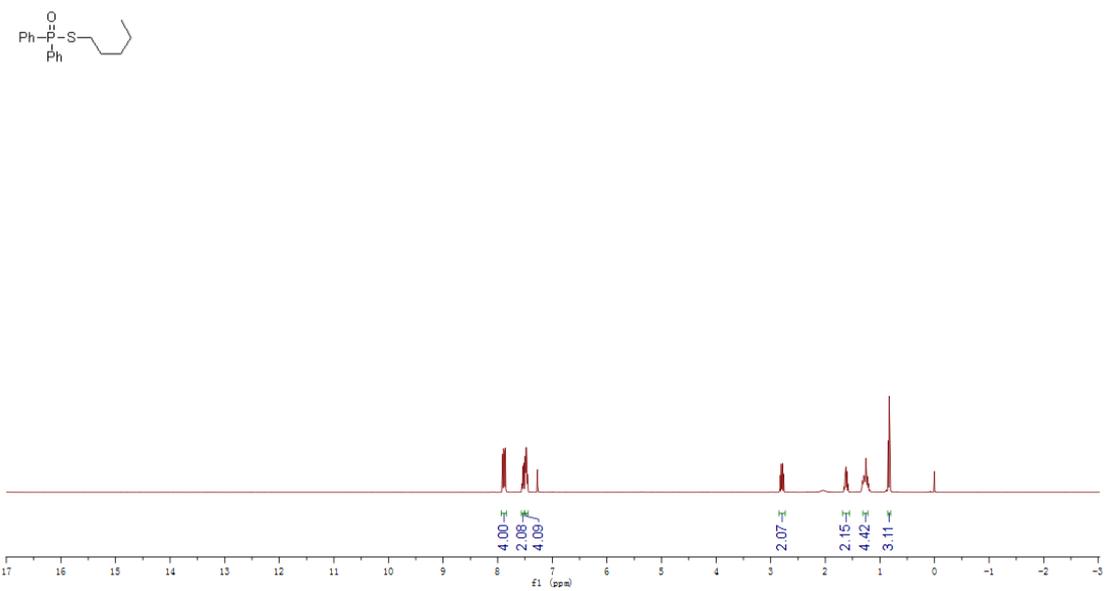
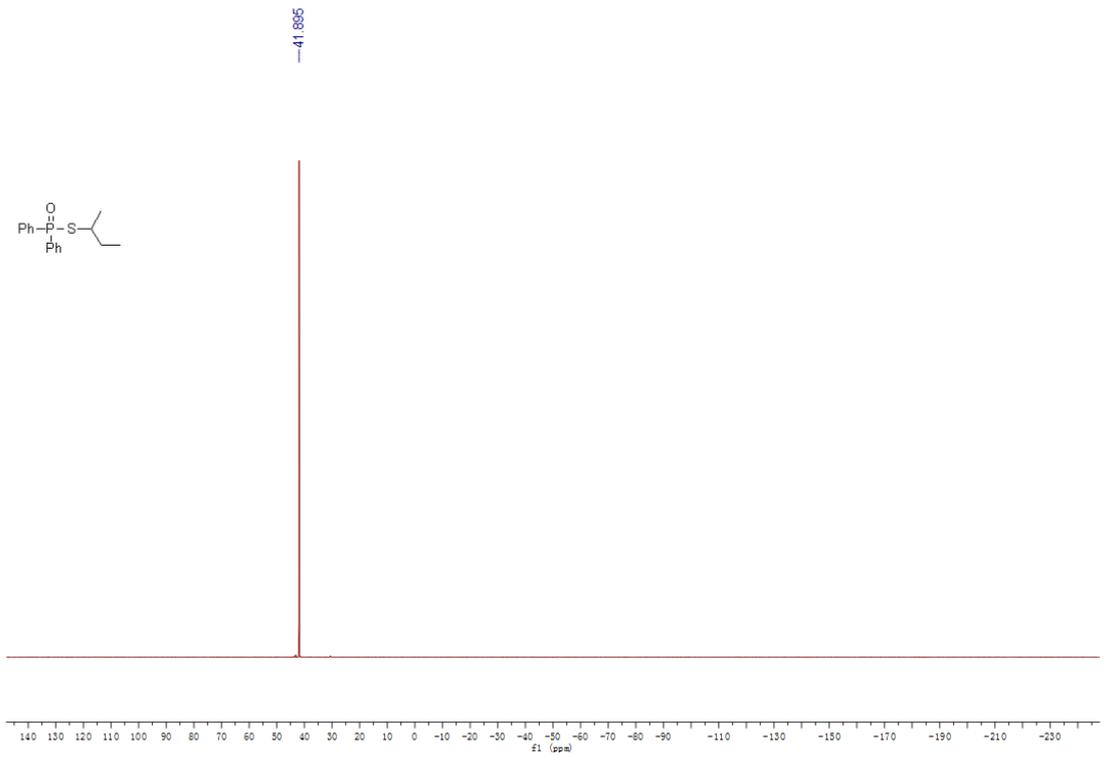


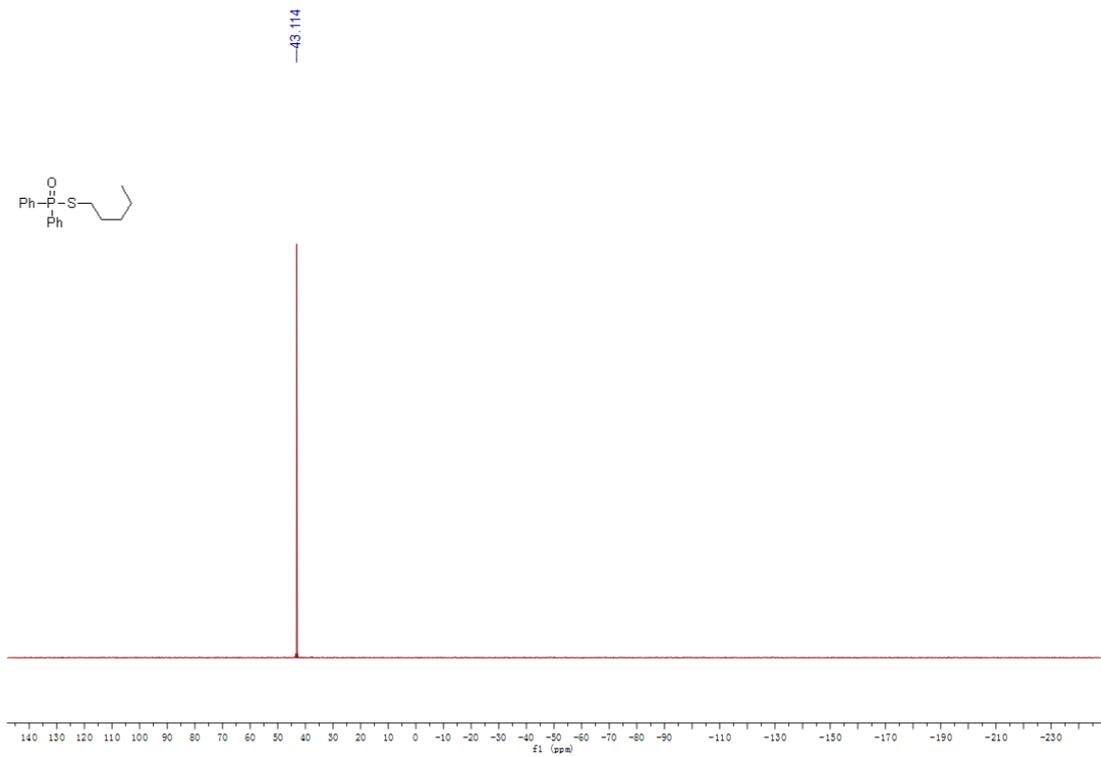
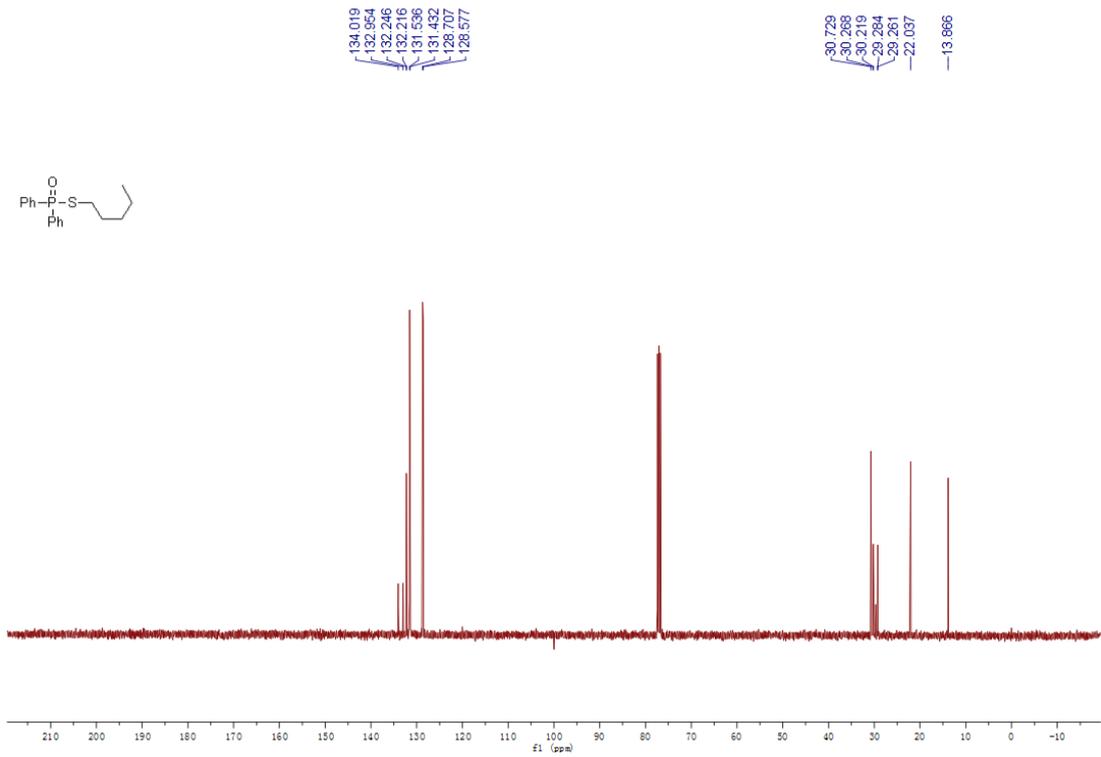


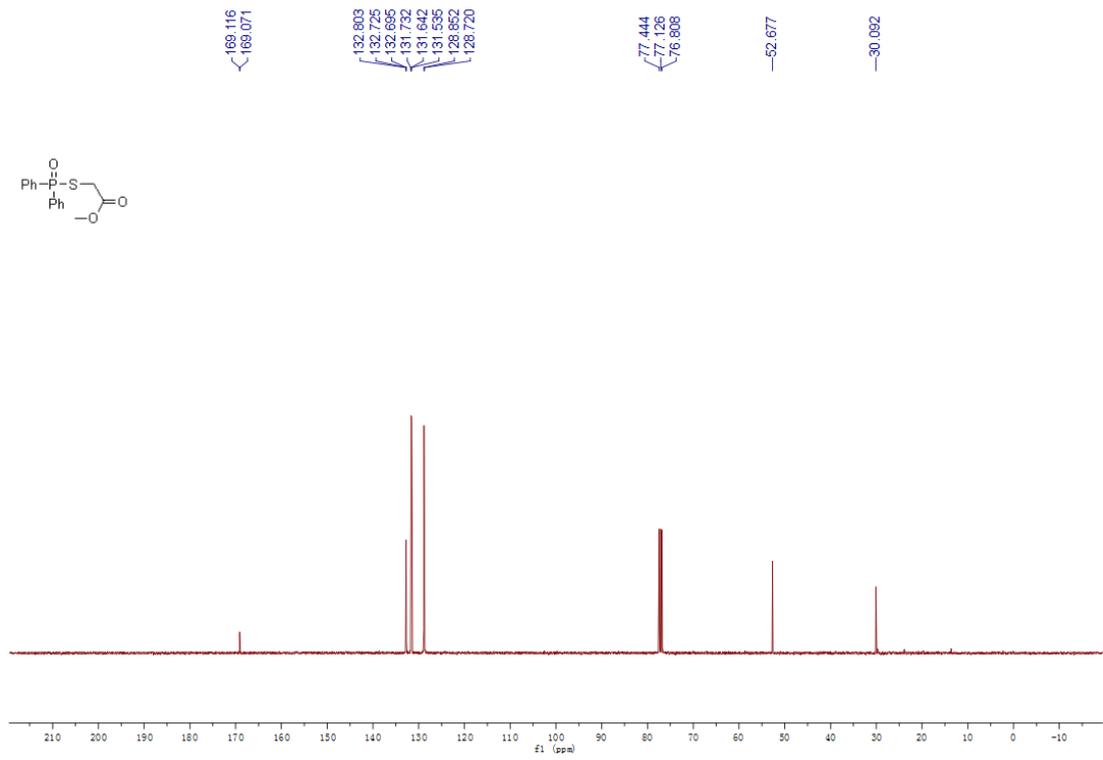
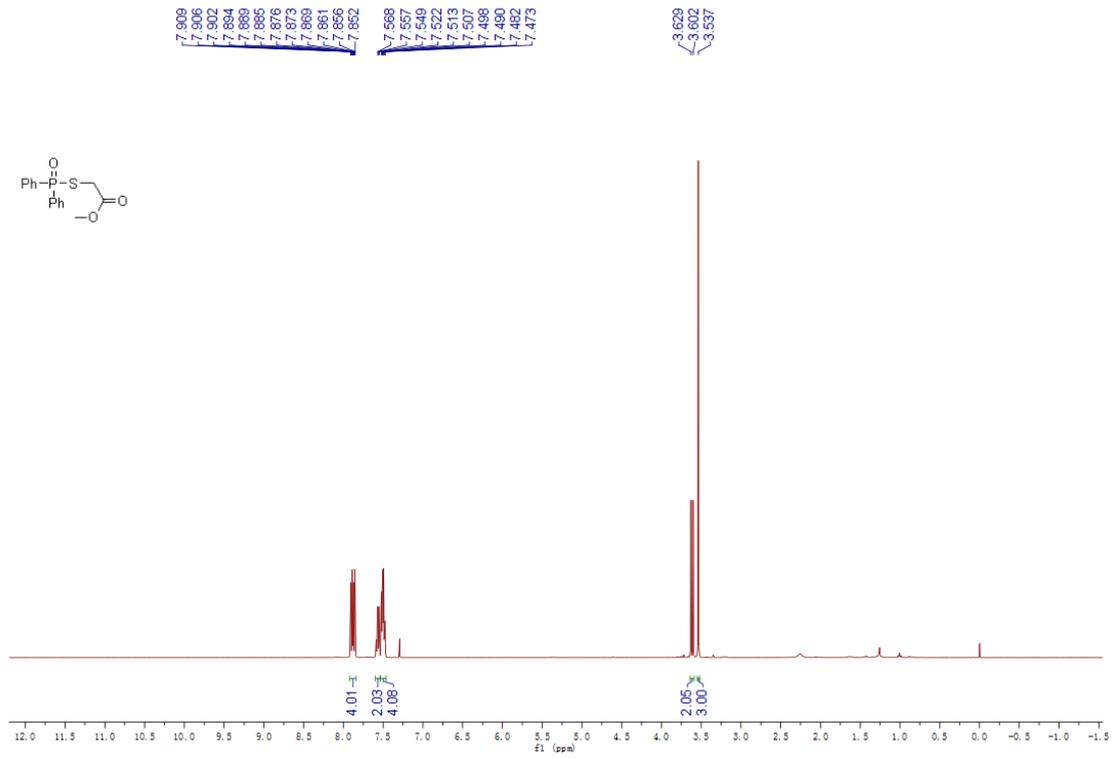


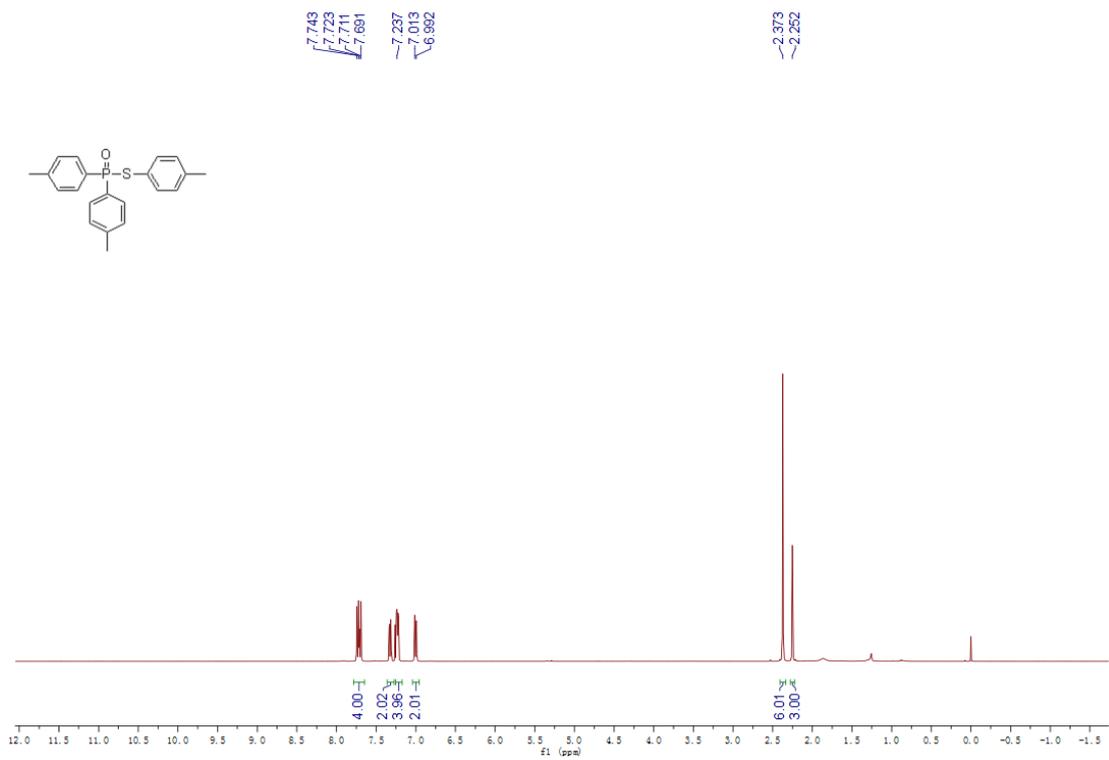
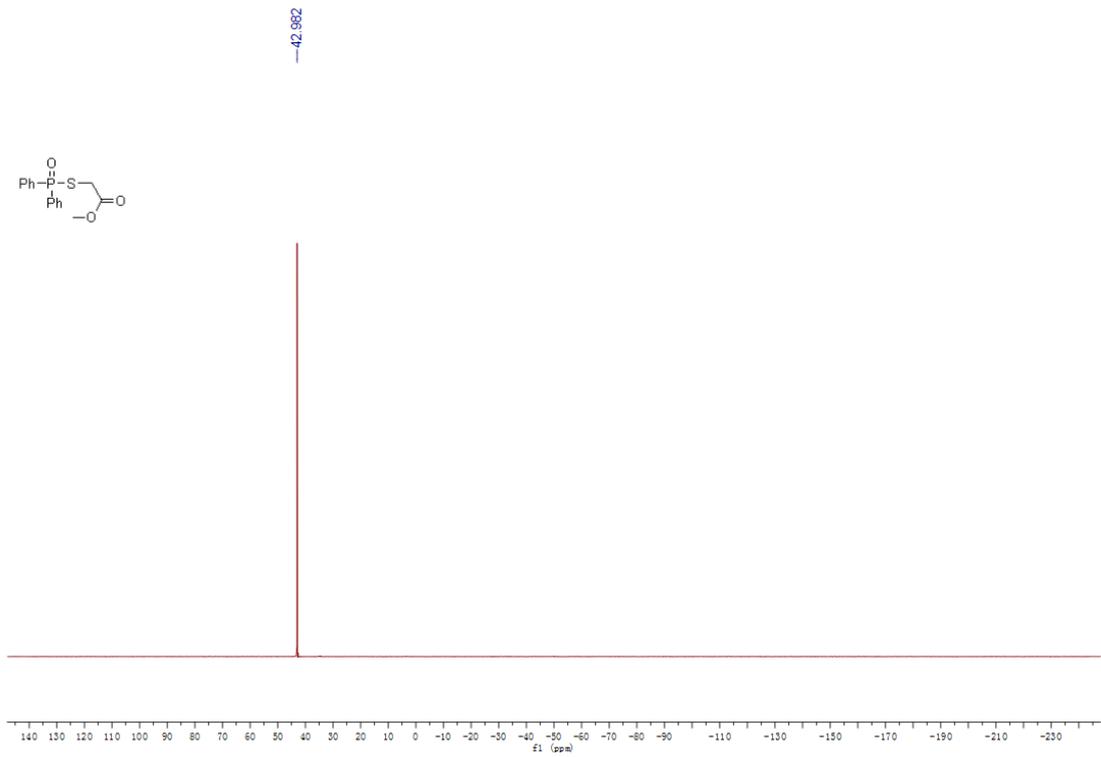


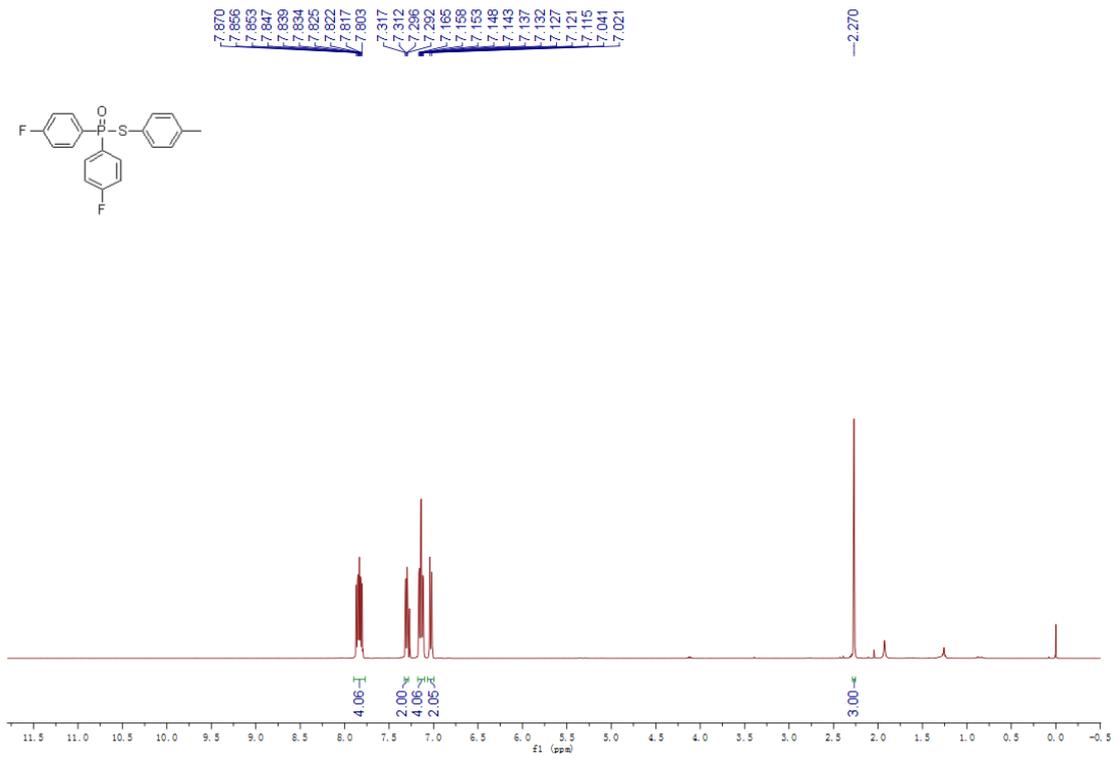
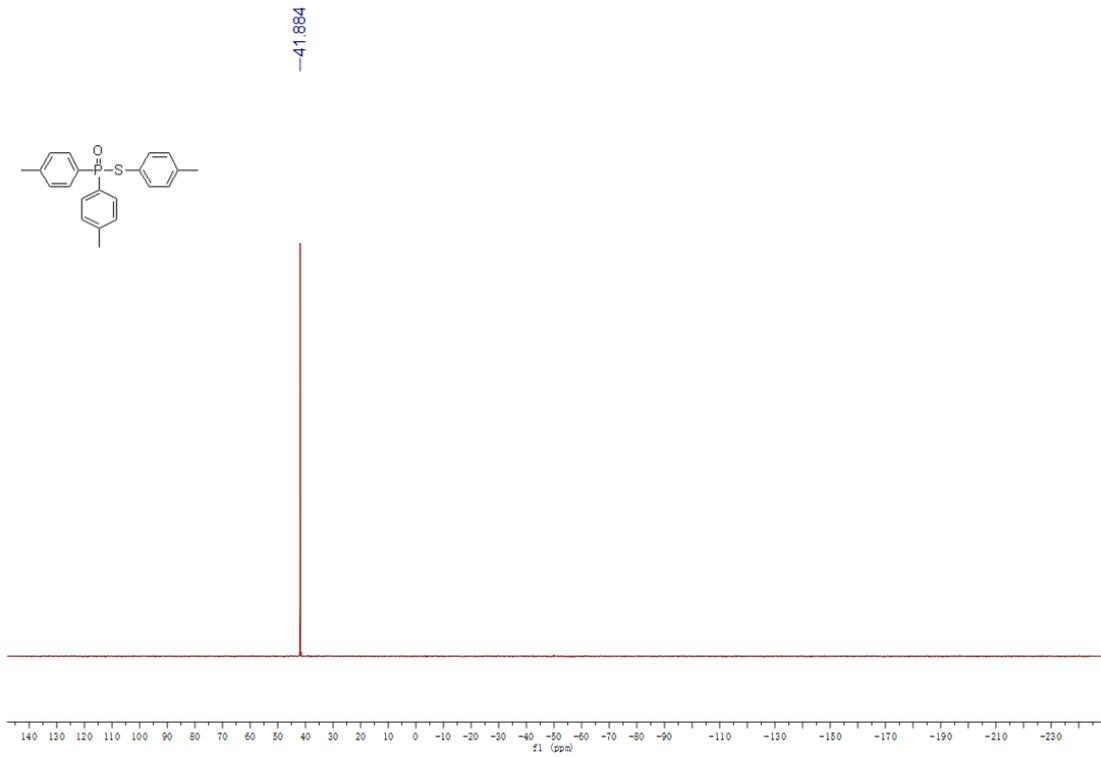


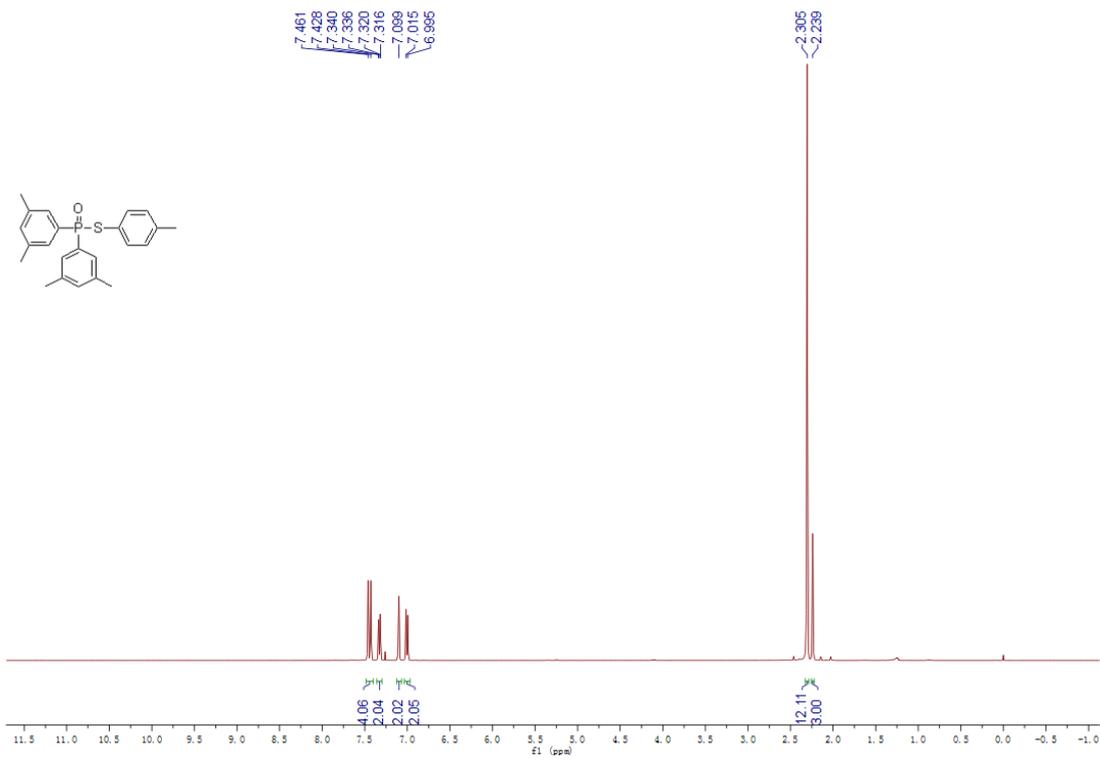
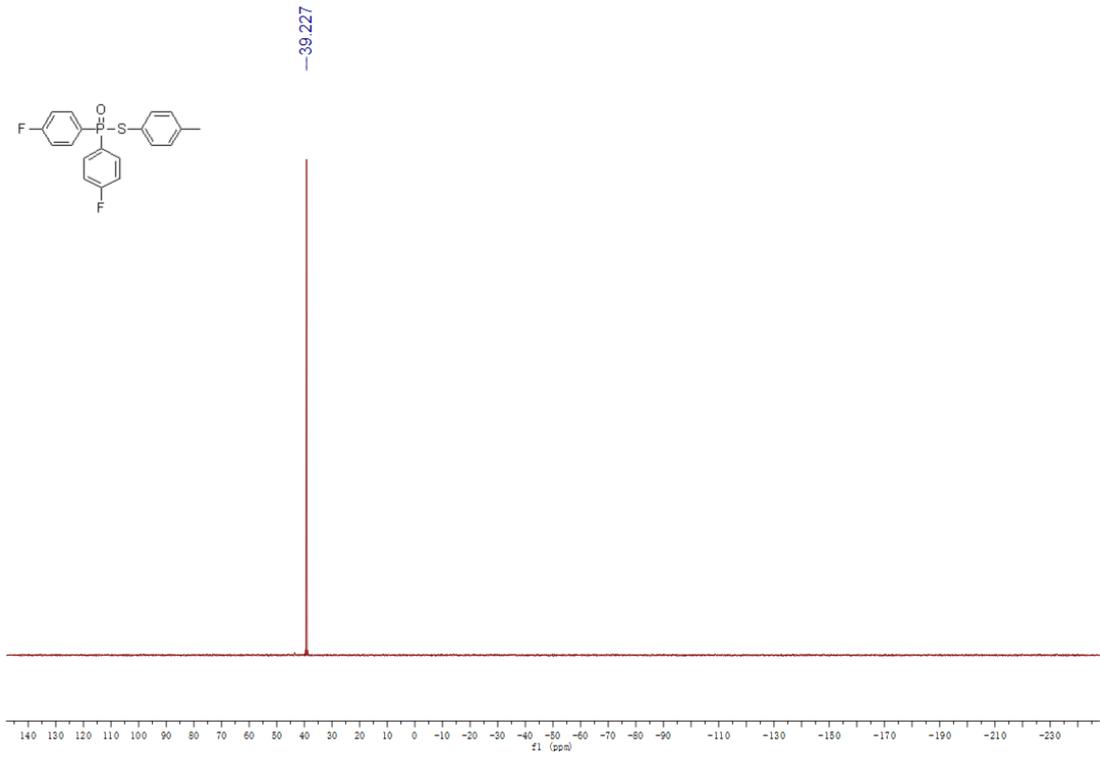


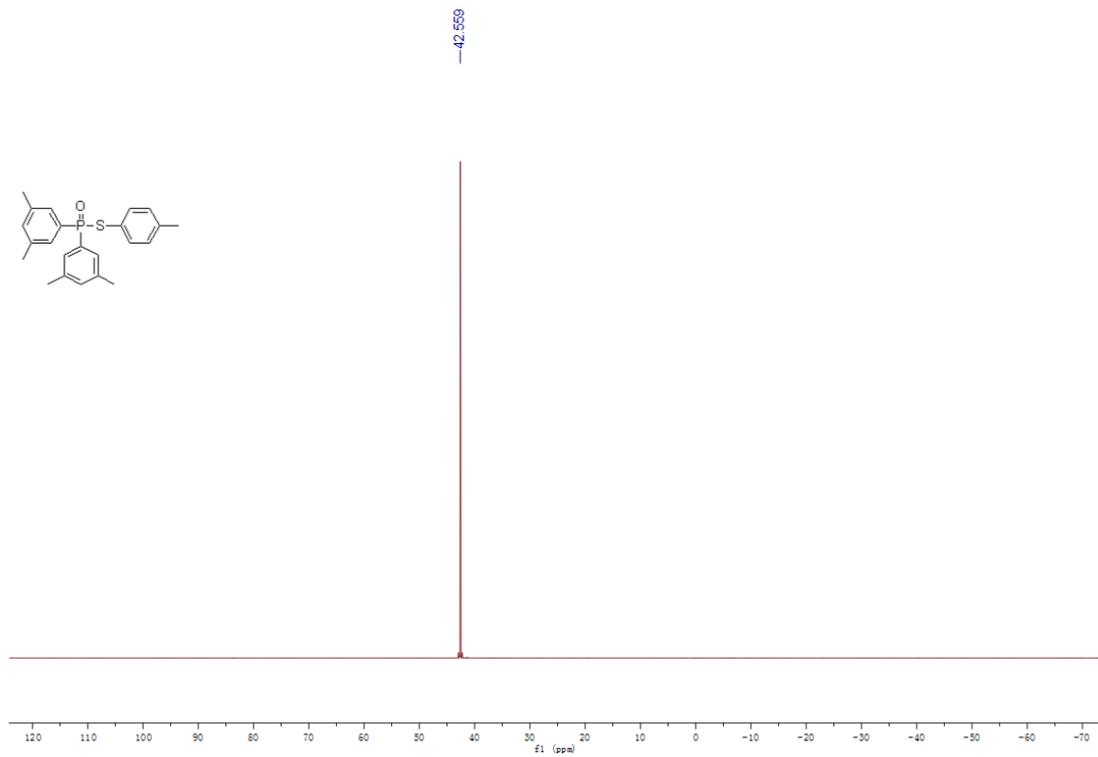
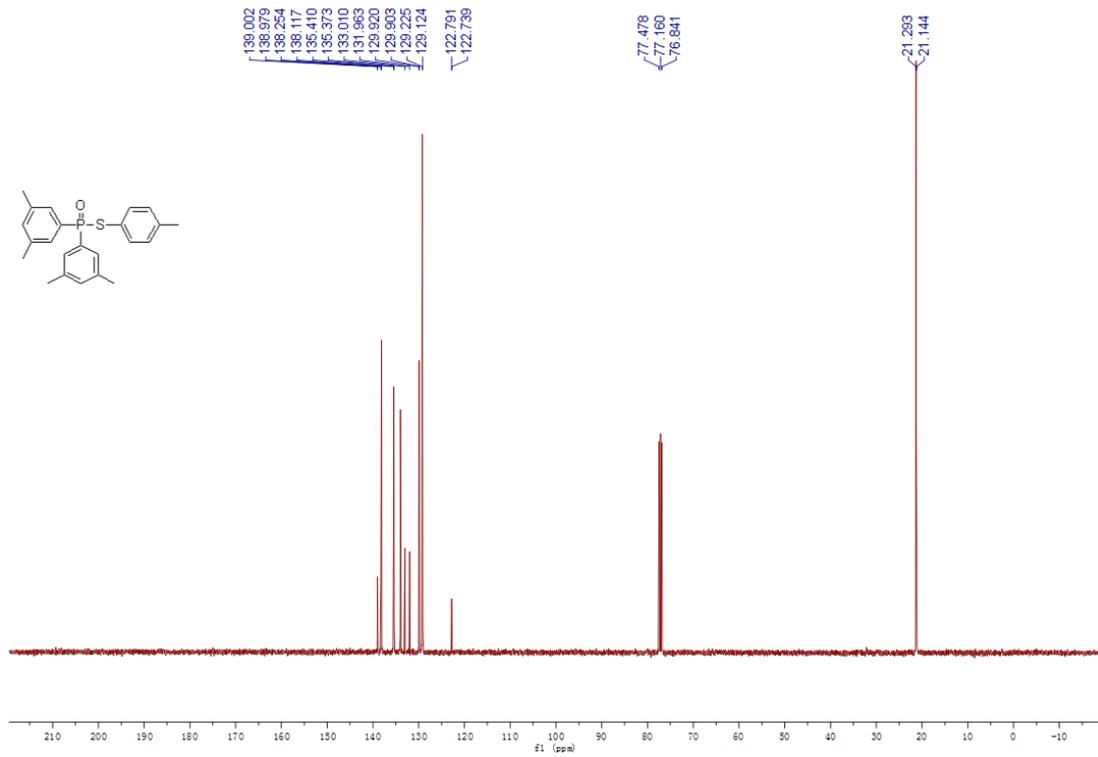


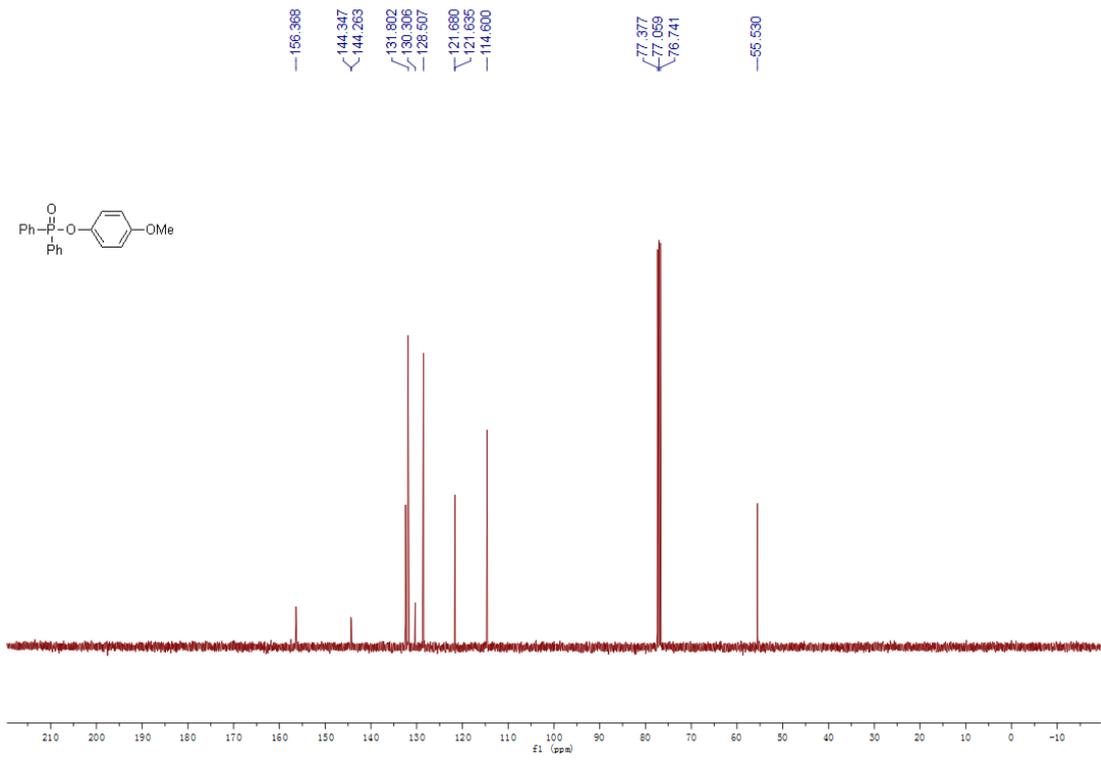
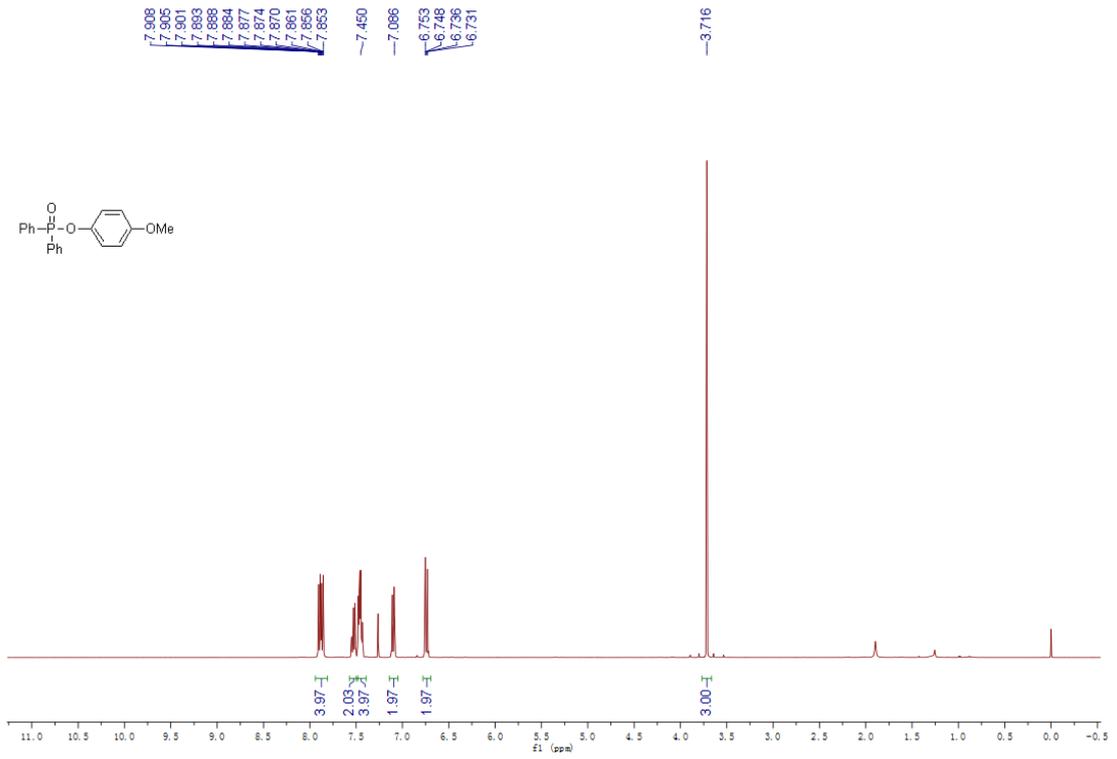


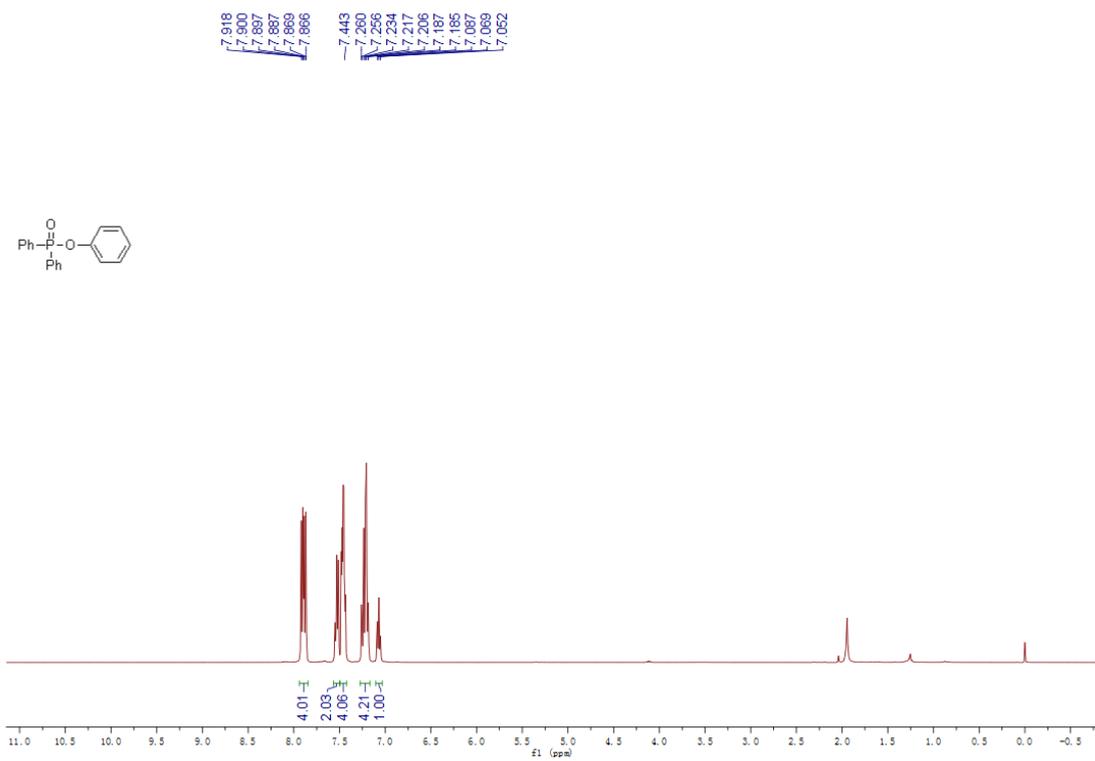
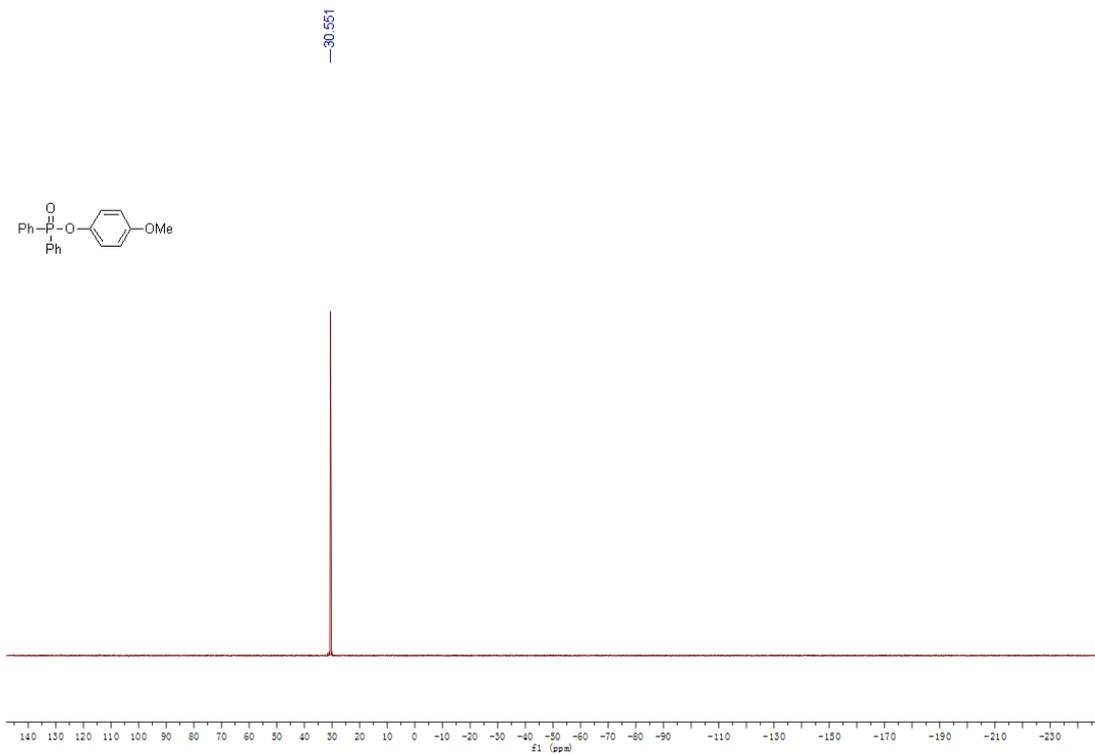


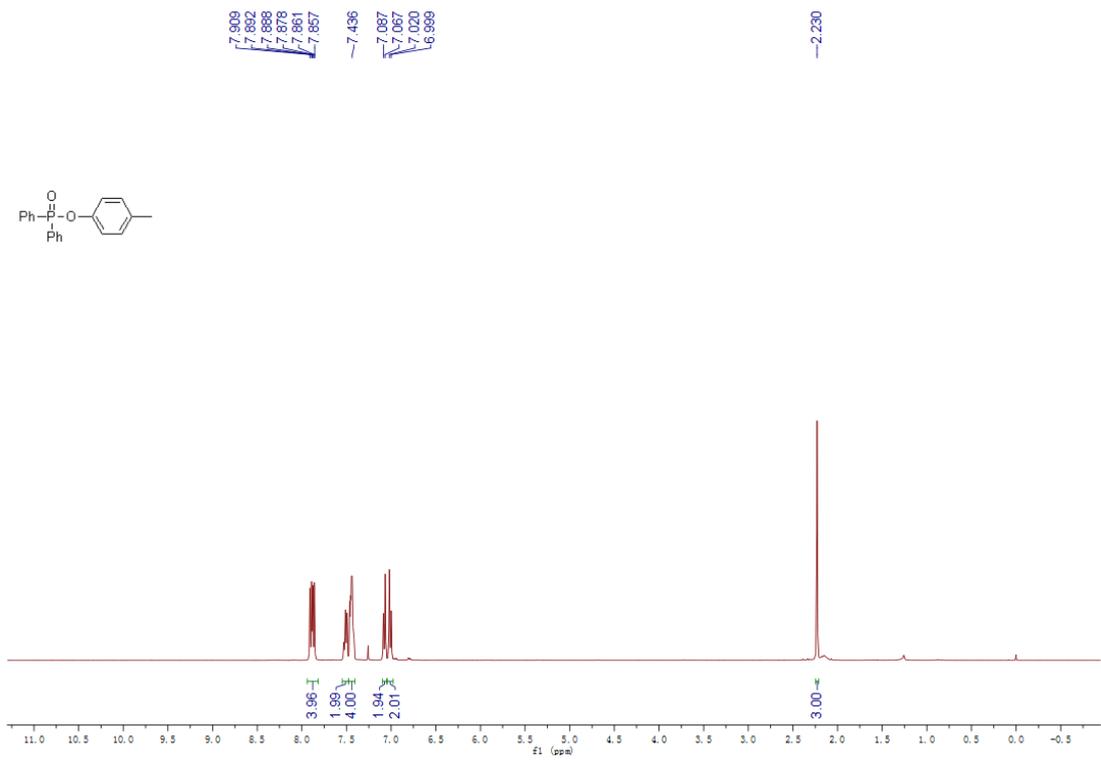
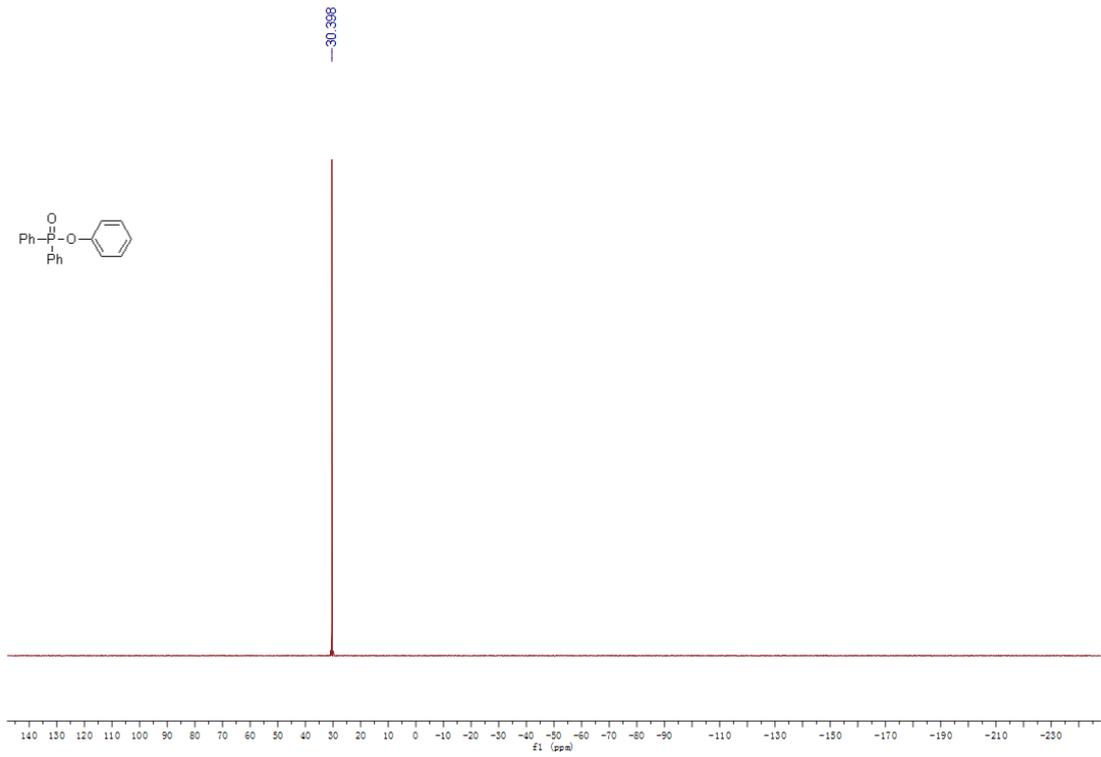


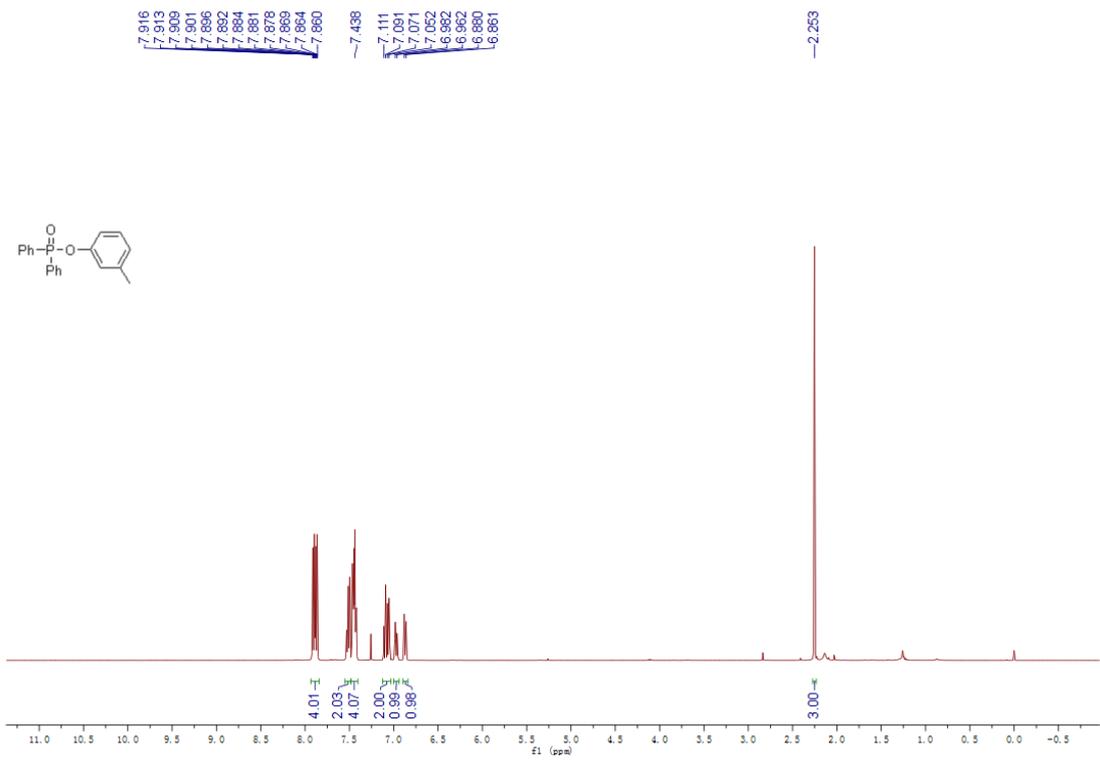
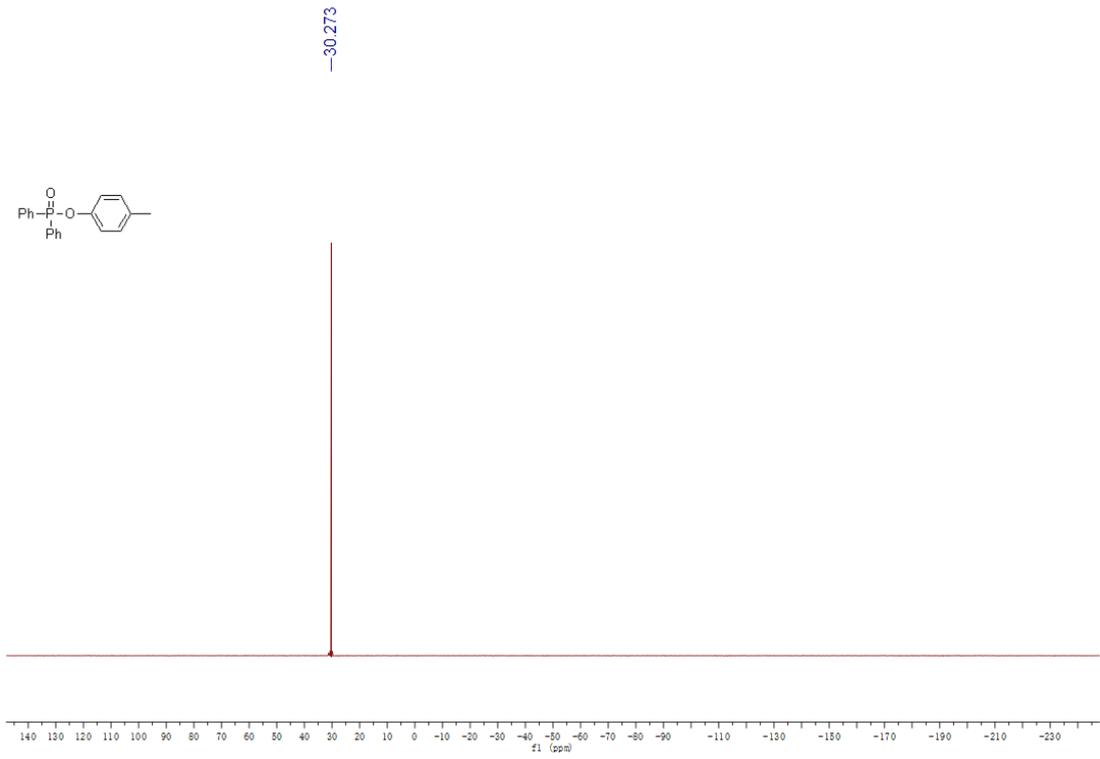


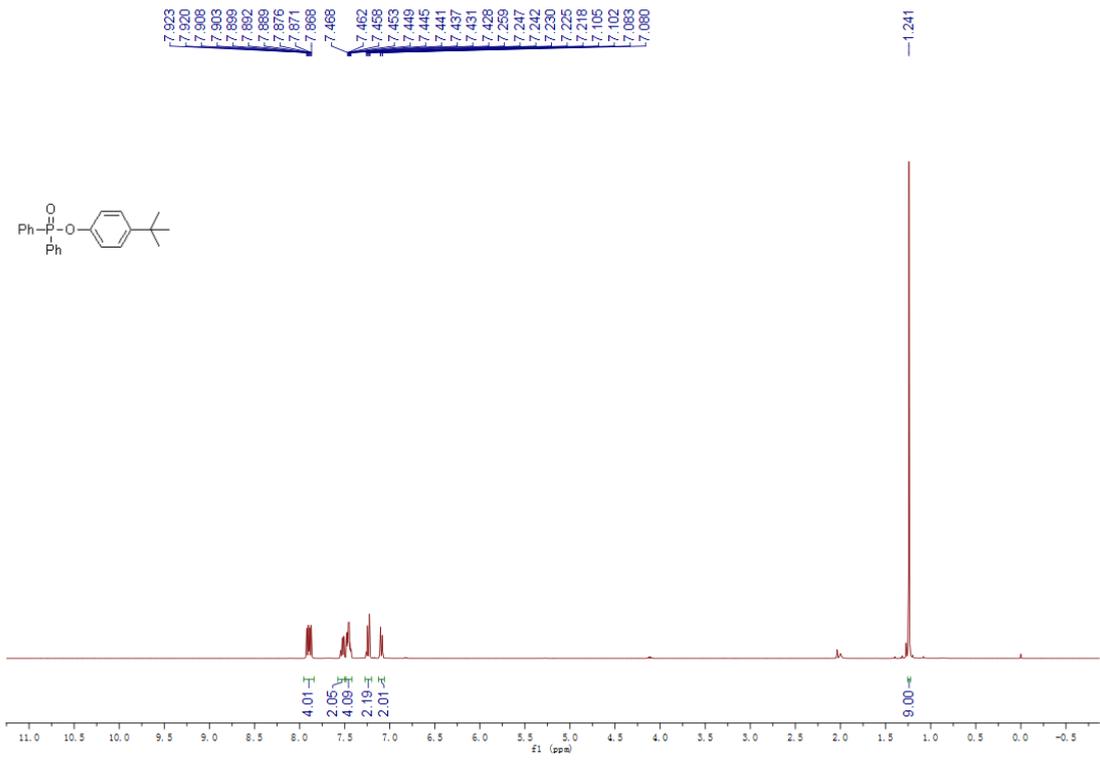
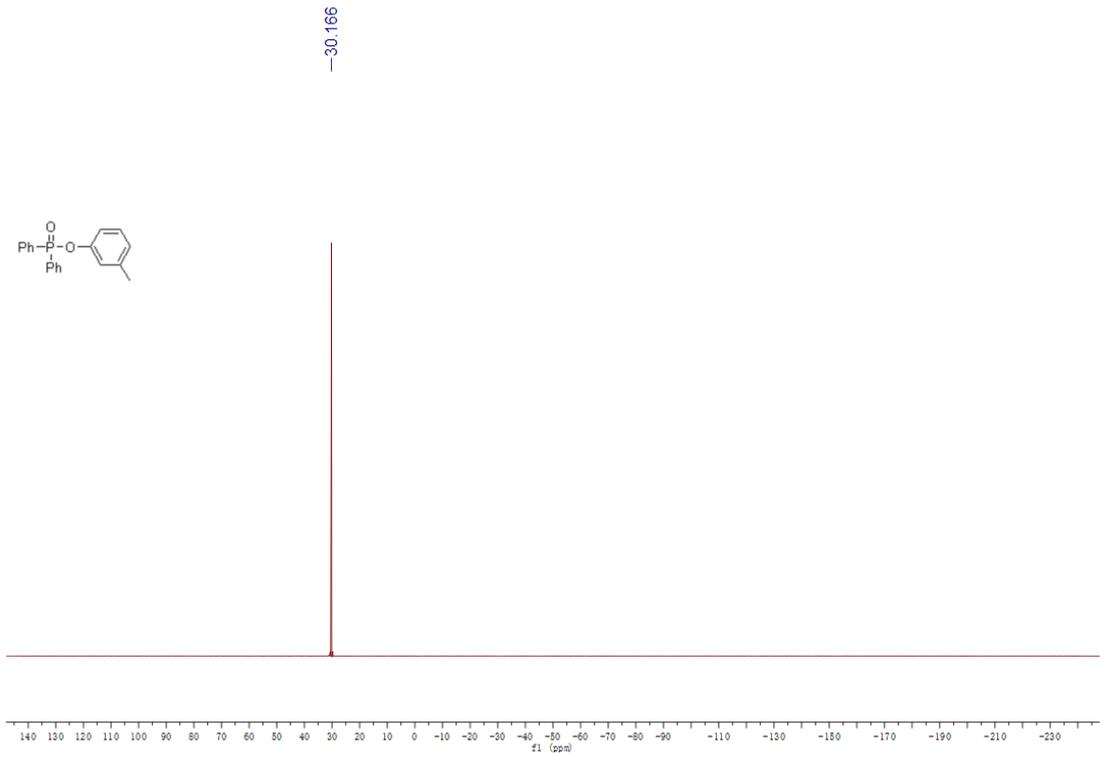


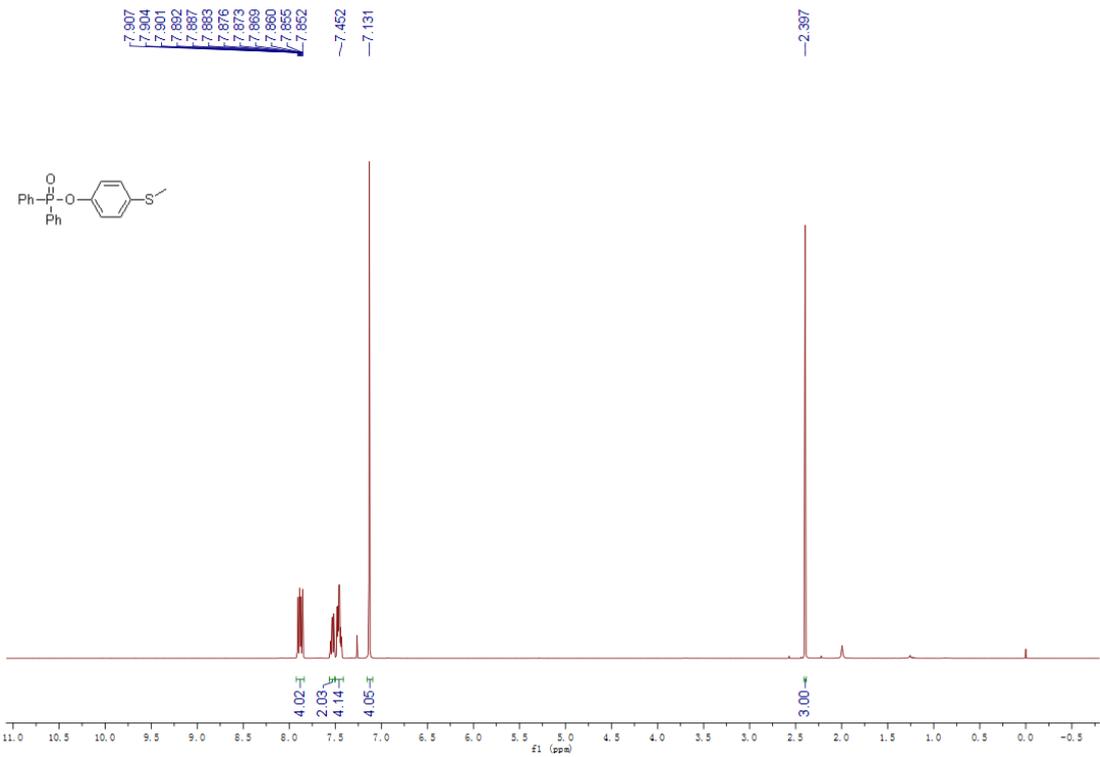
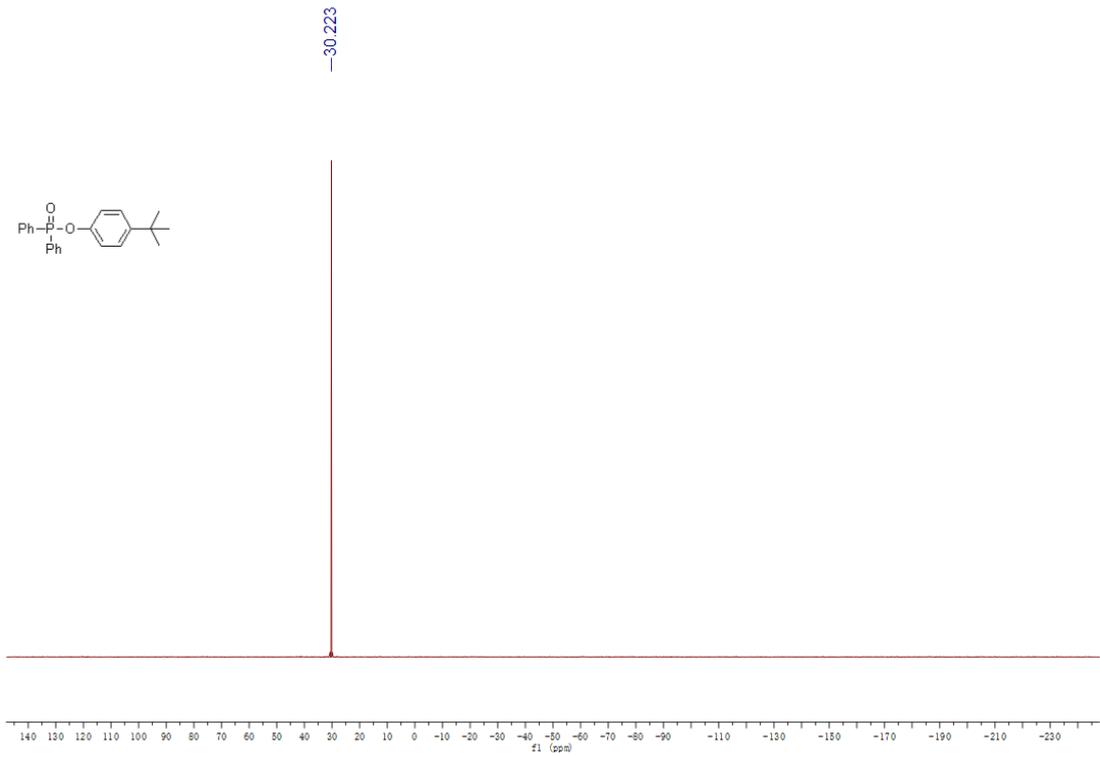


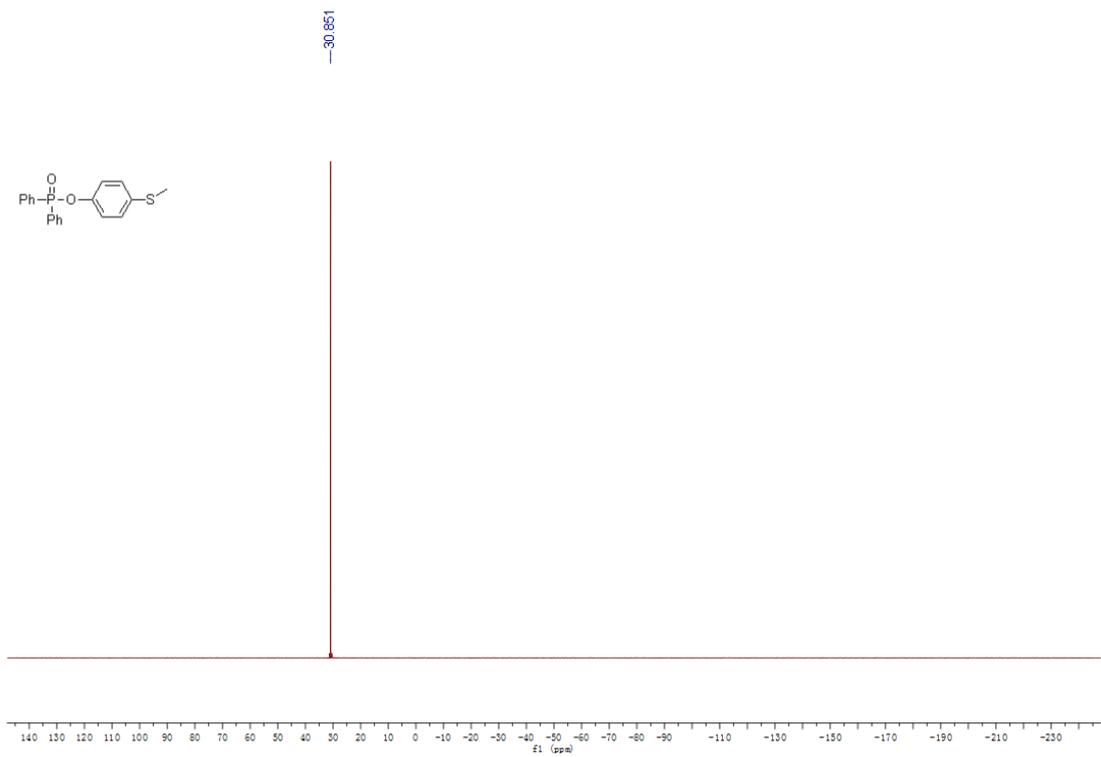
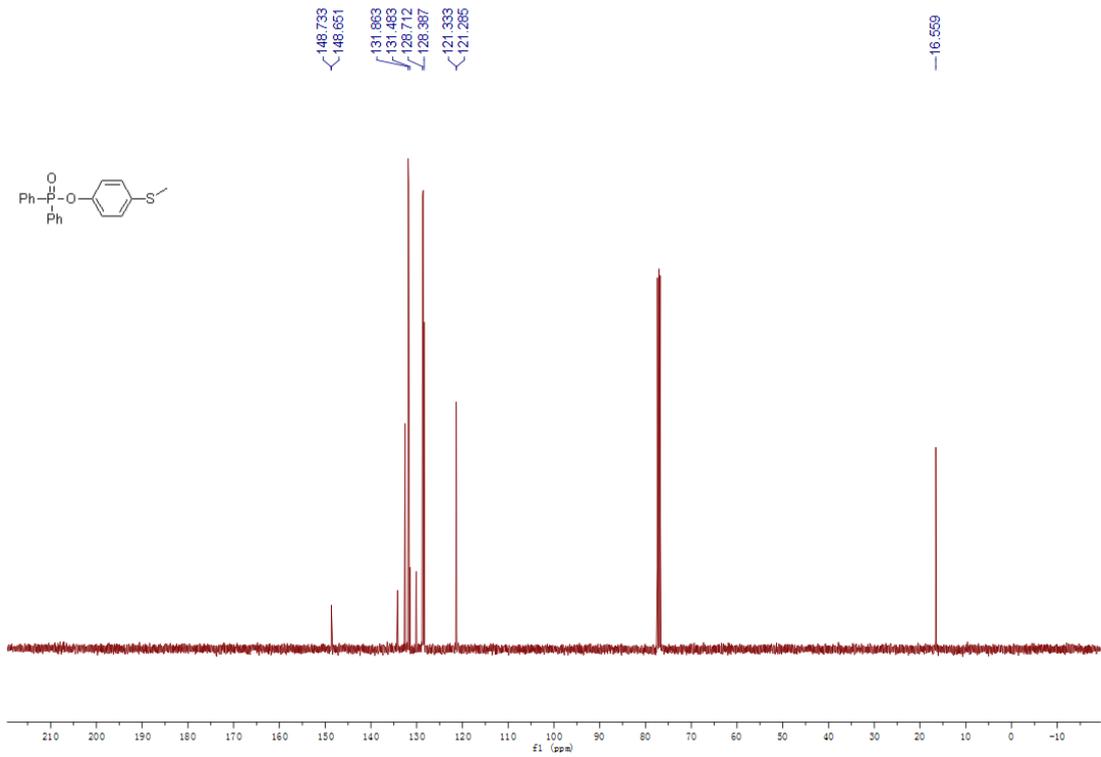


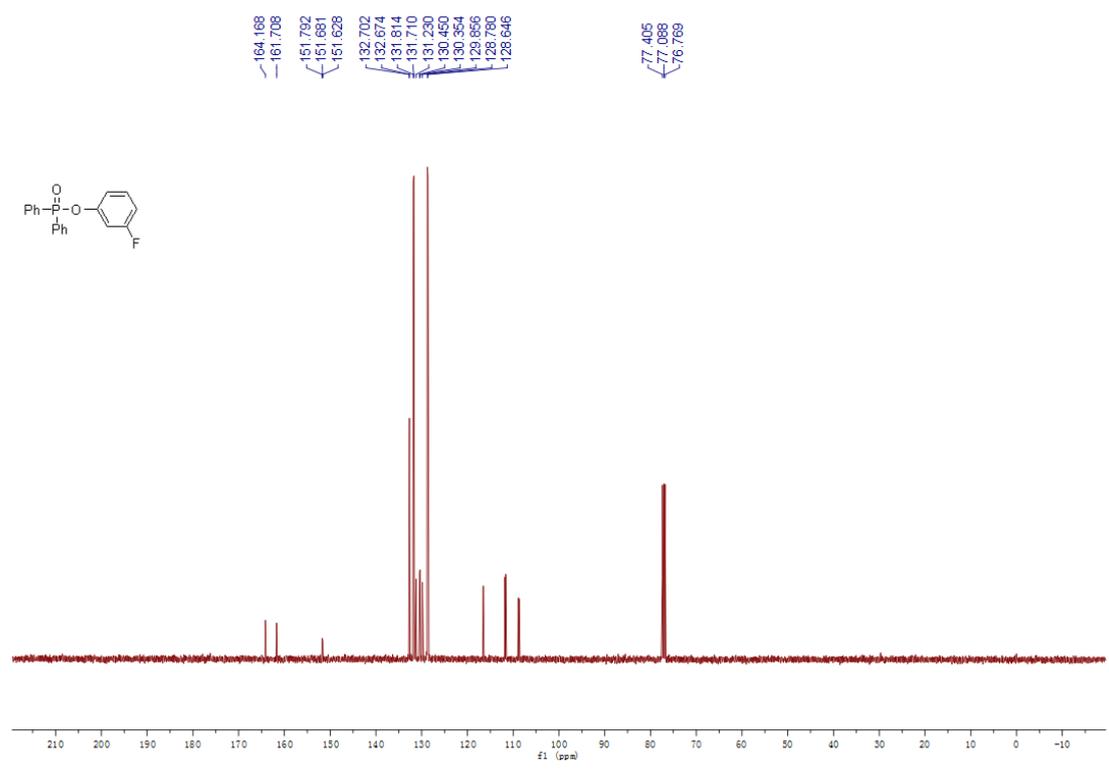
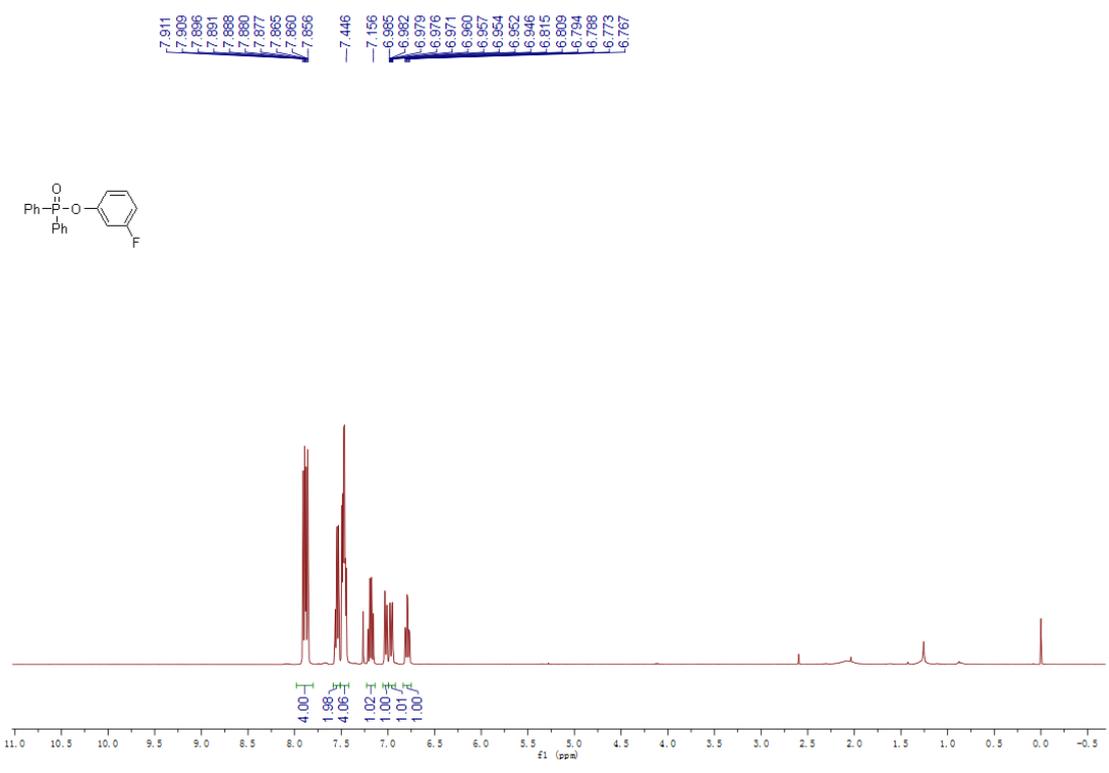


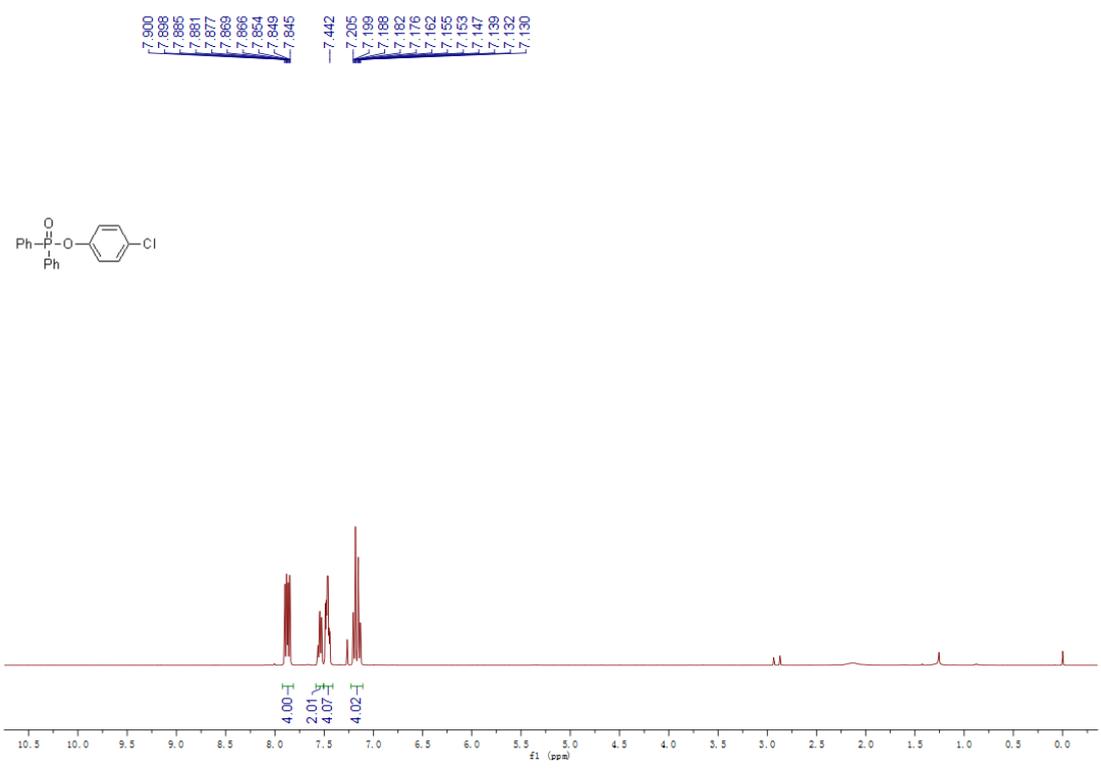
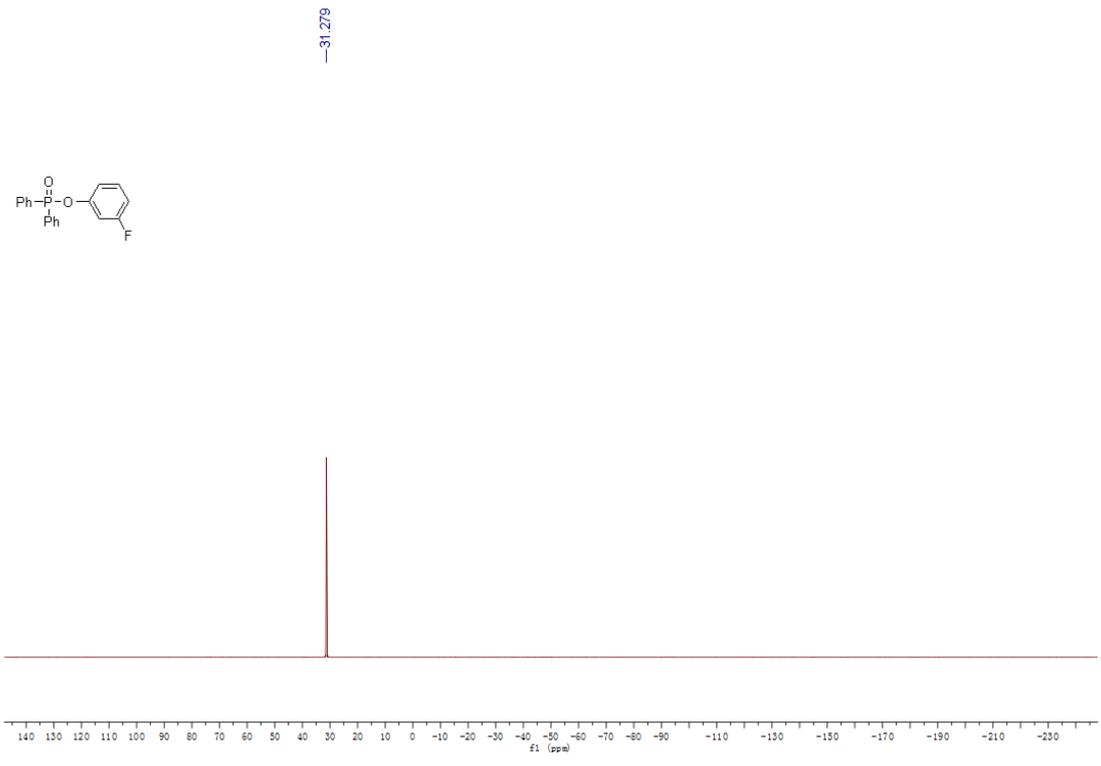


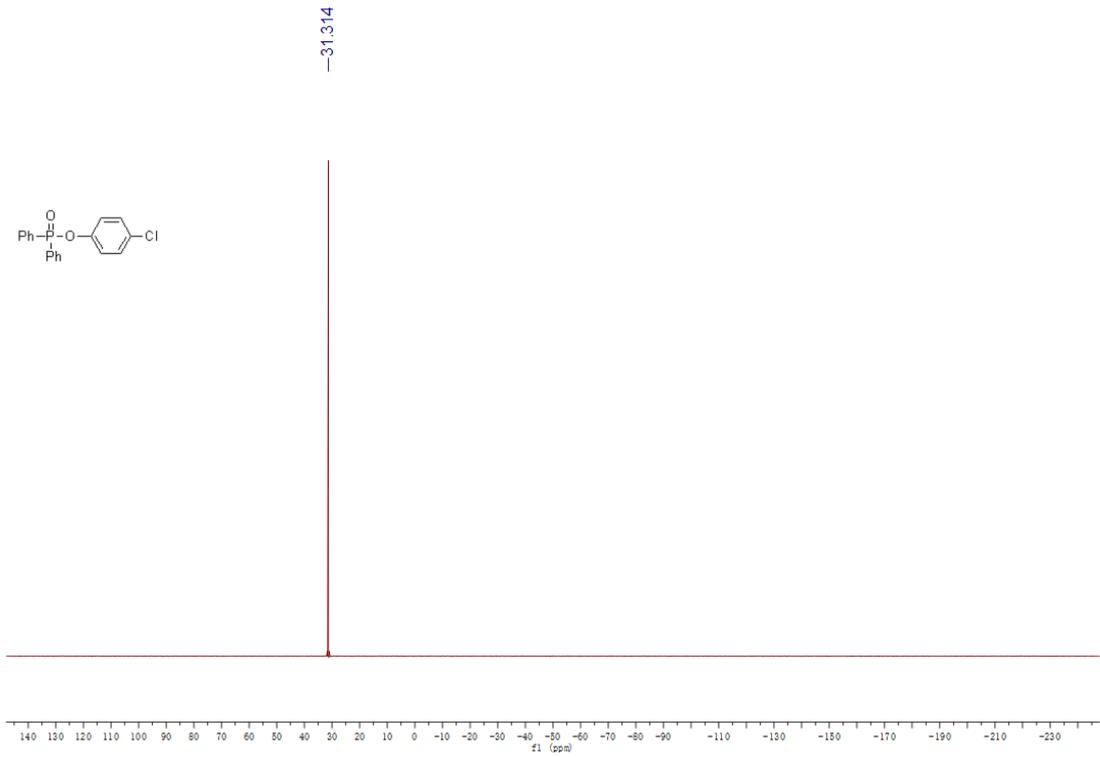




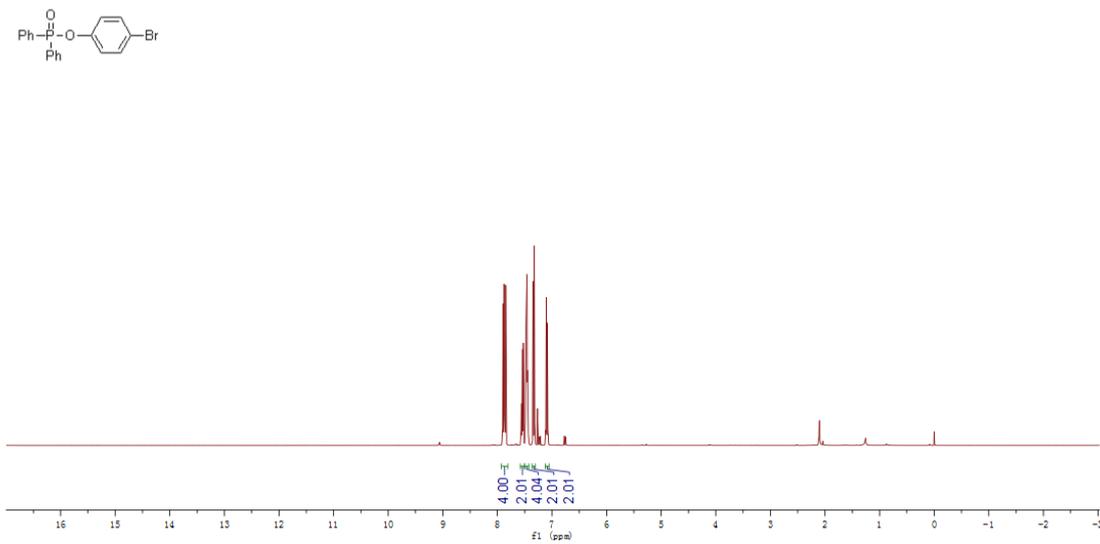


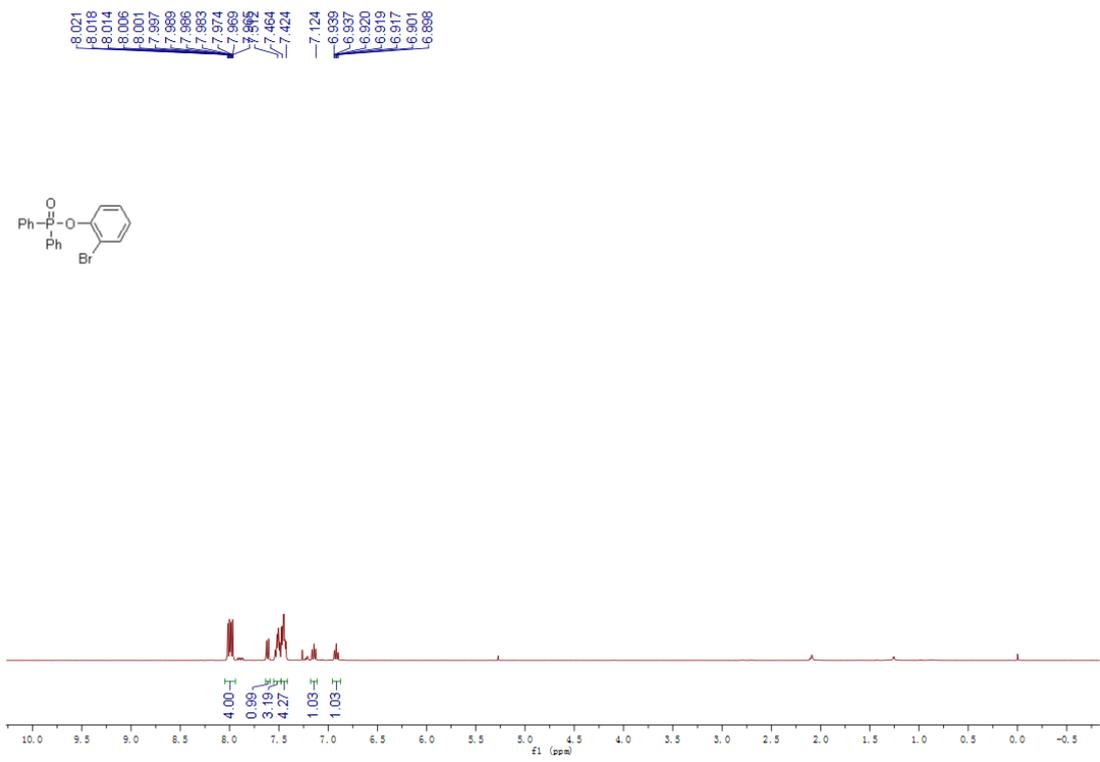
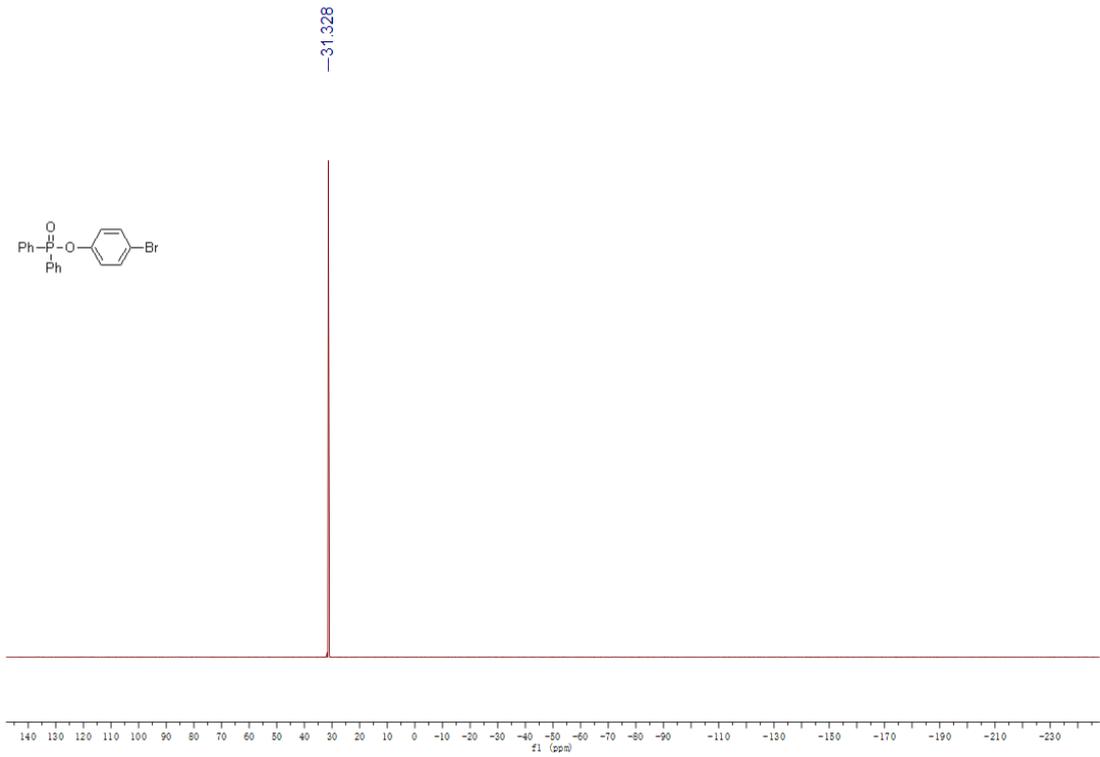


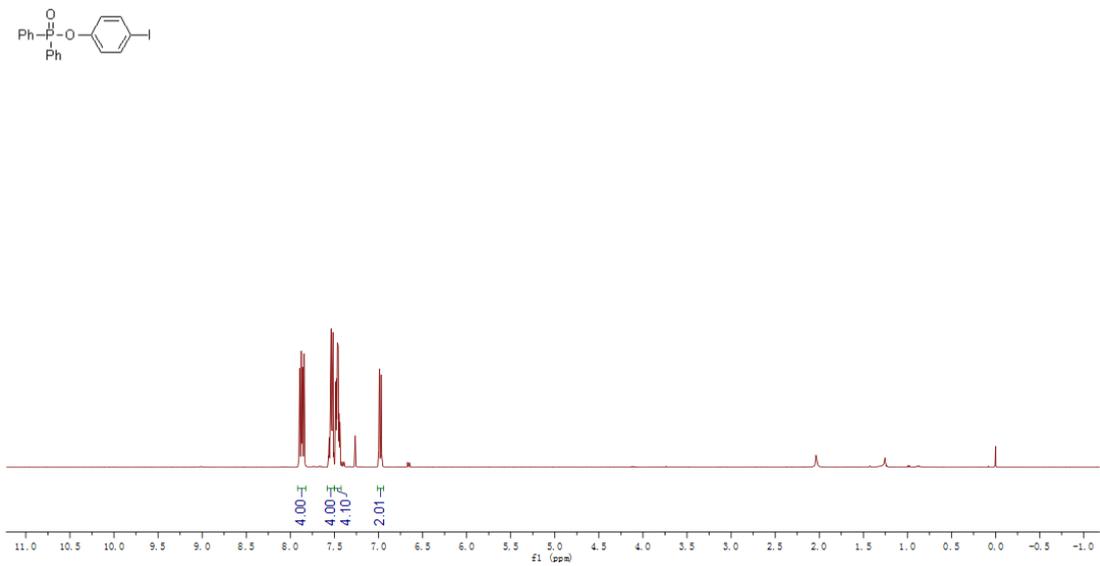
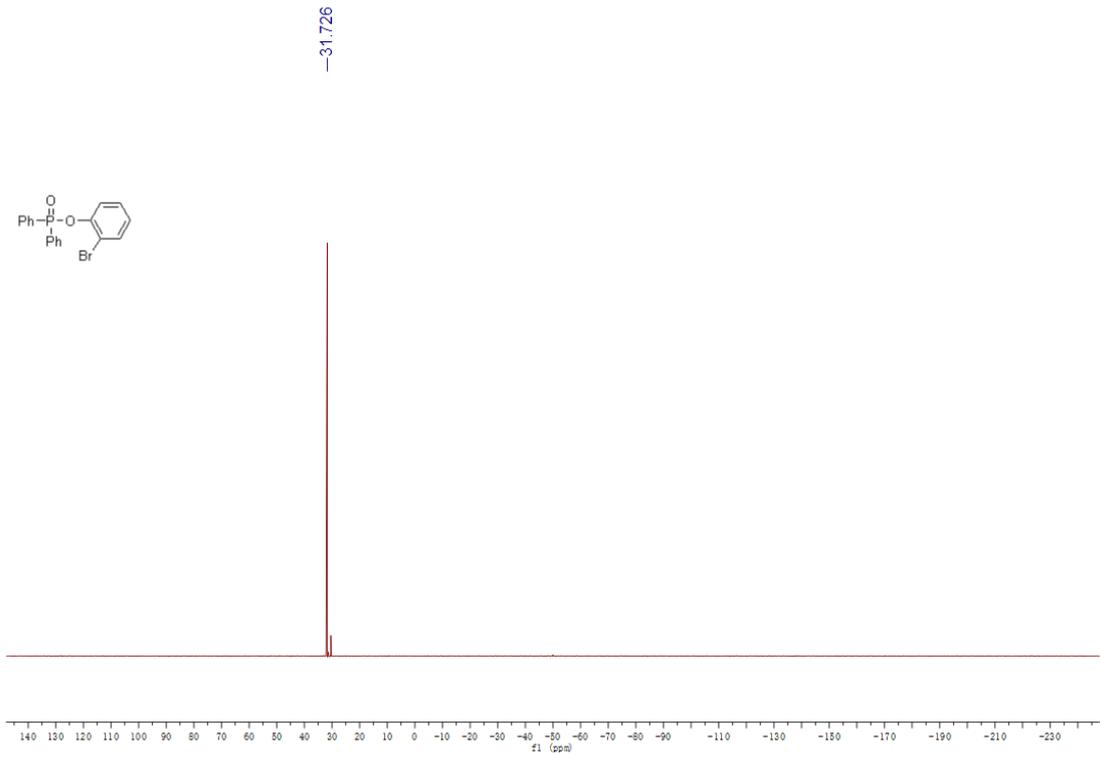


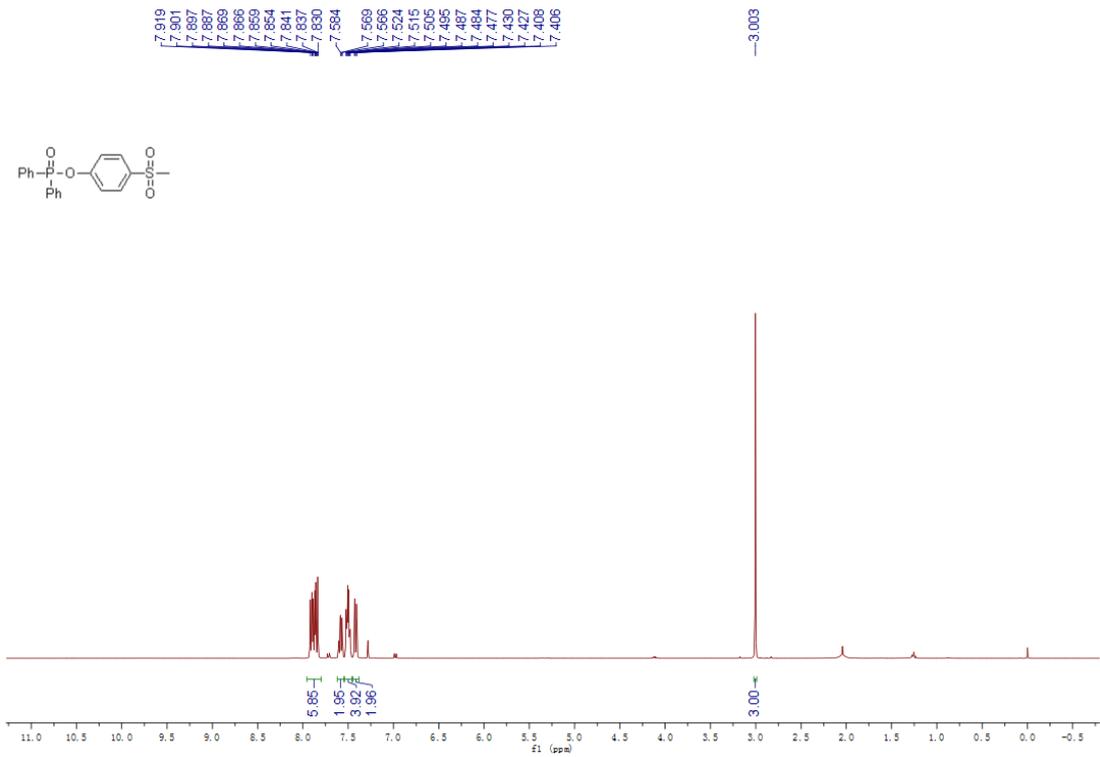
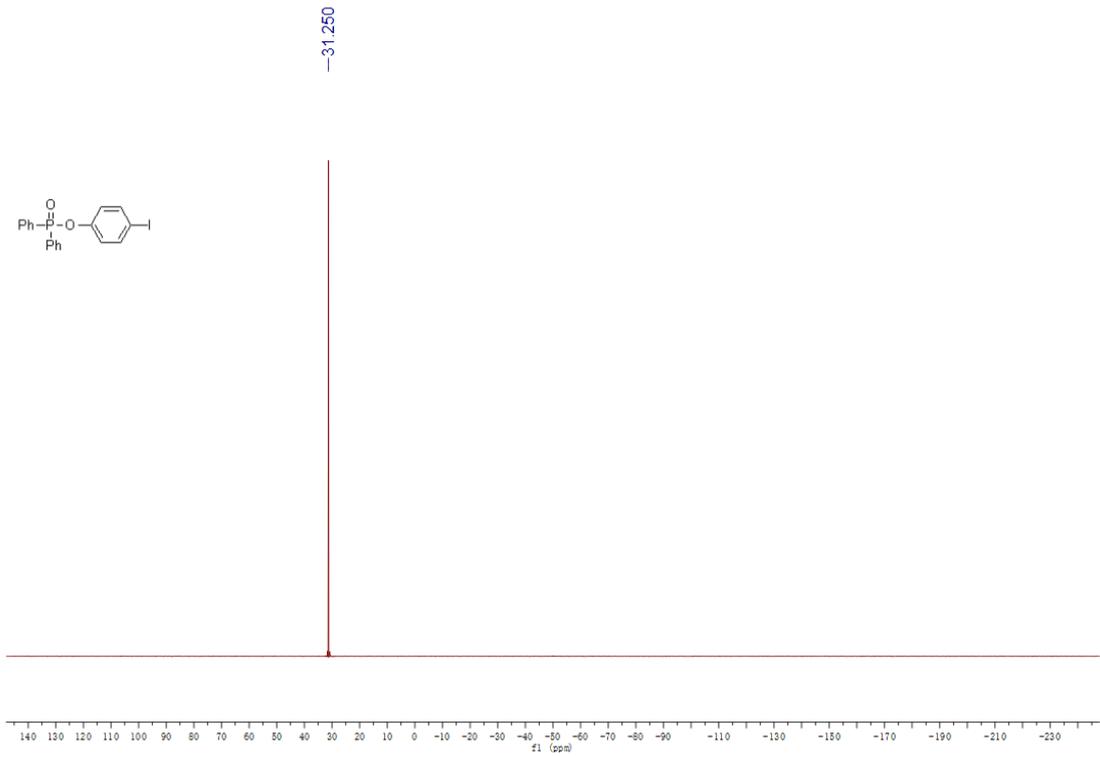


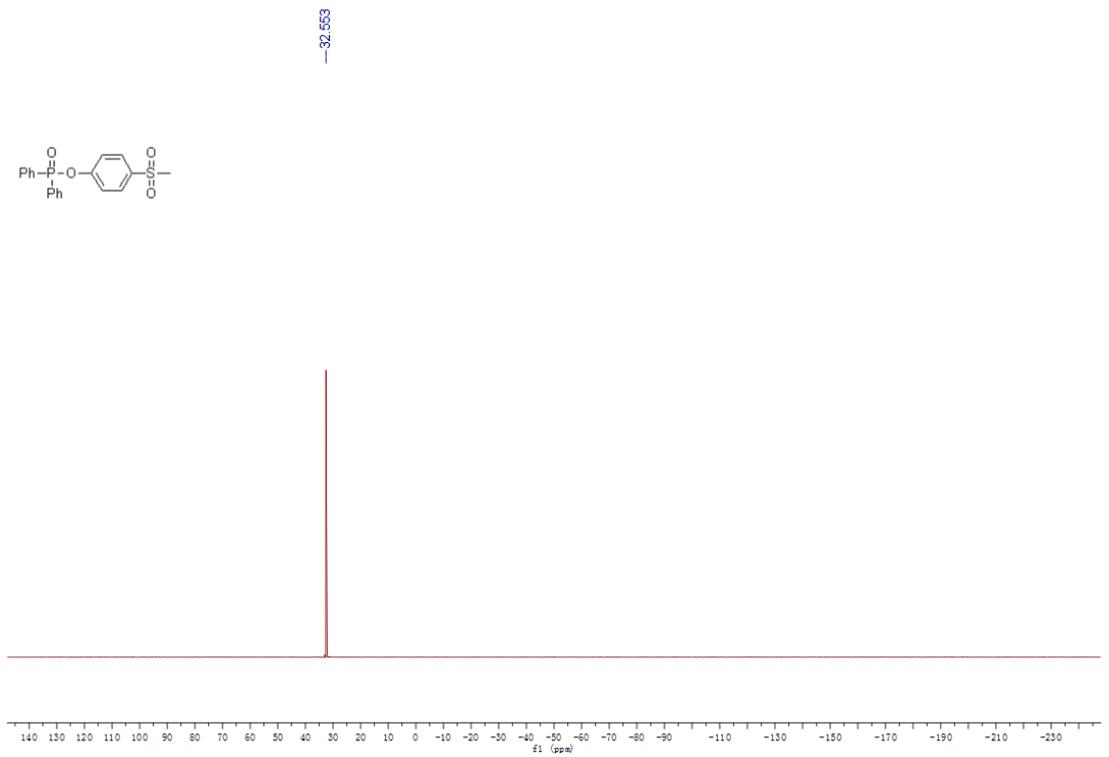
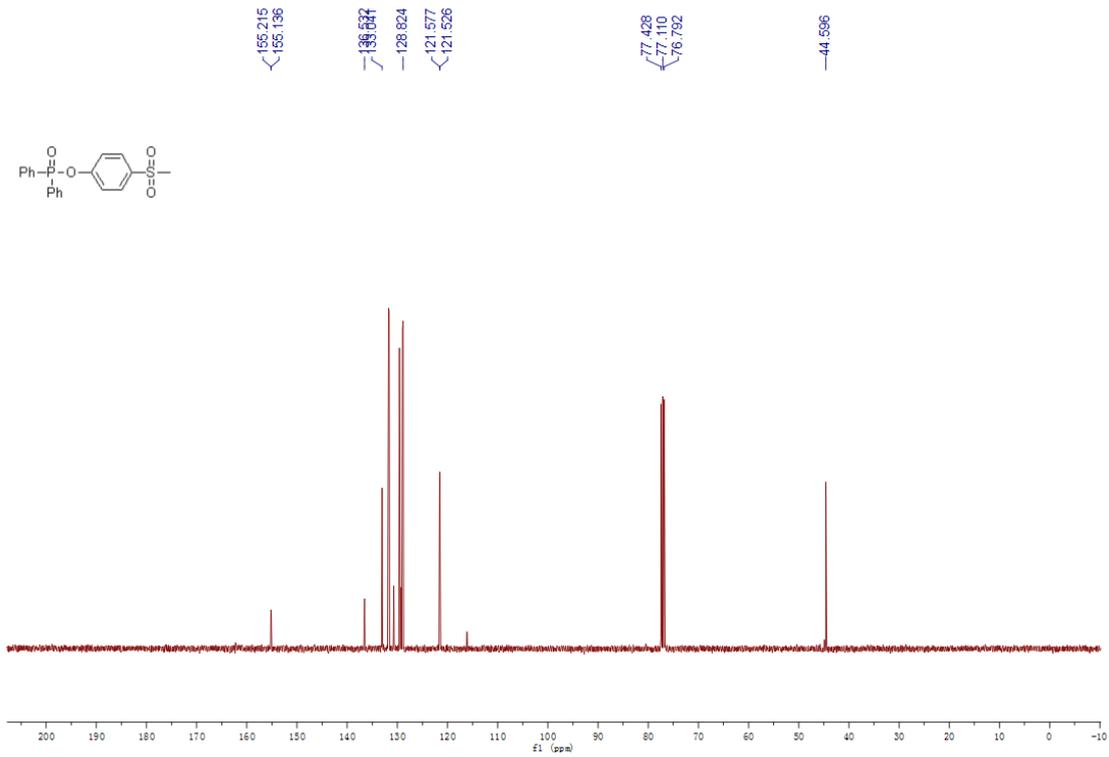
7.900
7.896
7.892
7.884
7.879
7.875
7.867
7.864
7.861
7.852
7.847
7.843
7.832
7.828
7.844
7.840
7.834
7.828
7.825
7.821
7.818
7.815
7.812
7.802
7.796
7.772
7.747
7.742
7.740
7.736
7.730
7.725
7.710
7.704
7.684
7.681

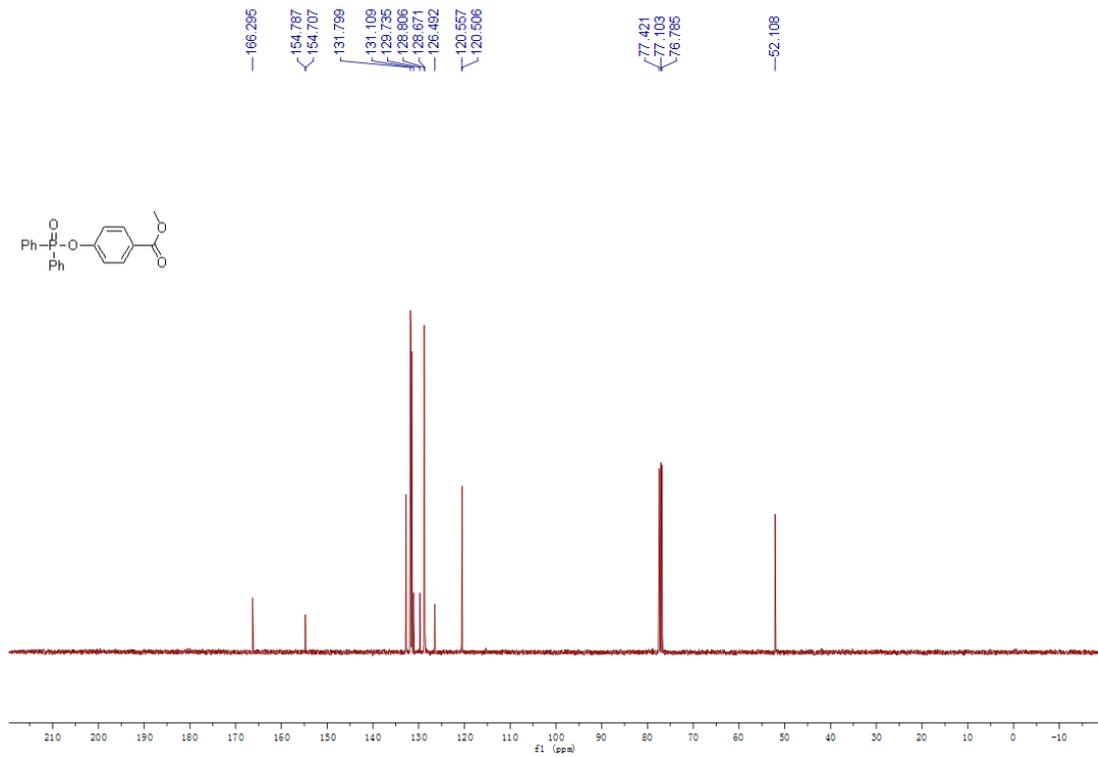
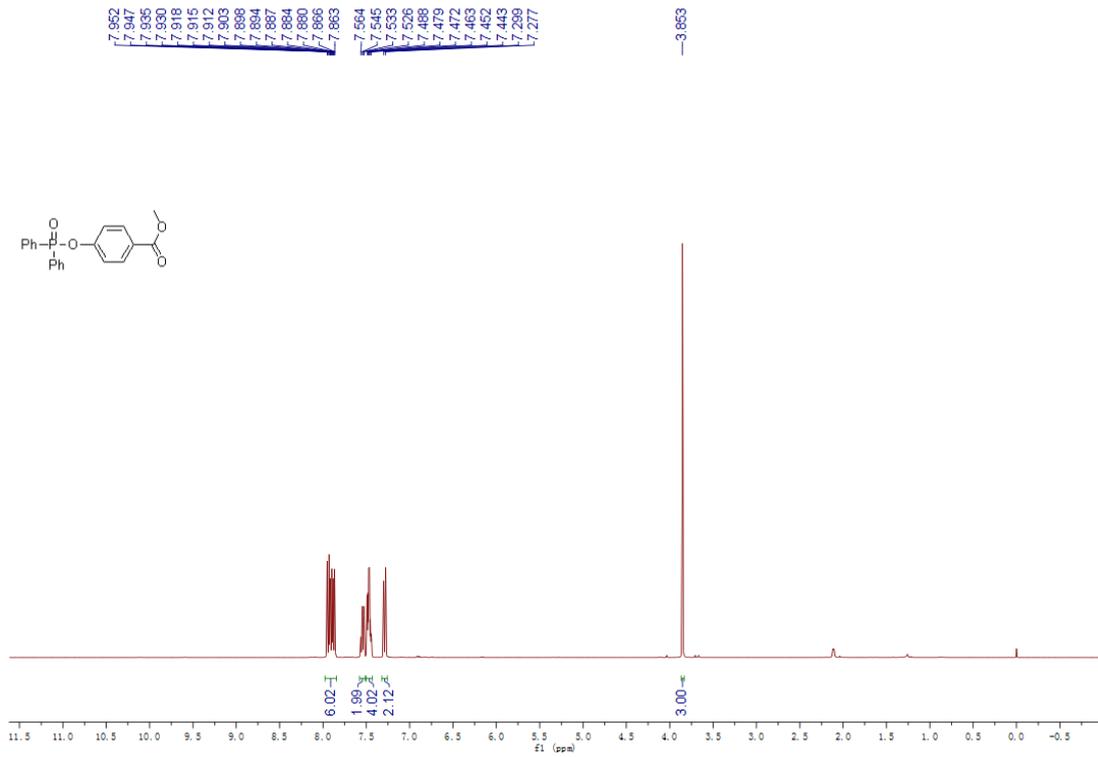




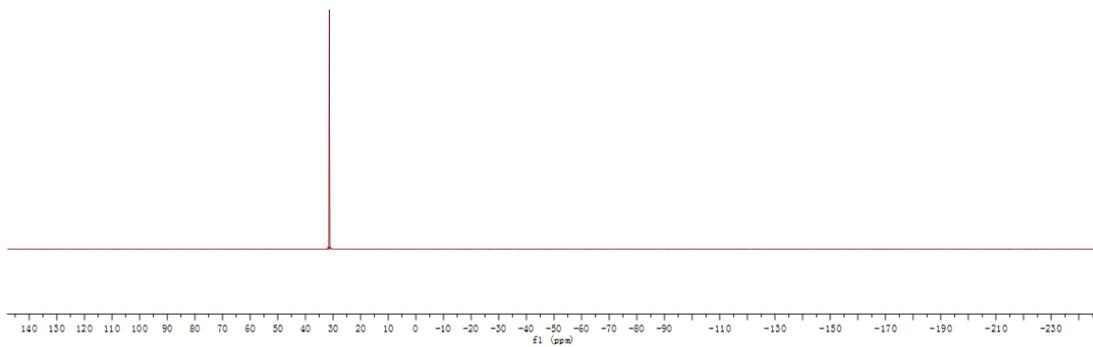
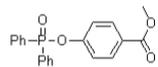




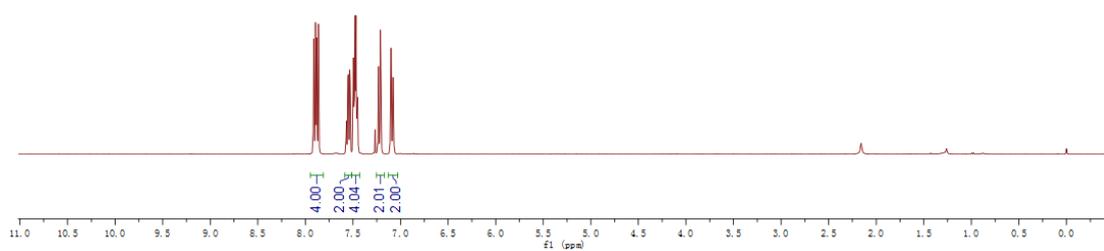
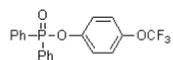


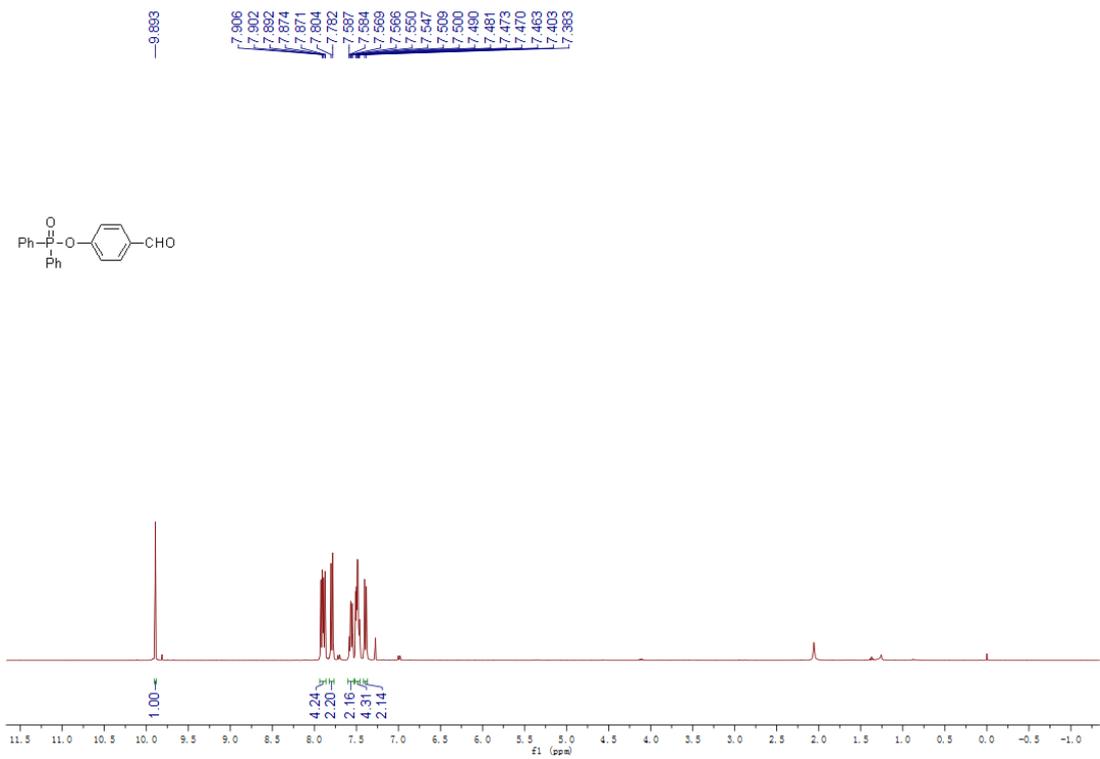
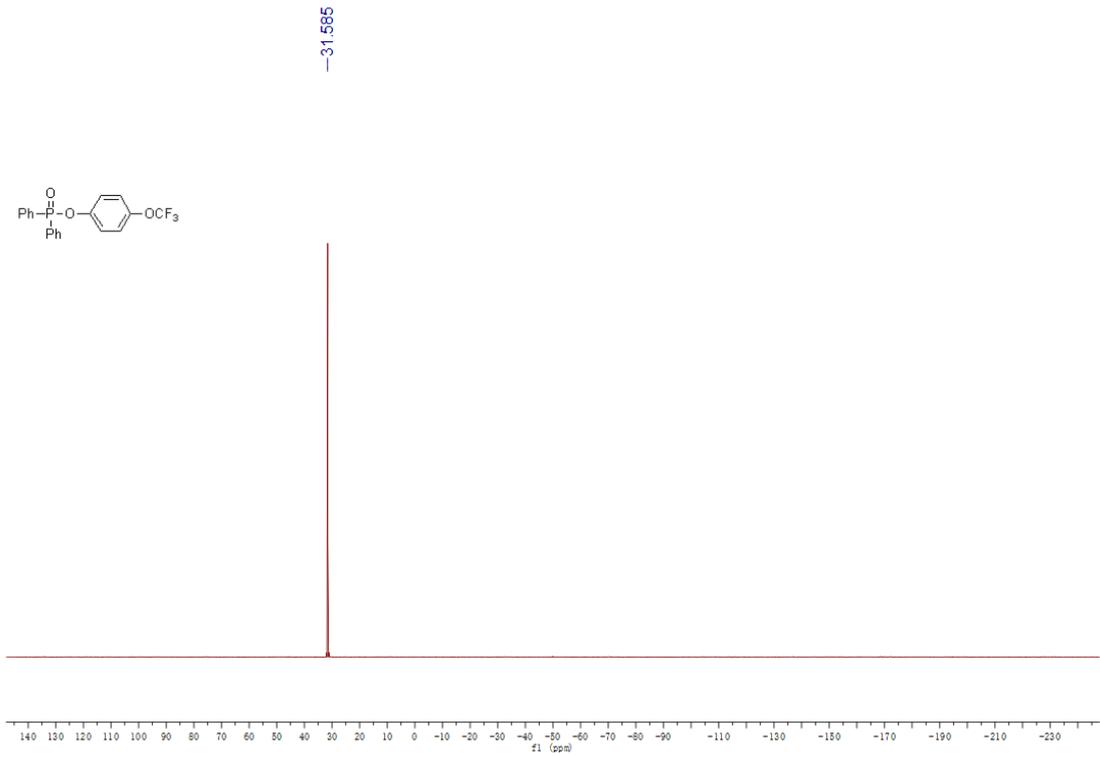


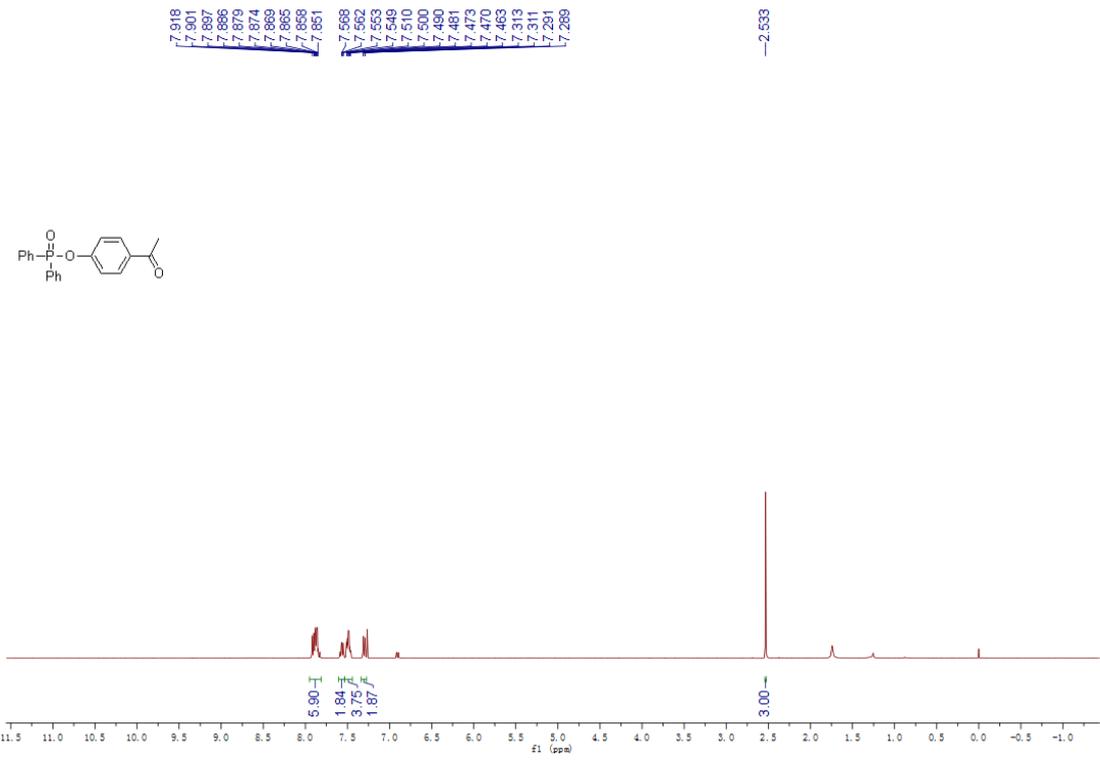
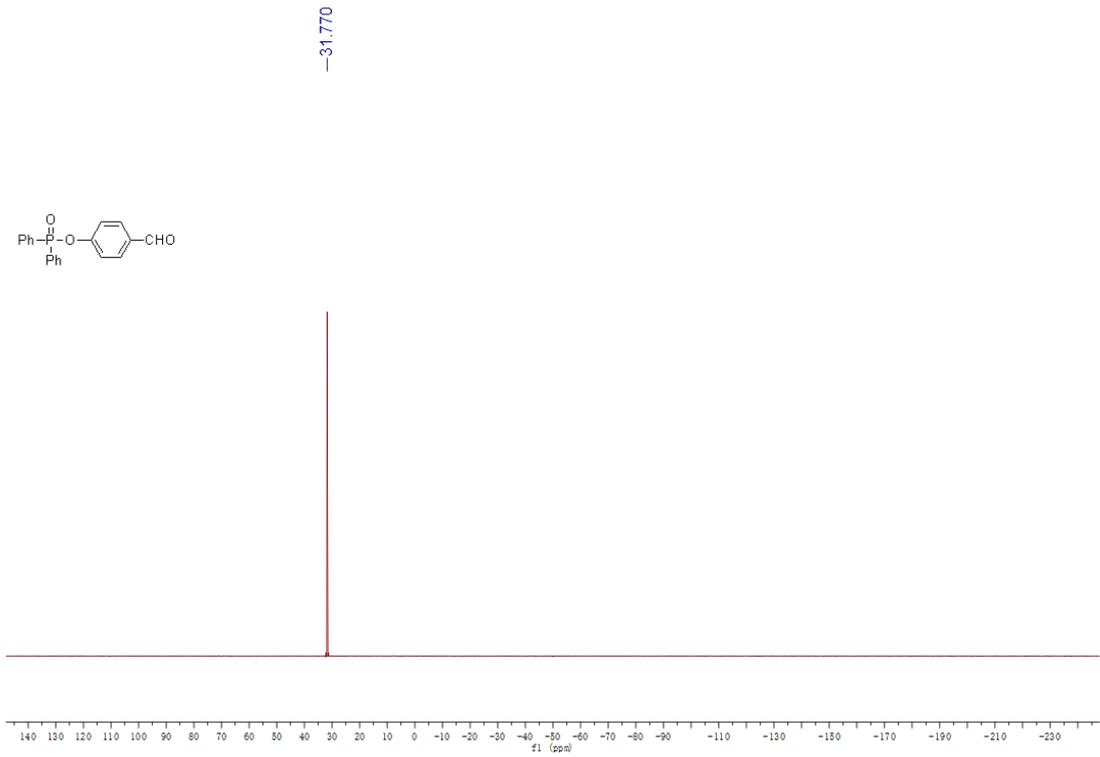
—31.359

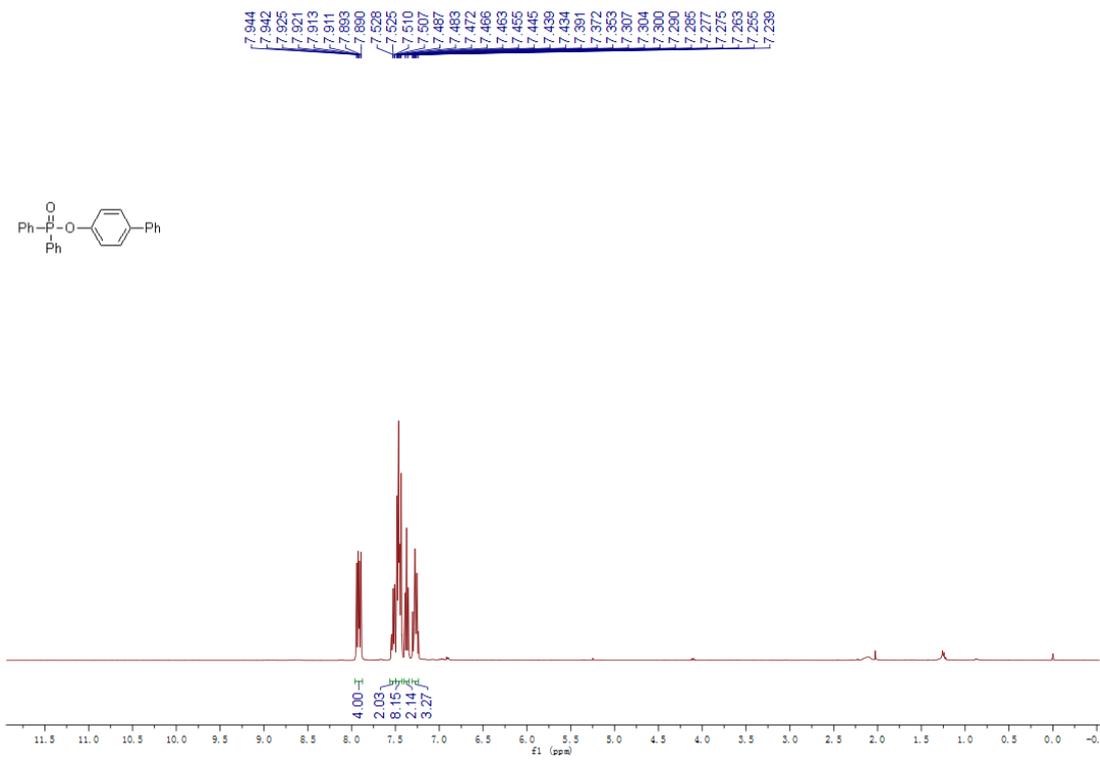
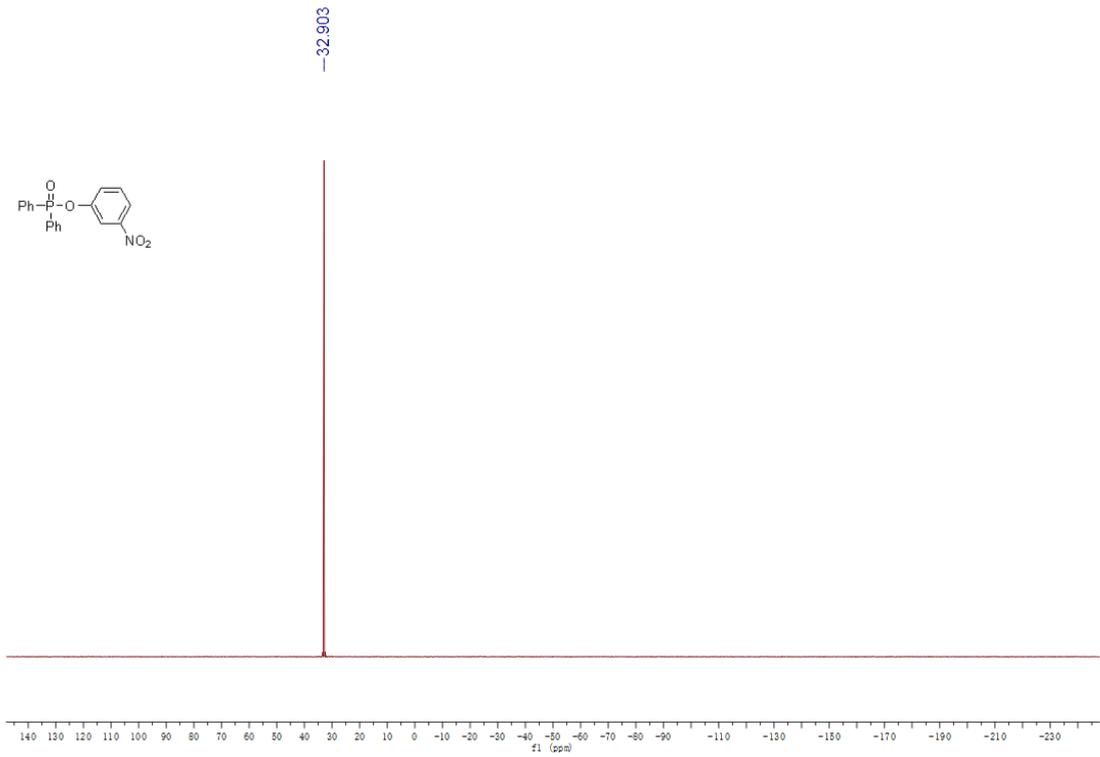


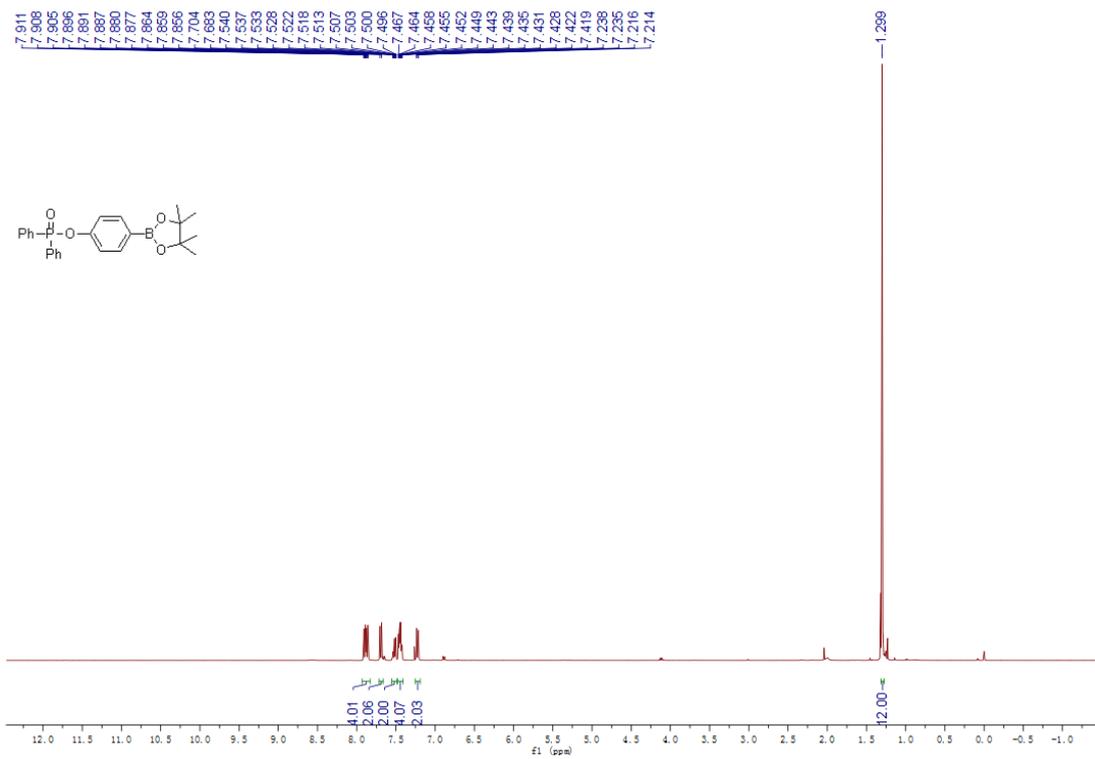
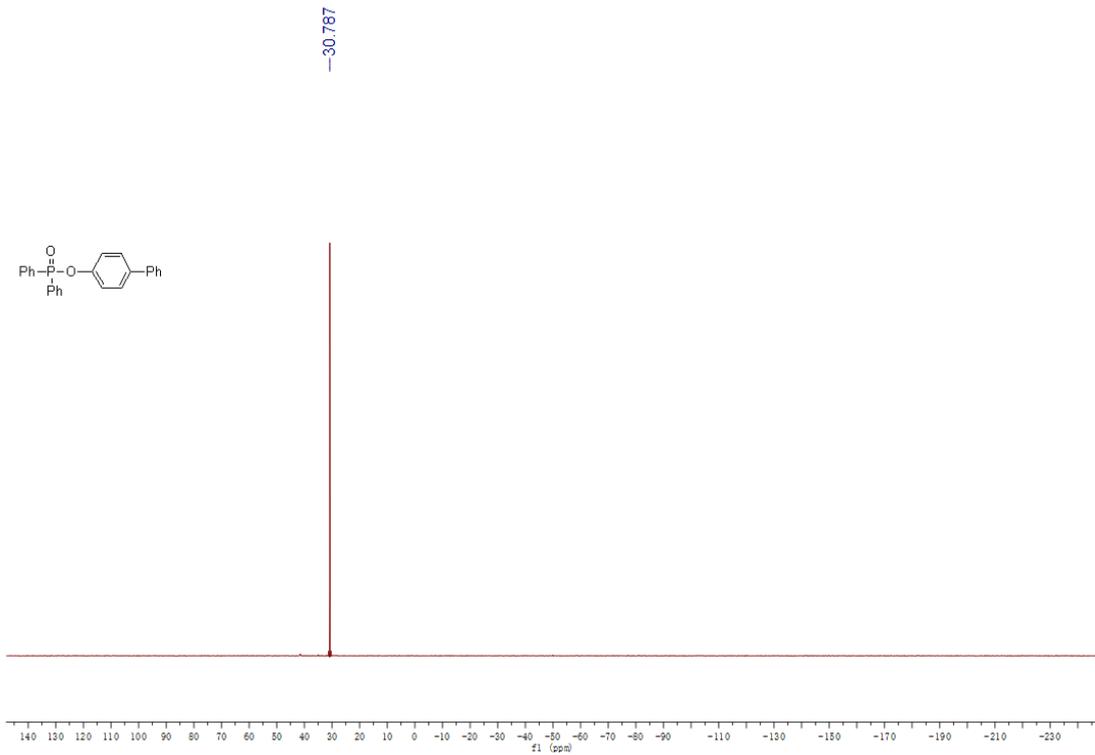
7.915
7.912
7.909
7.900
7.895
7.891
7.883
7.881
7.868
7.863
7.860
-7.468
7.234
7.231
7.225
7.217
7.211
7.208
7.100
7.078

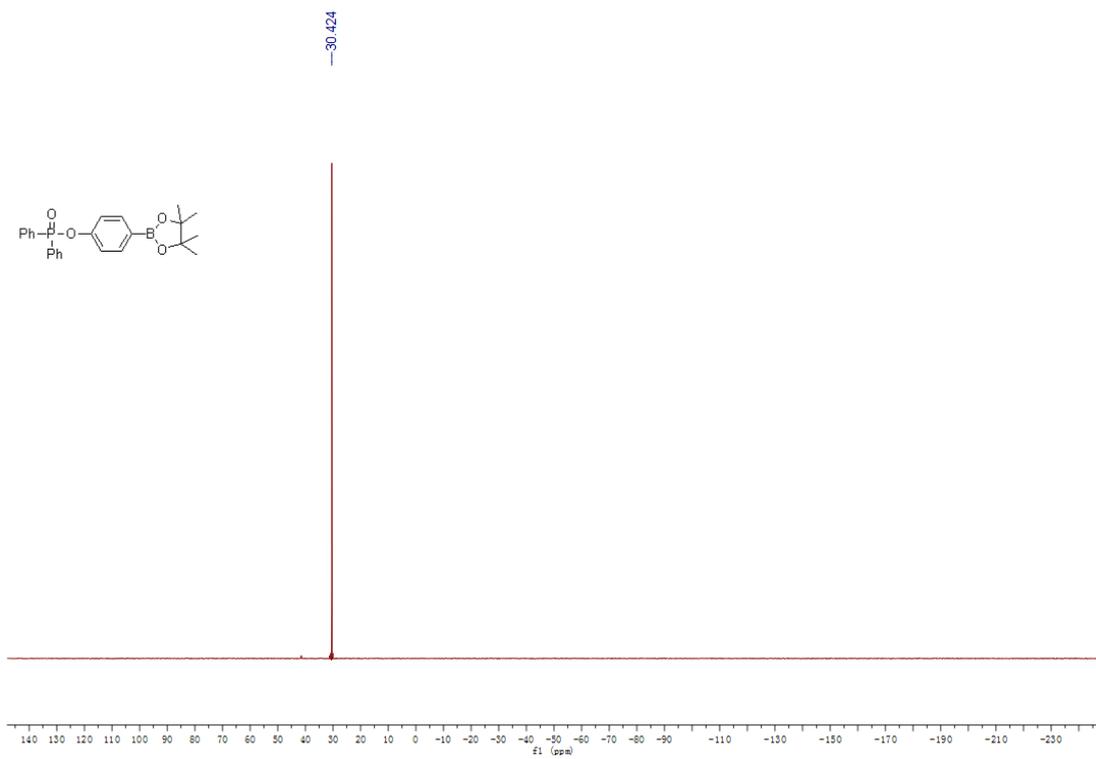
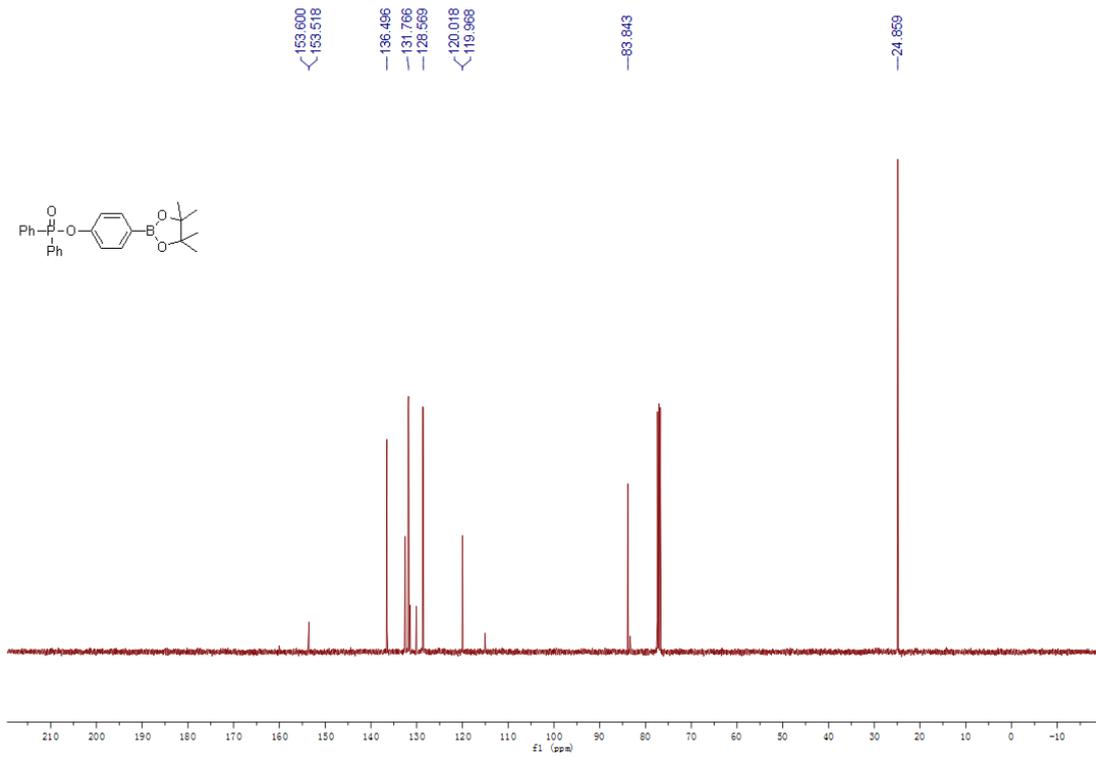


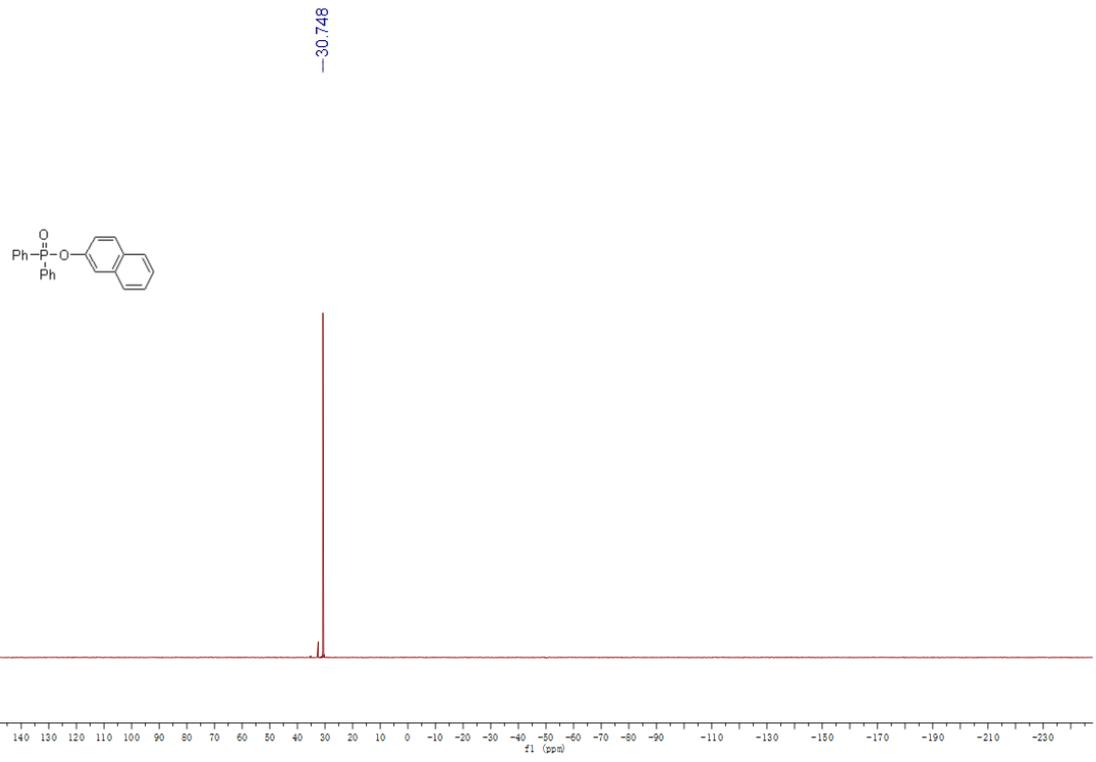
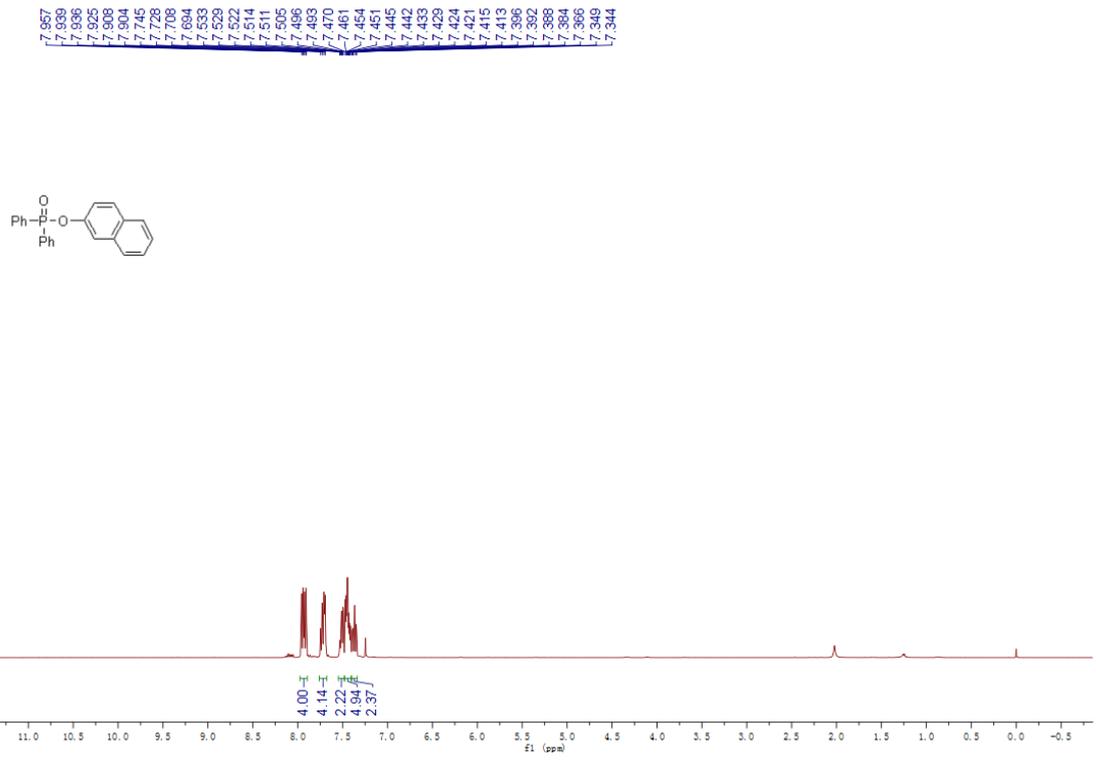


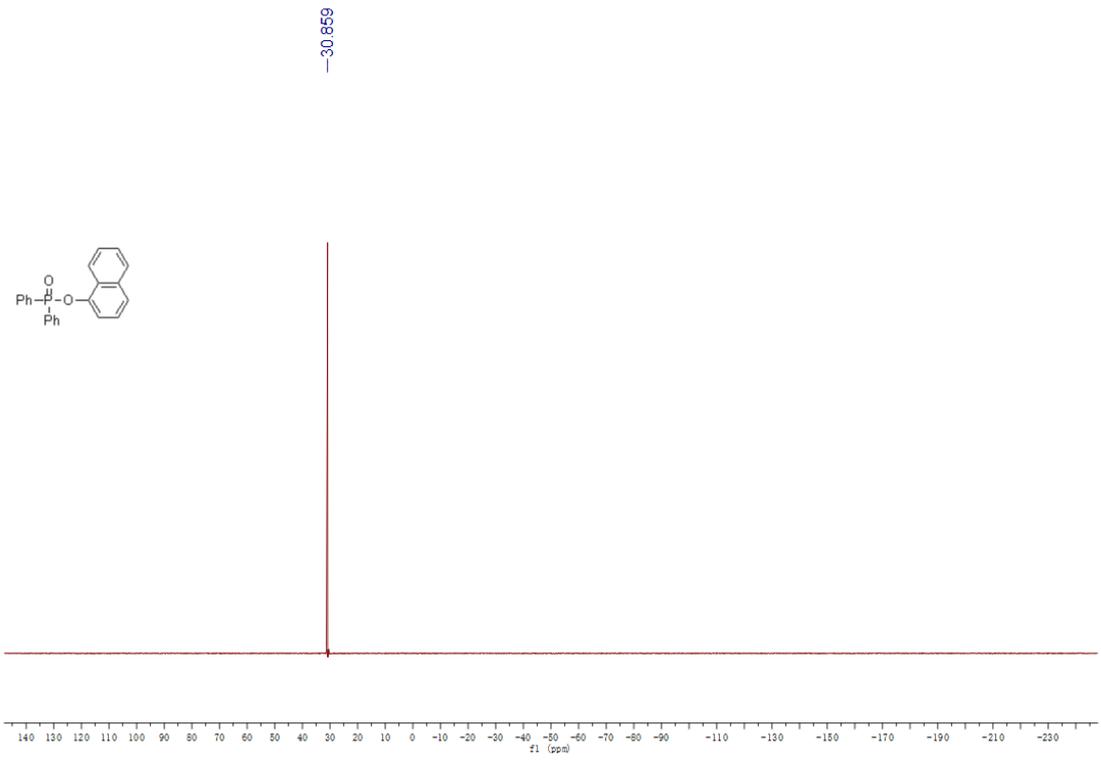
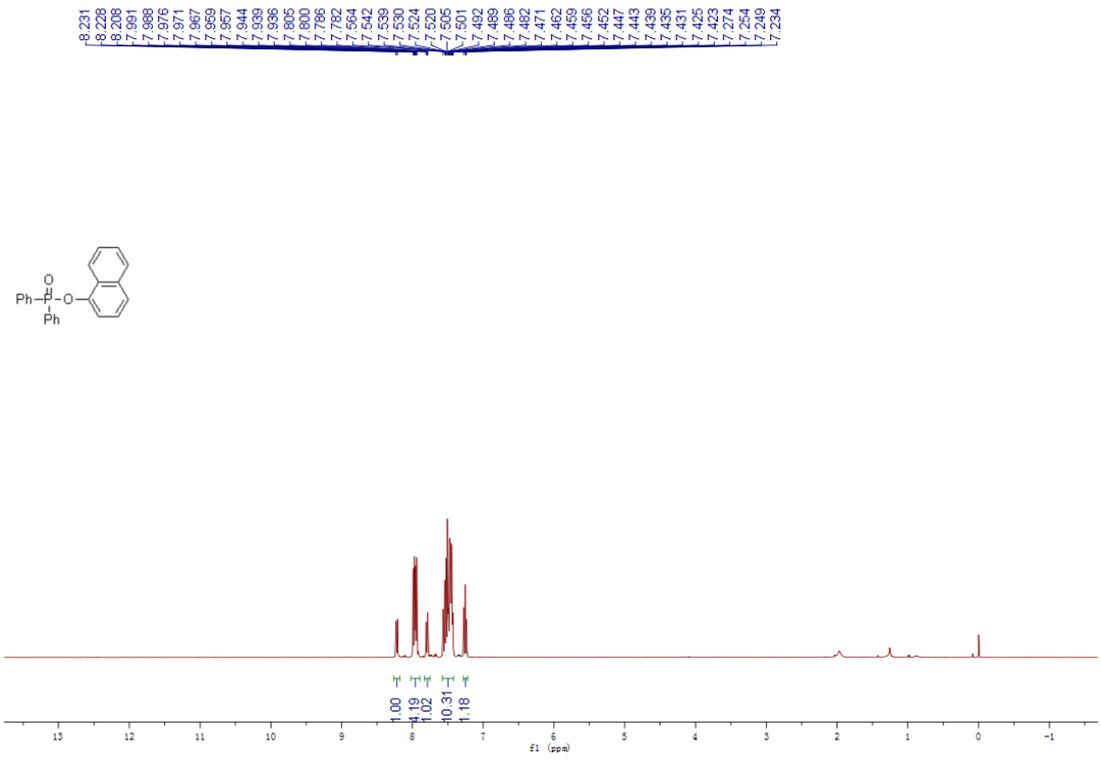


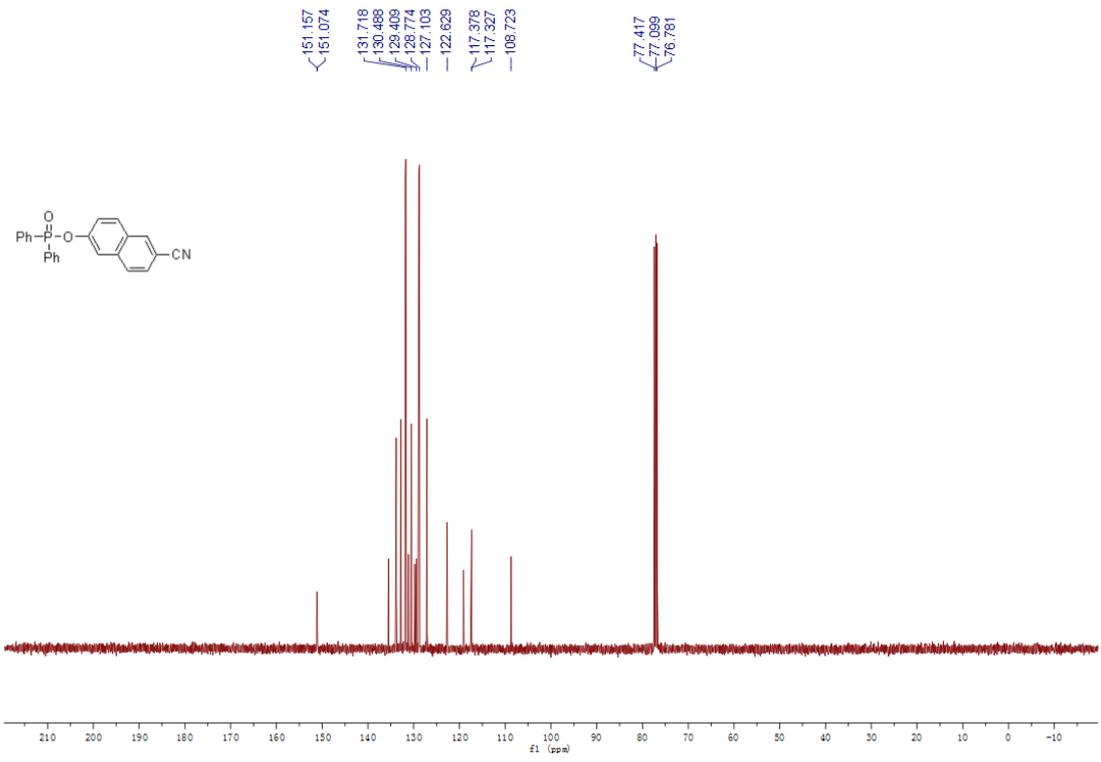
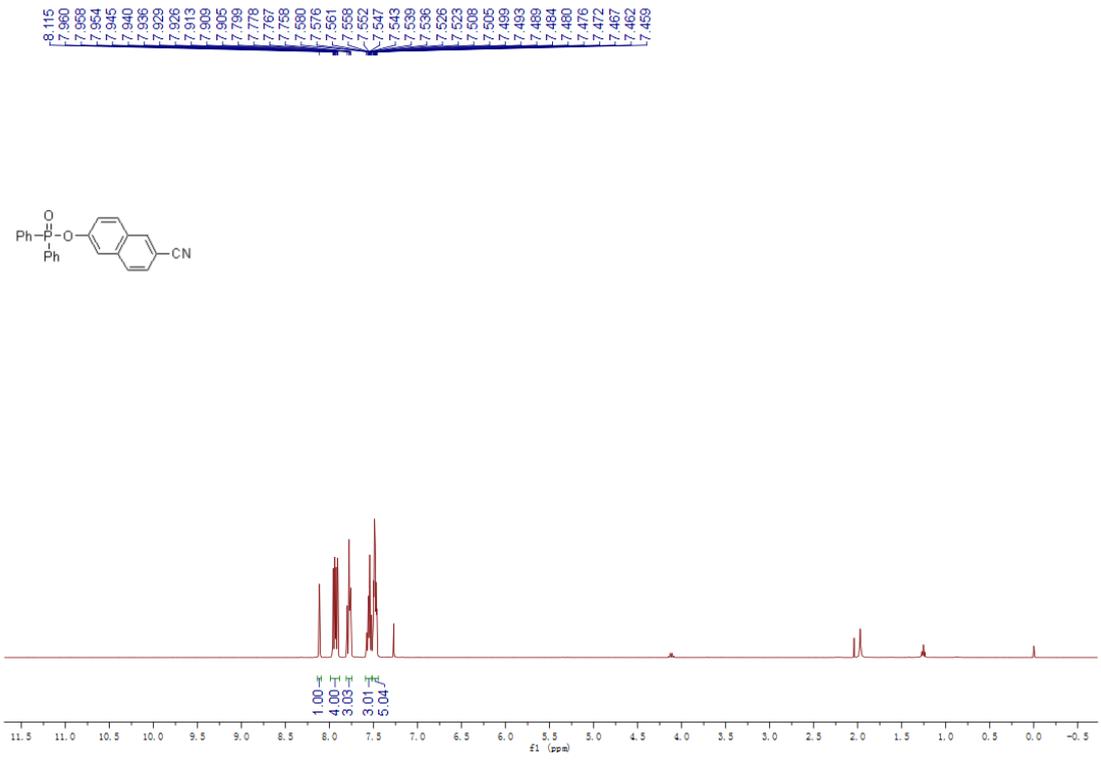


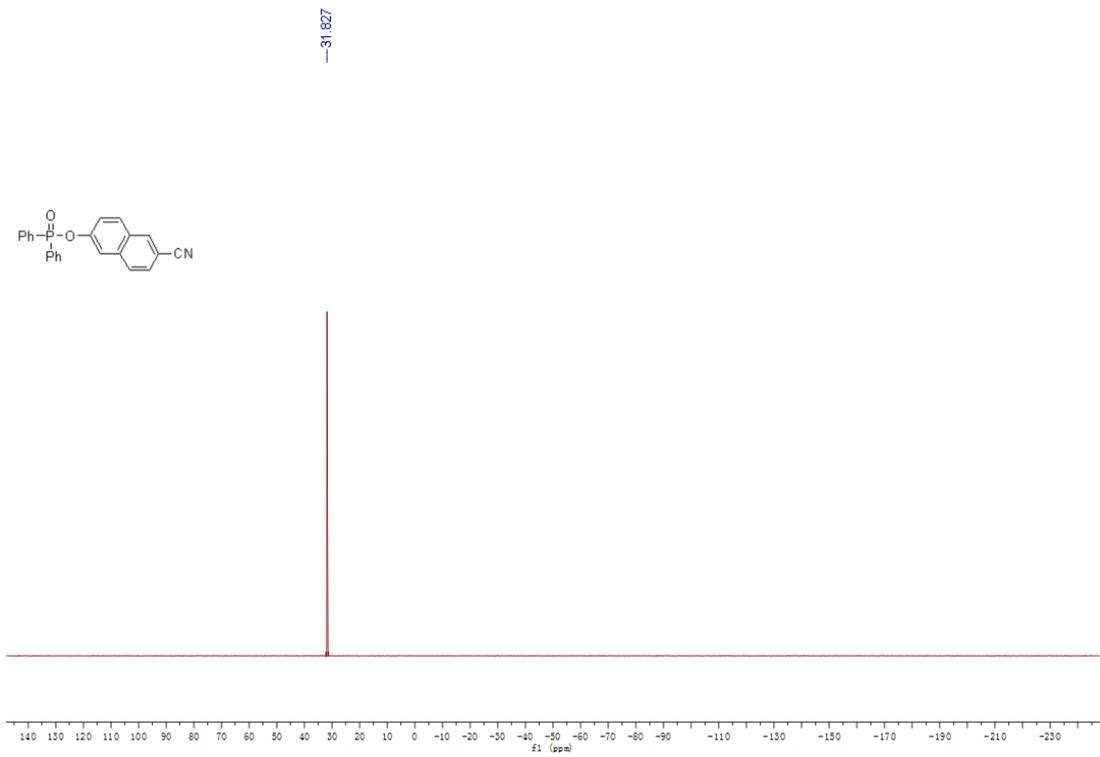




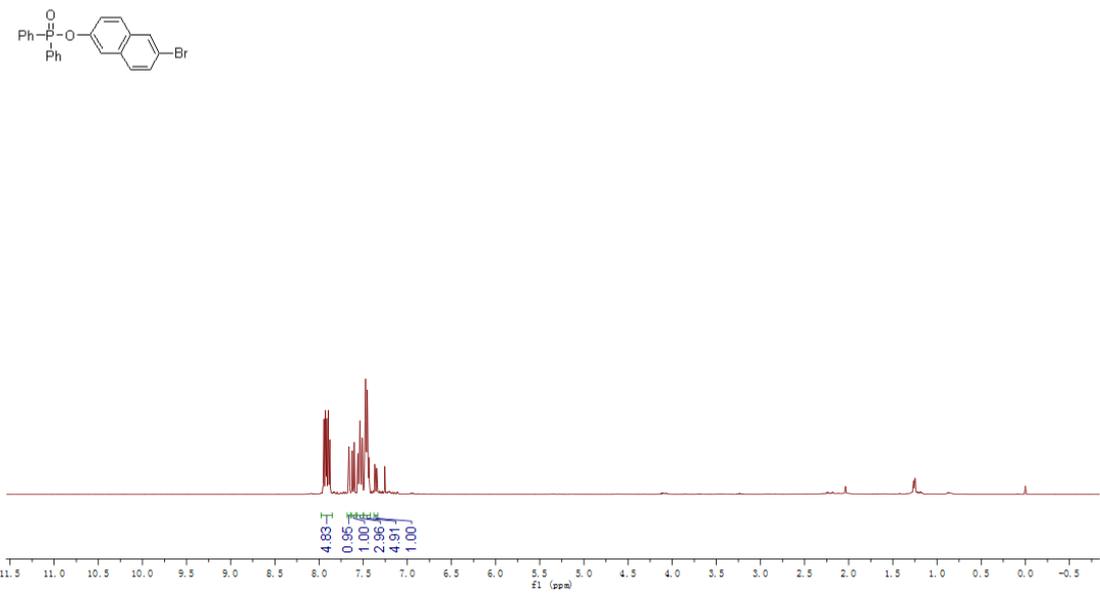


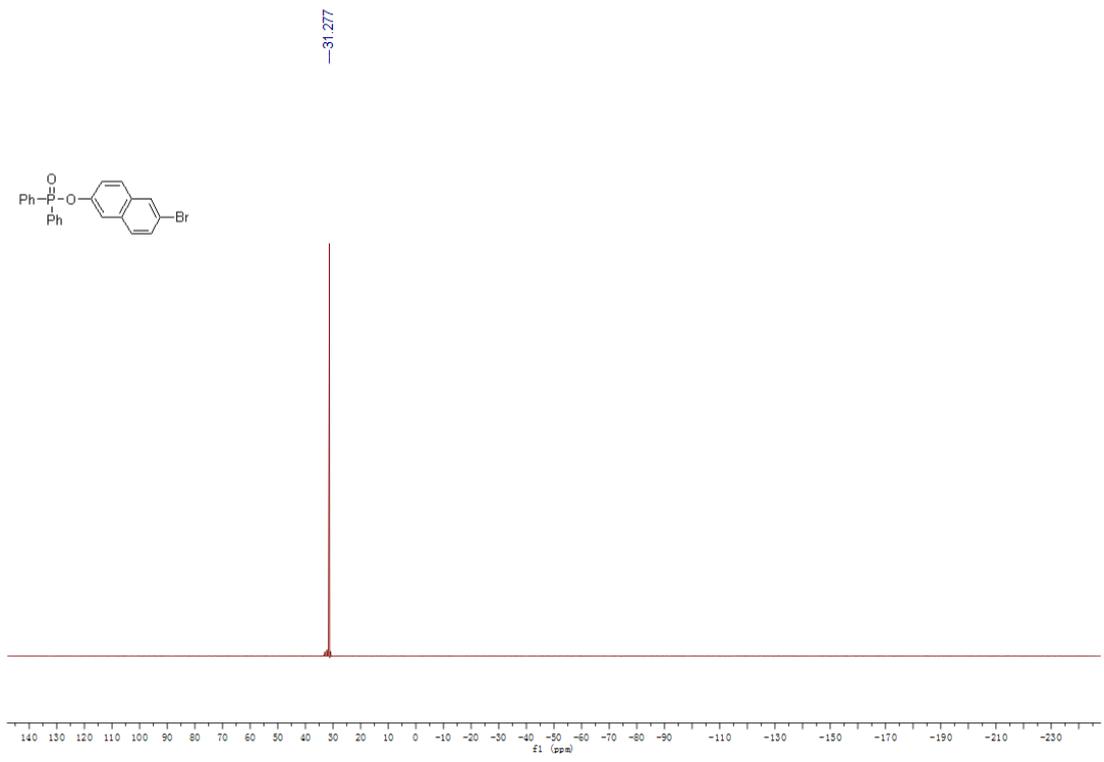
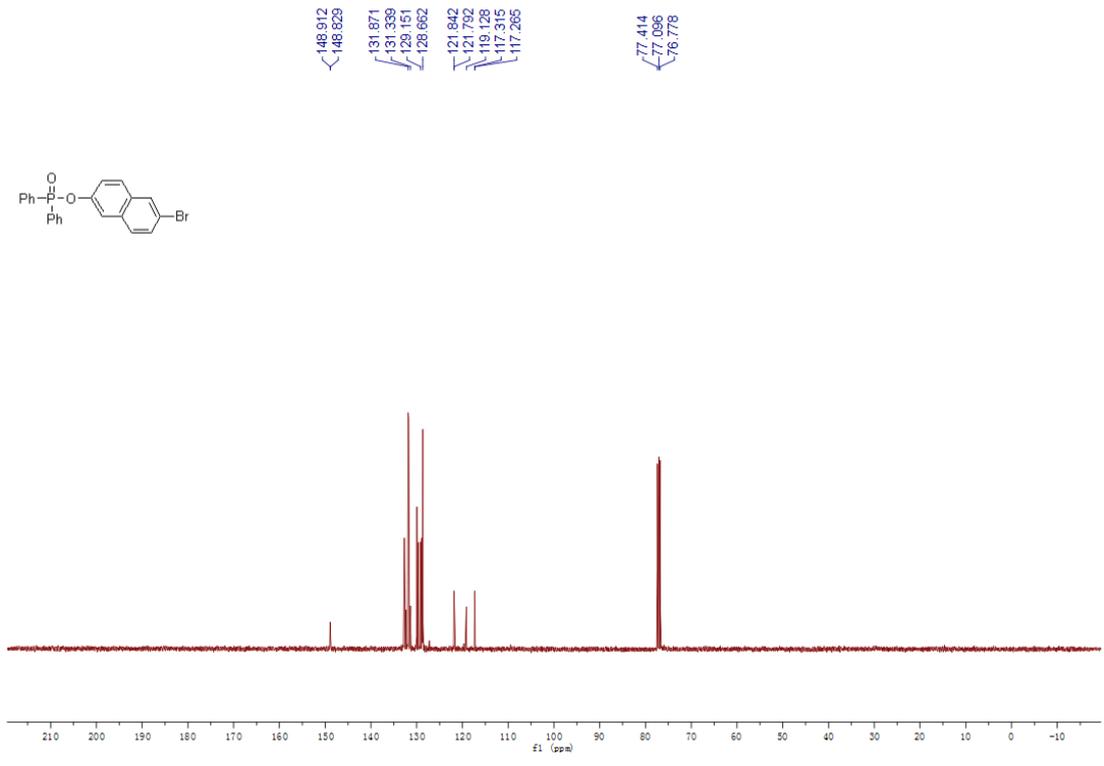


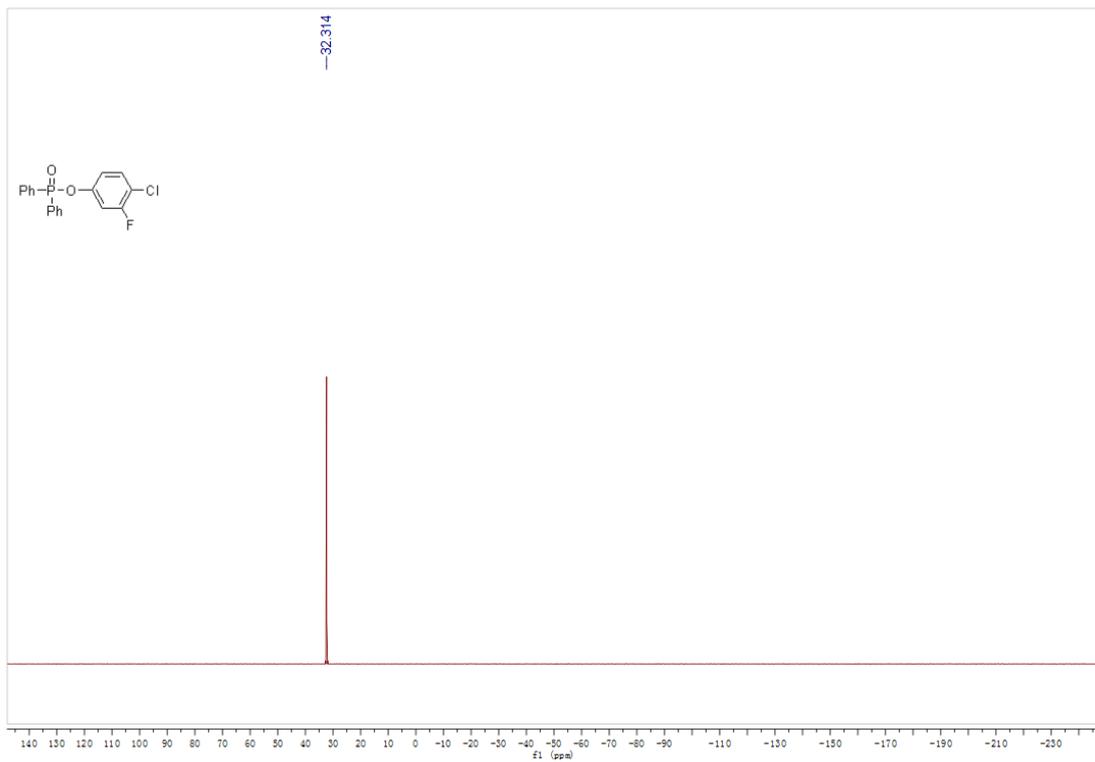




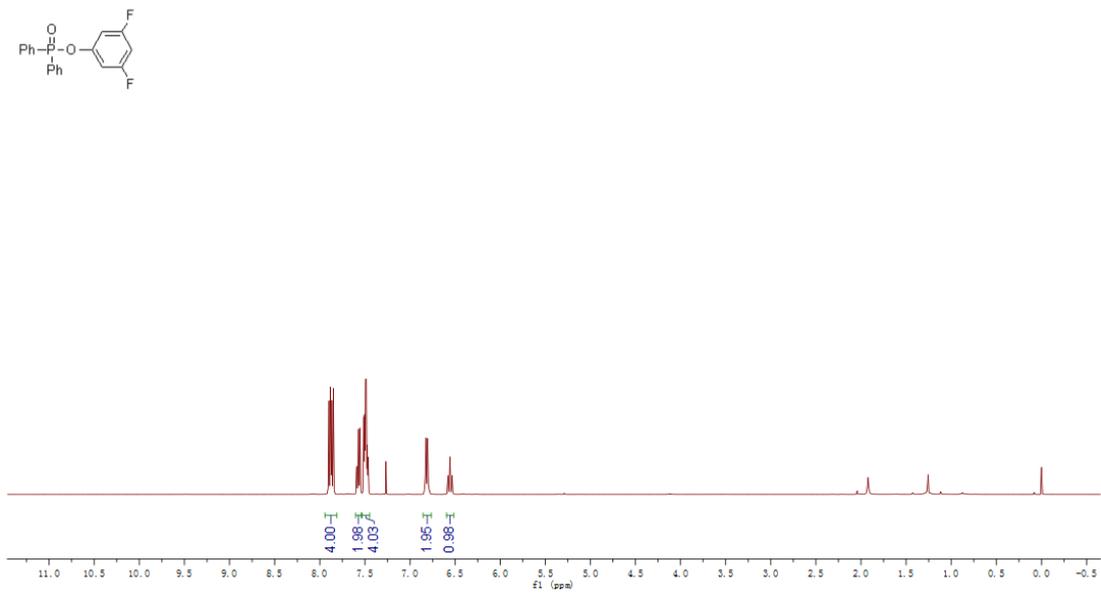
7.947
7.944
7.941
7.932
7.927
7.923
7.916
7.913
7.909
7.901
7.896
7.890
7.884
7.877
7.861
7.823
7.801
7.799
7.798
7.790
7.786
7.785
7.781
7.777
7.776
7.771
7.767
7.761
7.750
7.706
7.681
7.477
7.472
7.466
7.463
7.454
7.445
7.441
7.436
7.433
7.369
7.364
7.346
7.342

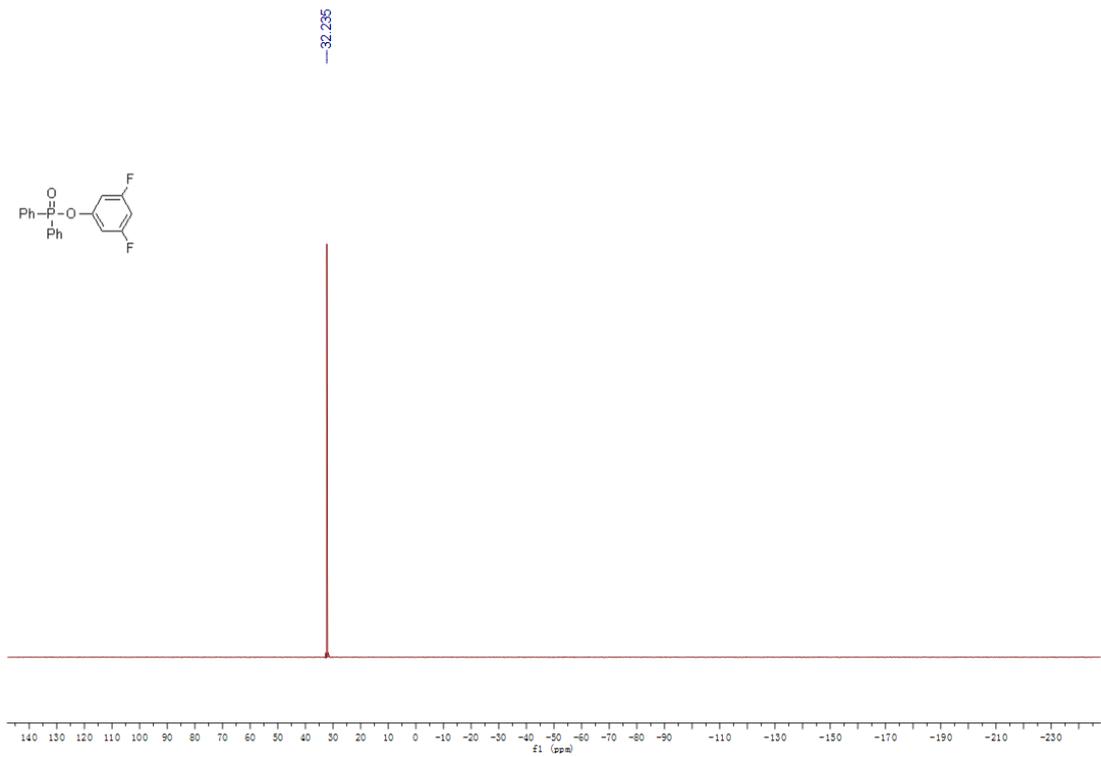
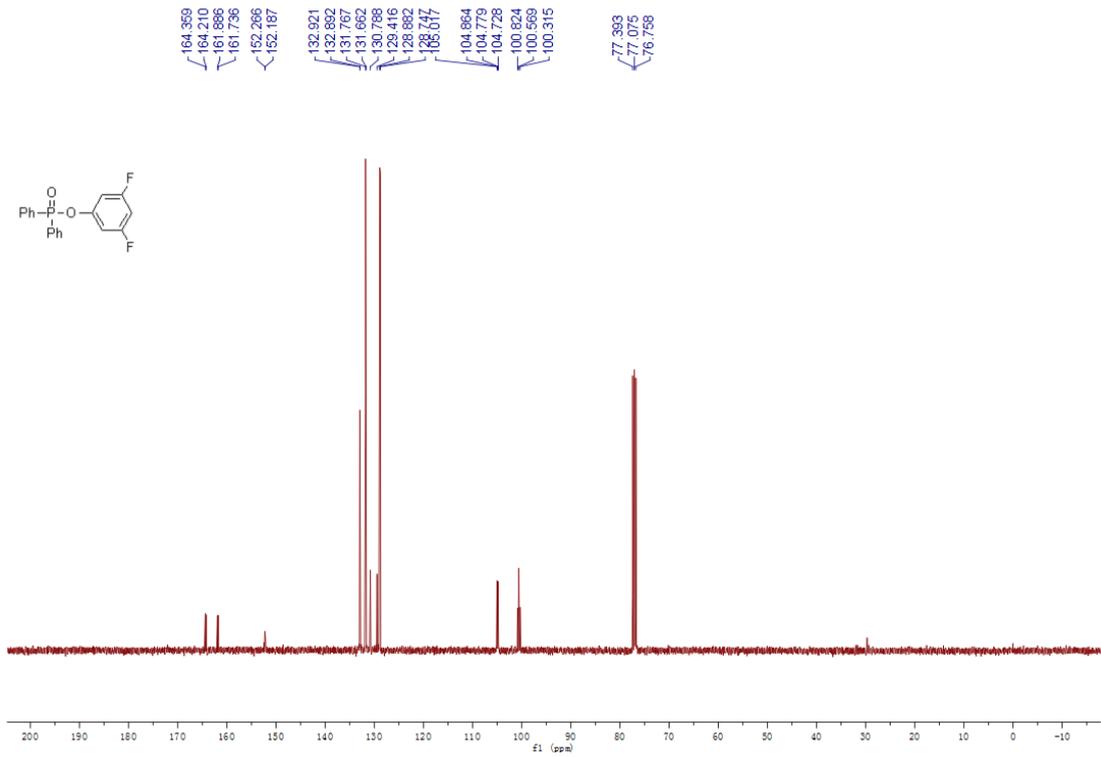


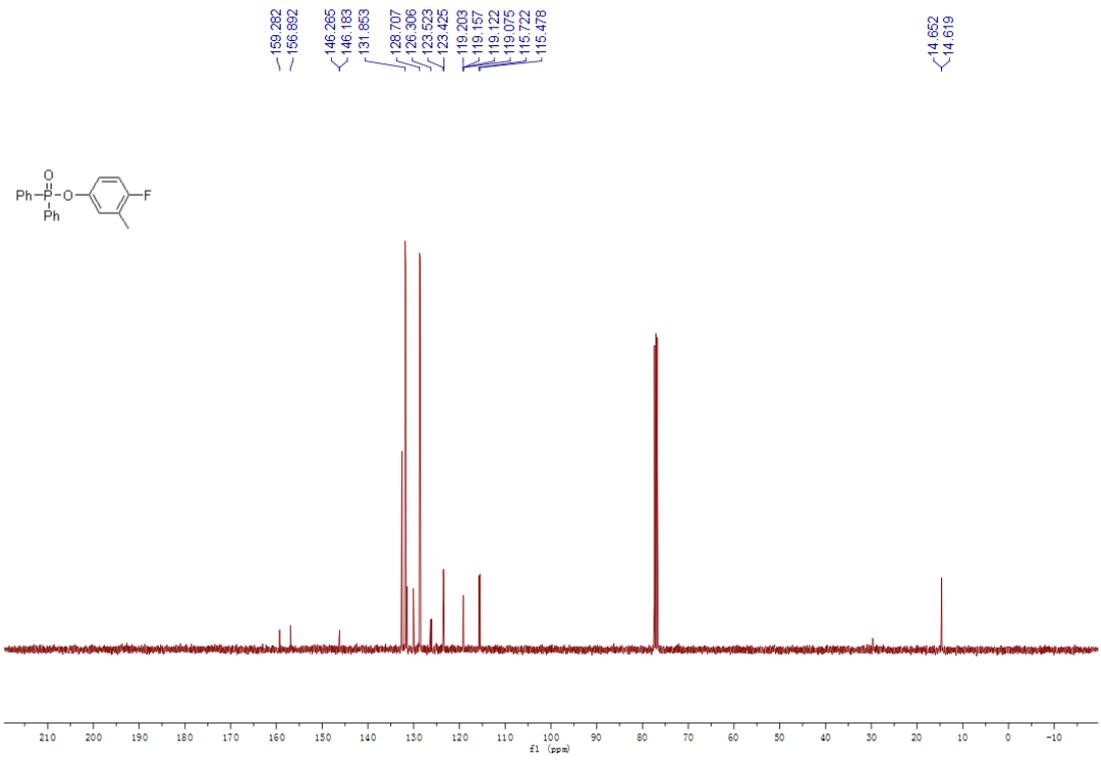
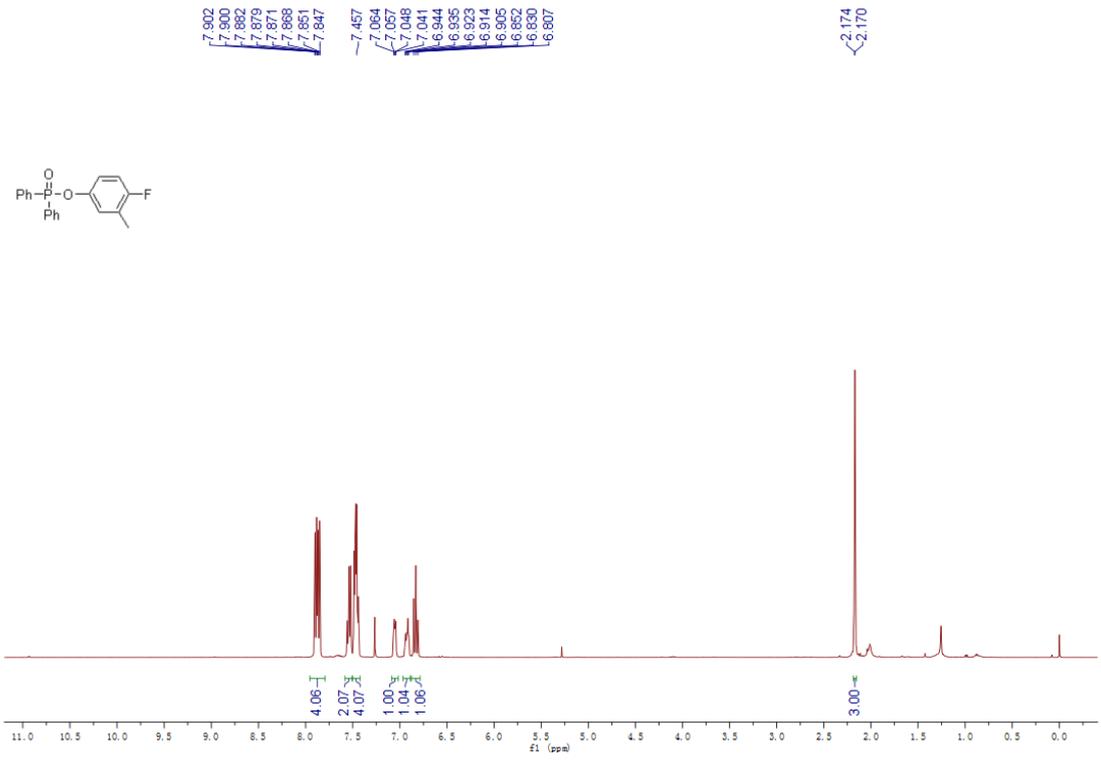


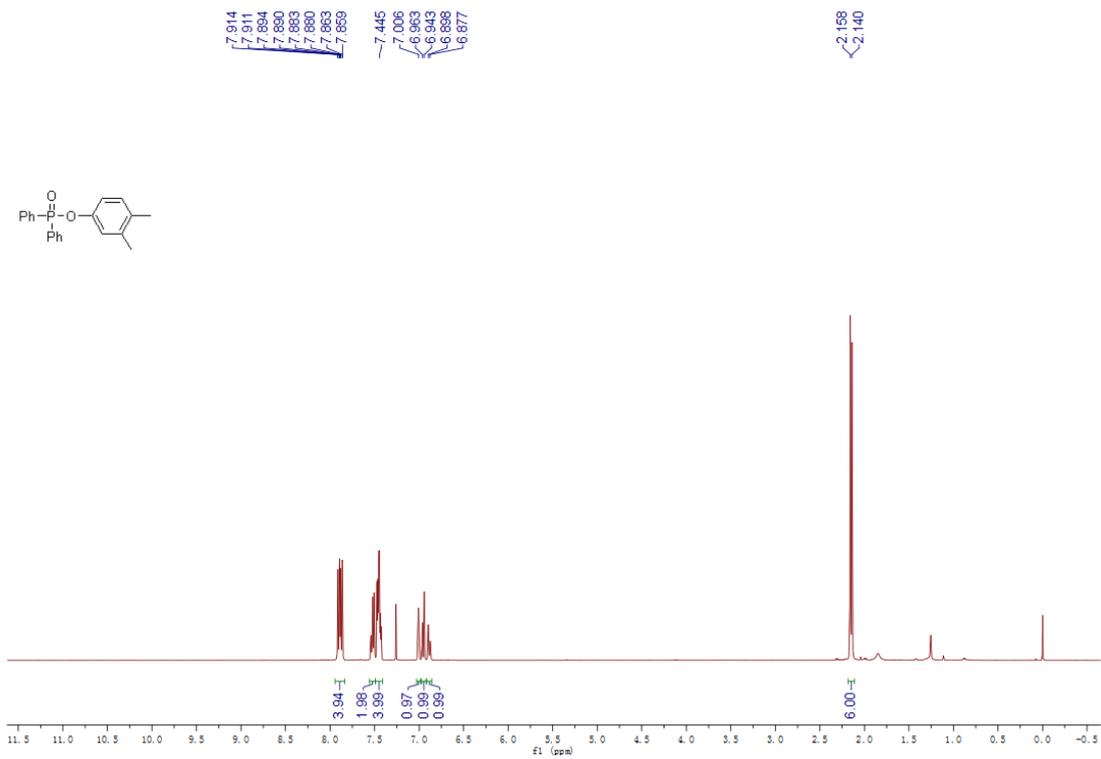
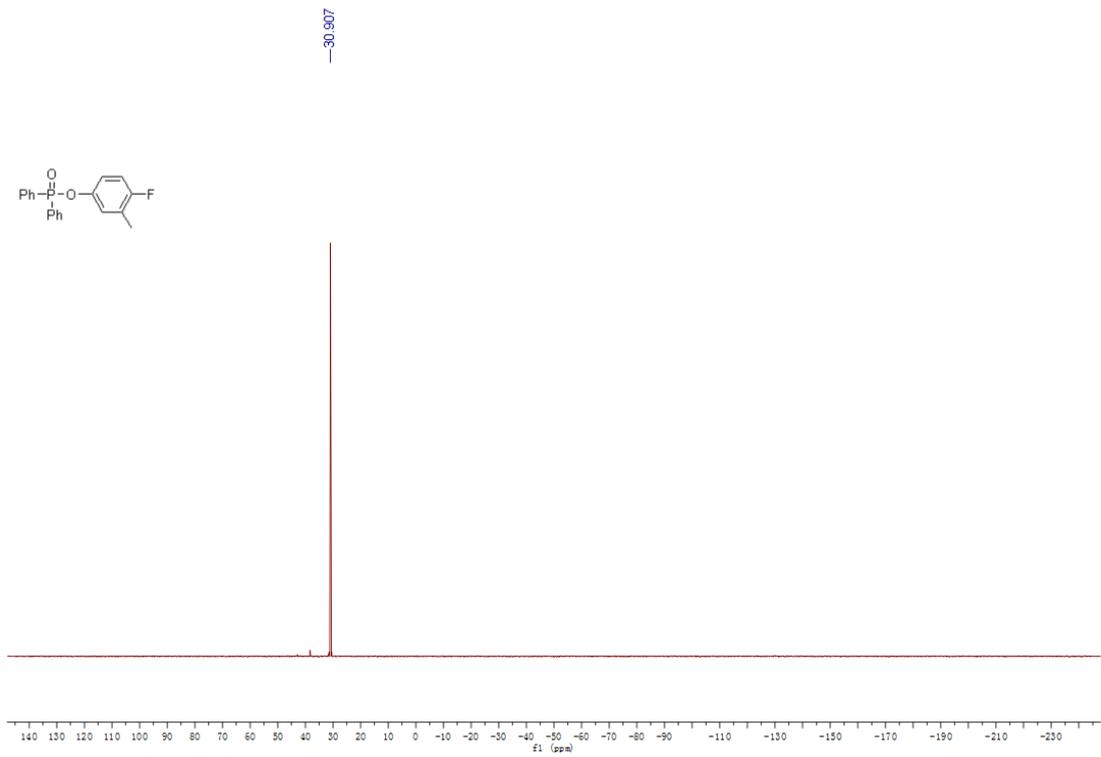


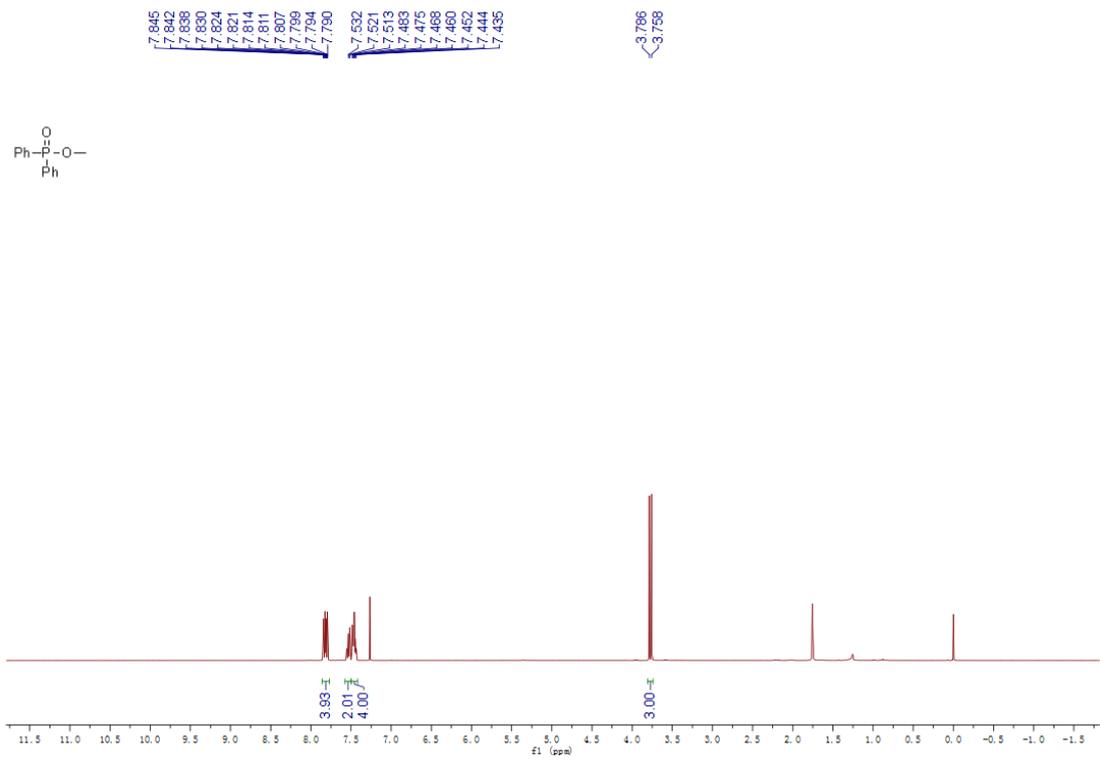
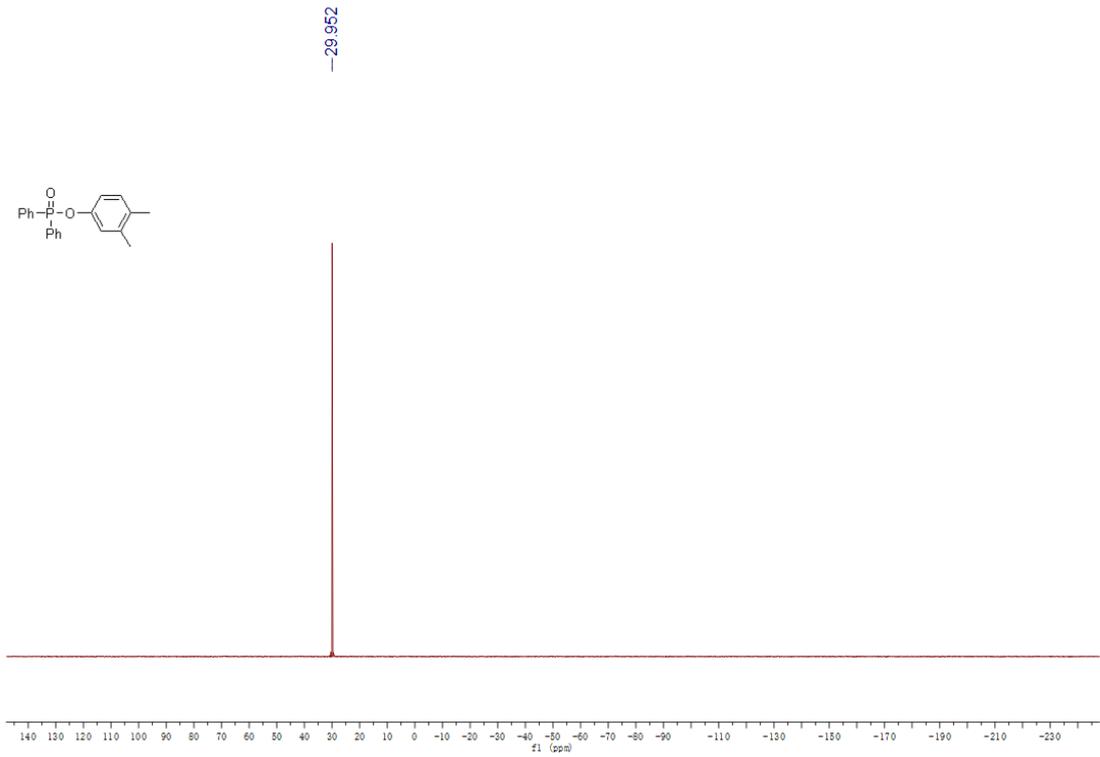
7.902
7.899
7.895
7.886
7.881
7.878
7.870
7.867
7.854
7.849
7.846
7.555
7.493
7.483
6.819
6.800
6.883
6.578
6.572
6.861
6.856
6.850
6.839
6.833
6.828

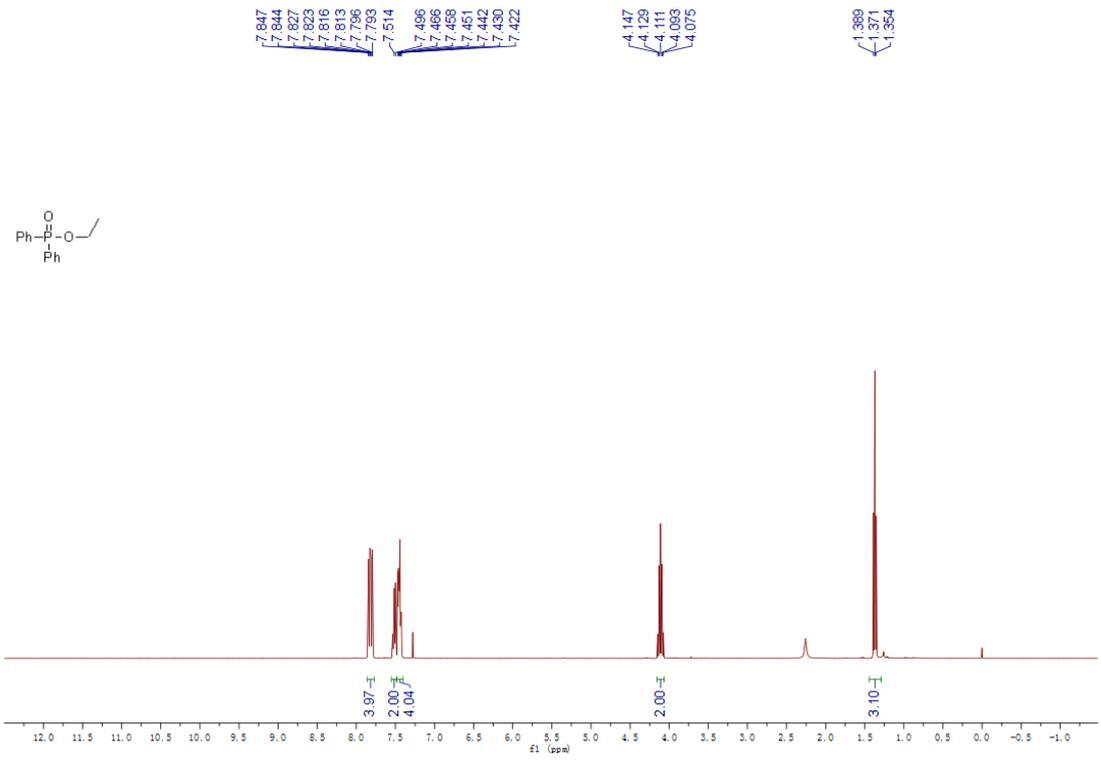
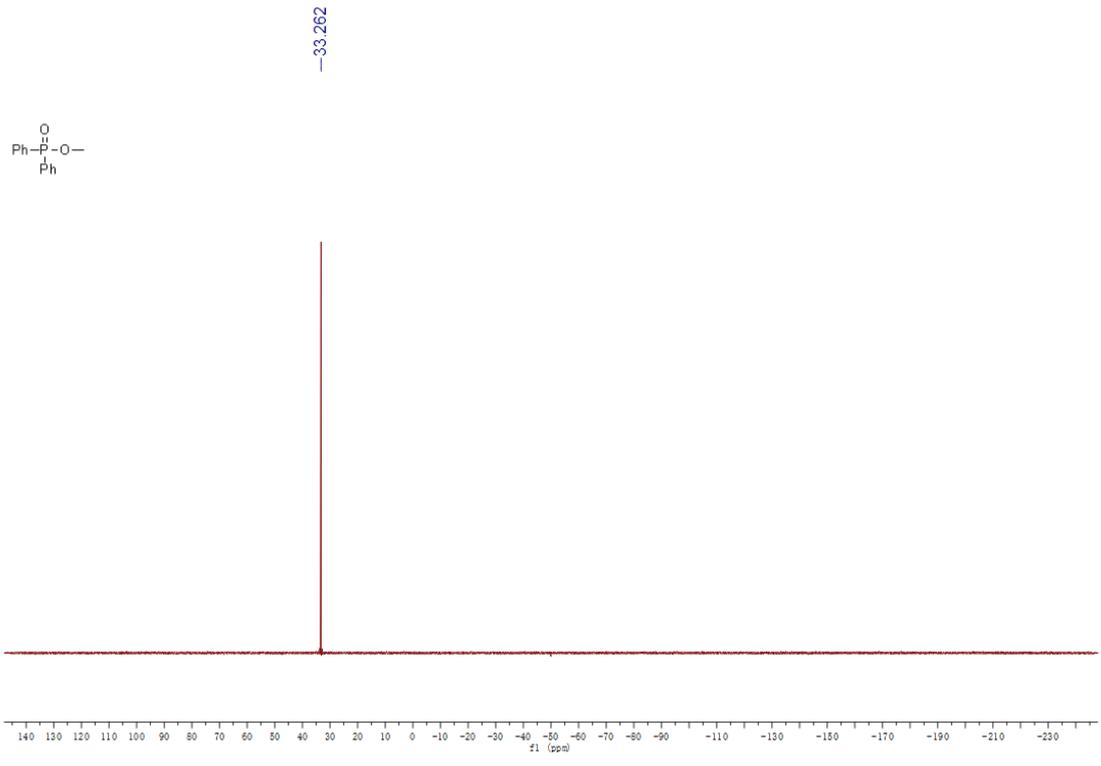


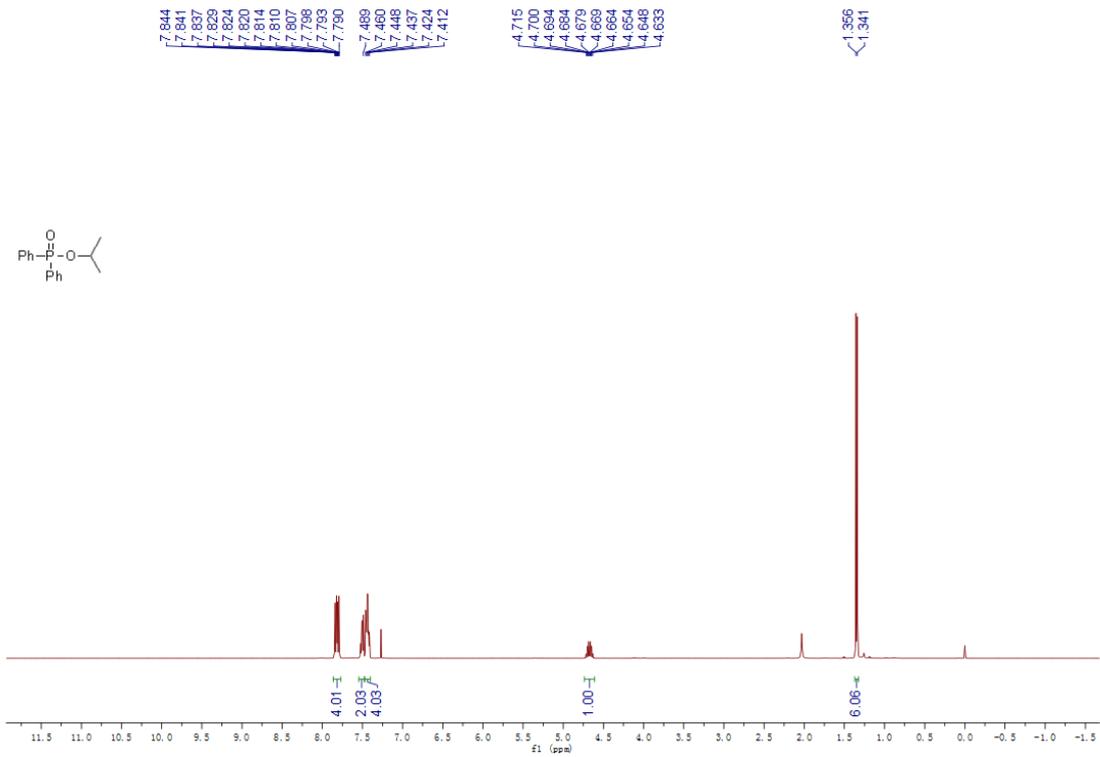
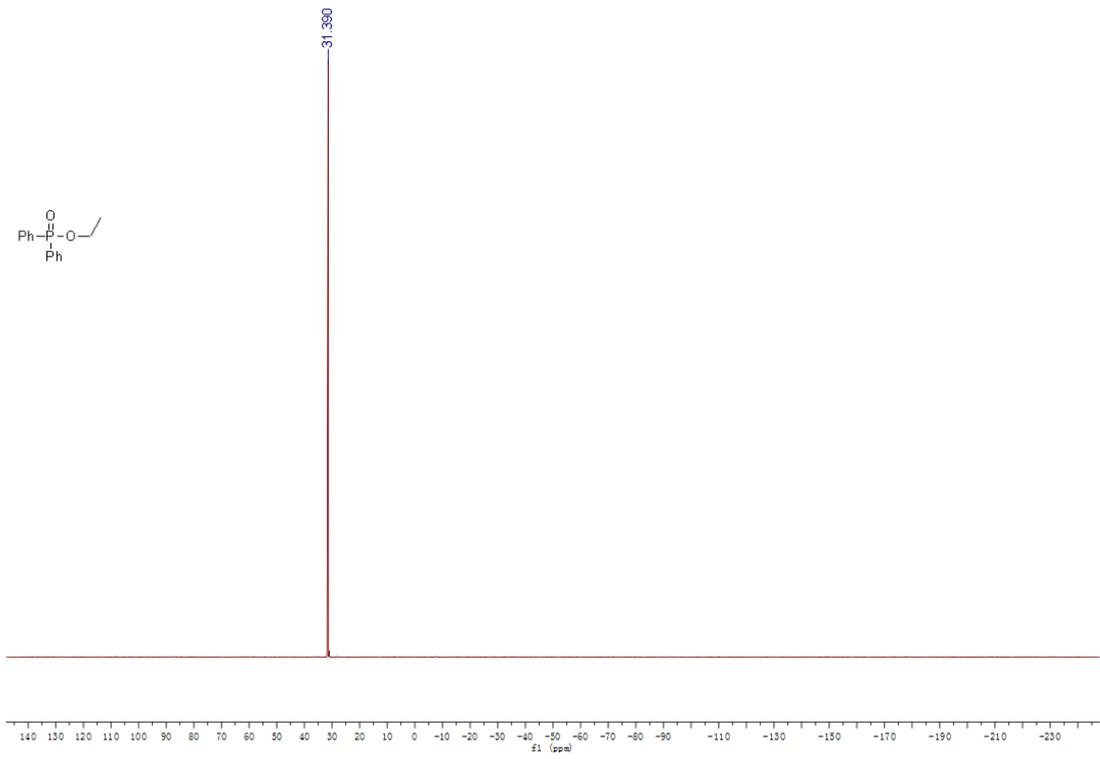


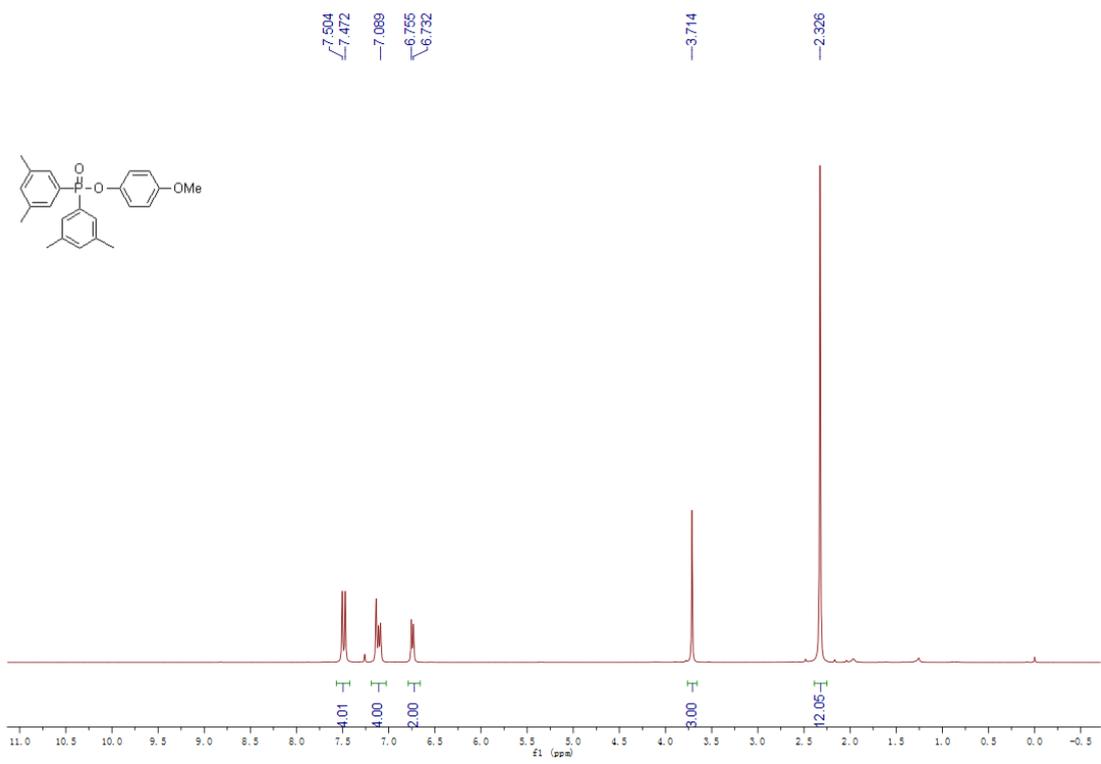
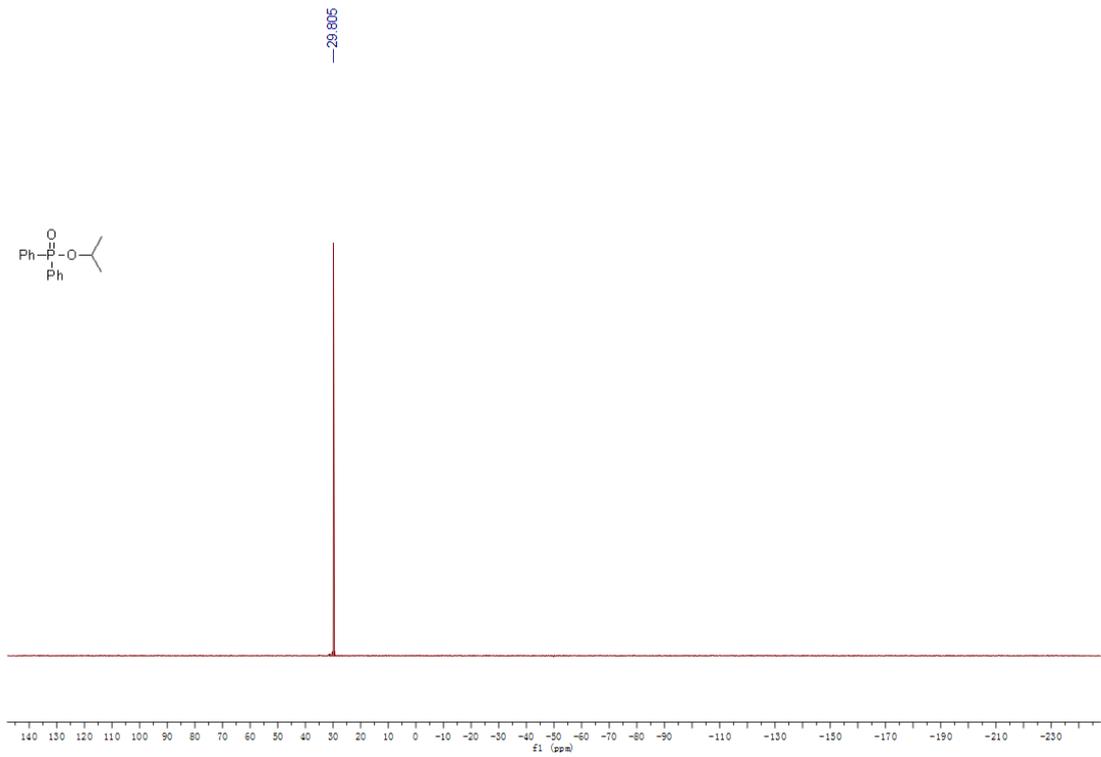


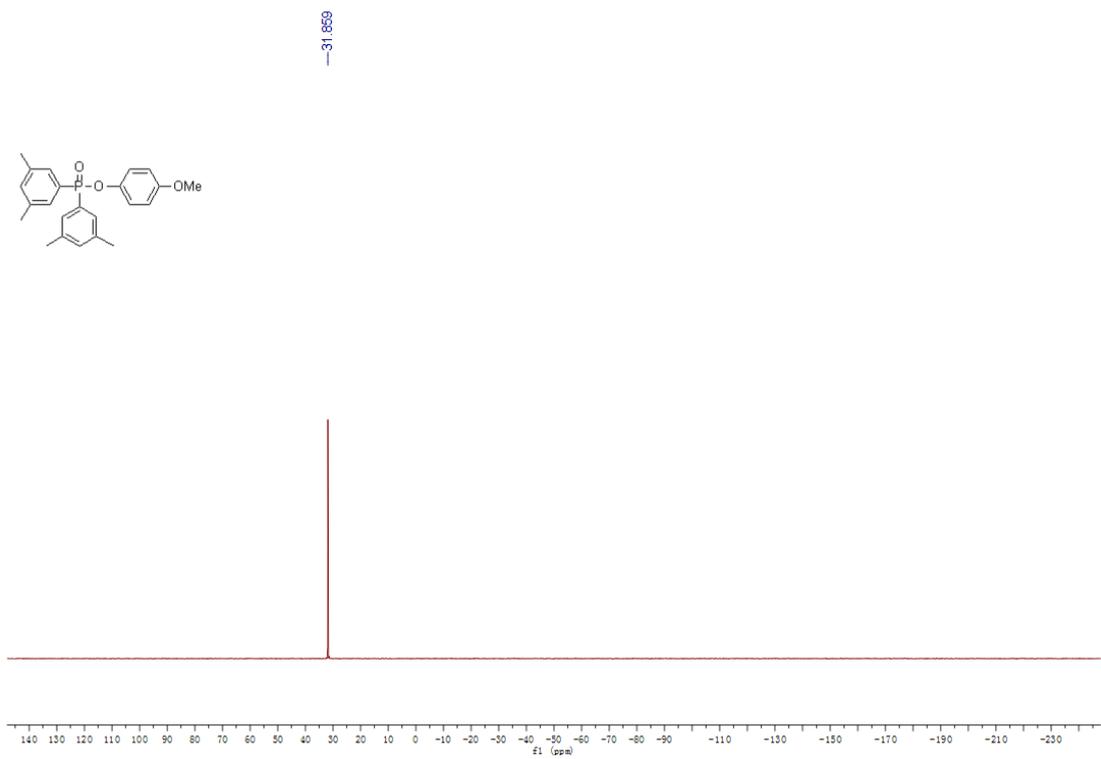
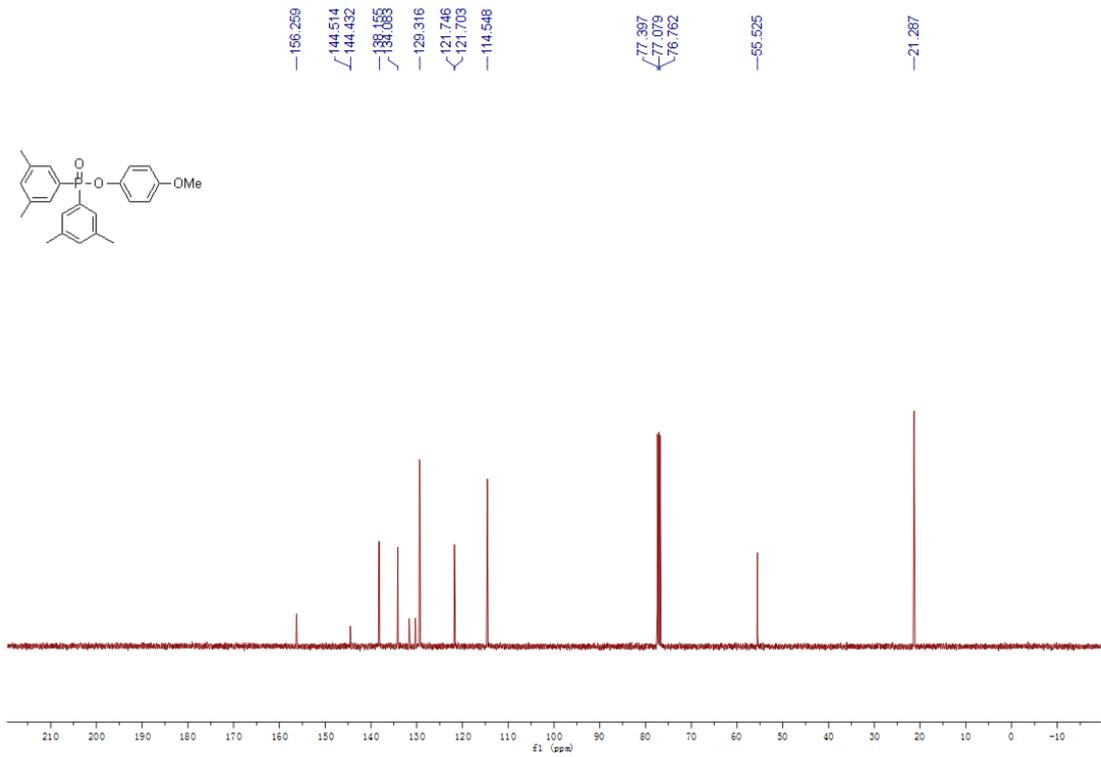


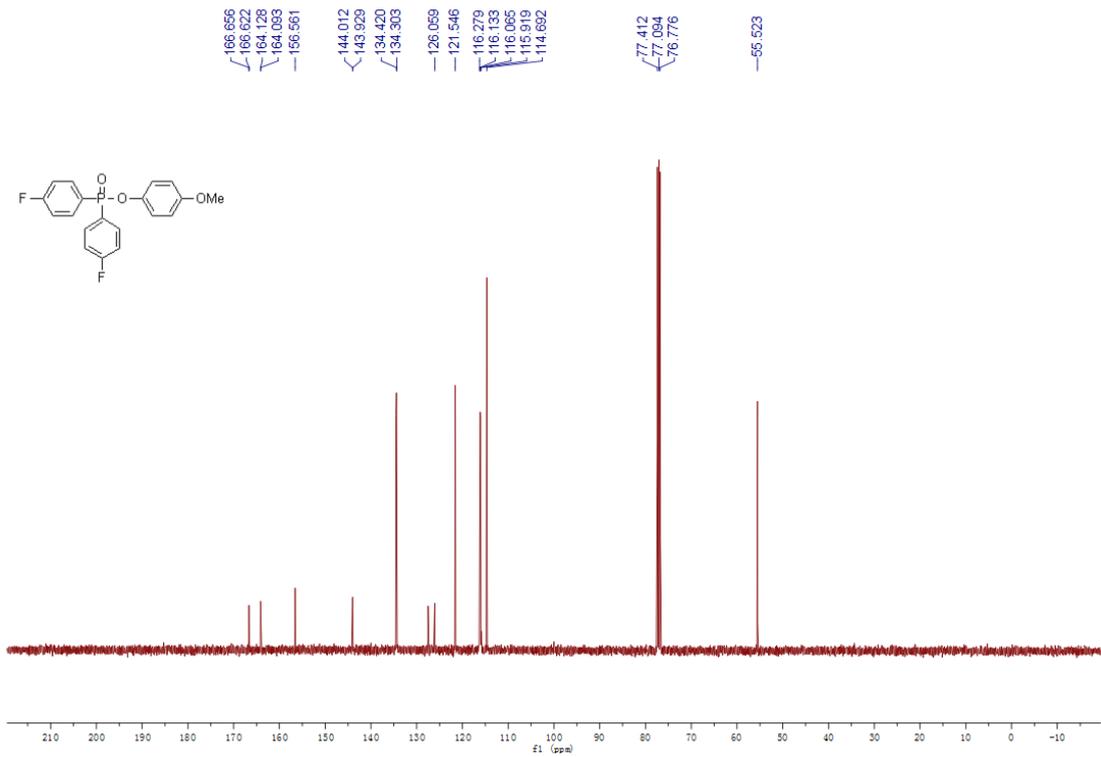
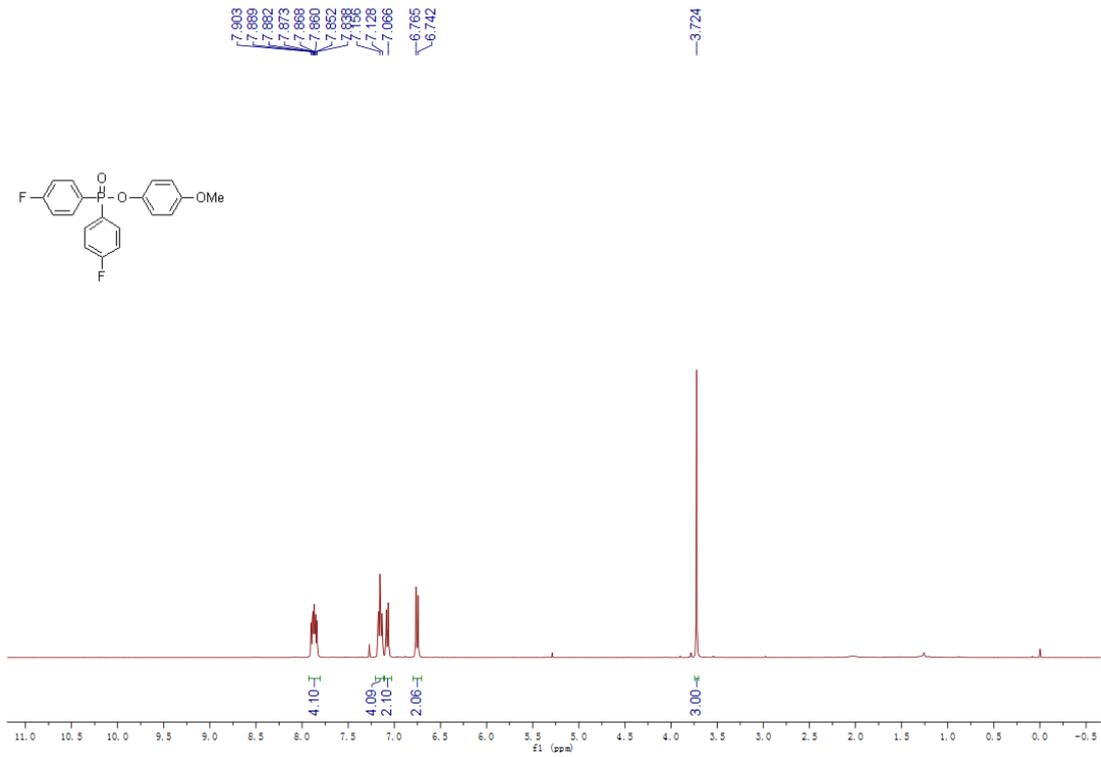


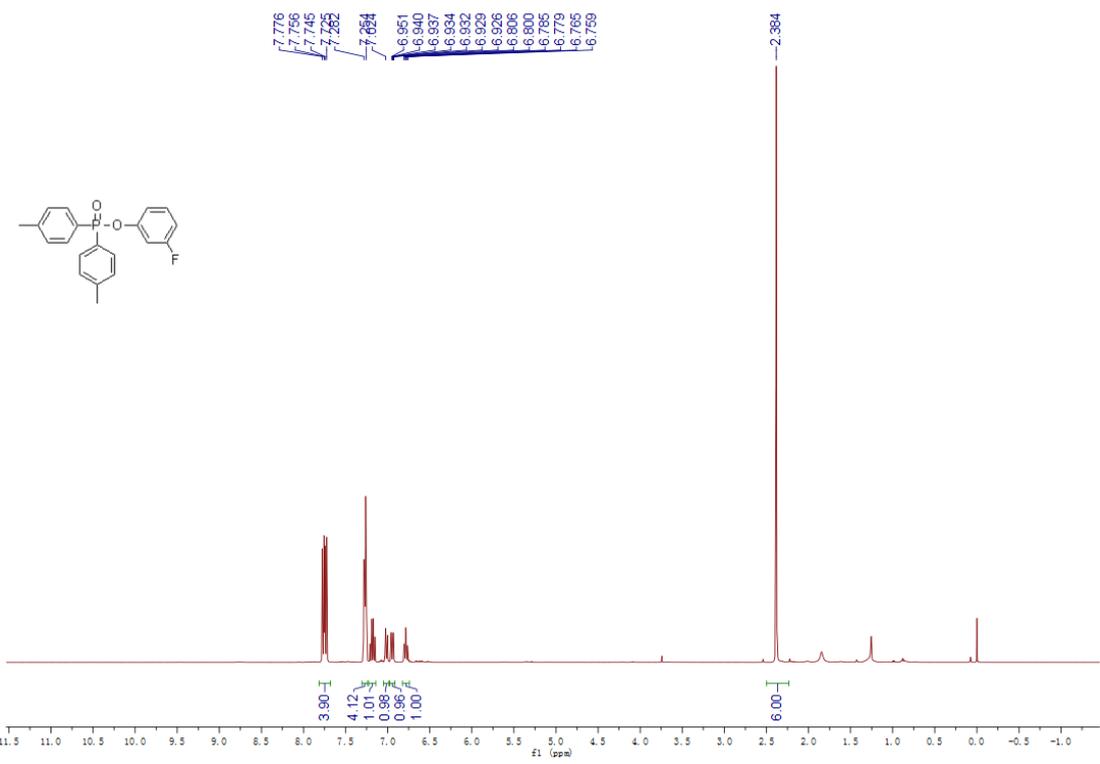
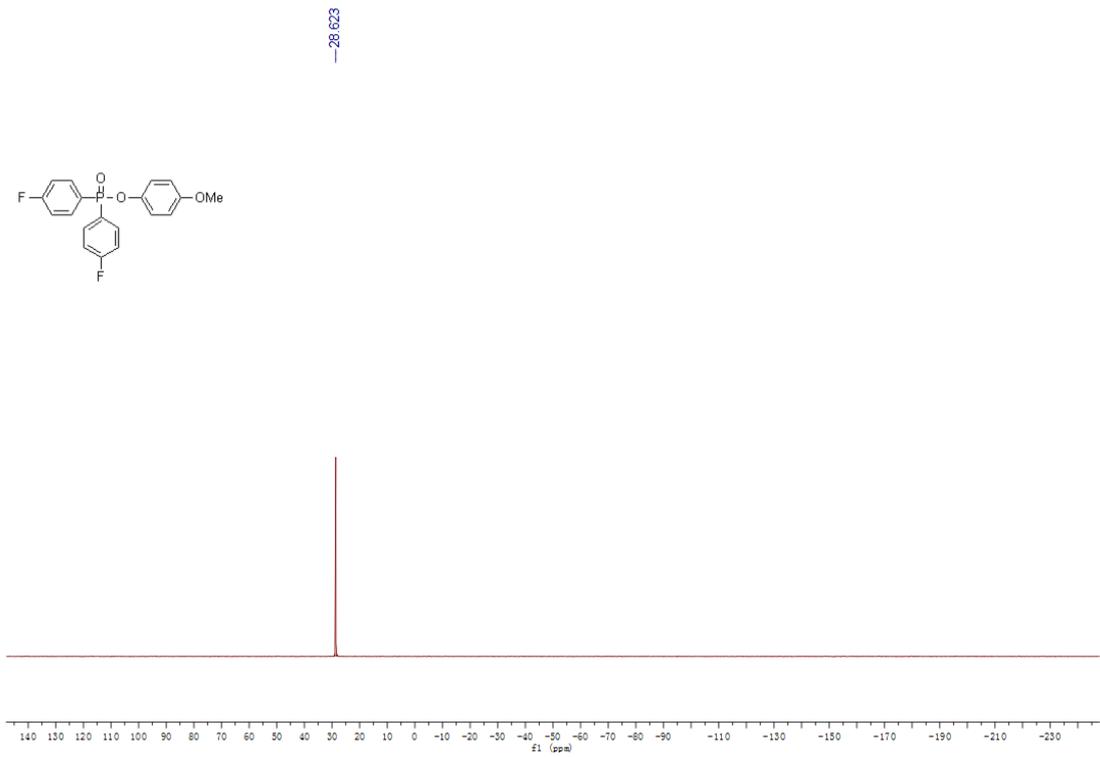


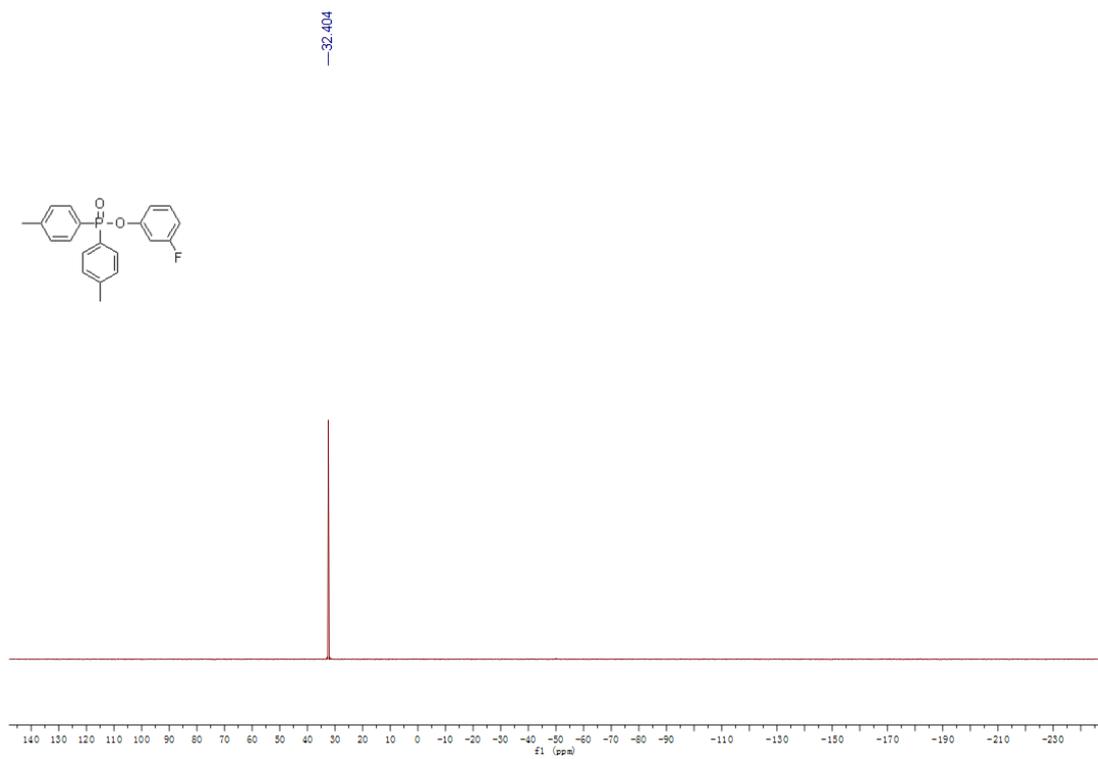
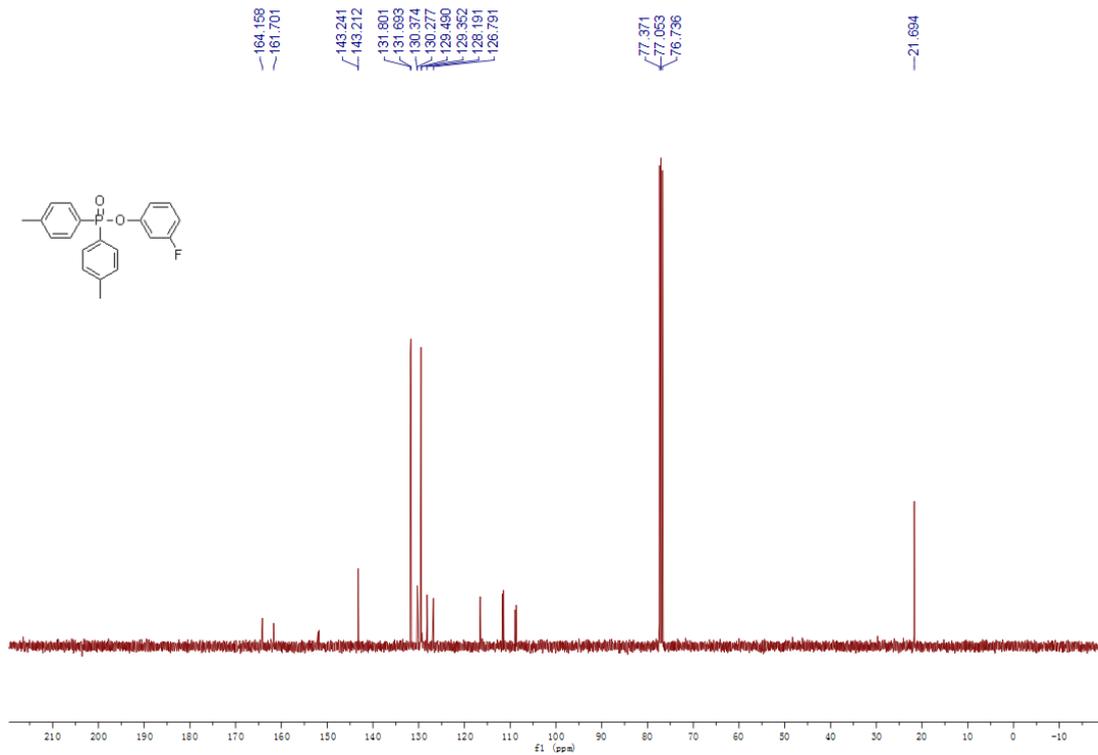


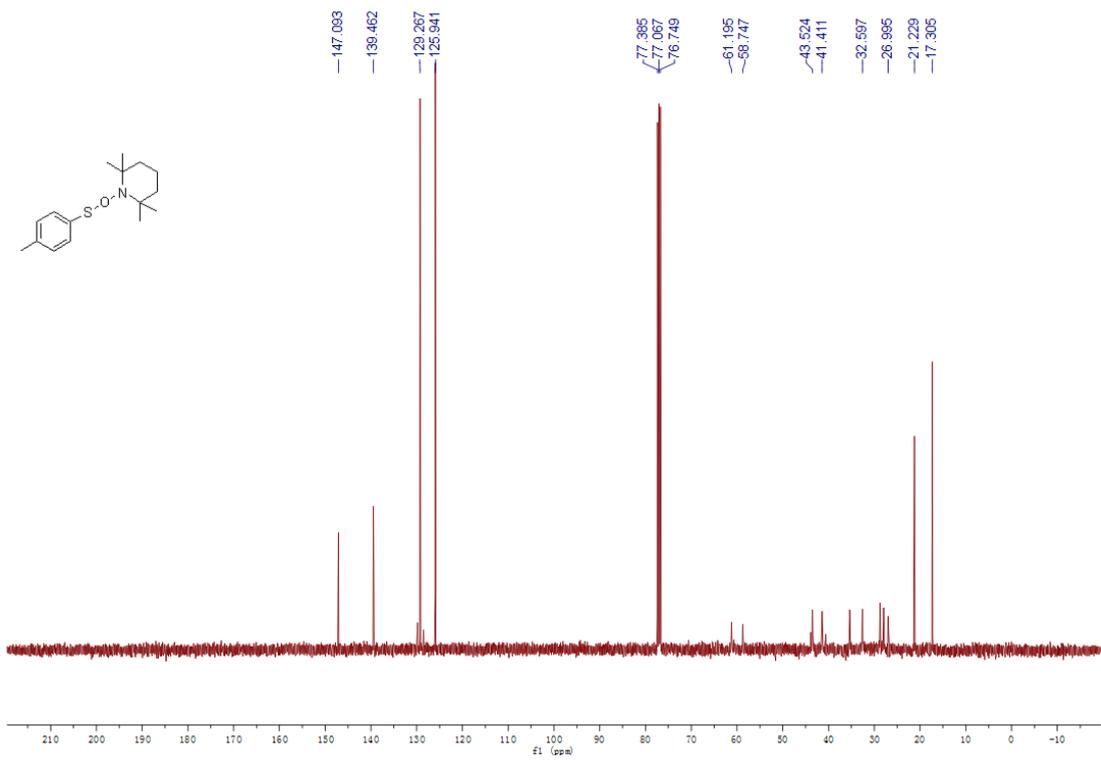
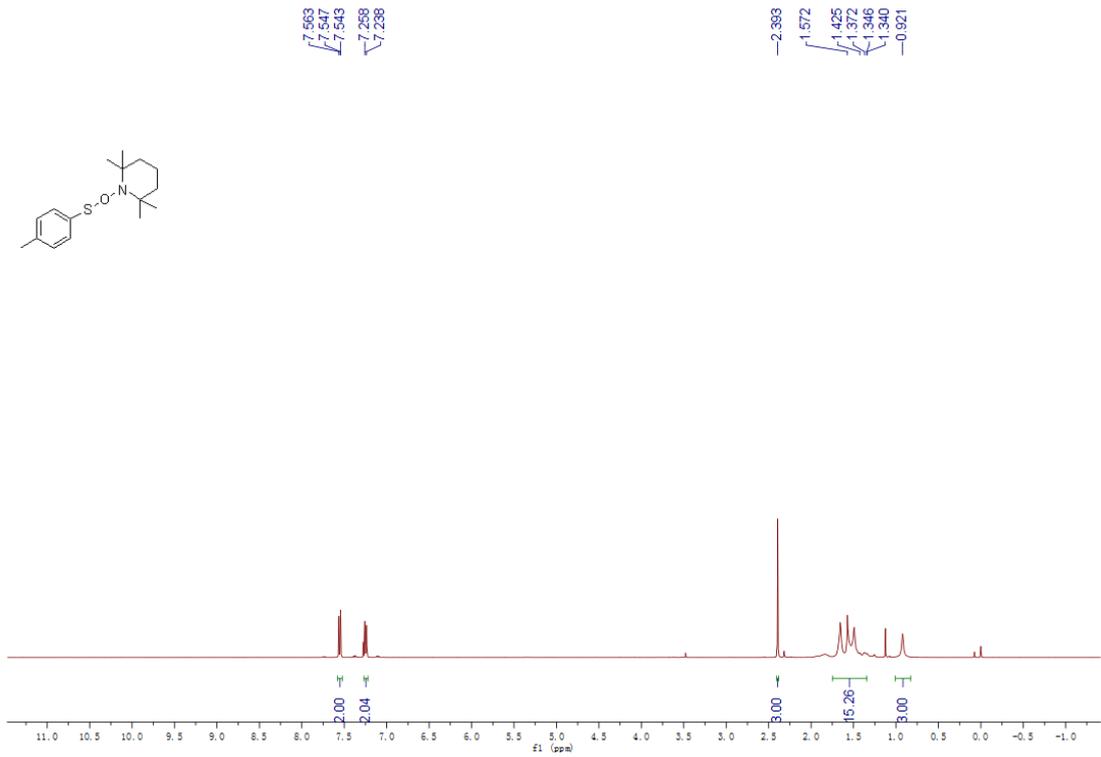


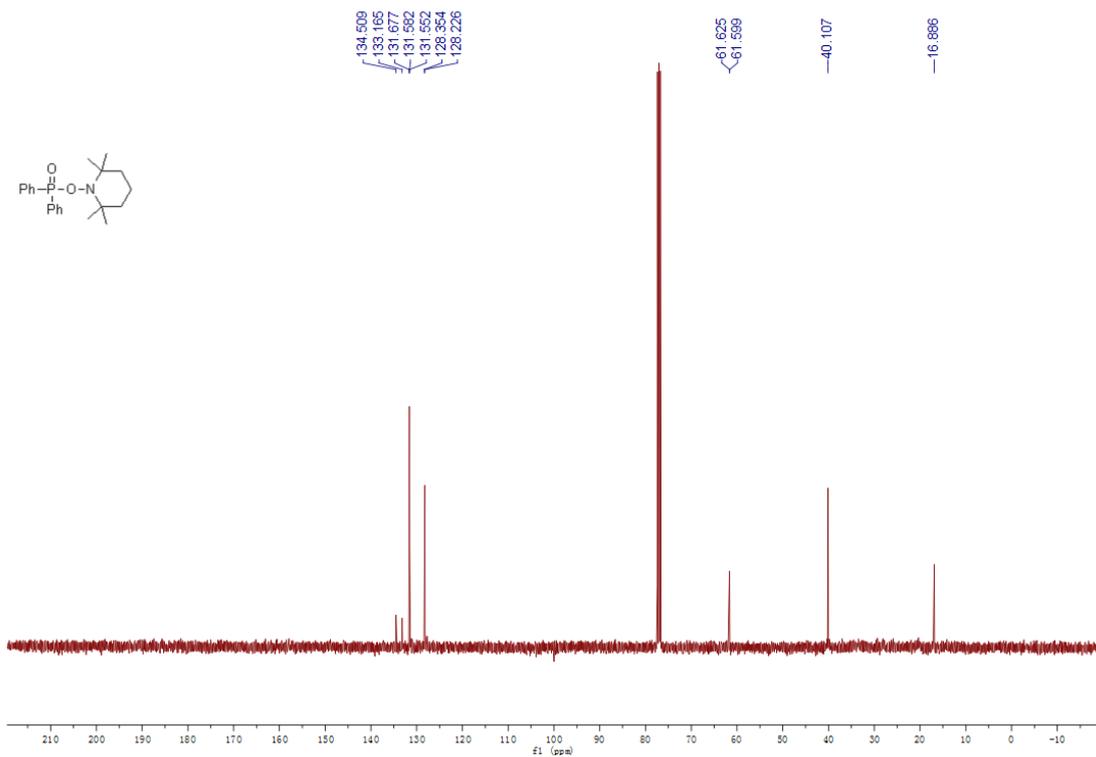
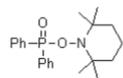
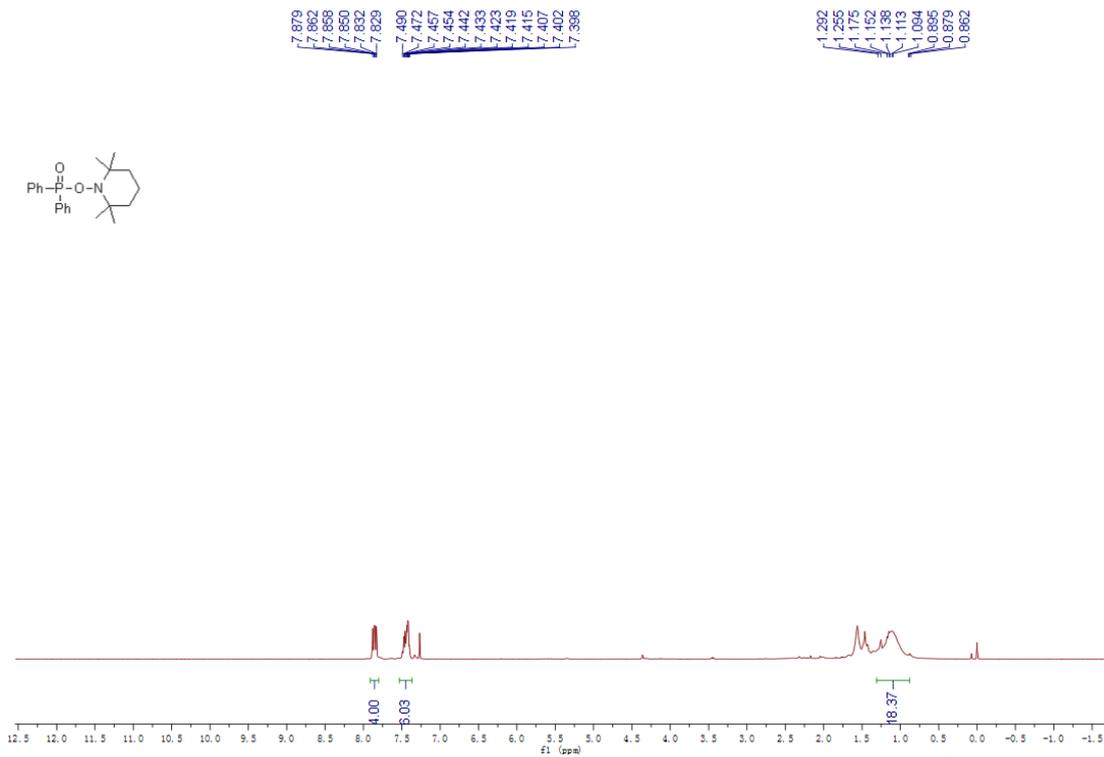
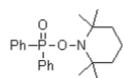


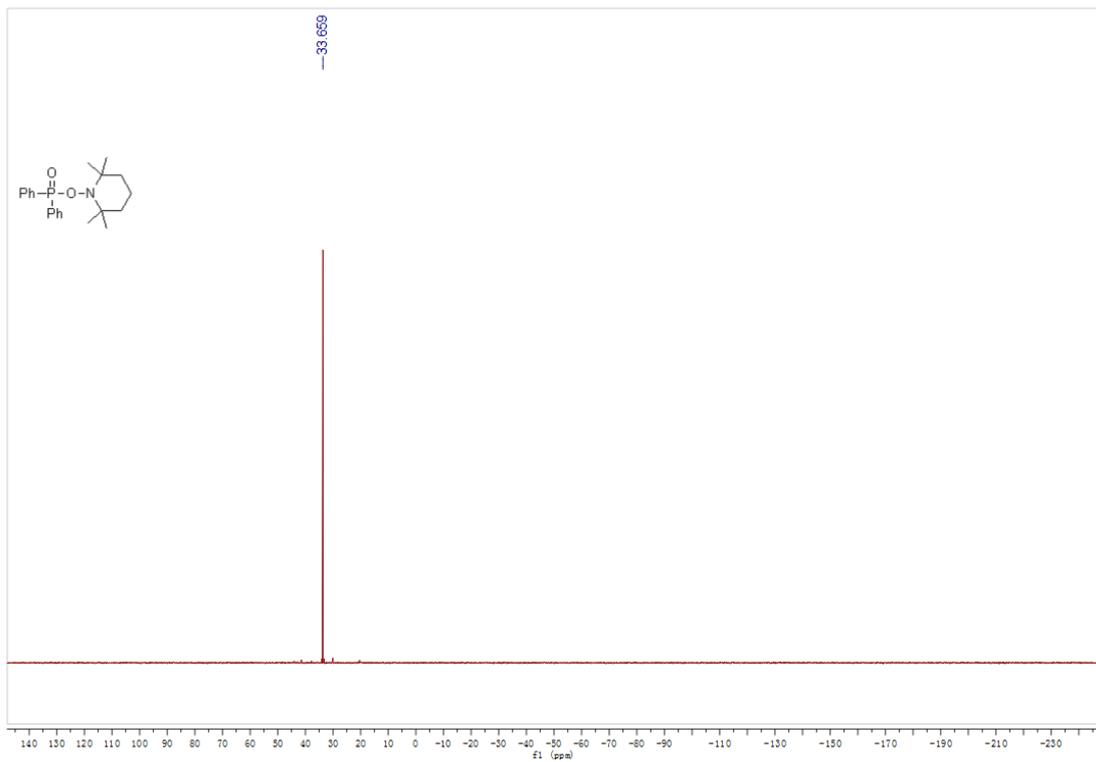












7.266
7.265
7.246
7.238
7.236
7.214
7.205
7.204
7.286
7.283
7.273
7.267
7.261
7.240
7.137
7.117

4.677
4.669
4.653
4.645

3.283
3.275
3.249
3.240

2.988
2.957

-2.334

