

# Supporting Information

## of

### A Facile and Practical Preparation for P-Chiral Phosphine Oxides

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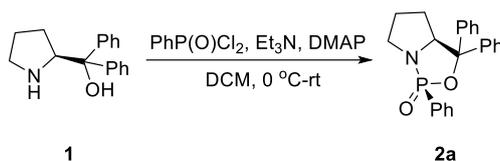
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## 1. General Considerations.

All reactions were carried out under the designated conditions. Unless otherwise noted, commercialized reagents were used without further purifications. Toluene and hexafluorobenzene were purchased from Sigma-Aldrich Chemical Co. All other solvents were purified and dried according to standard methods prior to use.

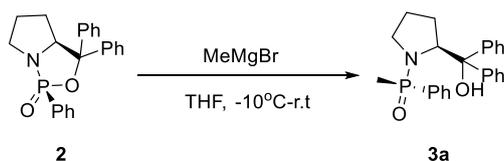
$^1\text{H}$  NMR,  $^{19}\text{F}$  NMR and  $^{13}\text{C}$  NMR data were recorded on a Bruker-Ultrashield PLUS 400 or 500 NMR Agilent spectrometer with Chloroform-d as the solvent.  $^1\text{H}$  chemical shifts were referenced to Chloroform-d at 7.26 ppm.  $^{13}\text{C}$  chemical shifts were referenced to Chloroform-d at 77.16 ppm and obtained with  $^1\text{H}$  decoupling. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), quintet (quint), sextet (sextet), septet (septet), multiplet (m), and broad (br). MS was measured on Agilent 7890A/5975C Series GC/MSD mass spectrometer. HPLC yield were determined on Agilent 1200 Infinity Series.

## 2. General procedures for Substrates 2

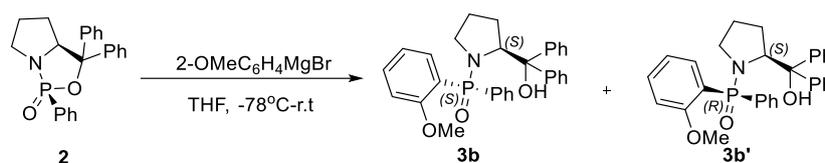


**2a**<sup>[1]</sup>: A Schlenk tube was dried under vacuum. After cooling, the tube was placed under N<sub>2</sub> atmosphere. Under a N<sub>2</sub> atmosphere, to a stirred solution of *S*-Diphenylprolinol (**1**, 1 equiv) in dry DCM was added triethylamine (3 equiv) followed by 4-Dimethylaminopyridine (DMAP, 0.3 equiv). To the mixture at 0 °C was added Phenylphosphonic dichloride (1.5 equiv) and the mixture remained at 0 °C. After adding the Phenylphosphonic dichloride, the cooling bath was removed and the solution was stirred at r.t. overnight (20 h). The mixture was carefully quenched with sat. NaHCO<sub>3</sub>. The water layer was washed with DCM for three times. The organic layer was washed with sat. NaHCO<sub>3</sub> for three times, dried over sodium sulfate, and concentrated. The residue was slurried by EA and the crude product was recrystallized with hexane: DCM= 1:3 to give the substrate **2a** as yellow solid.

### 3. General procedures for Substrates 3



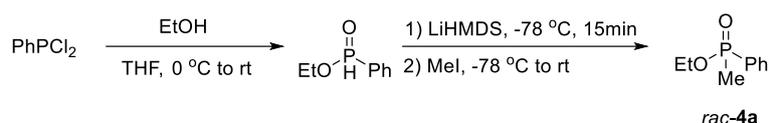
**3a**<sup>[2]</sup>: A Schlenk tube was dried under vacuum. After cooling, the tube was placed under N<sub>2</sub> atmosphere. Under a N<sub>2</sub> atmosphere, (1*S*,3*αS*)-1,3,3-triphenyltetrahydro-3H-pyrrolo[1,2-*c*][1,3,2]oxazaphosphole 1-oxide (**2a**, 1 equiv) was solved in dry THF. To the mixture at -10 °C was added Methyl magnesium bromide (1 equiv) and the mixture remained at -10 °C. After adding the Methyl magnesium bromide, the cooling bath was removed and the solution was stirred at rt overnight (12 h). The mixture was carefully quenched with sat. NH<sub>4</sub>Cl at 0°C. The organic layer was separated and the aqueous layer was washed with EA (once) and DCM (twice), dried over sodium sulfate, and concentrated. The residue was slurried by EA to give the substrate **3a** as pale yellow solid.



**3b**<sup>[3]</sup>: Step A: A 1L-Schlenk tube was dried under vacuum. After cooling, the tube was placed under N<sub>2</sub> atmosphere. Under a N<sub>2</sub> atmosphere, Mg turnings (1.1 equiv.), iodine (a few grains) and THF (20 mL) were added. In a separate flask under N<sub>2</sub> atmosphere, a solution of 2-methoxy bromobenzene (5.0 equiv.) in THF (20 mL) was prepared. A few drops of the aryl bromide solution in THF was added to the tube containing Mg, and the mixture was gently heated with a heat gun until the solution color changed from brown to colorless. The remaining aryl bromide solution was then slowly added. Upon complete addition, the mixture was stirred for 1-2 hr.

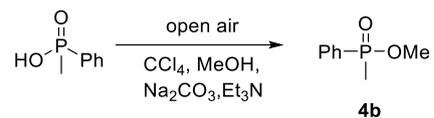
Step B: A 1L-Schlenk tube was dried under vacuum. After cooling, the tube was placed under N<sub>2</sub> atmosphere. Under a N<sub>2</sub> atmosphere, (1*S*,3*αS*)-1,3,3-triphenyltetrahydro-3*H*-pyrrolo[1,2-*c*][1,3,2]oxazaphosphole 1-oxide (**2a**, 1 equiv) was solved in dry THF. To the mixture at -10 °C was added 2-Methoxyphenyl Magnesium Bromide (1 equiv) and the mixture remained at 0 °C. After adding the 2-Methoxyphenyl Magnesium Bromide, the cooling bath was removed and the solution was stirred at r.t. overnight (12 h). The mixture was carefully quenched with sat. NH<sub>4</sub>Cl at 0°C. The organic layer was separated and the aqueous layer was washed with EA (once) and DCM (twice), dried over sodium sulfate, and concentrated. The residue was purified by silica gel column chromatography and the crude product was slurried by hexane: DCM= 1:3 to give the substrate **3b** and **3b'** as a white solid.

#### 4. General procedures for racemic Substrates 4

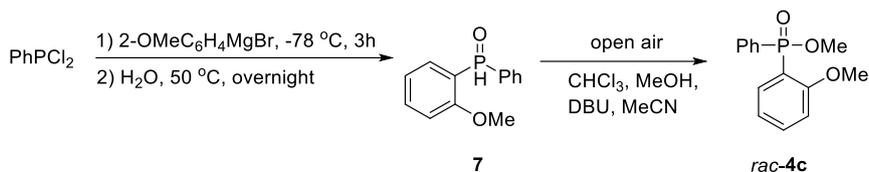


**Ethyl Phenylphosphinate** <sup>[4]</sup>: A Schlenk tube was dried under vacuum. After cooling, the tube was placed under N<sub>2</sub> atmosphere. Under a N<sub>2</sub> atmosphere, Phenyl Phosphorus Dichloride (**7a**, 1 equiv) was solved in dry THF. To the mixture at 0 °C was added dry ethanol (1 equiv) and the mixture remained at 0 °C. After adding the dry ethanol, the cooling bath was removed and the solution was stirred at rt overnight (12 h). The mixture was concentrated to give the substrate **7a** as colorless oil. It showed characterization data in full agreement with previously reported data<sup>[4]</sup>.

*rac-4a* <sup>[5]</sup>: A Schlenk tube was dried under vacuum. After cooling, the tube was placed under N<sub>2</sub> atmosphere. Under a N<sub>2</sub> atmosphere, ethyl phenylphosphinate (1 equiv) was solved in dry THF. To the mixture at -78 °C was added dropwise LiHMDS (Lithium bis(trimethylsilyl)amide, 1 equiv) and the mixture remained at -78 °C. After adding the Ethanol, the cooling bath was remained for 15 minutes and the MeI (Iodomethane, 1 equiv) was added dropwise, then the cooling bath was removed and the mixture stirred at rt overnight (12 h). The organic layer was separated and the aqueous layer was washed with EA (once) and DCM (twice), dried over sodium sulfate, concentrated, and purified by silica gel column chromatography to provide the to give the substrate *rac-4a* as light yellow oil.



*rac-4b*<sup>[6]</sup>: A mixture of methyl(phenyl)phosphinic acid (1 mmol), Na<sub>2</sub>CO<sub>3</sub> (2 mmol), CCl<sub>4</sub> (3 mmol), Et<sub>3</sub>N (1 mmol) and CuI (0.1 mmol) in MeOH (1 ml) was stirred at 80 °C under air atmosphere for 12 h. Removal of the solvent under a reduced pressure gave the crude product; pure product was obtained by passing the crude product through a short silica gel column using EtOAc as eluent to give the substrate *rac-4b* as light yellow oil and *rac-4c* as dark brown liquid.



**7:** A Schlenk tube was dried under vacuum. After cooling, the tube was placed under  $\text{N}_2$  atmosphere. Under a  $\text{N}_2$  atmosphere, Phenyl Phosphorus Dichloride (1 equiv) was solved in dry THF. To the mixture at  $-78\text{ }^\circ\text{C}$  was added 2-OMeC<sub>6</sub>H<sub>4</sub>MgBr (1 equiv) and the mixture remained at  $-78\text{ }^\circ\text{C}$ . After adding the 2-OMeC<sub>6</sub>H<sub>4</sub>MgBr, the cooling bath was removed and the solution was stirred at rt for 3h. After <sup>31</sup>P-NMR showed that the reaction was over, water (10 equiv) was added. The mixture was heated to  $50^\circ\text{C}$  overnight. After <sup>31</sup>P-NMR showed that the reaction was over, the mixture was washed with EA (once) and DCM (twice), dried over sodium sulfate, concentrated, and purified by silica gel column chromatography to provide the to give the substrate **7** as light yellow oil.

*rac-4d*<sup>[7]</sup>: A Schlenk tube was dried under vacuum. Under an air atmosphere, To a solution of (2-methoxyphenyl)(phenyl)phosphine oxide (**7b**, 40 mg, 0.2 mmol) and methanol (46mg, 1 mmol) in CH<sub>3</sub>CN (2 mL) were added CHCl<sub>3</sub> (24 mg, 0.2 mmol) and DBU (46mg, 0.3 mmol). The mixture was stirred at  $80\text{ }^\circ\text{C}$  under air atmosphere for 3 h. The reaction mixture was then concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel with petrol /ethyl acetate (2:1) to afford substrate *rac-4d* (48 mg, 98%) as a colorless oil.

## 5. General procedures for optimization of acidic alcoholysis of **3**<sup>[8]</sup>

A Schlenk tube was dried under vacuum. After cooling, the flask was placed under N<sub>2</sub> atmosphere. Under a N<sub>2</sub> atmosphere, ((*S*)-2-(hydroxydiphenylmethyl)pyrrolidin-1-yl)(methyl)(phenyl)phosphine oxide (**3**, 1 mmol, 1 equiv) was solved in ROH (2 mL). The resulting mixture was cooled to T °C. A solution of H<sub>2</sub>SO<sub>4</sub>(x mmol, x eq) in EtOH (2 mL) was added dropwise into the mixture (**Caution:** A lot of heat will be released when preparing the corresponding alcohol solution of concentrated sulfuric acid. It can be dropped after cooling to room temperature. The rate of dropping must be slow enough to avoid the mixture from heating). The mixture was stirred at T °C for t h. After t h, the mixture was quenched with sat. NaHCO<sub>3</sub> to adjust pH to 7. The mixture was washed with DCM (3 times), dried over sodium sulfate, concentrated, and purified by silica gel column chromatography to give the yield of **4a**. The enantiomeric purity of **4a** was determined by chiral HPLC.

## 6. General procedures for chiral Substrates 4

A Schlenk tube was dried under vacuum. After cooling, the flask was placed under N<sub>2</sub> atmosphere. Under a N<sub>2</sub> atmosphere, ((*S*)-2-(hydroxydiphenylmethyl)pyrrolidin-1-yl)(methyl)(phenyl)phosphine oxide (**3**, 1 mmol, 1 equiv) was charged EtOH (2 mL). The resulting mixture was cooled to -78 °C. A solution of H<sub>2</sub>SO<sub>4</sub> (1 mmol, 1 eq) in EtOH (2 mL) was added dropwise into the mixture (**Caution:** A lot of heat will be released when preparing the ethanol solution of concentrated sulfuric acid. It can be dropped after cooling to room temperature. The rate of dropping must be slow enough to avoid the mixture from heating). The mixture was stirred at -78 °C for 2h. After 2h, the mixture was quenched with sat. NaHCO<sub>3</sub> to adjust pH to 7. The mixture was washed with DCM (3 times), dried over sodium sulfate, concentrated, and purified by silica gel column chromatography to give yield of **4a**. The enantiomeric purity of **4a** was determined by chiral HPLC.

## 7. General procedures for racemic substrates 5

All Grignard reagents were prepared from aryl bromides via Mg insertion in the presence of iodine or purchased from commercial sources.

Step A: A Schlenk tube was dried under vacuum. After cooling, the tube was placed under N<sub>2</sub> atmosphere. Under a N<sub>2</sub> atmosphere, Mg turnings (5.5 mmol, 5.5 equiv.), iodine (a few grains) and THF (2 mL) were added. In a separate flask under Ar atmosphere, a solution of aryl bromide (5 mmol, 5.0 equiv.) in THF (2 mL) was prepared. A few drops of the aryl bromide solution in THF was added to the tube containing Mg, and the mixture was gently heated with a heat gun until the solution color changed from brown to colorless. The remaining aryl bromide solution was then slowly added. Upon complete addition, the mixture was stirred for 1-2 hr.

Step B: A Schlenk tube was dried under vacuum. After cooling, the tube was placed under N<sub>2</sub> atmosphere. Under a N<sub>2</sub> atmosphere, ethyl methyl (phenyl) phosphinate (*rac-4a* or *rac-4b*, 1 mmol, 1 equiv) was solved in THF (3 mL). Grignard reagents (5 mmol, 5 eq) was added dropwise into the mixture at room temperature. The mixture was stirred at 70 °C overnight. After TLC showed the reaction was over, the mixture was cooled to 0 °C and quenched with sat. NH<sub>4</sub>Cl. The mixture was washed with DCM (3 times), dried over sodium sulfate, concentrated, and purified by silica gel column chromatography to give yield of *rac-5*.

## 8. General procedures for chiral substrates **5**<sup>[9]</sup>

All Grignard reagents were prepared from aryl bromides via Mg insertion in the presence of iodine or purchased from commercial sources.

Step A: A Schlenk tube was dried under vacuum. After cooling, the tube was placed under N<sub>2</sub> atmosphere. Under a N<sub>2</sub> atmosphere, Mg turnings (5.5 mmol, 5.5 equiv.), iodine (a few grains) and THF (2 mL) were added. In a separate flask under N<sub>2</sub> atmosphere, a solution of aryl bromide (5 mmol, 5.0 equiv.) in THF (2 mL) was prepared. A few drops of the aryl bromide solution in THF was added to the tube containing Mg, and the mixture was gently heated with a heat gun until the solution color changed from brown to colorless. The remaining aryl bromide solution was then slowly added. Upon complete addition, the mixture was stirred for 1-2 hr.

Step B: A Schlenk tube was dried under vacuum. After cooling, the tube was placed under N<sub>2</sub> atmosphere. Under a N<sub>2</sub> atmosphere, ethyl methyl (phenyl) phosphinate (**4a** or **4b**, 1 mmol, 1 equiv) was solved in THF (3 mL). Grignard reagents (5 mmol, 5 equiv) was added dropwise into the mixture at room temperature. The mixture was stirred at room temperature overnight. After TLC showed the reaction was over, the mixture was cooled to 0 °C and quenched with sat. NH<sub>4</sub>Cl. The mixture was washed with DCM (3 times), dried over sodium sulfate, concentrated, and purified by silica gel column chromatography to give yield of **5**. The enantiomeric purity of **5** was determined by chiral HPLC.

## 9. Gram-scale synthesis of **5b**.

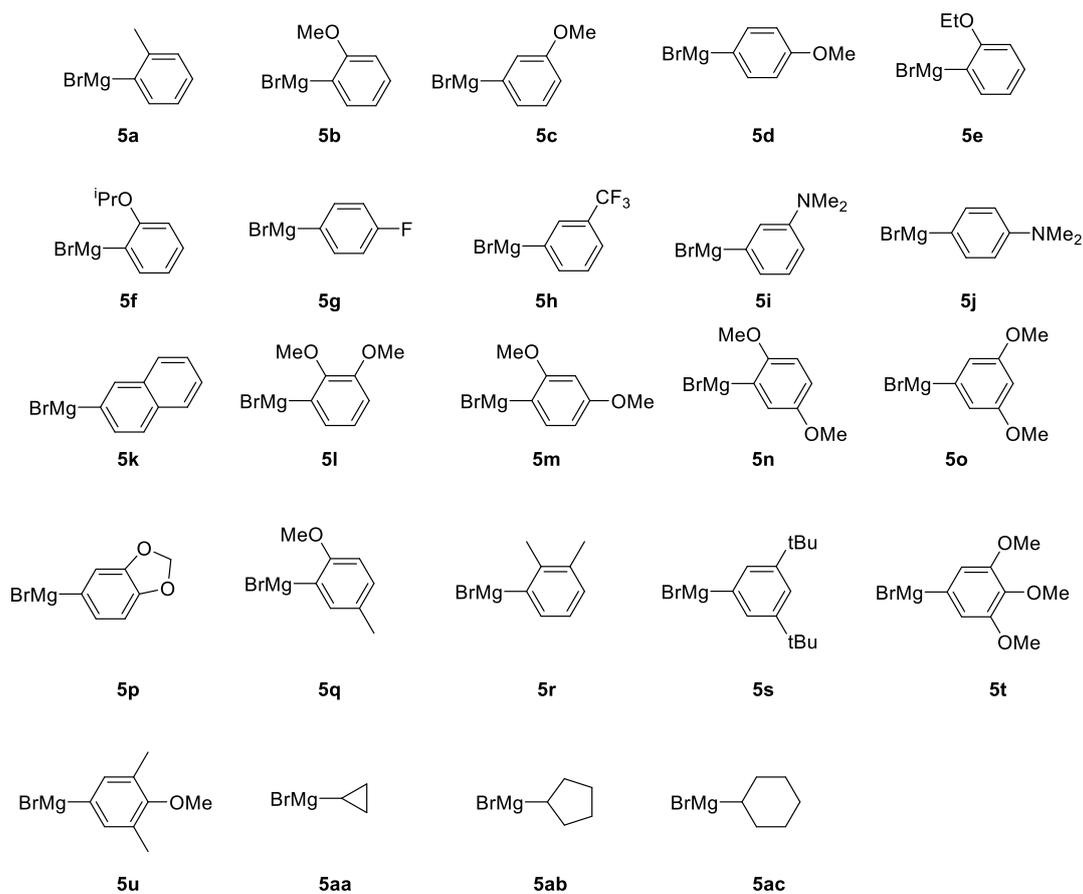
Step A: A 1L-Schlenk tube was dried under vacuum. After cooling, the tube was placed under N<sub>2</sub> atmosphere. Under a N<sub>2</sub> atmosphere, Mg turnings (597.63 mmol, 5.5 equiv.), iodine (a few grains) and THF (200 mL) were added. In a separate flask under N<sub>2</sub> atmosphere, a solution of 2-methoxy bromobenzene (543.30 mmol, 5.0 equiv.) in THF (2 mL) was prepared. A few drops of the aryl bromide solution in THF was added to the tube containing Mg, and the mixture was gently heated with a heat gun until the solution color changed from brown to colorless. The remaining aryl bromide solution was then slowly added. Upon complete addition, the mixture was stirred for 1-2 hr.

Step B: A 1L-Schlenk tube was dried under vacuum. After cooling, the tube was placed under N<sub>2</sub> atmosphere. Under a N<sub>2</sub> atmosphere, ethyl methyl (phenyl) phosphinate (**4a**, 108.66 mmol, 1 equiv) was solved in THF (3 mL). 2-Methoxyphenyl Magnesium Bromide (543.30 mmol, 5 equiv) in was added dropwise into the mixture at room temperature. The mixture was stirred at room temperature overnight. After TLC showed the reaction was over, the mixture was cooled to 0 °C and quenched with sat. NH<sub>4</sub>Cl. The mixture was washed with DCM (3 times), dried over sodium sulfate, concentrated, and purified by silica gel column chromatography to give yield of **5b**. The enantiomeric purity of **5b** was determined by chiral HPLC.

## 10. Synthesis of substrate **6z**<sup>[10]</sup>

A Schlenk tube was dried under vacuum. After cooling, the tube was placed under N<sub>2</sub> atmosphere. Under a N<sub>2</sub> atmosphere, to a stirred solution of (R)-cyclopropyl(methyl)(phenyl)phosphine oxide (**5z**, 1 mmol, 1 equiv) in dry THF was added triethylamine (5 mmol, 5 equiv). Trichlorosilane (5 mmol, 5 equiv) in was added dropwise into the mixture at room temperature. The mixture was stirred at 80 °C for 5h. After <sup>31</sup>P-NMR showed the reaction was over, sulfur was added. The mixture was stirred for overnight. After TLC showed the reaction was over, the mixture was cooled to 0 °C and quenched with NaOH. The mixture was heated at 60 °C for 30 minutes, and cooled to room room temperature, washed with DCM (3 times), dried over sodium sulfate, concentrated, and purified by silica gel column chromatography to give crude **6z**. The crude product was recrystallized with methanol to give the product **6z** as colorless crystal. It showed characterization data in full agreement with previously reported data<sup>[11]</sup>.

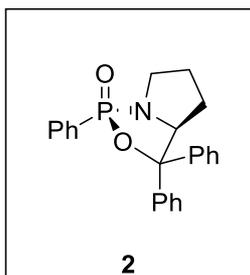
The following Grignard reagents which were used above were synthesized using the above procedures (step A)



The following Grignard reagents which were purchased by Sigma-Aldrich

MeMgBr	EtMgBr	nPrMgBr	iPrMgBr	nBuMgBr	sBuMgBr
3.0 M in THF	3.4 M in THF	1.0 M in THF	1.3 M in THF	2 M in THF	2 M in THF
<b>3'</b>	<b>5v</b>	<b>5w</b>	<b>5x</b>	<b>5y</b>	<b>5z</b>

## 11. Analytical data of Substrates 2-7



**Name:** (1*R*,3*aS*)-1,3,3-triphenyltetrahydro-3H-pyrrolo[1,2-*c*][1,3,2]oxazaphosphole 1-oxide

**Physical State:** pale yellow solid

**Yield:** 80% yield

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  1.50 – 1.60 (m, 1H), 1.60 – 1.69 (m, 1H), 1.69 – 1.78 (m, 2H), 1.78 – 1.88 (m, 1H), 3.00 (ddt,  $J = 12.5, 10.2, 7.1$  Hz, 1H), 3.73 (tdd,  $J = 10.4, 7.9, 4.6$  Hz, 1H), 4.70 (dt,  $J = 12.9, 6.5$  Hz, 1H), 7.25 (d,  $J = 7.8$  Hz, 1H), 7.27 – 7.37 (m, 7H), 7.38 – 7.48 (m, 3H), 7.50 – 7.60 (m, 4H).

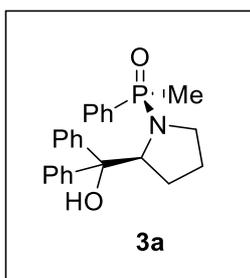
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  26.37 (d,  $J = 2.4$  Hz, 1C), 30.25 (d,  $J = 3.3$  Hz, 1C), 44.85, 71.37 (d,  $J = 7.4$  Hz, 1C), 88.75, 126.72 (d,  $J = 17.8$  Hz, 1C), 127.46, 128.02, 128.18, 128.34, 130.37, 131.72 (d,  $J = 10.7$  Hz, 1C), 132.18, 141.24 (d,  $J = 2.9$  Hz, 1C), 143.72 (d,  $J = 4.7$  Hz, 1C).

**<sup>31</sup>P NMR (162 MHz, Chloroform-*d*)**  $\delta$  35.21

**ESI-MS:**  $m/z$  376.35 [M+H]<sup>+</sup>, 398.30 [M+Na]<sup>+</sup>

**HRMS (ESI)** calculated for [M+Na, C<sub>23</sub>H<sub>22</sub>O<sub>2</sub>NaNP]<sup>+</sup>: 398.1280; found: 398.1274.

**$[\alpha]_D^{25}$ :** -52.0240 ( $c = 1.3720$ g/100 ml, CHCl<sub>3</sub>).



**Name:** (*R*)-((*S*)-2-(hydroxydiphenylmethyl)pyrrolidin-1-yl)(methyl)(phenyl)phosphine oxide

**Physical State:** pale yellow solid,

**Yield:** 65% yield,

**<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)**  $\delta$  1.00 (ddd,  $J = 12.9, 8.0, 5.5$  Hz, 1H), 1.43 (dddd,  $J = 14.9, 12.7, 8.4, 6.1$  Hz, 1H), 1.61 (d,  $J = 13.9$  Hz, 3H), 1.95 – 2.10 (m, 2H), 2.63 (dq,  $J = 9.6, 7.0$  Hz, 1H), 2.97 (dd,  $J = 8.9, 5.5$  Hz, 1H), 4.69 (td,  $J = 8.7, 4.0$  Hz, 1H), 6.40 (s, 1H), 7.21 – 7.33 (m, 6H), 7.41 (d,  $J = 7.7$  Hz, 2H), 7.45 – 7.56 (m, 5H), 7.70 (dd,  $J = 11.7, 7.4$  Hz, 2H).

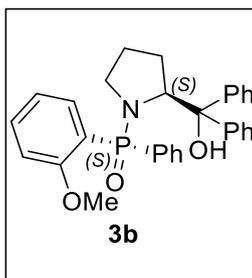
**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 14.68, 15.43, 24.83 (d, *J* = 5.2 Hz, 1C), 30.75 (d, *J* = 4.5 Hz, 1C), 48.71 (d, *J* = 3.5 Hz, 1C), 66.59, 106.57, 126.96 (d, *J* = 17.8 Hz, 1C), 127.29, 127.91 (d, *J* = 12.3 Hz, 1C), 128.54, 128.65, 128.75, 130.43 (d, *J* = 9.8 Hz, 1C), 131.80 (d, *J* = 3.2 Hz, 1C), 133.04 (d, *J* = 116.3 Hz, 1C), 145.53 (d, *J* = 213.7 Hz, 1C).

**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** δ 39.55.,

**ESI-MS:** *m/z* 414.45 [M+Na]<sup>+</sup>;

**HRMS (ESI)** calculated for [M+Na, C<sub>24</sub>H<sub>26</sub>O<sub>2</sub>NaNP]<sup>+</sup>: 414.1593; found: 414.1599.

[α]<sub>D</sub><sup>25</sup>: -200.9557 (c = 1.7320g/100ml, CHCl<sub>3</sub>).



**Name:** (S)-((S)-2-(hydroxydiphenylmethyl)pyrrolidin-1-yl)(2-methoxyphenyl)(phenyl)phosphine oxide (**3b**):

**Physical State:** white solid

**Yield:** 35% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 0.97 – 1.08 (m, 1H), 1.33 – 1.46 (m, 1H), 2.00 – 2.05 (m, 1H), 2.06 – 2.21 (m, 2H), 3.00 (qd, *J* = 9.5, 4.1 Hz, 1H), 3.73 (s, 3H), 4.68 (td, *J* = 8.6, 4.7 Hz, 1H), 6.99 (dd, *J* = 8.4, 5.5 Hz, 1H), 7.09 – 7.14 (m, 1H), 7.19 – 7.25 (m, 2H), 7.27 – 7.33 (m, 4H), 7.36 – 7.42 (m, 4H), 7.46 – 7.60 (m, 7H), 7.94 (ddd, *J* = 13.2, 7.5, 1.8 Hz, 1H).

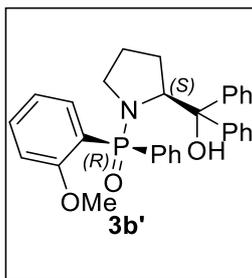
**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 24.75 (d, *J* = 4.9 Hz, 1C), 31.00 (d, *J* = 5.3 Hz, 1C), 50.06 (d, *J* = 5.6 Hz, 1C), 55.10, 67.62 (d, *J* = 3.4 Hz, 1C), 80.08, 110.64 (d, *J* = 7.8 Hz, 1C), 117.72, 118.65, 121.13 (d, *J* = 12.2 Hz, 1C), 126.72, 126.89, 127.02, 127.80, 128.02 – 128.49 (m), 129.08, 131.23 (d, *J* = 10.4 Hz), 131.64 – 131.98 (m), 132.75, 134.22, 137.01 (d, *J* = 6.7 Hz, 1C), 145.38 (d, *J* = 219.2 Hz).

**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** δ 32.60.,

**ESI-MS:** *m/z* 484.35 [M+H]<sup>+</sup>, 506.35 [M+Na]<sup>+</sup>;

**HRMS (ESI)** calculated for [M+H, C<sub>30</sub>H<sub>31</sub>O<sub>3</sub>NP]<sup>+</sup>: 484.2036; found: 484.2036 [M+Na, C<sub>30</sub>H<sub>30</sub>O<sub>3</sub>NaNP]<sup>+</sup>: 506.1856; found: 506.1860.

[α]<sub>D</sub><sup>25</sup>: -48.4027 (c = 0.4760g/100 ml, CHCl<sub>3</sub>).



**Name:** (R)-((S)-2-(hydroxydiphenylmethyl)pyrrolidin-1-yl)(2-methoxyphenyl)(phenyl)phosphine oxide (3b')

**Physical State:** pale yellow solid

**Yield:** 45% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 1.14 (ddd, *J* = 17.0, 8.2, 4.4 Hz, 1H), 1.23 – 1.43 (m, 2H), 1.98 (dtd, *J* = 13.1, 7.8, 5.0 Hz, 1H), 2.14 (ddt, *J* = 14.2, 9.0, 4.5 Hz, 1H), 2.45 (ddt, *J* = 10.3, 8.4, 7.0 Hz, 1H), 2.94 (dtd, *J* = 10.0, 8.4, 3.8 Hz, 1H), 3.71 (s, 3H), 4.96 (td, *J* = 8.2, 5.0 Hz, 1H), 6.64 (s, 1H), 6.86 – 6.92 (m, 1H), 6.96 (tdd, *J* = 7.5, 2.5, 0.9 Hz, 1H), 7.12 – 7.25 (m, 6H), 7.36 – 7.45 (m, 4H), 7.45 – 7.52 (m, 5H), 7.62 – 7.69 (m, 2H).

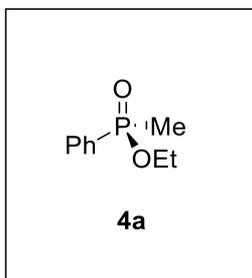
**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 25.19 (d, *J* = 5.5 Hz, 1C), 30.73 (d, *J* = 5.5 Hz, 1C), 49.81 (d, *J* = 4.6 Hz, 1C), 55.32, 67.10 (d, *J* = 3.2 Hz, 1C), 80.18, 110.93 (d, *J* = 7.7 Hz, 1C), 118.89, 119.92, 120.83 (d, *J* = 12.5 Hz, 1C), 126.53, 126.82, 127.10, 127.73, 127.87, 128.27 (d, *J* = 13.4 Hz, 1C), 128.49, 131.32 (d, *J* = 10.2 Hz, 1C), 131.42, 132.16, 133.15, 134.10, 134.91 (d, *J* = 7.0 Hz, 1C), 145.50 (d, *J* = 184.2 Hz, 1C).

**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** δ 31.18.,

**ESI-MS:** *m/z* 506.25 [M+Na]<sup>+</sup>;

**HRMS (ESI)** calculated for [M+H, C<sub>30</sub>H<sub>31</sub>O<sub>3</sub>NP]<sup>+</sup>: 484.2036; found: 484.2036 [M+Na, C<sub>30</sub>H<sub>30</sub>O<sub>3</sub>NaNP]<sup>+</sup>: 506.1856; found: 506.1853

[α]<sub>D</sub><sup>25</sup>: -72.7482 (c = 05480g/100 ml, CHCl<sub>3</sub>).



**Name:** ethyl (S)-methyl(phenyl)phosphinate

**Physical State:** yellow oil

**Yield:** 95% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 1.12 (t, *J* = 7.1 Hz, 3H), 1.50 (d, *J* = 14.6 Hz, 3H), 3.66 (dp, *J* = 10.1, 7.2 Hz, 1H), 3.87 – 3.93 (m, 1H), 7.32 (ddd, *J* = 8.5, 6.8, 3.3 Hz, 2H), 7.39 (td, *J* = 7.3, 1.5 Hz, 1H), 7.64 (ddd, *J* = 12.0, 8.2, 1.5 Hz, 2H).

**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 15.35, 16.29 (d, *J* = 6.6 Hz, 1C), 60.32 (d, *J* = 6.7 Hz, 1C), 128.51 (d, *J* = 13.1 Hz, 2C), 131.07 (d, *J* = 10.1 Hz, 2C), 132.12, 170.86

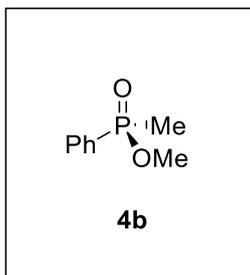
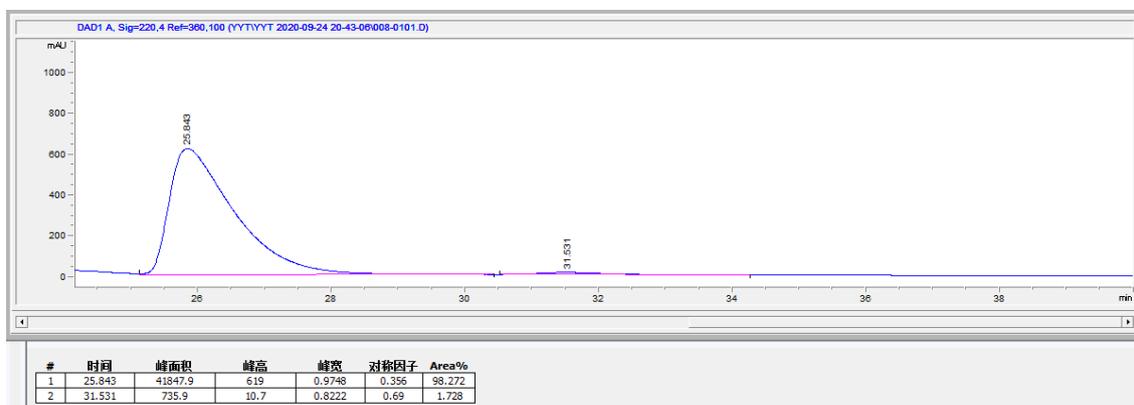
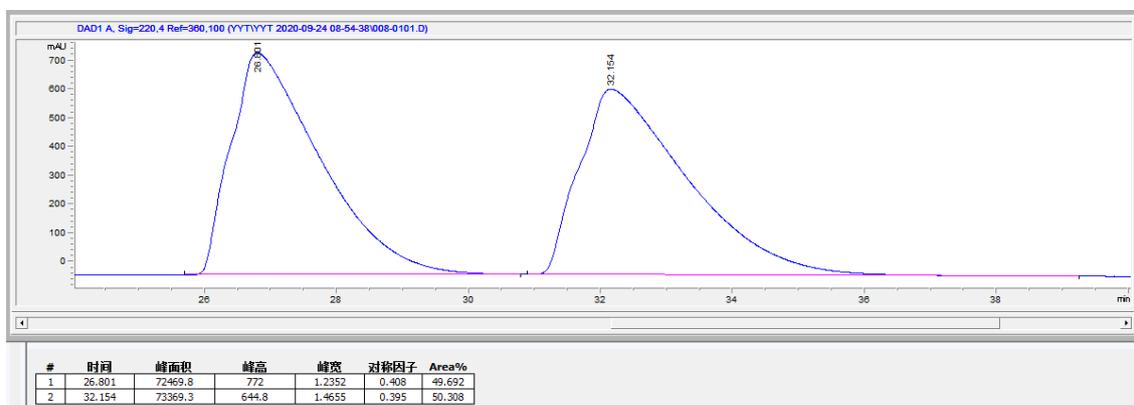
**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** δ 42.67..

**ESI-MS:** *m/z* 369.15 [2M+H]<sup>+</sup>, 391.30 [2M+Na]<sup>+</sup>

**HRMS (ESI)** calculated for [M+H, C<sub>19</sub>H<sub>13</sub>O<sub>2</sub>NaP]<sup>+</sup>: 207.0545; found: 207.0548.

[α]<sub>D</sub><sup>25</sup>: -4.3518 (*c* = 1.0560g/100ml, CHCl<sub>3</sub>).

**Chiral HPLC conditions:** OD-H, *i*-PrOH-hexane 2.5/97.5, flow rate 0.8 mL/min, 220 nm. *t*<sub>1</sub> = 26 min, *t*<sub>2</sub> = 32 min. 97% ee.



**Name:** methyl (*S*)-methyl(phenyl)phosphinate

**Physical State:** yellow oil

**Yield:** 90% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 1.66 (d, *J* = 14.6 Hz, 3H), 3.59 (d, *J* = 11.3 Hz, 3H), 7.46 – 7.51 (m, 2H), 7.53 – 7.58 (m, 1H), 7.77 (ddt, *J* = 12.0, 6.9, 1.4 Hz, 2H).

**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 15.54 (d, *J* = 102.5 Hz, 1C), 50.97 – 51.15 (m, 1C), 128.72 (d, *J* = 12.5 Hz, 2C), 131.33 (d, *J* = 10.2 Hz, 2C), 132.37, 170.86.

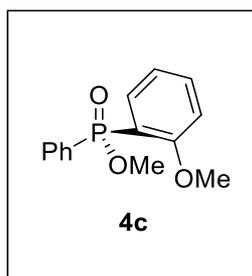
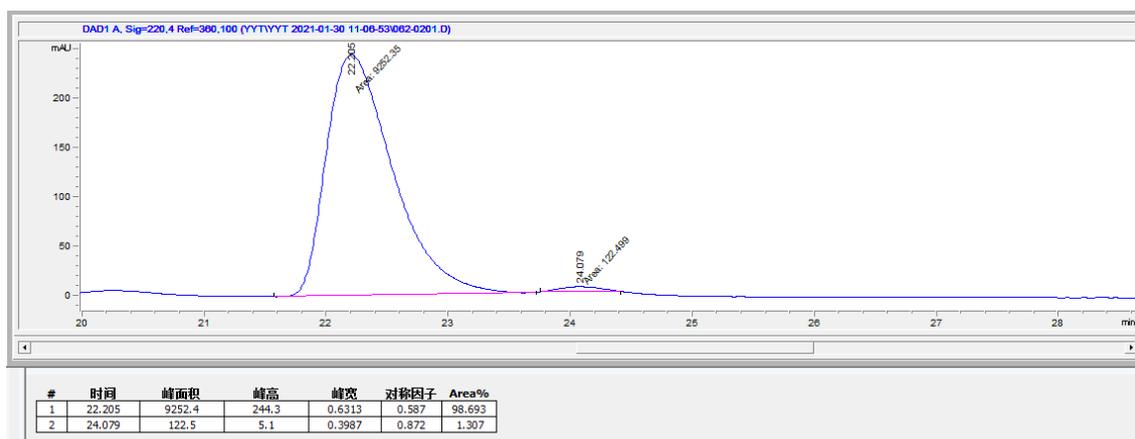
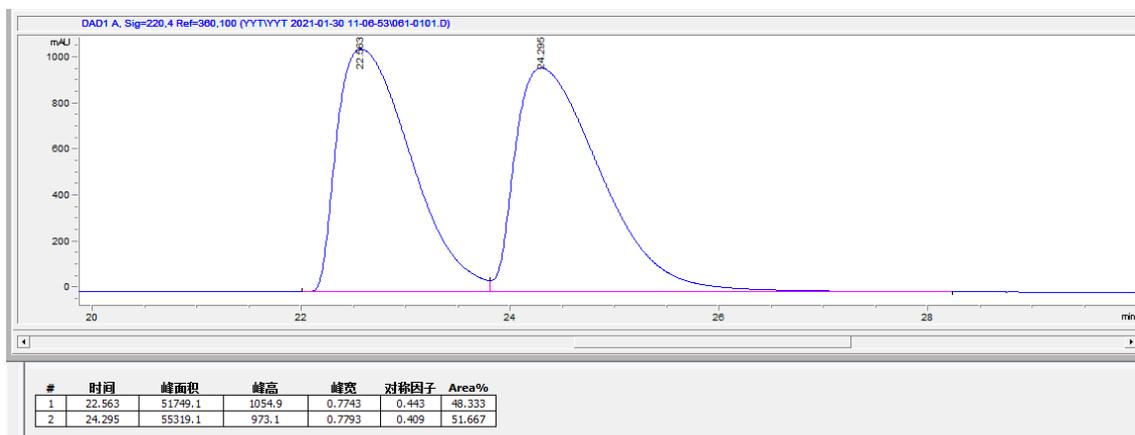
**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** δ 43.10

**ESI-MS:** *m/z* 170.85 [M+H]<sup>+</sup>, 192.90 [M+Na]<sup>+</sup>

**HRMS (ESI)** calculated for [M+H, C<sub>8</sub>H<sub>12</sub>O<sub>2</sub>P]<sup>+</sup>: 171.0569; found: 171.0573. calculated for [M+Na, C<sub>8</sub>H<sub>11</sub>O<sub>2</sub>PNa]<sup>+</sup>: 193.0389; found: 193.0394.

[α]<sub>D</sub><sup>25</sup>: -4.9510 (c = 0.8240g/100 ml, CHCl<sub>3</sub>).

Chiral HPLC conditions: OD-H, *i*-PrOH-hexane 5/95, flow rate 0.8 mL/min, 220 nm. *t*<sub>1</sub> = 22.363 min (*S*), *t*<sub>2</sub> = 24.295 min (*R*). 98% ee.



SI-20

**Name: methyl (S)-(2-methoxyphenyl)(phenyl)phosphinate**

**Physical State:** yellow oil

**Yield:** 80% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 3.70 (s, 3H), 3.74 (d, *J* = 11.4 Hz, 3H), 6.86 (dd, *J* = 8.3, 6.0 Hz, 1H), 7.06 (tdd, *J* = 7.5, 2.6, 0.9 Hz, 1H), 7.38 – 7.46 (m, 2H), 7.47 – 7.56 (m, 2H), 7.80 – 7.89 (m, 2H), 7.97 (ddd, *J* = 13.3, 7.6, 1.8 Hz, 1H).

**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 51.43 (d, *J* = 5.7 Hz, 1C), 55.53, 111.24 (d, *J* = 7.9 Hz, 2C), 118.85 (d, *J* = 135.6 Hz, 2C), 120.65 (d, *J* = 12.4 Hz, 2C), 128.05 (d, *J* = 13.6 Hz, 1C), 131.40, 131.81 (d, *J* = 10.2 Hz, 1C), 132.52, 133.93 – 136.36 (m).

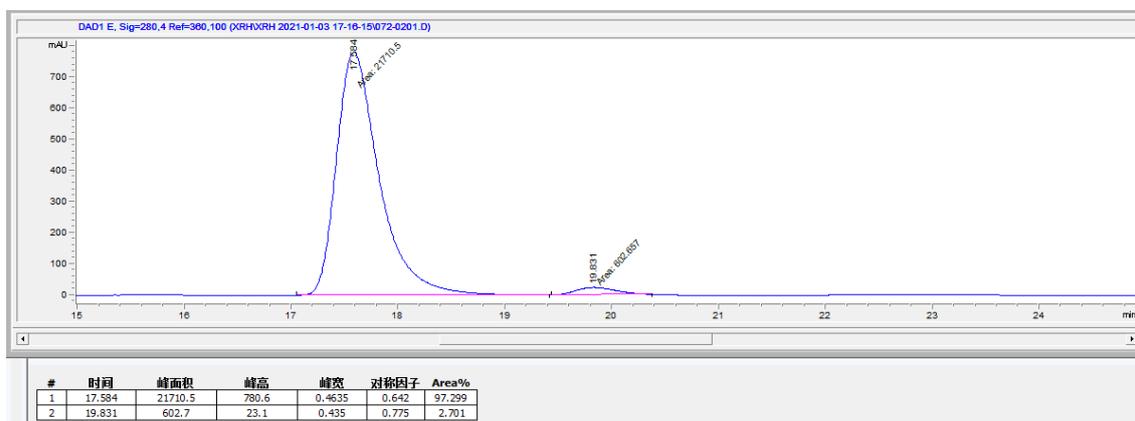
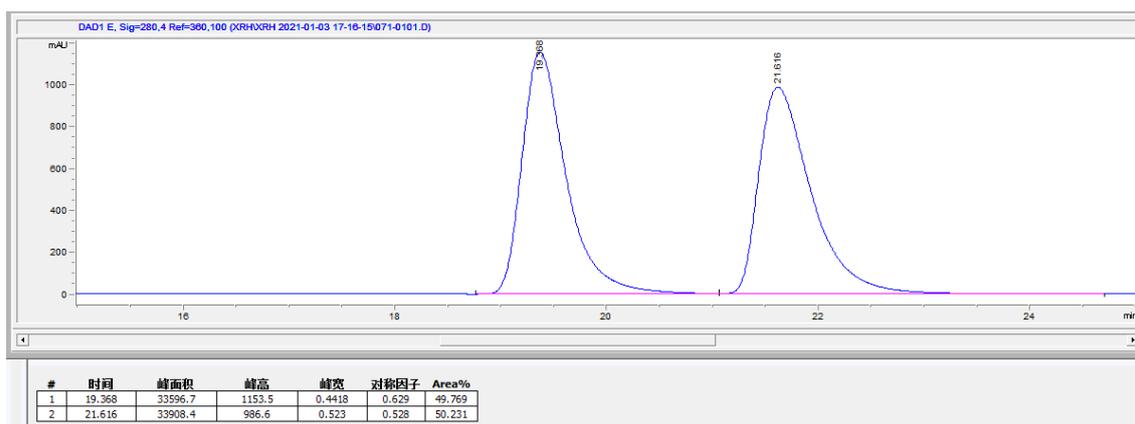
**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** δ 30.73..,

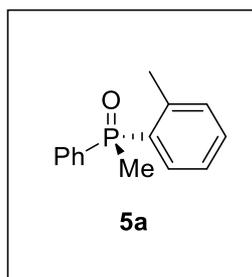
**ESI-MS:** *m/z* 263.15 [M+H]<sup>+</sup>, 285.15 [M+Na]<sup>+</sup>;

**HRMS (ESI)** calculated for [M+H, C<sub>14</sub>H<sub>16</sub>O<sub>3</sub>P]<sup>+</sup>: 263.0832; found: 263.0835. calculated for [M+Na, C<sub>14</sub>H<sub>15</sub>O<sub>3</sub>PNa]<sup>+</sup>: 285.0561; found: 285.0654.

[α]<sub>D</sub><sup>25</sup>: -25.0713 (c = 0.13g/100ml, CHCl<sub>3</sub>).

**Chiral HPLC conditions:** AD-3, *i*-PrOH-hexane 12.5/87.5, flow rate 0.8 mL/min, 280 nm. *t*<sub>1</sub> = 19.363 min (*S*), *t*<sub>2</sub> = 19 min (*R*). 21.626% ee.





**Name:** (S)-methyl(phenyl)(o-tolyl)phosphine oxide

**Physical State:** yellow oil

**Yield:** 60% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 2.06 (d, *J* = 12.9 Hz, 3H), 2.38 (s, 3H), 7.21 – 7.25 (m, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.42 – 7.48 (m, 3H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.66 (td, *J* = 12.4, 11.8, 7.4 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 17.14 (d, *J* = 73.7 Hz, 1C), 21.37 (d, *J* = 4.6 Hz, 1C), 125.64 (d, *J* = 12.3 Hz, 1C), 128.71 (d, *J* = 11.8 Hz, 1C), 130.44 (d, *J* = 9.9 Hz, 1C), 131.53 (d, *J* = 11.3 Hz, 1C), 131.68, 132.00, 132.25, 134.32 (d, *J* = 99.8 Hz, 1C), 142.17 (d, *J* = 8.1 Hz, 1C).

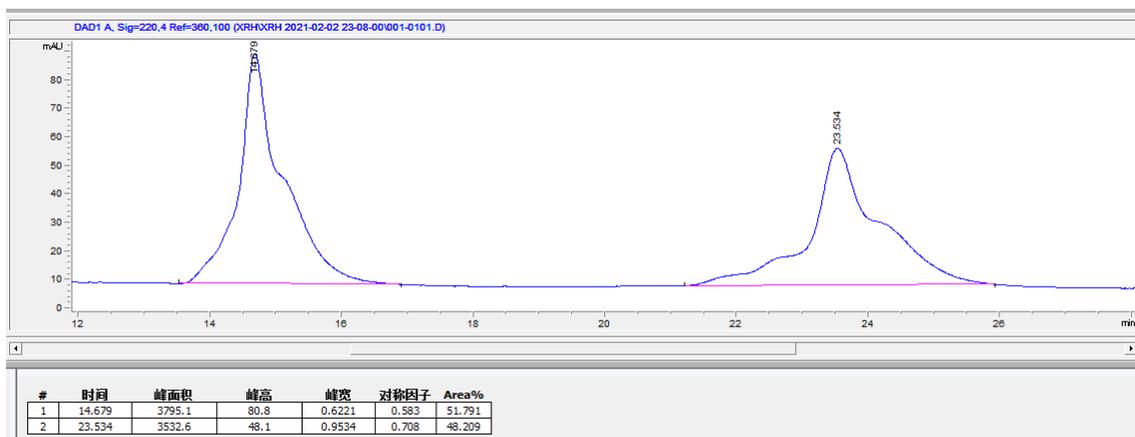
**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** δ 33.33.

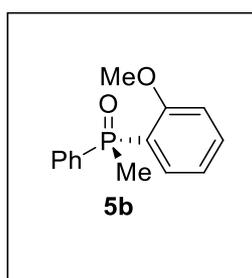
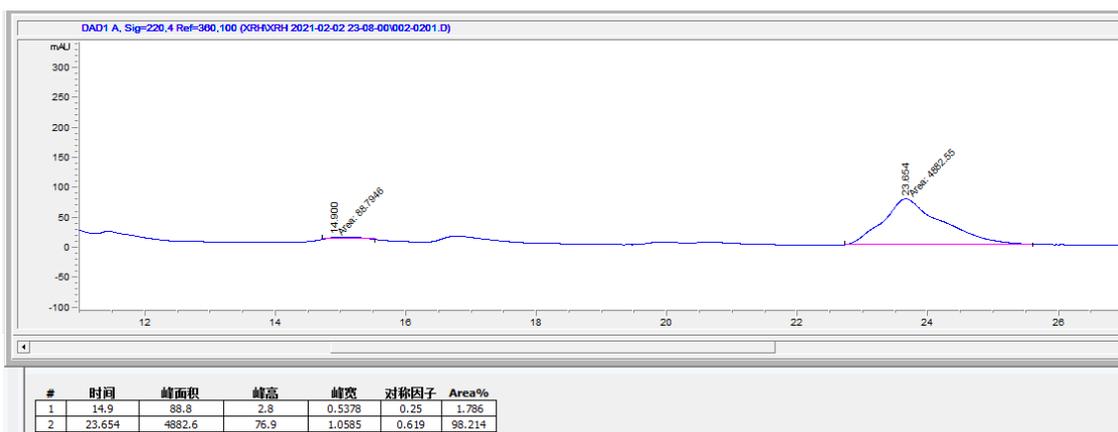
**ESI-MS:** *m/z* 253.15 [M+Na]<sup>+</sup>

**HRMS (ESI)** calculated for [M+Na, C<sub>14</sub>H<sub>15</sub>OPNa]<sup>+</sup>: 253.0753; found:253.0746.

[α]<sub>D</sub><sup>25</sup>: 9.1285 (c = 1.0667g/100ml, CHCl<sub>3</sub>).

Chiral HPLC conditions: AD-3, *i*-PrOH-hexane 10/90, flow rate 1.00 mL/min, 220 nm. *t*<sub>1</sub> = 14.679 min, *t*<sub>2</sub> = 23.534 min. 97% ee





**Name:** (S)-(2-methoxyphenyl)(methyl)(phenyl)phosphine oxide

**Physical State:** colorless solid

**Yield:** 70% yield

**<sup>1</sup>H NMR (400 MHz, Chloroform-d)** δ 7.95 (ddd, *J* = 13.0, 7.5, 1.4 Hz, 1H), 7.79 – 7.66 (m, 2H), 7.52 – 7.37 (m, 4H), 7.17 – 7.05 (m, 1H), 6.88 (dd, *J* = 8.2, 5.4 Hz, 1H), 3.71 (s, 3H), 2.07 (d, *J* = 14.0 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-d)** δ 160.01, 134.00, 131.36, 131.74 – 129.07 (m, 3C), 128.30 (d, *J* = 12.2 Hz, 2C), 121.15 (d, *J* = 11.3 Hz, 2C), 110.99 (d, *J* = 6.5 Hz, 2C), 55.39, 16.26 (d, *J* = 75.3 Hz, 1C).

**<sup>31</sup>P NMR (162 MHz, Chloroform-d)** δ 25.09 ,

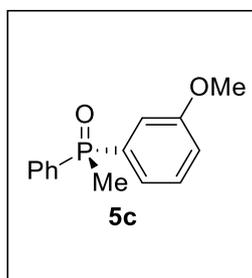
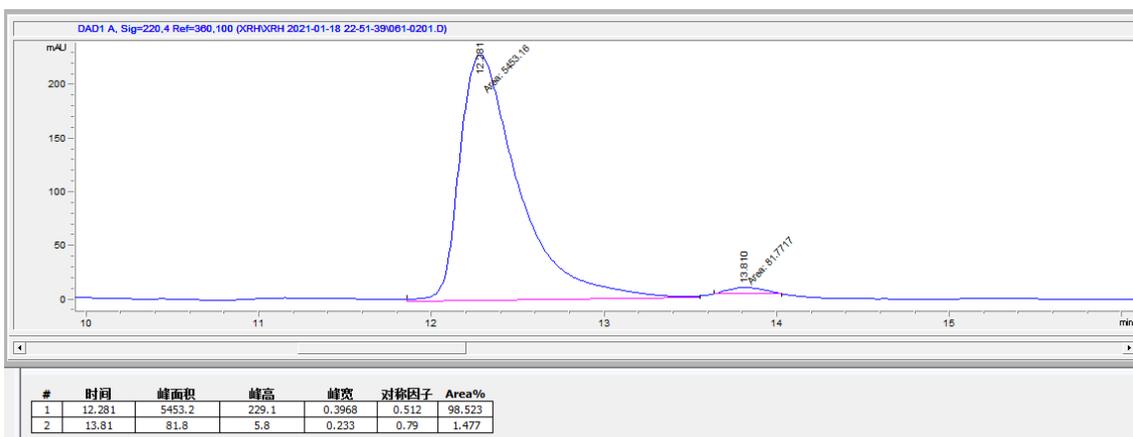
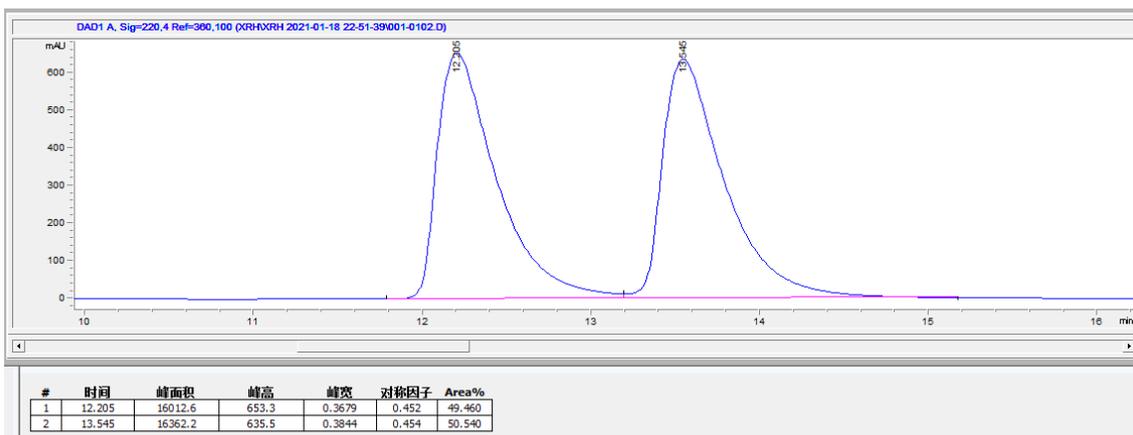
**ESI-MS:** *m/z* 247.00 [M+H]<sup>+</sup>, 269.10 [M+Na]<sup>+</sup>

**HRMS (ESI)**calculated for [M+Na, C<sub>14</sub>H<sub>15</sub>O<sub>2</sub>PNa]<sup>+</sup>: 269.0702; found: 269.0704.

[α]<sub>D</sub><sup>25</sup>: 15.1150 (*c* = 2.5400g/100ml, CHCl<sub>3</sub>).

Chiral HPLC conditions: IA-3, *i*-PrOH-hexane 15/85, flow rate 1.00 mL/min, 220 nm.

*t*<sub>1</sub> = 12.205 min, *t*<sub>2</sub> = 13.545 min. 97% ee.



**Name:** (S)-3-methoxyphenyl(methyl)(phenyl)phosphine oxide

**Physical States:** yellow oil

**Yield:** 70% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 7.74 (ddd, *J* = 8.4, 3.4, 1.7 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.47 (dd, *J* = 4.2, 2.9 Hz, 1H), 7.38 (dd, *J* = 13.7, 9.9 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.25 – 7.19 (m, 1H), 7.06 (d, *J* = 2.3 Hz, 1H), 3.84 (s, 3H), 2.06 – 1.98 (m, 3H).

**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 159.67 (d, *J* = 14.7 Hz, 1C), 131.85, 130.50 (d, *J* = 10.0 Hz, 1C), 129.87, 128.69 (d, *J* = 11.7 Hz, 1C), 122.56 (d, *J* = 10.1 Hz, 1C), 117.90 (d, *J* = 1.4 Hz, 1C), 115.53 (d, *J* = 10.8 Hz, 1C), 55.49, 16.59 (d, *J* = 73.8 Hz, 1C).

**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** δ 31.26 (d, *J* = 21.6 Hz).

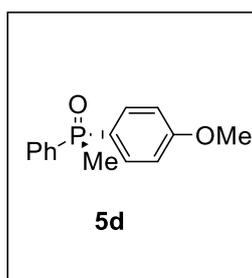
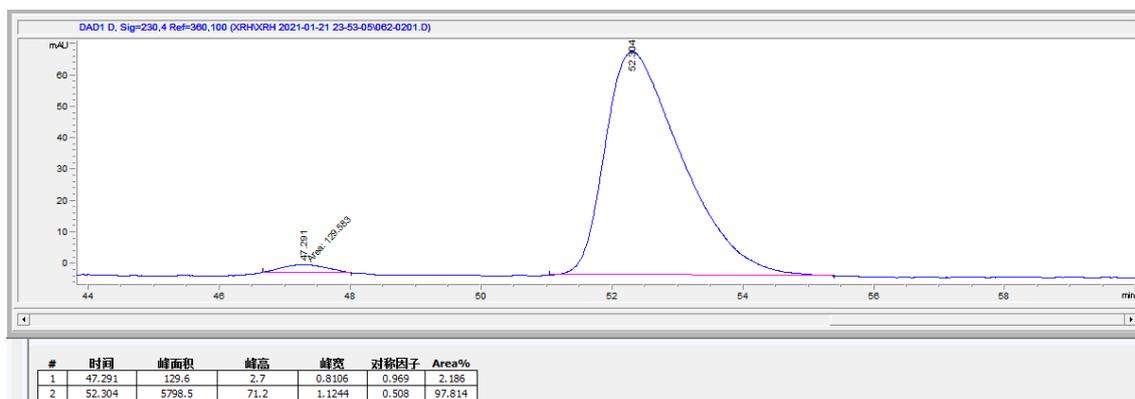
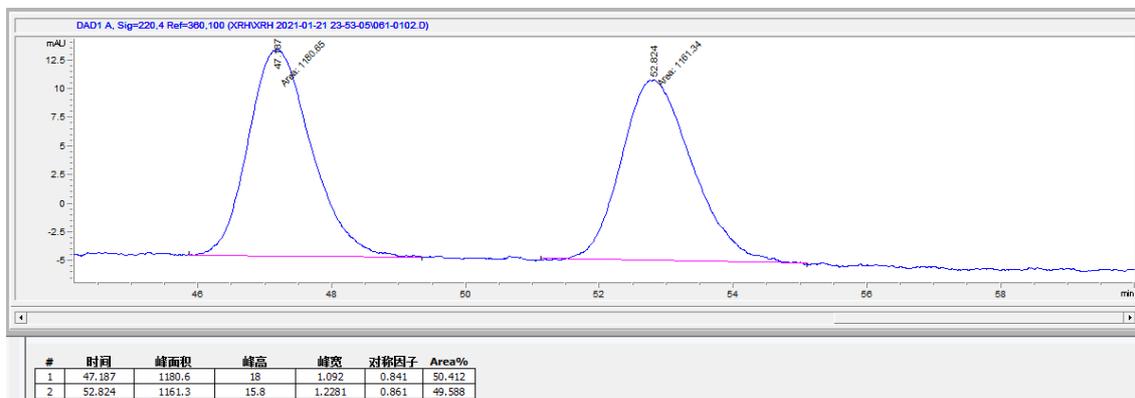
**ESI-MS:** *m/z* 247.35 [M+H]<sup>+</sup>

**HRMS (ESI)** calculated for  $[M+H, C_{14}H_{16}O_2P]^+$ : 247.0882; found: 247.0884, calculated for  $[M+Na, C_{14}H_{15}O_2PNa]^+$ : 269.0702; found: 269.0706.

$[\alpha]_D^{25}$ : -13.7510 ( $c = 0.2933\text{g}/100\text{ml}$ ,  $\text{CHCl}_3$ ).

Chiral HPLC conditions: ID-3, *i*-PrOH-hexane 10/90, flow rate 1.00 mL/min, 220 nm.

$t_1 = 47.187\text{ min}$ ,  $t_2 = 52.824\text{ min}$  97% ee



**Name:** (S)-(4-methoxyphenyl)(methyl)(phenyl)phosphine oxide

**Physical States:** yellow oil

**Yield:** 70% yield

**$^1\text{H}$  NMR (500 MHz, Chloroform-d)**  $\delta$  7.74 – 7.61 (m, 4H), 7.54 – 7.41 (m, 3H), 7.00 – 6.94 (m, 2H), 3.83 (d,  $J = 0.9\text{ Hz}$ , 3H), 1.98 (dd,  $J = 13.1, 0.9\text{ Hz}$ , 2H).

**$^{13}\text{C}$  NMR (126 MHz, Chloroform-d)**  $\delta$  162.37 (d,  $J = 3.1\text{ Hz}$ , 2C), 132.42 (d,  $J = 11.3\text{ Hz}$ , 2C), 131.67 (d,  $J = 3.1\text{ Hz}$ , 2C), 130.48 (d,  $J = 10.1\text{ Hz}$ , 2C), 128.62 (d,  $J = 11.3\text{ Hz}$ , 2C), 114.23 (d,  $J = 12.5\text{ Hz}$ , 2C), 55.37, 16.78 (d,  $J = 73.6\text{ Hz}$ , 1C).

**$^{31}\text{P}$  NMR (202 MHz, Chloroform-d)**  $\delta$  30.95 (d,  $J = 7.8\text{ Hz}$ ).

SI-25

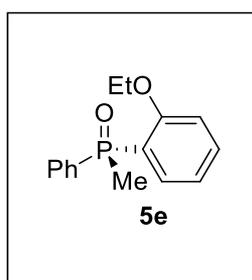
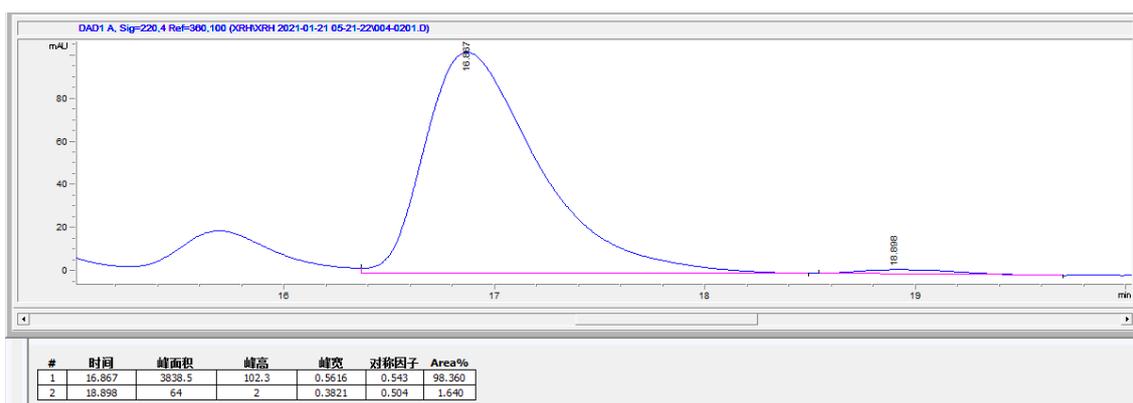
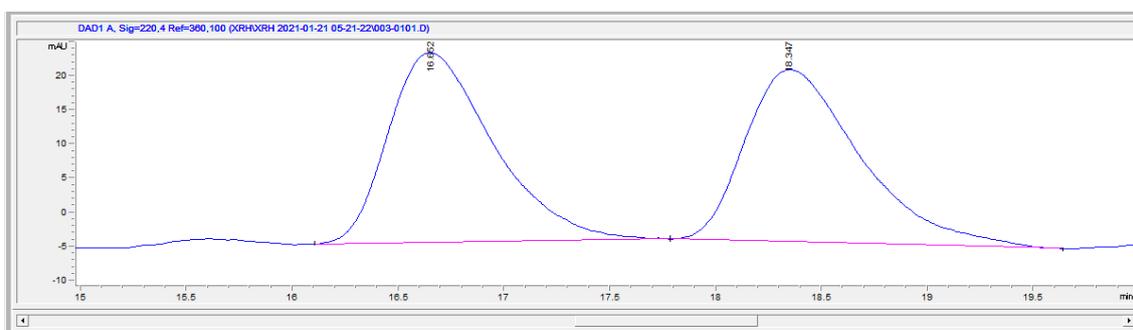
**ESI-MS:** m/z 247.35 [M+H]<sup>+</sup>;

**HRMS (ESI)** calculated for [M+H, C<sub>14</sub>H<sub>16</sub>O<sub>2</sub>P]<sup>+</sup>:247.0882; found:247.0881,calculated for [M+Na, C<sub>14</sub>H<sub>15</sub>O<sub>2</sub>PNa]<sup>+</sup>: 269.0702; found: 269.0702

[α]<sub>D</sub><sup>25</sup>: -1.1764 (c = 0.3400g/100ml, CHCl<sub>3</sub>).

Chiral HPLC conditions: OD-3, *i*-PrOH-hexane 10/90, flow rate 1.00mL/min, 220 nm.

*t*<sub>1</sub> = 16.652 min, *t*<sub>2</sub>=18.347 min. 97% ee



**Name:** (*S*)-(2-ethoxyphenyl)(methyl)(phenyl)phosphine oxide (**5g**)

**Physical States:** colorless solid

**Yield:** 70% yield

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.02 (ddd, *J* = 13.0, 7.5, 1.5 Hz, 1H), 7.71 (dt, *J* = 36.9, 18.4 Hz, 2H), 7.54 – 7.35 (m, 4H), 7.08 (dd, *J* = 18.0, 10.6 Hz, 1H), 6.83 (dd, *J* = 8.2, 5.4 Hz, 1H), 4.08 – 3.97 (m, 1H), 3.91 – 3.83 (m, 1H), 2.09 (d, *J* = 14.0 Hz, 3H), 1.19 (t, *J* = 7.0 Hz, 3H).

$^{13}\text{C}$  NMR (126 MHz, Chloroform- $d$ )  $\delta$  159.11 (d,  $J = 4.5$  Hz, 1C), 134.28 – 133.81 (m, 1C), 131.25, 130.24 (d,  $J = 10.1$  Hz, 1C), 128.16 (d,  $J = 12.4$  Hz, 1C), 120.80 (d,  $J = 11.1$  Hz, 1C), 111.27 (d,  $J = 6.7$  Hz, 1C), 63.76, 16.21, 15.61, 14.35.

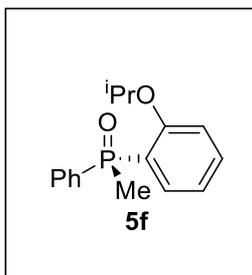
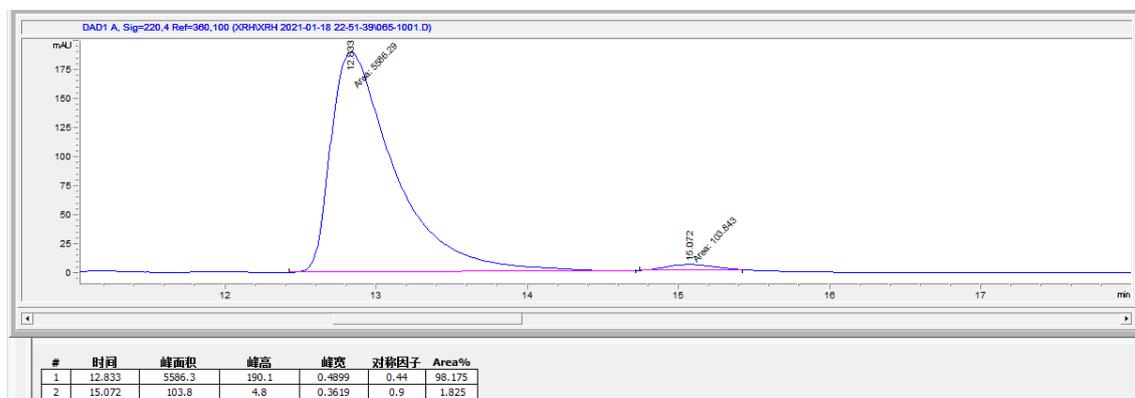
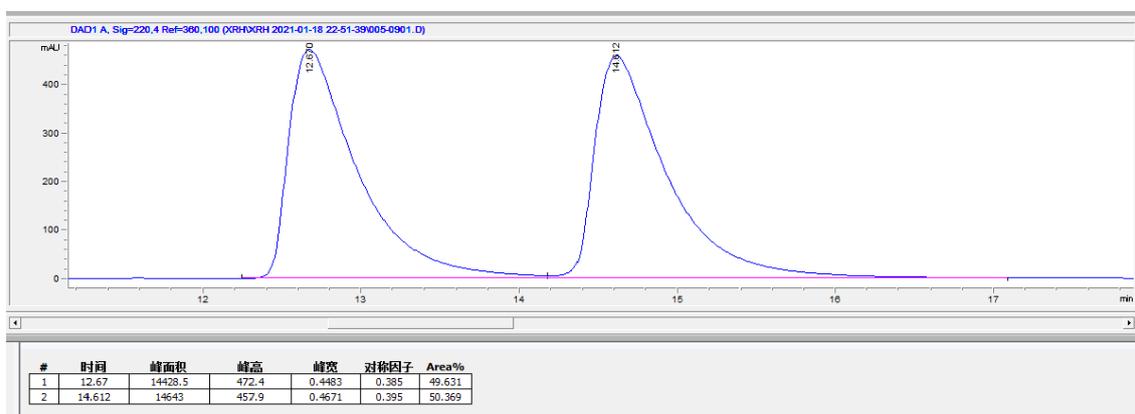
$^{31}\text{P}$  NMR (202 MHz, Chloroform- $d$ )  $\delta$  29.48

ESI-MS:  $m/z$  283.35  $[\text{M}+\text{Na}]^+$

HRMS (ESI) calculated for  $[\text{M}+\text{H}, \text{C}_{15}\text{H}_{18}\text{O}_2\text{P}]^+$ : 261.1039; found:261.1033. calculated for  $[\text{M}+\text{Na}, \text{C}_{15}\text{H}_{17}\text{O}_2\text{PNa}]^+$ : 283.0858; found:283.0855

$[\alpha]_{\text{D}}^{25}$ : 8.6349 ( $c = 0.2800\text{g}/100\text{ml}$ ,  $\text{CHCl}_3$ ).

Chiral HPLC conditions: IA-3, *i*-PrOH-hexane 15/85, flow rate 1.00 mL/min, 220 nm.  $t_1 = 12.670$  min,  $t_2 = 14.612$  min. 97% ee.



Name: (S)-(2-isopropoxyphenyl)(methyl)(phenyl)phosphine oxide

Physical States: yellow oil

**Yield:** 70% yield

**$^1\text{H}$  NMR (500 MHz, Chloroform- $d$ )**  $\delta$  0.91 (d,  $J$  = 6.1 Hz, 3H), 1.24 (d,  $J$  = 6.0 Hz, 3H), 2.10 (d,  $J$  = 14.1 Hz, 3H), 4.54 (p,  $J$  = 6.0 Hz, 1H), 6.81 (dd,  $J$  = 8.4, 5.4 Hz, 1H), 7.04 – 7.11 (m, 1H), 7.39 (td,  $J$  = 7.5, 2.9 Hz, 2H), 7.43 – 7.51 (m, 2H), 7.67 – 7.74 (m, 2H), 8.07 (ddd,  $J$  = 13.1, 7.5, 1.9 Hz, 1H).

**$^{13}\text{C}$  NMR (126 MHz, Chloroform- $d$ )**  $\delta$  15.53 (d,  $J$  = 75.5 Hz, 1C), 21.42 (d,  $J$  = 93.8 Hz, 1C), 69.64, 111.75 (d,  $J$  = 6.7 Hz, 1C), 120.35 (d,  $J$  = 11.1 Hz, 1C), 128.12 (d,  $J$  = 12.4 Hz, 1C), 130.25 (d,  $J$  = 10.2 Hz, 1C), 131.23 (d,  $J$  = 3.1 Hz, 1C), 133.77, 134.36 (d,  $J$  = 5.6 Hz, 1C), 157.83 (d,  $J$  = 4.5 Hz, 1C).

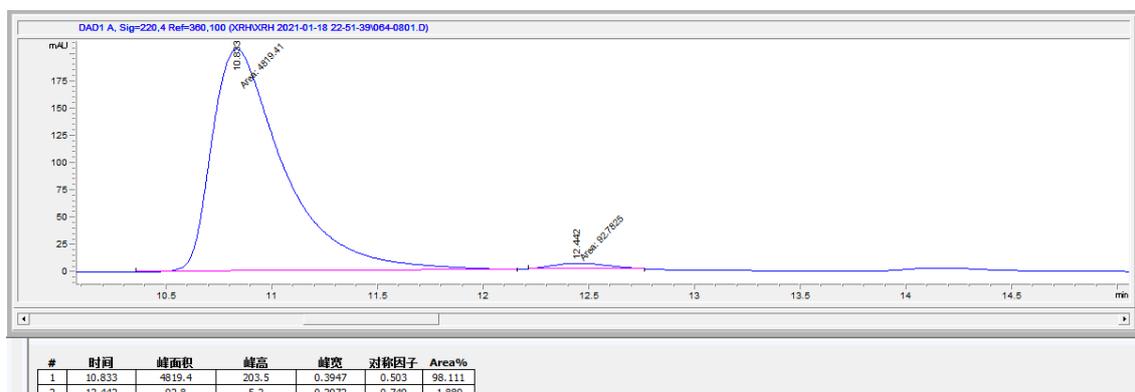
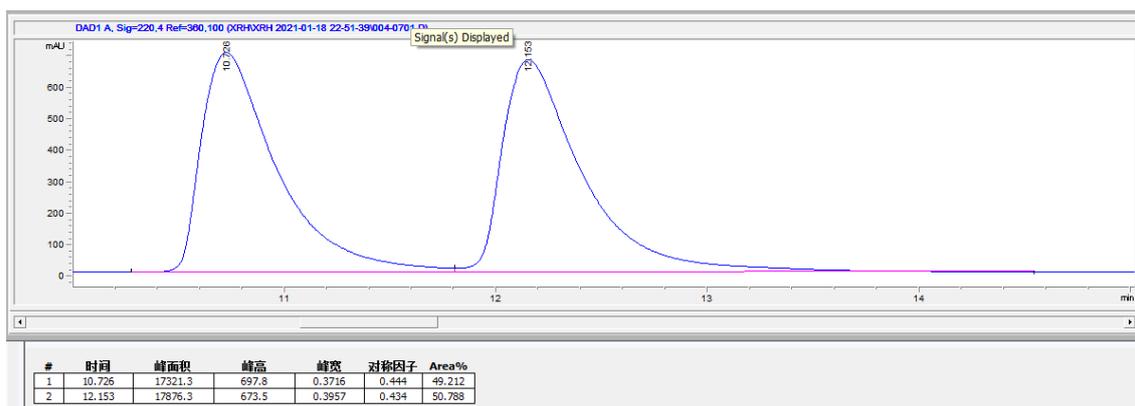
**$^{31}\text{P}$  NMR (202 MHz, Chloroform- $d$ )**  $\delta$  29.81 (d,  $J$  = 7.5 Hz)

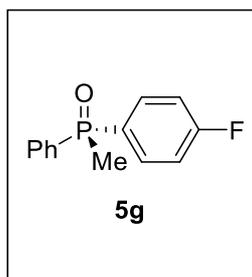
**ESI-MS:**  $m/z$  275.35  $[\text{M}+\text{H}]^+$ , 297.35  $[\text{M}+\text{Na}]^+$

**HRMS (ESI)** calculated for  $[\text{M}+\text{H}, \text{C}_{16}\text{H}_{20}\text{O}_2\text{P}]^+$ : 275.1195 found 275.1196; calculated for  $[\text{M}+\text{Na}, \text{C}_{16}\text{H}_{19}\text{O}_2\text{PNa}]^+$ : 297.1015 found: 297.1016.

$[\alpha]_{\text{D}}^{25}$ : 3.7337 ( $c$  = 0.3133g/100ml,  $\text{CHCl}_3$ ).

Chiral HPLC conditions: IA-3, *i*-PrOH-hexane 10/90, flow rate 1.00 mL/min, 220 nm.  $t_1$  = 10.726 min,  $t_2$  = 12.153 min. 97% ee.





**Name:** (S)-(4-fluorophenyl)(methyl)(phenyl)phosphine oxide

**Physical States:** white solid

**Yield:**70% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 2.02 (dd, *J* = 13.0, 4.1 Hz, 3H), 7.15 (td, *J* = 8.7, 2.0 Hz, 1H), 7.43 – 7.56 (m, 4H), 7.66 – 7.76 (m, 4H).

**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 16.72 (d, *J* = 74.4 Hz, 1C), 116.07 (dd, *J* = 21.4, 13.4 Hz, 1C), 128.74 (t, *J* = 11.5 Hz, 1C), 130.51 (t, *J* = 10.0 Hz, 1C), 131.83 (d, *J* = 2.5 Hz, 1C), 131.98, 133.04 (dd, *J* = 11.2, 8.2 Hz, 1C), 161.11 – 173.11 (m, 1C).

**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** δ 30.53 (d, *J* = 148.1 Hz).

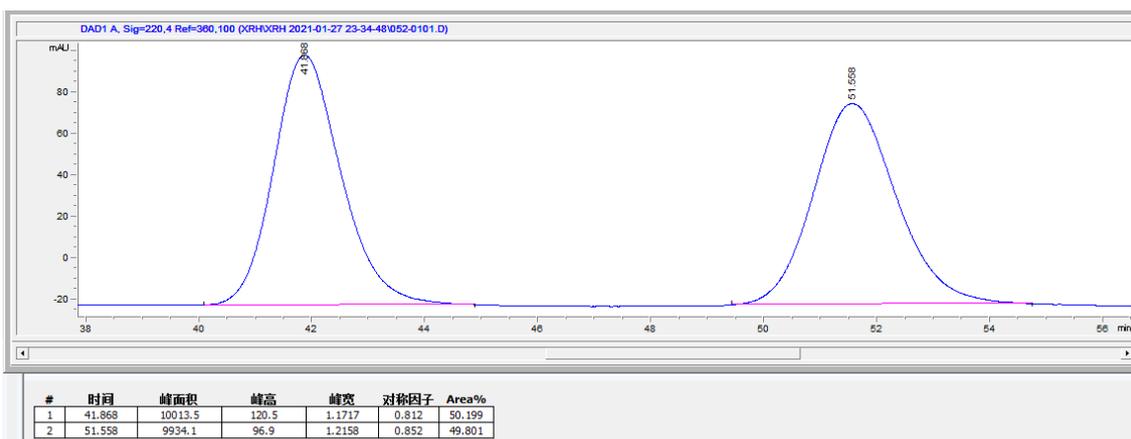
**<sup>19</sup>F NMR (471 MHz, Chloroform-d)** δ -106.97 (t, *J* = 8.1 Hz).

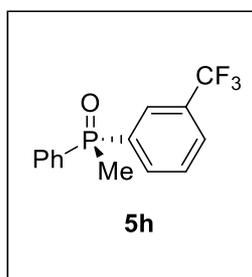
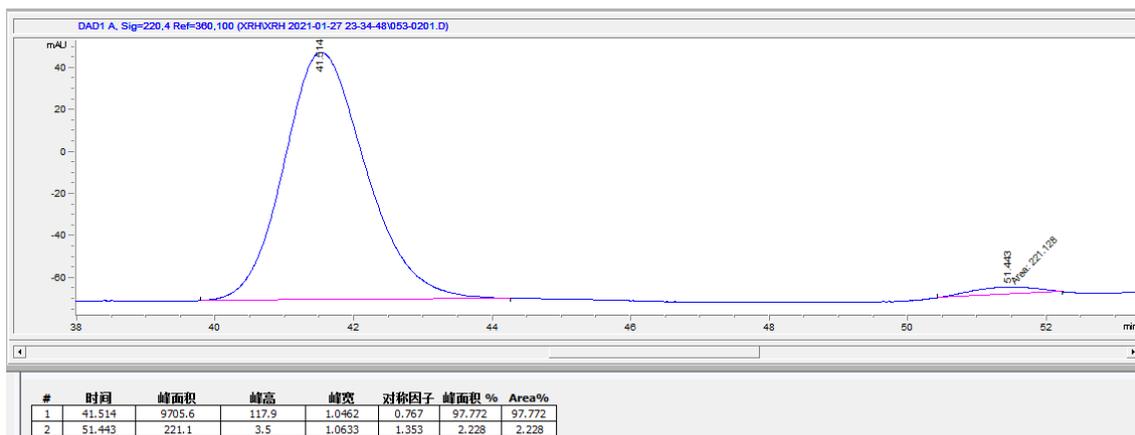
ESI-MS: *m/z* 275.35 [M+H]<sup>+</sup>, 297.35 [M+Na]<sup>+</sup>;

HRMS (ESI) calculated for [M+H, C<sub>16</sub>H<sub>20</sub>O<sub>2</sub>P]<sup>+</sup>: 275.1195 found 275.1196; calculated for [M+Na, C<sub>16</sub>H<sub>19</sub>O<sub>2</sub>PNa]<sup>+</sup>: 297.1015 found: 297.1016.

[α]<sub>D</sub><sup>25</sup>: -8.3305 (c = 6g/100ml, CHCl<sub>3</sub>).

Chiral HPLC conditions: Cellulose-2, *i*-PrOH-hexane 10/90, flow rate 1.00 mL/min, 220 nm. *t*<sub>1</sub> = 42.152 min, *t*<sub>2</sub> = 51.899 min. 97% ee





**Name:** (S)-methyl(phenyl)(3-(trifluoromethyl)phenyl)phosphine oxide

**Physical States:** white solid

**Yield:** 70% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)**  $\delta$  2.06 (dd,  $J = 13.3, 1.2$  Hz, 3H), 7.49 (dddd,  $J = 8.4, 6.9, 3.2, 1.5$  Hz, 2H), 7.53 – 7.63 (m, 2H), 7.69 – 7.79 (m, 3H), 7.86 – 7.91 (m, 1H), 8.00 (d,  $J = 11.8$  Hz, 1H).

**<sup>13</sup>C NMR (126 MHz, Chloroform-d)**  $\delta$  16.48 (d,  $J = 74.5$  Hz, 1C), 127.13 – 127.55 (m, 1C), 128.40 – 128.61 (m, 1C), 128.92 (d,  $J = 12.3$  Hz, 1C), 129.28 (d,  $J = 11.3$  Hz, 1C), 130.45 (d,  $J = 10.1$  Hz, 1C), 132.24, 132.61, 133.43, 133.82 (d,  $J = 9.4$  Hz, 1C), 135.74 (d,  $J = 98.9$  Hz, 1C).

**<sup>31</sup>P NMR (202 MHz, Chloroform-d)**  $\delta$  29.61 ,

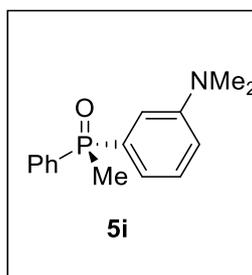
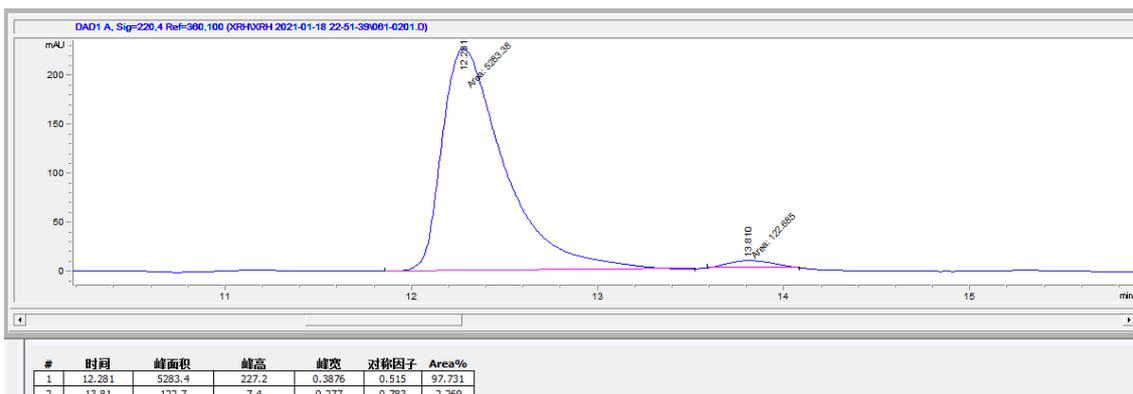
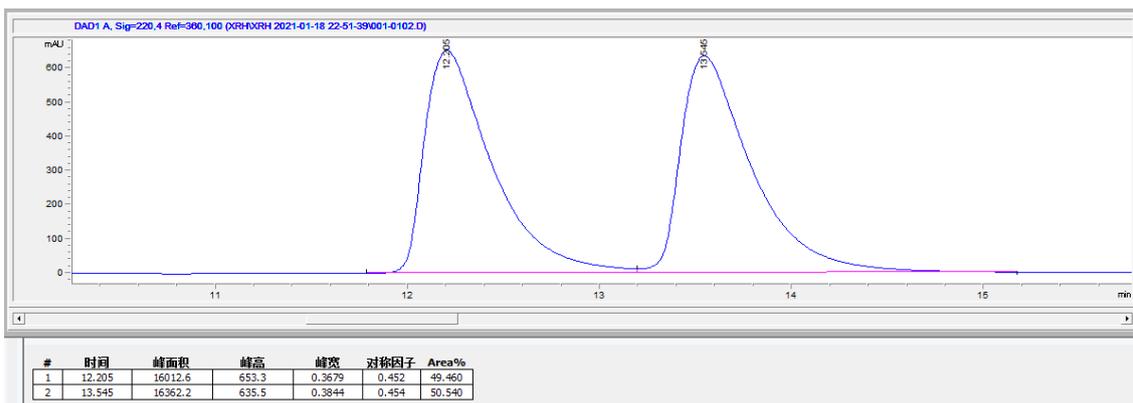
**<sup>19</sup>F NMR (471 MHz, Chloroform-d)**  $\delta$  -62.76

**ESI-MS:**  $m/z$  285.15 [M+H]<sup>+</sup>, 307.15 [M+Na]<sup>+</sup>;

**HRMS (ESI)** calculated for [M+H, C<sub>14</sub>H<sub>13</sub>F<sub>3</sub>OP]<sup>+</sup>: 285.0651 found 285.0653; calculated for [M+Na, C<sub>14</sub>H<sub>12</sub>F<sub>3</sub>OPNa]<sup>+</sup>: 307.0470 found: 307.0473.

$[\alpha]_D^{25}$ : -23.1499 ( $c = 0.4600$ g/100ml, CHCl<sub>3</sub>).

Chiral HPLC conditions: IA-3, *i*-PrOH-hexane 10/90, flow rate 1.00 mL/min, 220 nm.  $t_1 = 12.205$  min,  $t_2 = 13.81$  min. 97% ee.



**Name:** (*S*)-3-(dimethylamino)phenyl(methyl)(phenyl)phosphine oxide

**Physical States:** white solid

**Yield:** 70% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 1.99 (d, *J* = 13.1 Hz, 3H), 2.96 (d, *J* = 1.1 Hz, 6H), 6.80 – 6.92 (m, 2H), 7.13 – 7.18 (m, 1H), 7.28 (td, *J* = 7.8, 3.9 Hz, 1H), 7.40 – 7.52 (m, 3H), 7.72 (ddt, *J* = 11.8, 6.9, 1.4 Hz, 2H).

**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 16.67 (d, *J* = 73.5 Hz, 1C), 40.46, 114.13 (d, *J* = 10.8 Hz, 1C), 115.37, 117.86, 128.60, 129.32 (d, *J* = 14.7 Hz, 1C), 130.49 (d, *J* = 9.2 Hz, 1C), 131.60, 133.96 (d, *J* = 31.8 Hz, 1C), 134.76 (d, *J* = 30.7 Hz, 1C), 150.32 (d, *J* = 13.3 Hz, 1C).

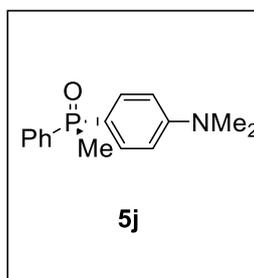
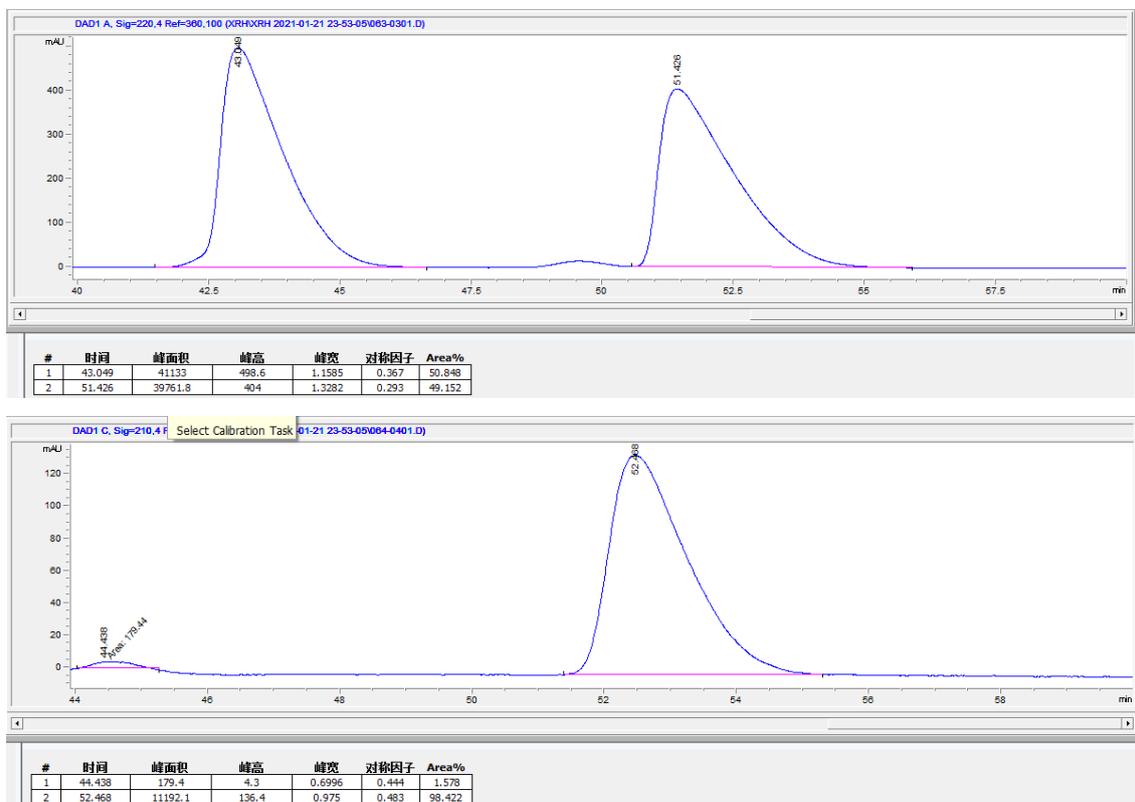
**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** δ 31.48.

**ESI-MS:** *m/z* 260.10 [M+H]<sup>+</sup>, 282.05 [M+Na]<sup>+</sup>

**HRMS (ESI)** calculated for [M+H, C<sub>15</sub>H<sub>19</sub>NOP]<sup>+</sup>: 260.1199 found 260.1205; calculated for [M+Na, C<sub>15</sub>H<sub>18</sub>NOPNa]<sup>+</sup>: 282.1018 found: 282.1024.

$[\alpha]_D^{25}$ : -48.4142 ( $c = 0.1667\text{g}/100\text{ml}$ ,  $\text{CHCl}_3$ ).

Chiral HPLC conditions: ID-3, *i*-PrOH-hexane 10/90, flow rate 1.00 mL/min, 220 nm.  $t_1 = 43.049$  min,  $t_2 = 51.426$  min. 97% ee.



**Name:** (S)-4-(dimethylamino)phenyl(methyl)(phenyl)phosphine oxide

**Physical States:** white solid

**Yield:** 70% yield

**$^1\text{H}$  NMR (500 MHz, Chloroform-d)**  $\delta$  1.89 (dd,  $J = 13.1, 1.3$  Hz, 3H), 2.94 (d,  $J = 1.2$  Hz, 6H), 6.67 (dd,  $J = 8.2, 2.8$  Hz, 2H), 7.32 – 7.51 (m, 5H), 7.59 – 7.67 (m, 2H).

**$^{13}\text{C}$  NMR (126 MHz, Chloroform-d)**  $\delta$  16.86 (d,  $J = 73.9$  Hz, 1C), 40.13, 111.59 (d,  $J = 12.4$  Hz, 1C), 128.48 (d,  $J = 11.4$  Hz, 1C), 130.50 (d,  $J = 9.2$  Hz, 1C), 131.33 (d,  $J = 3.2$  Hz, 1C), 131.96 (d,  $J = 11.2$  Hz, 1C), 152.25,

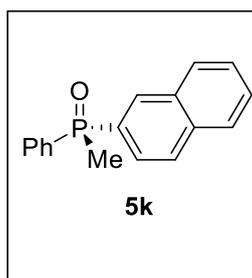
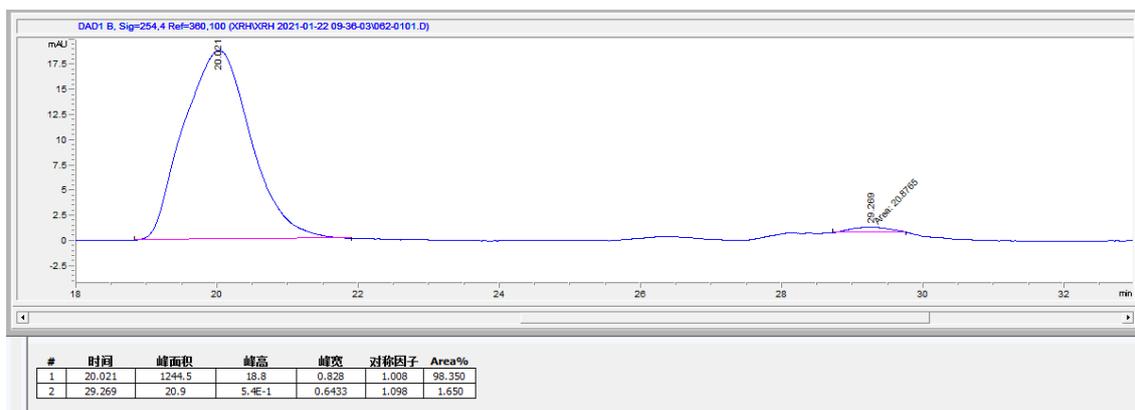
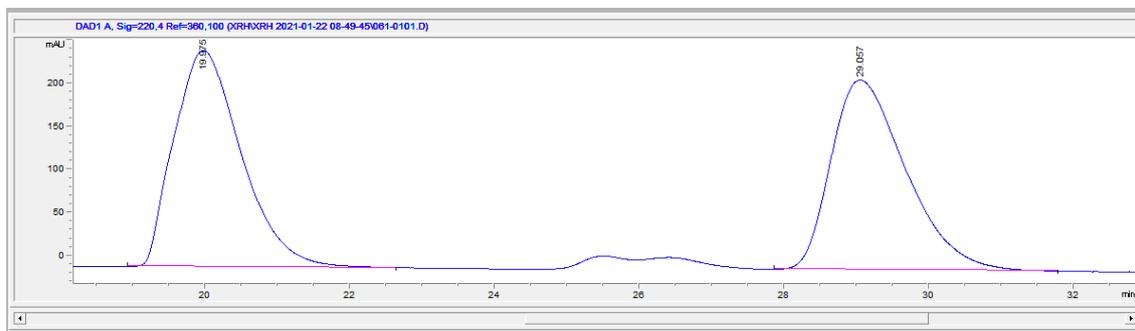
**$^{31}\text{P}$  NMR (202 MHz, Chloroform-d)**  $\delta$  30.89.

**ESI-MS:**  $m/z$  260.10  $[\text{M}+\text{H}]^+$ , 282.10  $[\text{M}+\text{Na}]^+$ ;

**HRMS (ESI)** calculated for  $[M+H, C_{15}H_{19}NOP]^+$ : 260.1199 found 260.1200; calculated for  $[M+Na, C_{15}H_{18}NOPNa]^+$ : 282.1018 found: 282.1021.

$[\alpha]_D^{25}$ : 5.9894 ( $c = 0.2000\text{g}/100\text{ml}$ ,  $\text{CHCl}_3$ ).

Chiral HPLC conditions: OJ-3, *i*-PrOH-hexane 10/90, flow rate 1.00 mL/min, 220 nm.  $t_1 = 19.075$  min,  $t_2 = 29.057$  min. 97% ee



**Name:** (S)-methyl(naphthalen-2-yl)(phenyl)phosphine oxide (**5k**)

**Physical States:** white solid

**Yield:** 70% yield

$^1\text{H NMR}$  (500 MHz, Chloroform- $d$ )  $\delta$  2.11 (dd,  $J = 13.2, 1.8$  Hz, 3H), 7.43 – 7.67 (m, 6H), 7.72 – 7.81 (m, 2H), 7.84 – 7.95 (m, 3H), 8.37 (d,  $J = 13.6$  Hz, 1H).

$^{13}\text{C}$  NMR (126 MHz, Chloroform- $d$ )  $\delta$  16.57 (d,  $J = 73.6$  Hz, 1C), 127.07, 127.86, 128.20, 128.55, 128.64, 128.69, 128.79, 128.89, 130.57 (d,  $J = 10.0$  Hz, 1C), 131.87, 132.36, 132.45 (d,  $J = 3.5$  Hz, 1C), 132.57, 134.63

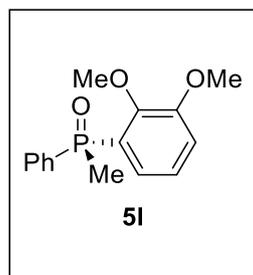
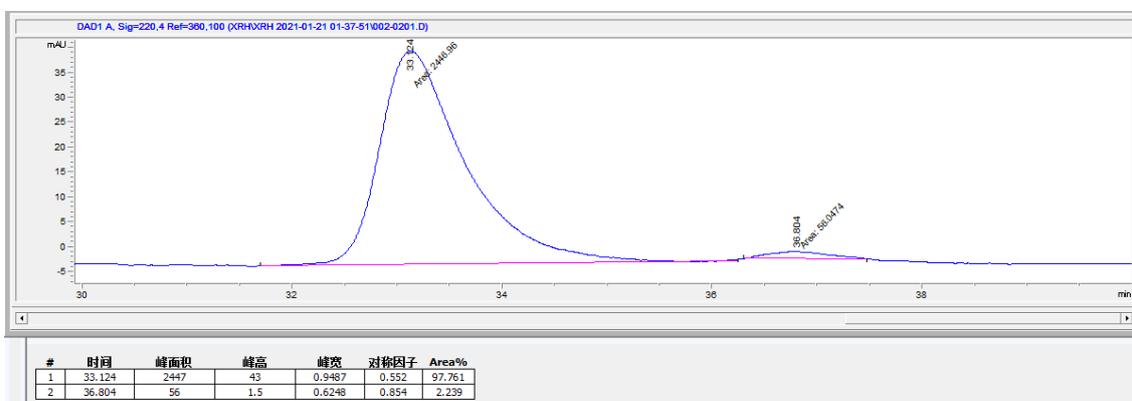
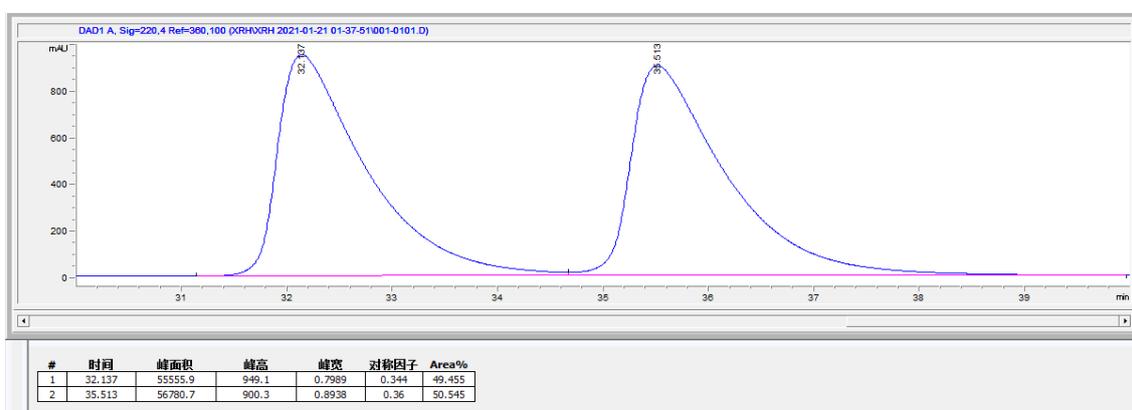
$^{31}\text{P}$  NMR (202 MHz, Chloroform- $d$ )  $\delta$  30.86

ESI-MS:  $m/z$  267.10  $[\text{M}+\text{H}]^+$ , 289.05  $[\text{M}+\text{Na}]^+$

HRMS (ESI) calculated for  $[\text{M}+\text{H}, \text{C}_{17}\text{H}_{16}\text{OP}]^+$ : 267.0933 found 267.0939; calculated for  $[\text{M}+\text{Na}, \text{C}_{17}\text{H}_{15}\text{OPNa}]^+$ : 289.0753 found: 289.0759.

$[\alpha]_{\text{D}}^{25}$ : 11.6679 ( $c = 0.1267\text{g}/100\text{ml}$ ,  $\text{CHCl}_3$ ).

Chiral HPLC conditions: IA-3, *i*-PrOH-hexane 10/90, flow rate 1.00 mL/min, 220 nm.  $t_1 = 32.137\text{min}$ ,  $t_2 = 35.513\text{ min}$ . 97% ee



Name: (*S*)-(2,3-dimethoxyphenyl)(methyl)(phenyl)phosphine oxide

Physical States: white solid

**Yield:** 70% yield

**$^1\text{H}$  NMR (500 MHz, Chloroform- $d$ )**  $\delta$  2.09 (d,  $J = 14.0$  Hz, 3H), 3.45 (s, 3H), 3.84 (s, 3H), 7.09 (dd,  $J = 8.1, 1.5$  Hz, 1H), 7.17 (td,  $J = 7.9, 2.8$  Hz, 1H), 7.42 – 7.51 (m, 4H), 7.71 – 7.77 (m, 2H)

**$^{13}\text{C}$  NMR (126 MHz, Chloroform- $d$ )**  $\delta$  16.04 (d,  $J = 75.7$  Hz, 1C), 55.84, 60.18, 116.71, 124.09 (d,  $J = 13.1$  Hz, 1C), 124.42 (d,  $J = 6.5$  Hz, 1C), 126.91, 127.70, 128.39 (d,  $J = 12.4$  Hz, 1C), 130.32 (d,  $J = 10.3$  Hz, 1C), 131.45 (d,  $J = 2.5$  Hz, 1C), 134.80, 135.62, 149.65 (d,  $J = 4.5$  Hz, 1C), 152.28 (d,  $J = 10.1$  Hz, 1C).

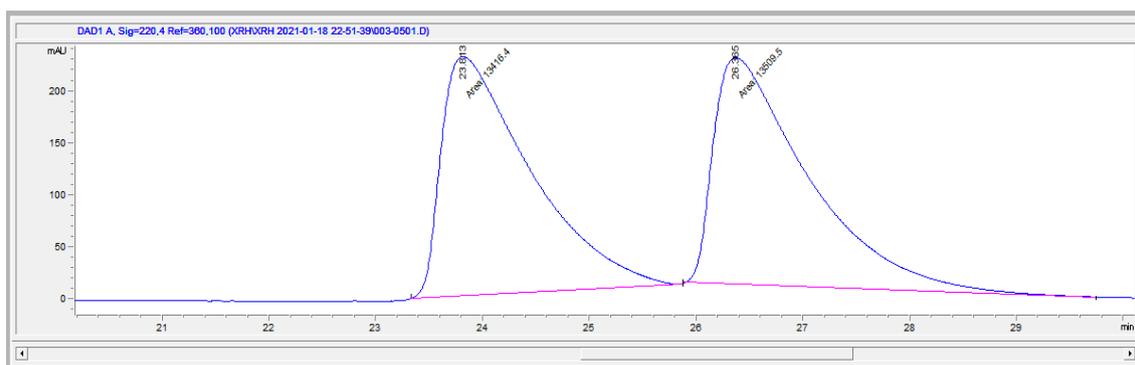
**$^{31}\text{P}$  NMR (202 MHz, Chloroform- $d$ )**  $\delta$  29.30.

**ESI-MS:**  $m/z$  277.05  $[\text{M}+\text{H}]^+$ ,

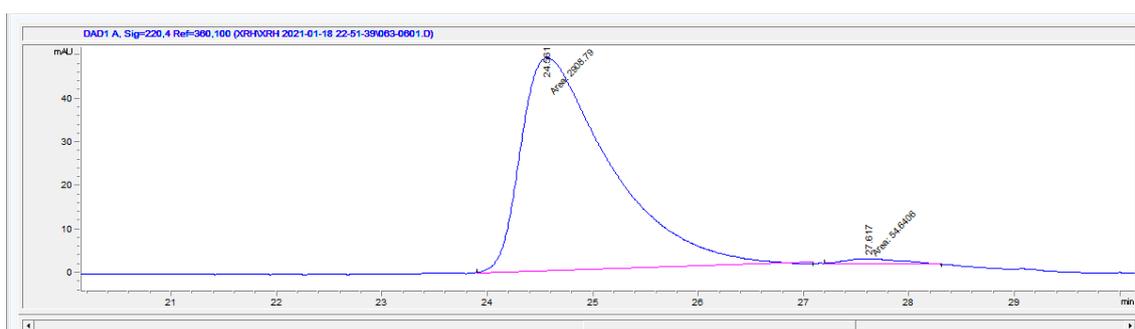
**HRMS (ESI)** calculated for  $[\text{M}+\text{H}, \text{C}_{15}\text{H}_{18}\text{O}_3\text{P}]^+$ : 277.0988 found 277.0991; calculated for  $[\text{M}+\text{Na}, \text{C}_{15}\text{H}_{17}\text{O}_3\text{PNa}]^+$ : 299.0808 found: 299.0811.

$[\alpha]_{\text{D}}^{25}$ : -12.1588 ( $c = 0.1000\text{g}/100\text{ml}$ ,  $\text{CHCl}_3$ ).

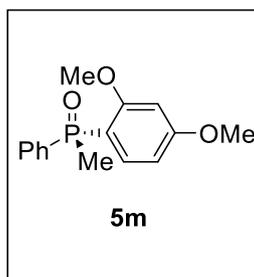
Chiral HPLC conditions: IA-3, *i*-PrOH-hexane 10/90, flow rate 1.00 mL/min, 220 nm.  $t_1 = 23.813$  min,  $t_2 = 26.365$  min. 97% ee.



#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	23.813	13416.4	230.5	0.9703	0.316	49.827
2	26.365	13509.5	218	1.0327	0.293	50.173



#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	24.561	2908.8	49.1	0.9865	0.398	98.156
2	27.617	54.6	1.3	0.6786	0.71	1.844



**Name:** (S)-(2,4-dimethoxyphenyl)(methyl)(phenyl)phosphine oxide

**Physical States:** white solid

**Yield:** 70% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 2.03 (dd, *J* = 14.1, 0.8 Hz, 3H), 3.69 (s, 3H), 3.83 (s, 3H), 6.41 (dd, *J* = 4.8, 2.2 Hz, 1H), 6.60 (dt, *J* = 8.5, 1.7 Hz, 1H), 7.37 – 7.49 (m, 3H), 7.71 (ddt, *J* = 12.1, 6.9, 1.5 Hz, 2H), 7.85 (dd, *J* = 12.9, 8.5 Hz, 1H).

**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 16.38 (d, *J* = 75.7 Hz, 1C), 55.43 (d, *J* = 28.3 Hz, 1C), 98.70, 104.97 (d, *J* = 11.4 Hz, 1C), 128.21 (d, *J* = 12.4 Hz, 1C), 130.16 (d, *J* = 10.1 Hz, 1C), 131.19 (d, *J* = 3.2 Hz, 1C), 135.37 (d, *J* = 6.7 Hz, 1C), 163.04 (d, *J* = 415.4 Hz, 1C)

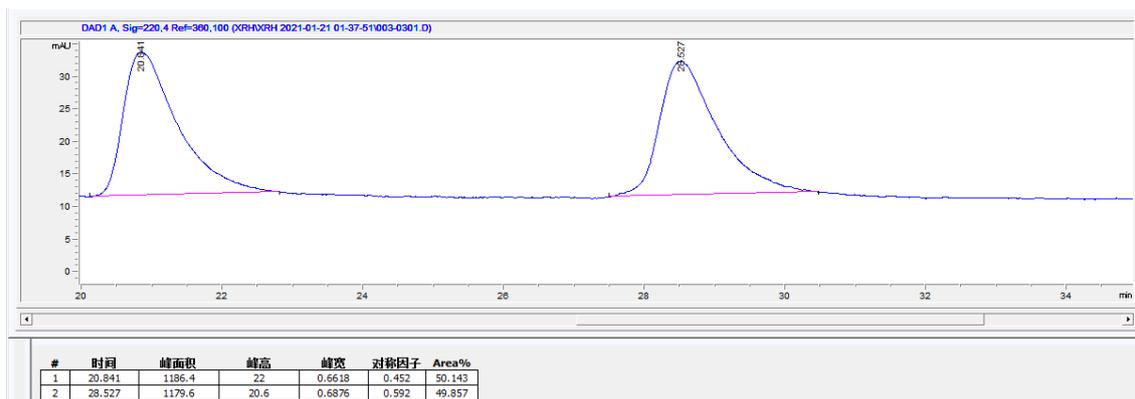
**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** δ 29.77 (d, *J* = 8.6 Hz)

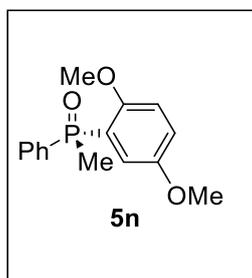
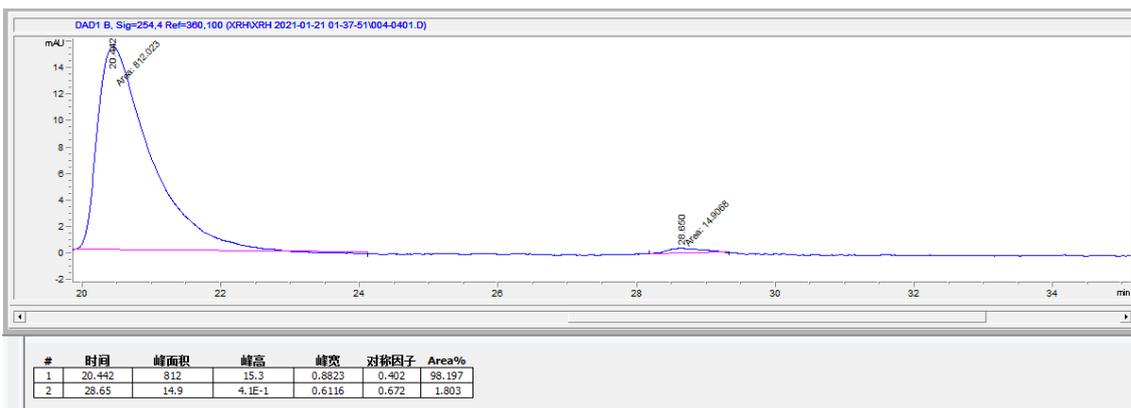
**ESI-MS:** *m/z* 299.30 [M+Na]<sup>+</sup>

**HRMS (ESI)** calculated for [M+H, C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>P]<sup>+</sup>: 277.0988 found 277.0987; calculated for [M+Na, C<sub>15</sub>H<sub>17</sub>O<sub>3</sub>PNa]<sup>+</sup>: 299.0808 found: 299.0809.

[α]<sub>D</sub><sup>25</sup>: -1.6675 (c = 0.2267g/100ml, CHCl<sub>3</sub>).

Chiral HPLC conditions: IA-3, *i*-PrOH-hexane 15/85, flow rate 1.00 mL/min, 220 nm. *t*<sub>1</sub> = 20.841 min, *t*<sub>2</sub> = 28.527 min. 97% ee.





**Name:** (S)-(2,5-dimethoxyphenyl)(methyl)(phenyl)phosphine oxide

**Physical States:** white solid

**Yield:** 70% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 2.03 (dd, *J* = 14.1, 0.8 Hz, 3H), 3.69 (s, 3H), 3.83 (s, 3H), 6.41 (dd, *J* = 4.8, 2.2 Hz, 1H), 6.60 (dt, *J* = 8.5, 1.7 Hz, 1H), 7.37 – 7.49 (m, 3H), 7.71 (ddt, *J* = 12.1, 6.9, 1.5 Hz, 2H), 7.85 (dd, *J* = 12.9, 8.5 Hz, 1H).

**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 16.00 (d, *J* = 75.0 Hz, 1C), 55.80, 56.01, 112.47 (d, *J* = 8.6 Hz, 1C), 117.67 (d, *J* = 6.5 Hz, 1C), 120.14, 128.25 (d, *J* = 12.3 Hz, 1C), 130.24 (d, *J* = 10.2 Hz, 1C), 131.39 (d, *J* = 3.2 Hz, 1C), 150.87 – 155.38 (m, 1C).

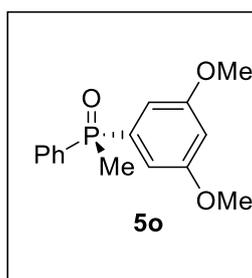
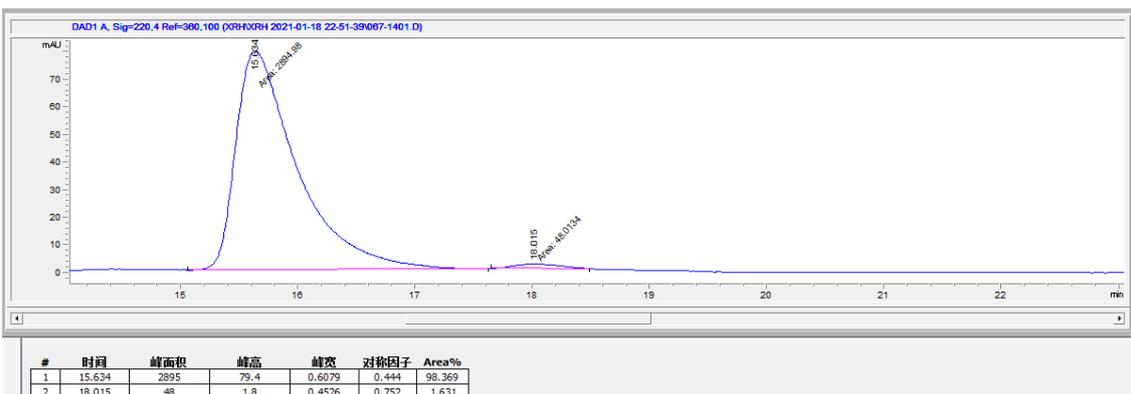
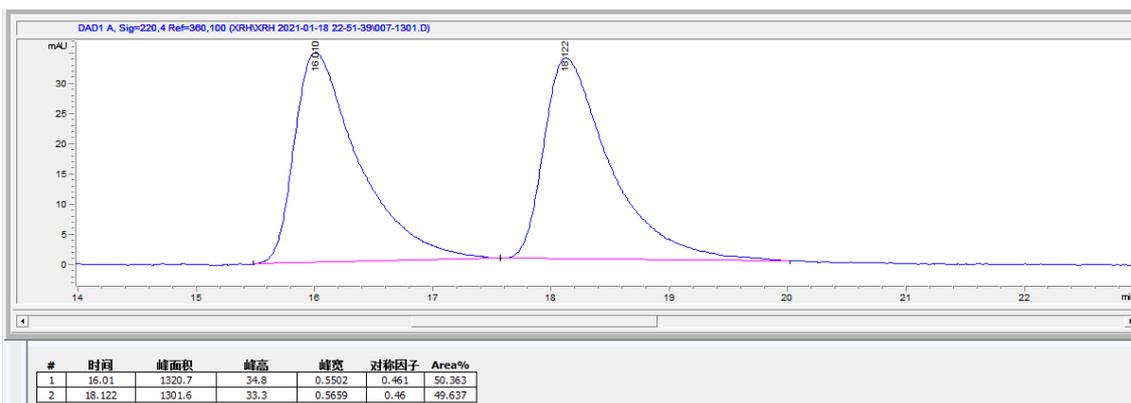
**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** δ 29.77 (d, *J* = 8.6 Hz)

**ESI-MS:** *m/z* 299.30 [M+Na]<sup>+</sup>

**HRMS (ESI)** calculated for [M+H, C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>P]<sup>+</sup>: 277.0988 found 277.0990; calculated for [M+Na, C<sub>15</sub>H<sub>17</sub>O<sub>3</sub>PNa]<sup>+</sup>: 299.0808 found: 299.0811.

[α]<sub>D</sub><sup>25</sup>: -16.4232 (c = 0.0944g/100ml, CHCl<sub>3</sub>).

Chiral HPLC conditions: IA-3, *i*-PrOH-hexane 15/85, flow rate 1.00 mL/min, 220 nm. *t*<sub>1</sub> = 16.01 min (*S*), *t*<sub>2</sub> = 18.122 min (*R*). 97% ee.



**Name:** *(S)*-(3,5-dimethoxyphenyl)(methyl)(phenyl)phosphine oxide

**Physical States:** white solid

**Yield:** 70% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 1.95 – 2.02 (m, 3H), 3.76 – 3.81 (m, 6H), 6.56 (q, *J* = 2.1 Hz, 1H), 6.83 (dd, *J* = 13.1, 2.2 Hz, 2H), 7.41 – 7.54 (m, 3H), 7.71 (ddt, *J* = 11.9, 6.9, 1.5 Hz, 2H)

**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 16.55 (d, *J* = 74.4 Hz, 1C), 55.61, 103.77, 108.18 (d, *J* = 11.2 Hz, 1C), 128.68 (d, *J* = 12.3 Hz, 1C), 130.45 (d, *J* = 9.3 Hz, 1C), 131.85 (d, *J* = 3.3 Hz, 1C), 133.78 (d, *J* = 101.7 Hz, 1C), 135.93 (d, *J* = 100.6 Hz, 1C), 160.98 (d, *J* = 18.0 Hz, 1C)

**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** δ 31.62 (d, *J* = 8.1 Hz)

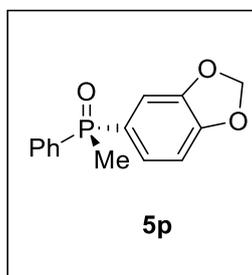
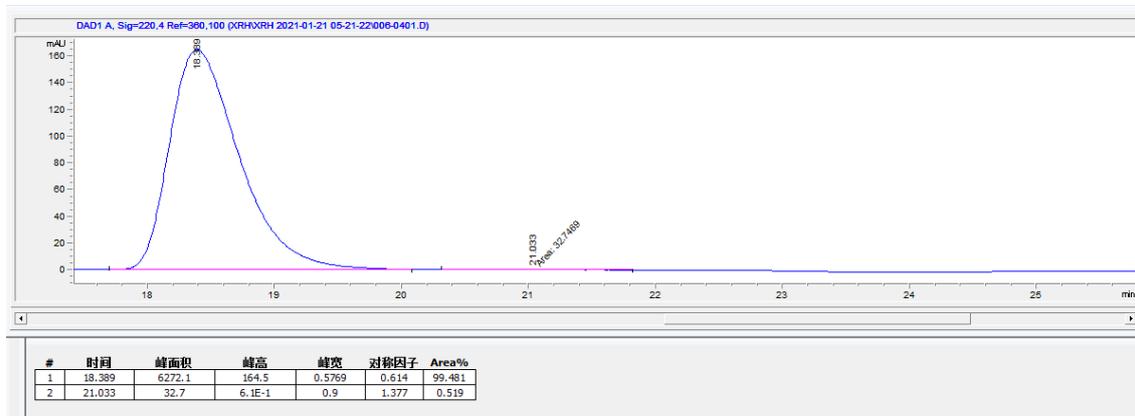
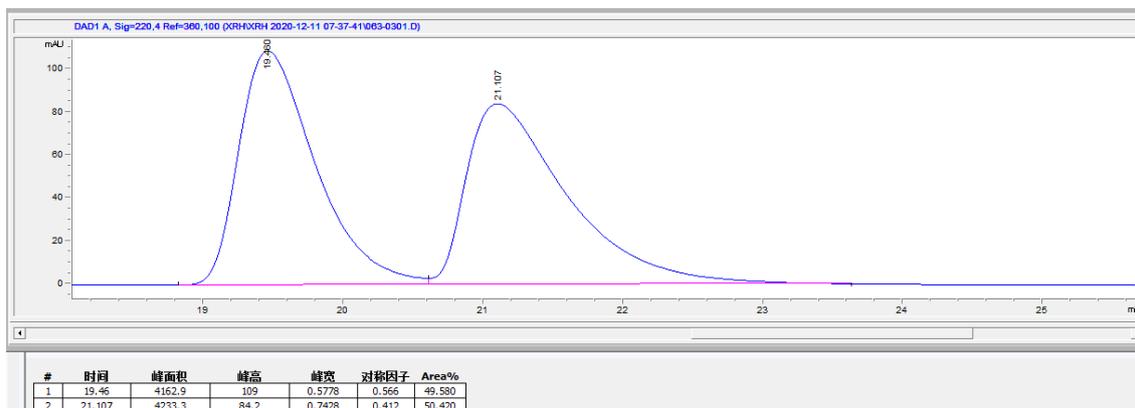
**ESI-MS:** *m/z* 277.35 [M+H]<sup>+</sup>,

**HRMS (ESI)** calculated for [M+H, C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>P]<sup>+</sup>: 277.0988 found 277.0988; calculated for [M+Na, C<sub>15</sub>H<sub>17</sub>O<sub>3</sub>PNa]<sup>+</sup>: 299.0808 found: 299.0810.

[α]<sub>D</sub><sup>25</sup>: -4.4995 (c = 0.2200g/100ml, CHCl<sub>3</sub>).

Chiral HPLC conditions: OD-3, *i*-PrOH-hexane 10/90, flow rate 1.00 mL/min, 220 nm.

$t_1 = 19.46$  min,  $t_2 = 21.107$  min. 97% ee.



**Name:** (*S*)-benzo[d][1,3]dioxol-5-yl(methyl)(phenyl)phosphine oxide

**Physical States:** white solid

**Yield:** 70% yield

**$^1\text{H}$  NMR (500 MHz, Chloroform-*d*)**  $\delta$  1.97 (dd,  $J = 13.1, 1.0$  Hz, 3H), 5.99 (d,  $J = 1.1$  Hz, 2H), 6.88 (dd,  $J = 7.9, 2.3$  Hz, 1H), 7.09 (dd,  $J = 11.4, 1.4$  Hz, 1H), 7.21 – 7.25 (m, 1H), 7.42 – 7.53 (m, 3H), 7.66 – 7.73 (m, 2H).

**$^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)**  $\delta$  16.71 (d,  $J = 74.5$  Hz, 1C), 101.64, 108.80 (d,  $J = 14.8$  Hz, 1C), 110.15 (d,  $J = 12.4$  Hz, 1C), 125.78 (d,  $J = 11.2$  Hz, 1C), 128.68 (d,  $J = 12.3$  Hz, 1C), 130.45 (d,  $J = 10.1$  Hz, 1C), 131.79 (d,  $J = 3.2$  Hz, 1C), 148.10 (d,  $J = 18.1$  Hz, 1C), 150.70 (d,  $J = 2.9$  Hz, 1C).

**$^{31}\text{P}$  NMR (202 MHz, Chloroform-*d*)**  $\delta$  31.20

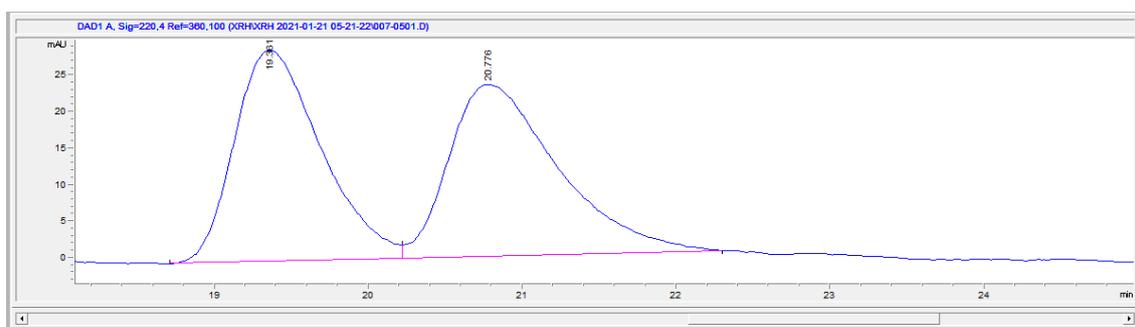
**ESI-MS:**  $m/z$  261.35  $[M+H]^+$ , 283.30  $[M+Na]^+$

**HRMS (ESI)** calculated for  $[M+H, C_{14}H_{14}O_3P]^+$ : 261.0675 found 261.0675; calculated for  $[M+Na, C_{14}H_{13}O_3PNa]^+$ : 283.0495 found: 283.0496.

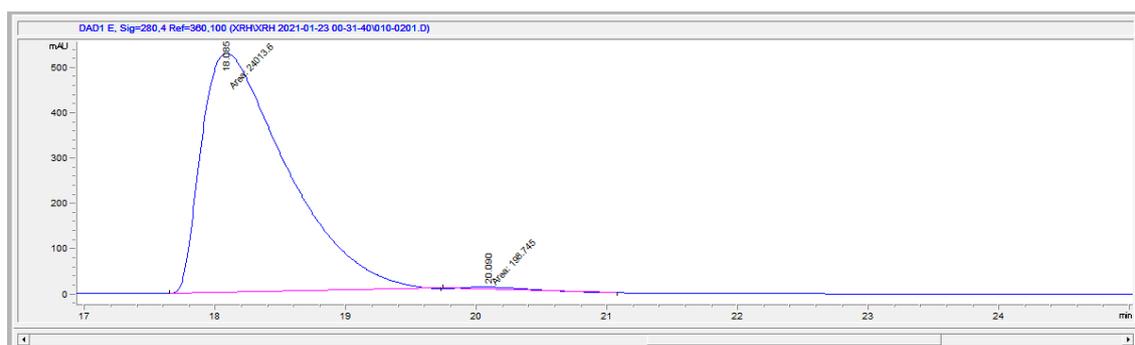
$[\alpha]_D^{25}$ : -0.8189 ( $c = 0.6667g/100ml, CHCl_3$ )

Chiral HPLC conditions: OD-3, *i*-PrOH-hexane 10/90, flow rate 1.00 mL/min, 220 nm.

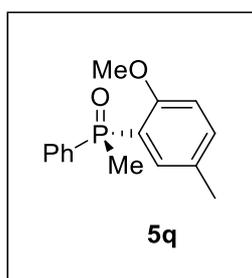
$t_1 = 19.361$  min,  $t_2 = 20.776$  min. 97% ee



#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	19.361	1132.2	28.9	0.5469	0.665	49.335
2	20.776	1162.7	23.6	0.611	0.529	50.665



#	时间	峰面积	峰高	峰宽	对称因子	Area%
1	18.085	24013.6	528.1	0.7579	0.404	99.179
2	20.09	198.7	5.9	0.5593	0.397	0.821



**Name:** (*S*)-(2-methoxy-5-methylphenyl)(methyl)(phenyl)phosphine oxide

**Physical States:** colorless oil

**Yield:** 70% yield

$^1H$  NMR (500 MHz, Chloroform-*d*)  $\delta$  2.07 (dd,  $J = 14.0, 1.2$  Hz, 3H), 2.32 (s, 3H), 3.68 (d,  $J = 0.9$  Hz, 3H), 6.78 (dd,  $J = 8.3, 5.6$  Hz, 1H), 7.27 – 7.31 (m, 1H), 7.40 (ddd,  $J = 8.2, 6.7, 2.8$  Hz, 2H), 7.43 – 7.49 (m, 1H), 7.73 (ddd,  $J = 12.2, 8.0, 1.4$  Hz, 2H), 7.81 (dd,  $J = 13.4, 2.3$  Hz, 1H).

SI-40

$^{13}\text{C}$  NMR (126 MHz, Chloroform- $d$ )  $\delta$  16.14 (d,  $J = 74.7$  Hz, 1C), 20.38, 55.36, 110.87 (d,  $J = 7.7$  Hz, 1C), 128.21 (d,  $J = 12.4$  Hz, 1C), 130.23 (d,  $J = 10.2$  Hz, 1C), 130.54 (d,  $J = 11.2$  Hz, 1C), 131.29, 134.20 (d,  $J = 5.6$  Hz, 1C), 134.34, 157.77

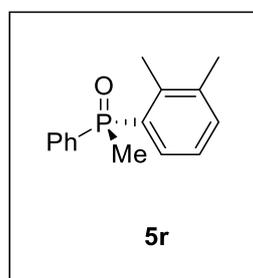
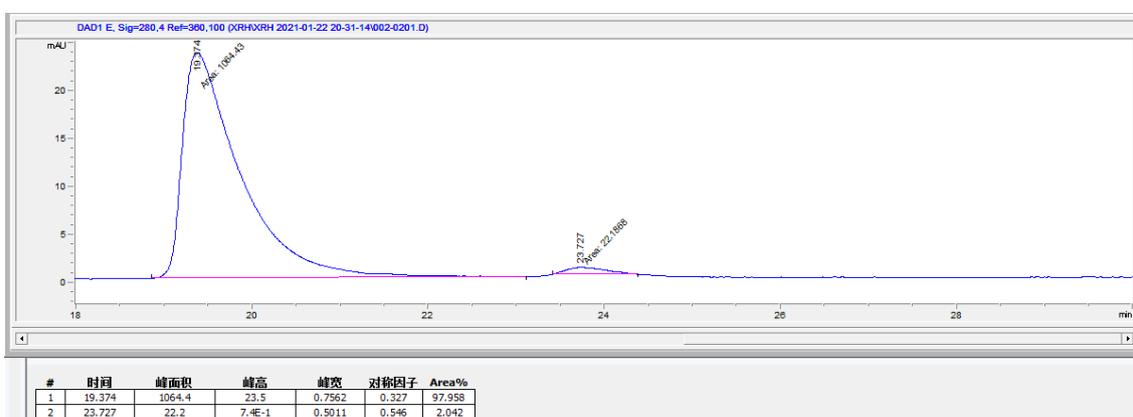
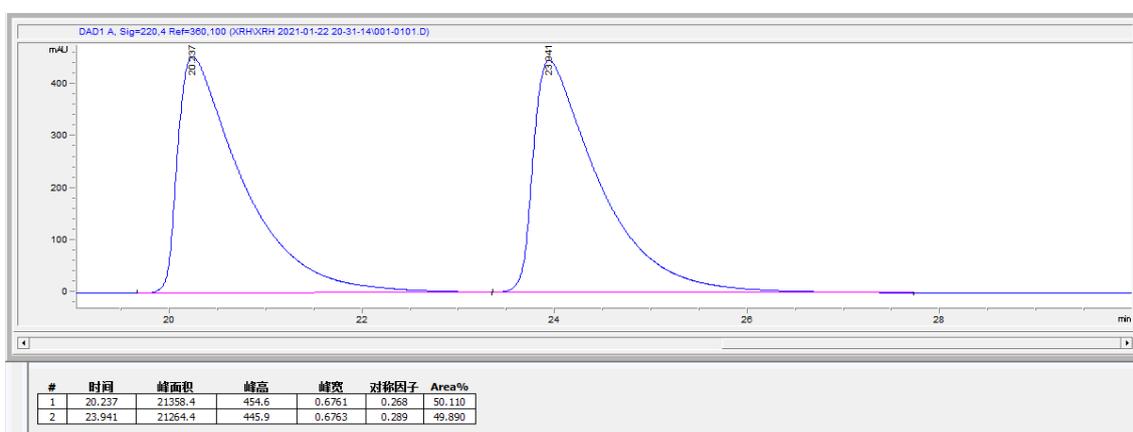
$^{31}\text{P}$  NMR (202 MHz, Chloroform- $d$ )  $\delta$  29.58

ESI-MS:  $m/z$  261.15  $[\text{M}+\text{H}]^+$ , 283.05  $[\text{M}+\text{Na}]^+$

HRMS (ESI) calculated for  $[\text{M}+\text{H}, \text{C}_{15}\text{H}_{18}\text{O}_2\text{P}]^+$ : 261.1039 found 261.1045; calculated for  $[\text{M}+\text{Na}, \text{C}_{15}\text{H}_{17}\text{O}_2\text{PNa}]^+$ : 283.0858 found: 283.0866.

$[\alpha]_{\text{D}}^{25}$ : -12.6854 ( $c = 0.3000\text{g}/100\text{ml}$ ,  $\text{CHCl}_3$ ).

Chiral HPLC conditions: IA-3, *i*-PrOH-hexane 10/90, flow rate 1.00 mL/min, 220 nm.  $t_1 = 20.237$  min,  $t_2 = 23.727$  min. 97% ee



Name: (*S*)-(2,3-dimethylphenyl)(methyl)(phenyl)phosphine oxide

Physical States: colorless oil

**Yield:** 70% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 2.04 (d, *J* = 13.0 Hz, 3H), 2.25 (s, 3H), 2.30 (s, 3H), 7.18 – 7.24 (m, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.45 (td, *J* = 7.5, 2.8 Hz, 2H), 7.48 – 7.55 (m, 2H), 7.65 (ddt, *J* = 11.9, 6.8, 1.4 Hz, 2H).

**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 17.62 (d, *J* = 74.6 Hz, 1C), 18.02 (d, *J* = 5.6 Hz, 1C), 20.34, 125.43 (d, *J* = 13.3 Hz, 1C), 128.65 (d, *J* = 12.1 Hz, 1C), 129.44 (d, *J* = 11.6 Hz, 1C), 130.34 (d, *J* = 10.0 Hz, 1C), 131.49, 133.87, 138.77 (d, *J* = 10.2 Hz, 1C), 140.63 (d, *J* = 8.2 Hz, 1C).

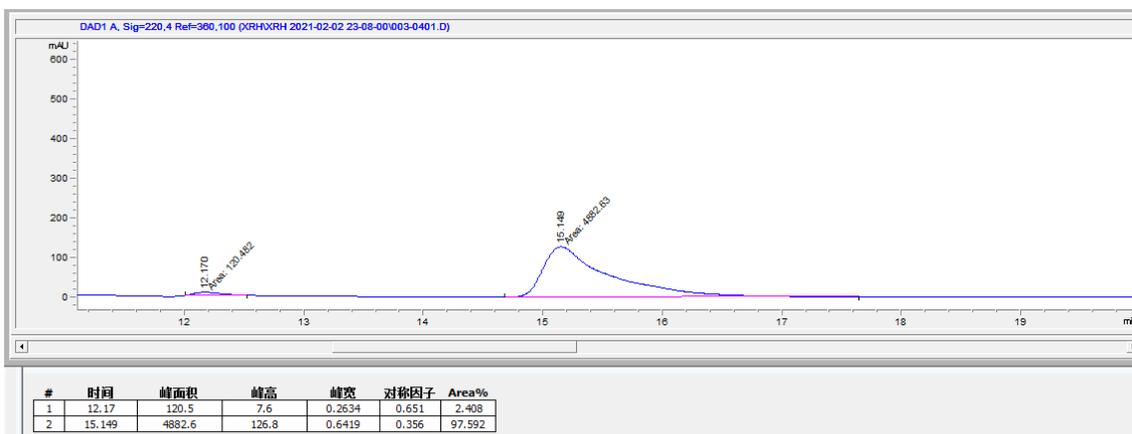
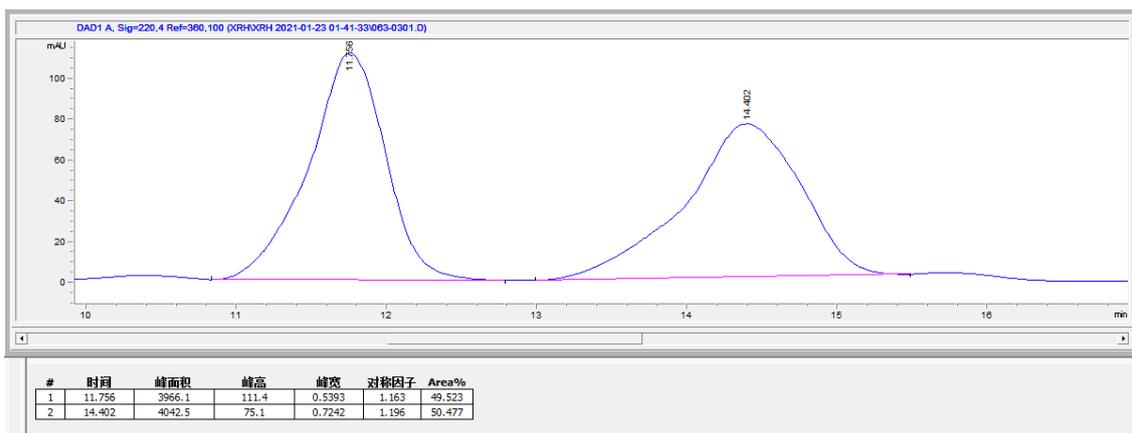
**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** δ 33.87

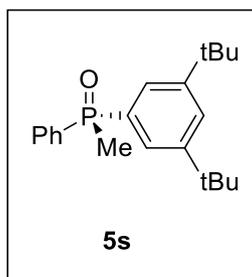
**ESI-MS:** *m/z* 245.20 [M+H]<sup>+</sup>, 266.90 [M+Na]<sup>+</sup>

**HRMS (ESI)** calculated for [M+H, C<sub>15</sub>H<sub>18</sub>OP]<sup>+</sup>: 245.1090 found 245.1082; calculated for [M+Na, C<sub>15</sub>H<sub>17</sub>OPNa]<sup>+</sup>: 267.0909 found: 267.0904.

[α]<sub>D</sub><sup>25</sup>: -39.0011 (c = 0.4000g/100ml, CHCl<sub>3</sub>).

Chiral HPLC conditions: AD-3, *i*-PrOH-hexane 10/90, flow rate 1.00mL/min, 220 nm. *t*<sub>1</sub> = 11.746 min, *t*<sub>2</sub> = 14.402 min (*R*). 95% ee.





**Name:** (S)-(3,5-di-tert-butylphenyl)(methyl)(phenyl)phosphine oxide

**Physical States:** colorless oil

**Yield:** 70% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 1.29 (d, *J* = 2.2 Hz, 18H), 2.00 (dd, *J* = 13.0, 1.8 Hz, 3H), 7.42 – 7.58 (m, 6H), 7.70 – 7.76 (m, 2H)

**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 16.93 (d, *J* = 73.4 Hz, 1C), 31.31, 35.03, 124.60 (d, *J* = 10.3 Hz, 1C), 126.02 (d, *J* = 3.1 Hz, 1C), 128.52 (d, *J* = 11.3 Hz, 1C), 130.54 (d, *J* = 10.1 Hz, 1C), 131.58 (d, *J* = 2.8 Hz, 1C), 151.16 (d, *J* = 11.4 Hz, 1C).

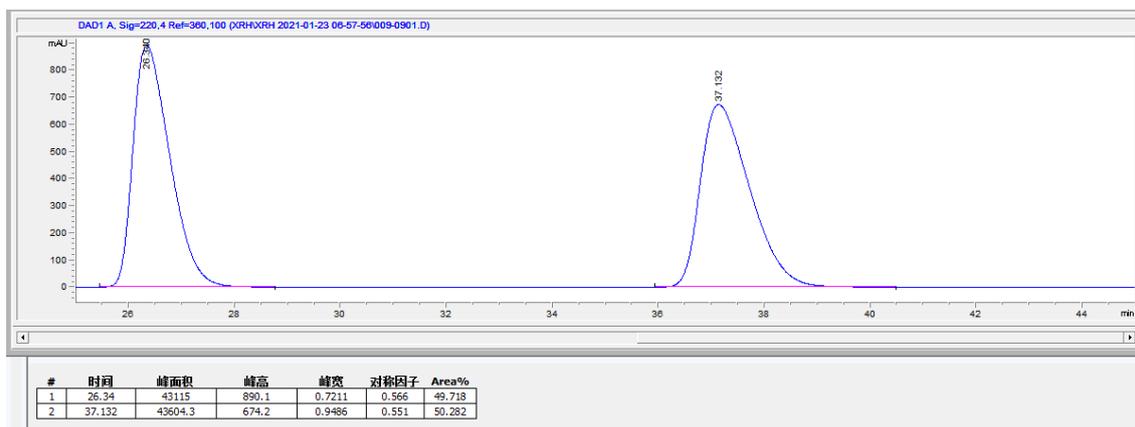
**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** 31.60

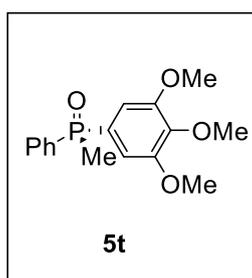
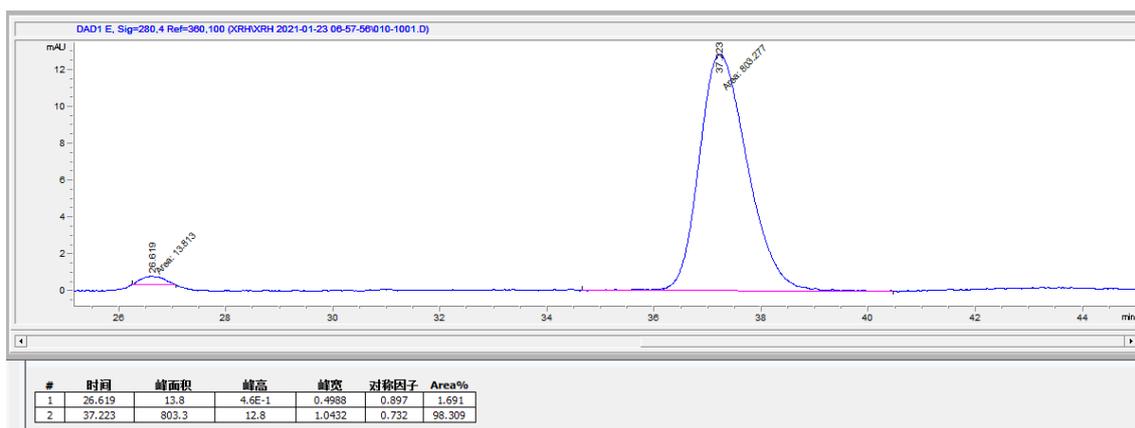
**ESI-MS:** *m/z* 329.25 [M+H]<sup>+</sup>,

**HRMS (ESI)** calculated for [M+H, C<sub>21</sub>H<sub>30</sub>OP]<sup>+</sup>: 329.2029 found 329.2032; calculated for [M+Na, C<sub>21</sub>H<sub>29</sub>OPNa]<sup>+</sup>: 351.1848 found: 351.1850.

[α]<sub>D</sub><sup>25</sup>: -11.2894 (c = 0.9769g/100ml, CHCl<sub>3</sub>)

Chiral HPLC conditions: IC-3, *i*-PrOH-hexane 10/90, flow rate 1.00 mL/min, 220 nm. *t*<sub>1</sub> = 26.34 min, *t*<sub>2</sub> = 37.132 min. 97% ee.





**Name:** (S)-methyl(phenyl)(3,4,5-trimethoxyphenyl)phosphine oxide

**Physical States:** white solid

**Yield:** 70% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 2.01 (d, *J* = 13.2 Hz, 3H), 3.86 (s, 6H), 3.88 (s, 3H), 6.91 (d, *J* = 13.0 Hz, 2H), 7.45 – 7.56 (m, 3H), 7.69 – 7.76 (m, 2H).

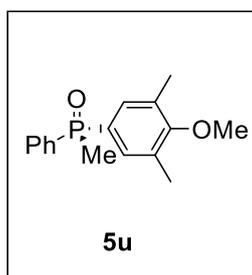
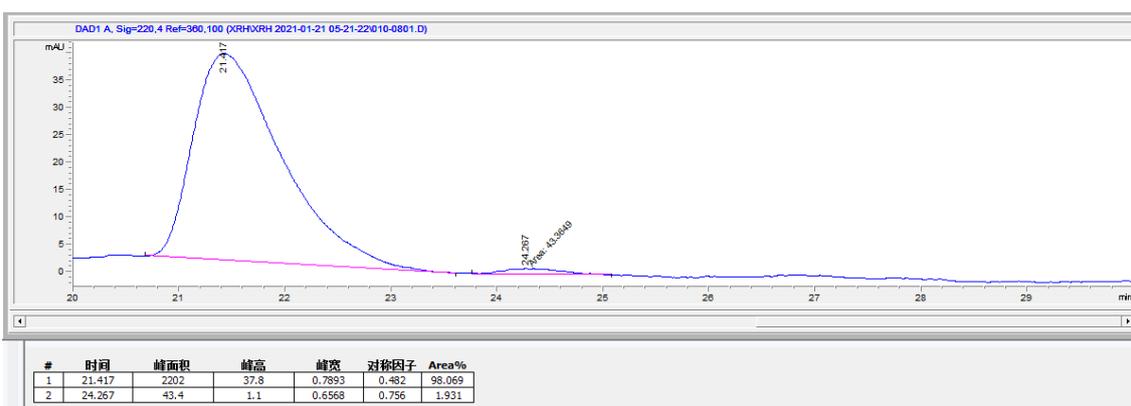
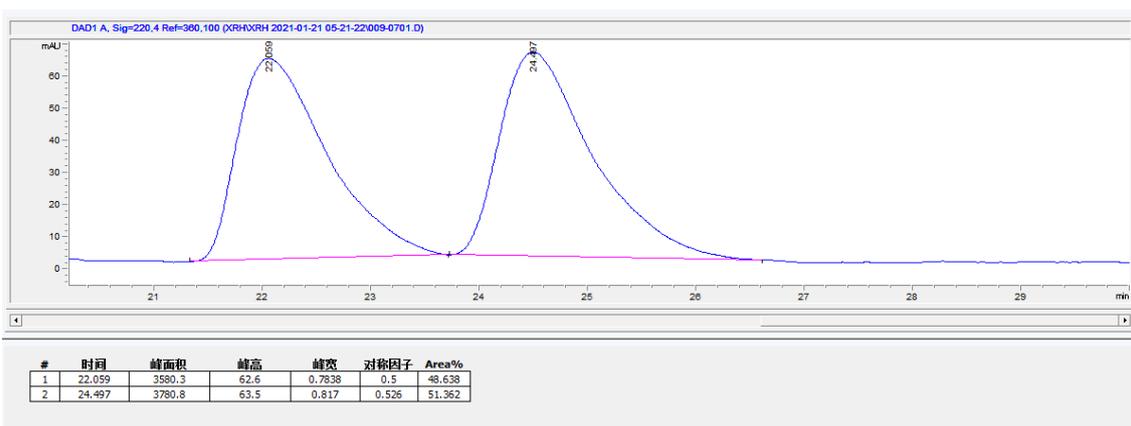
**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 16.68 (d, *J* = 74.3 Hz, 1C), 56.37, 60.89, 107.62 (d, *J* = 11.4 Hz, 1C), 128.69 (d, *J* = 11.4 Hz, 1C), 130.42 (d, *J* = 9.3 Hz, 1C), 131.86, 133.97 (d, *J* = 101.7 Hz, 1C), 140.97, 153.47 (d, *J* = 17.8 Hz, 1C).

**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** 31.23

**ESI-MS:** *m/z* 307.20 [M+H]<sup>+</sup>

**HRMS (ESI)** calculated for [M+Na, C<sub>16</sub>H<sub>19</sub>O<sub>4</sub>PNa]<sup>+</sup>: 329.0913 found: 329.0912. [α]<sub>D</sub><sup>25</sup>: -7.4990 (*c* = 0.0867g/100ml, CHCl<sub>3</sub>)

Chiral HPLC conditions: OD-3, *i*-PrOH-hexane 10/90, flow rate 1.00 mL/min, 220 nm. *t*<sub>1</sub> = 22.059 min, *t*<sub>2</sub> = 24.497 min. 97% ee.



**Name:** (S)-(4-methoxy-3,5-dimethylphenyl)(methyl)(phenyl)phosphine oxide

**Physical States:** white solid

**Yield:** 70% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 1.91 (dd, *J* = 13.1, 1.2 Hz, 3H), 2.22 (s, 6H), 3.66 (d, *J* = 1.2 Hz, 3H), 7.29 (d, *J* = 11.9 Hz, 2H), 7.37 – 7.47 (m, 3H), 7.62 – 7.69 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 16.21, 16.69 (d, *J* = 73.6 Hz, 1C), 59.68, 128.62 (d, *J* = 12.3 Hz, 1C), 130.48 (d, *J* = 10.1 Hz, 1C), 131.25 (d, *J* = 10.3 Hz, 1C), 131.60, 131.67 (t, *J* = 3.9 Hz, 1C), 160.05

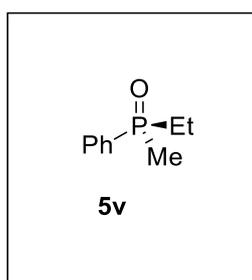
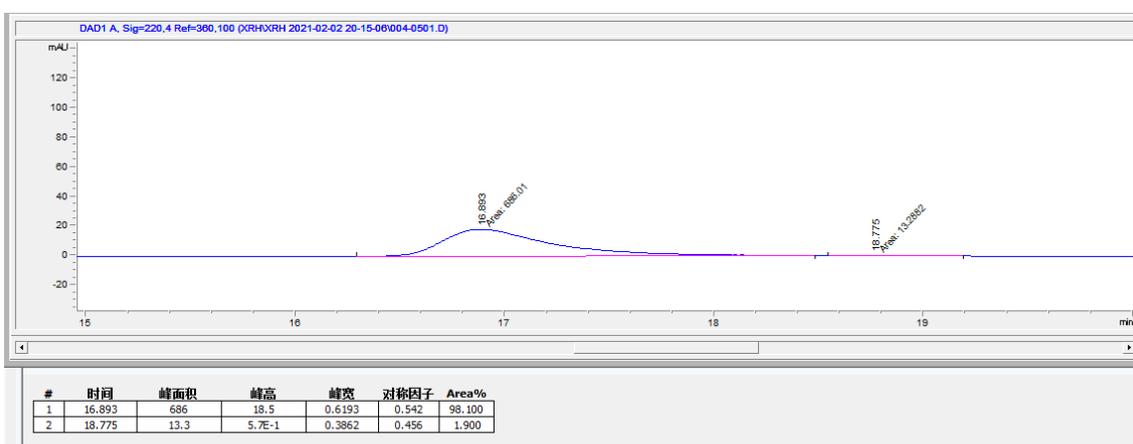
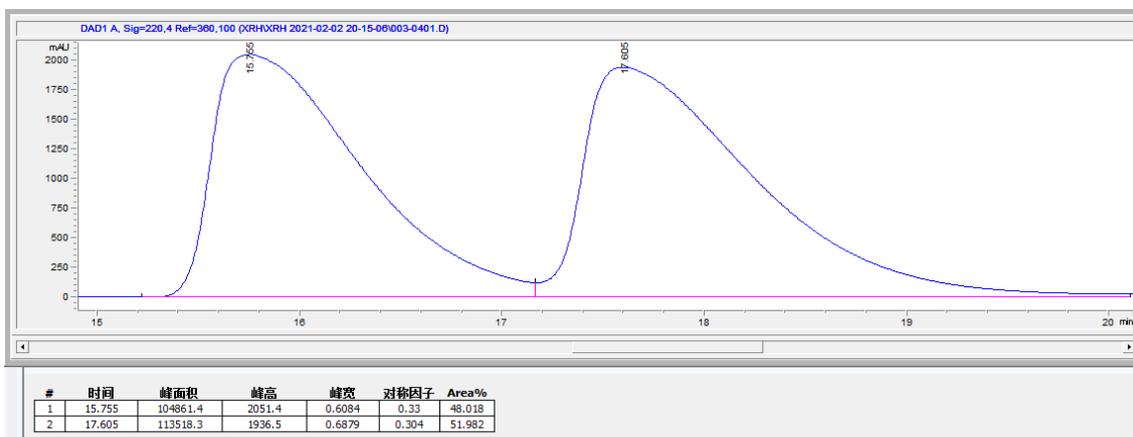
**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** 30.58

**ESI-MS:** *m/z* 275.35 [M+H]<sup>+</sup>, 297.35 [M+Na]<sup>+</sup>

**HRMS (ESI)** calculated for [M+H, C<sub>16</sub>H<sub>20</sub>O<sub>2</sub>P]<sup>+</sup>: 274.2741 found 274.2748; calculated for [M+Na, C<sub>16</sub>H<sub>19</sub>O<sub>2</sub>PNa]<sup>+</sup>: 297.1015 found: 297.1021.

$[\alpha]_D^{25}$ : 5.8794 ( $c = 0.1000\text{g}/100\text{ml}$ ,  $\text{CHCl}_3$ ).

Chiral HPLC conditions: IA-3, *i*-PrOH-hexane 10/90, flow rate 1.00 mL/min, 220 nm.  $t_1 = 16.192$  min,  $t_2 = 18.126$  min. 96% ee



**Name:** (*S*)-ethyl(methyl)(phenyl)phosphine oxide

**Physical States:** white solid

**Yield:** 70% yield,

$^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  1.08 (dt,  $J = 17.5, 7.6$  Hz, 3H), 1.65 (d,  $J = 12.7$  Hz, 3H), 1.89 (dddt,  $J = 26.3, 15.1, 11.0, 7.5$  Hz, 2H), 7.41 – 7.51 (m, 3H), 7.66 (ddt,  $J = 11.3, 6.7, 1.5$  Hz, 2H)..

$^{13}\text{C}$  NMR (126 MHz, Chloroform- $d$ )  $\delta$  5.74 (d,  $J$  = 5.2 Hz, 1C), 15.41 (d,  $J$  = 69.1 Hz, 1C), 24.63 (d,  $J$  = 71.2 Hz, 1C), 128.65 (d,  $J$  = 12.4 Hz, 1C), 130.07 (d,  $J$  = 10.0 Hz, 1C), 131.63 (d,  $J$  = 2.9 Hz, 1C), 133.21 (d,  $J$  = 95.1 Hz, 1C).

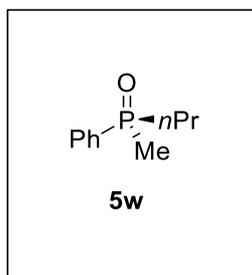
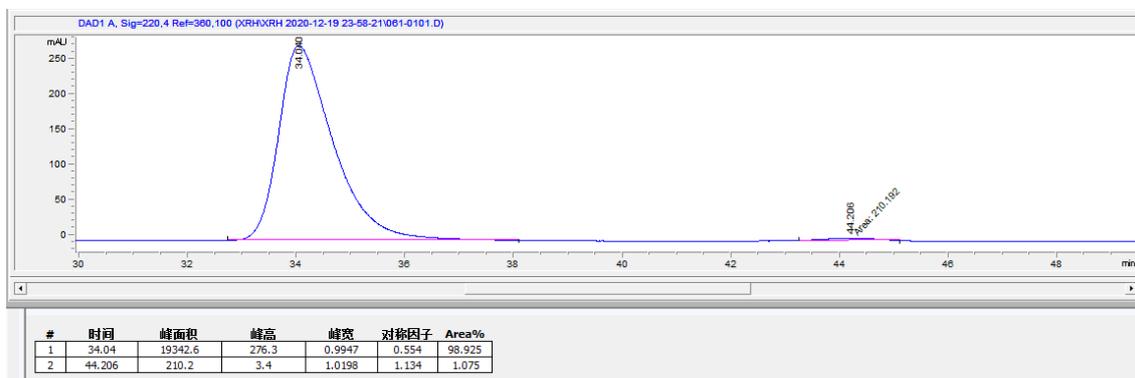
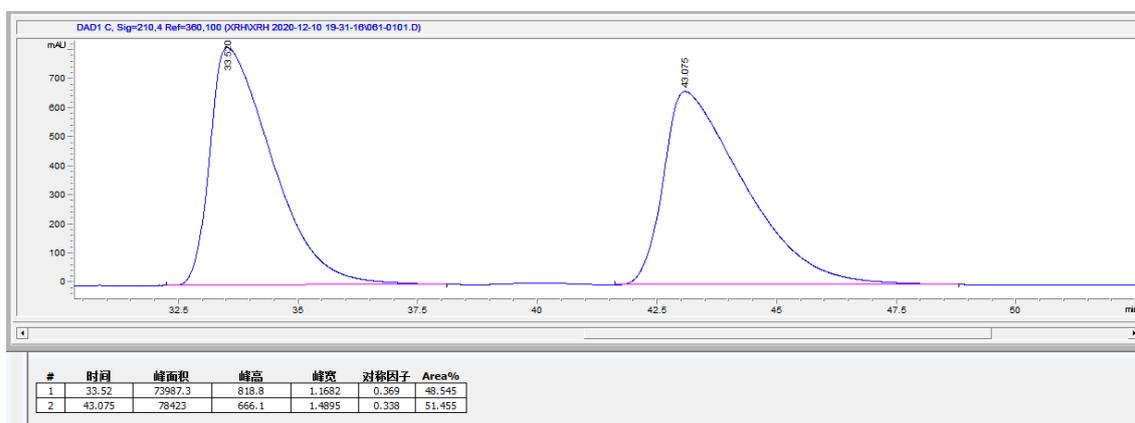
$^{31}\text{P}$  NMR (202 MHz, Chloroform- $d$ ) 39.58

ESI-MS:  $m/z$  169.00  $[\text{M}+\text{H}]^+$ ,

HRMS (ESI) calculated for  $[\text{M}+\text{H}, \text{C}_9\text{H}_{14}\text{OP}]^+$ : 169.0777 found 169.0784; calculated for  $[\text{M}+\text{Na}, \text{C}_9\text{H}_{13}\text{OPNa}]^+$ : 191.0596 found: 191.0604

$[\alpha]_{\text{D}}^{25}$ : -11.0239 ( $c=0.8000\text{g}/100\text{ml}$ ,  $\text{CHCl}_3$ ).

Chiral HPLC conditions: Cellulose-2,  $i$ -PrOH-hexane 10/90, flow rate 1.00 mL/min, 220 nm.  $t_1 = 32.52$  min,  $t_2 = 43.075$  min. 97% ee



Name: (S)-methyl(phenyl)(propyl)phosphine oxide

Physical States: colorless oil

Yield: 70% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 0.98 (td, *J* = 7.3, 1.0 Hz, 3H), 1.45 – 1.66 (m, 2H), 1.69 (d, *J* = 12.7 Hz, 3H), 1.80 – 2.00 (m, 2H), 7.45 – 7.56 (m, 3H), 7.70 (ddt, *J* = 11.3, 6.7, 1.5 Hz, 2H).

**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 15.42 (d, *J* = 3.5 Hz, 1C), 15.62 (d, *J* = 15.8 Hz, 1C), 16.02 (d, *J* = 69.9 Hz, 1C), 33.88 (d, *J* = 70.1 Hz, 1C), 128.65 (d, *J* = 11.3 Hz, 1C), 130.01 (d, *J* = 9.5 Hz, 1C), 131.57, 133.70 (d, *J* = 95.0 Hz, 1C)

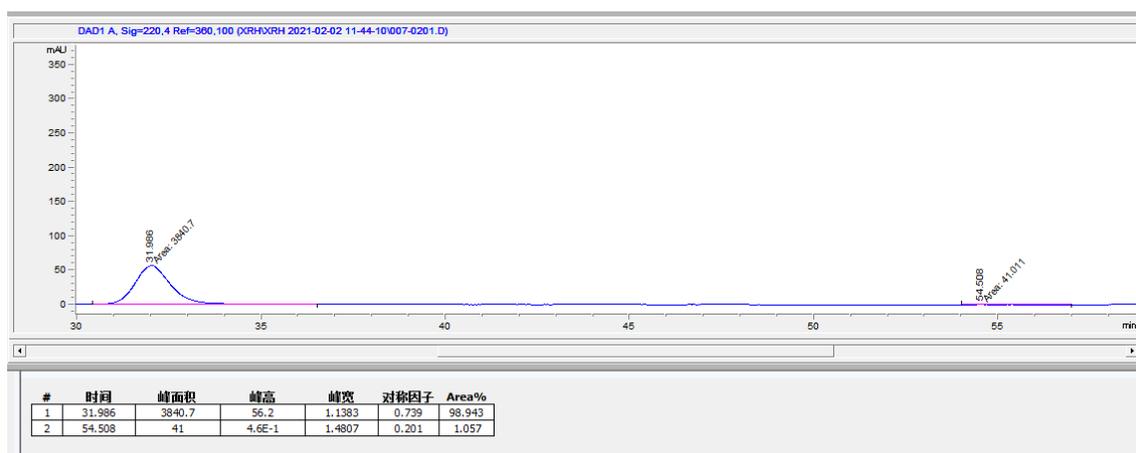
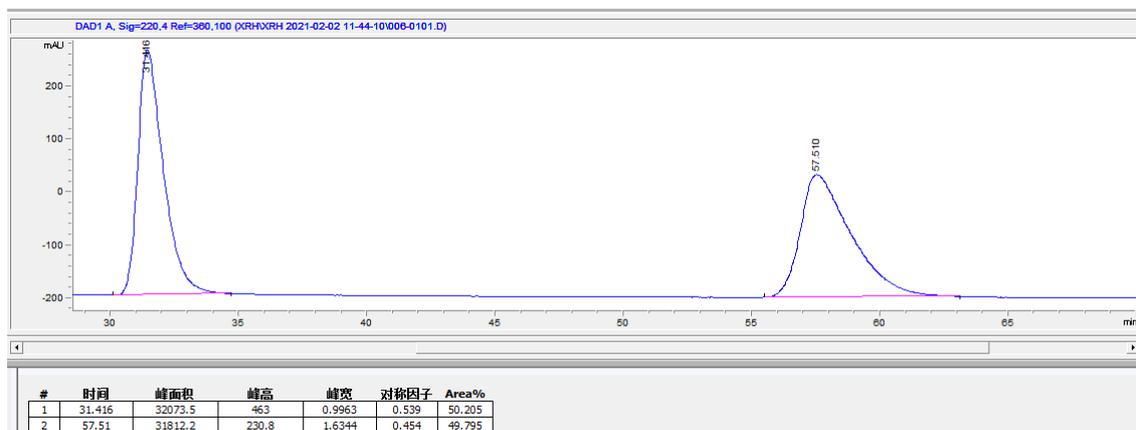
**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** 37.90

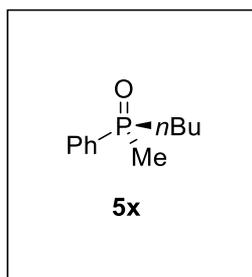
**ESI-MS:** *m/z* 183.00 [M+H]<sup>+</sup>, 205.00 [M+Na]<sup>+</sup>

**HRMS (ESI)** calculated for [M+H, C<sub>10</sub>H<sub>16</sub>OP]<sup>+</sup>: 183.0933 found 183.0937; calculated for [M+Na, C<sub>10</sub>H<sub>15</sub>OPNa]<sup>+</sup>: 205.0753 found: 205.0757

[α]<sub>D</sub><sup>25</sup>: -17.8696 (c = 0.1400g/100ml, CHCl<sub>3</sub>).

Chiral HPLC conditions: Cellulose-2, *i*-PrOH-hexane 10/90, flow rate 1.00 mL/min, 220 nm. *t*<sub>1</sub> = 25.011 min, *t*<sub>2</sub> = 37.728 min. 97% ee





**Name:** (S)-butyl(methyl)(phenyl)phosphine oxide

**Physical States:** colorless oil

**Yield:** 70% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 0.80 (t, *J* = 7.2 Hz, 3H), 1.31 (h, *J* = 7.1 Hz, 2H), 1.36 – 1.58 (m, 2H), 1.62 (s, 3H), 1.76 – 1.95 (m, 2H), 7.43 (tdd, *J* = 8.6, 6.5, 4.8 Hz, 3H), 7.61 – 7.69 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 13.55, 16.00 (d, *J* = 69.3 Hz, 1C), 22.67 – 25.03 (m, 1C), 31.46 (d, *J* = 70.8 Hz, 1C), 128.62 (d, *J* = 11.3 Hz, 1C), 129.97 (d, *J* = 9.0 Hz, 1C), 131.54, 133.65 (d, *J* = 95.2 Hz, 1C).

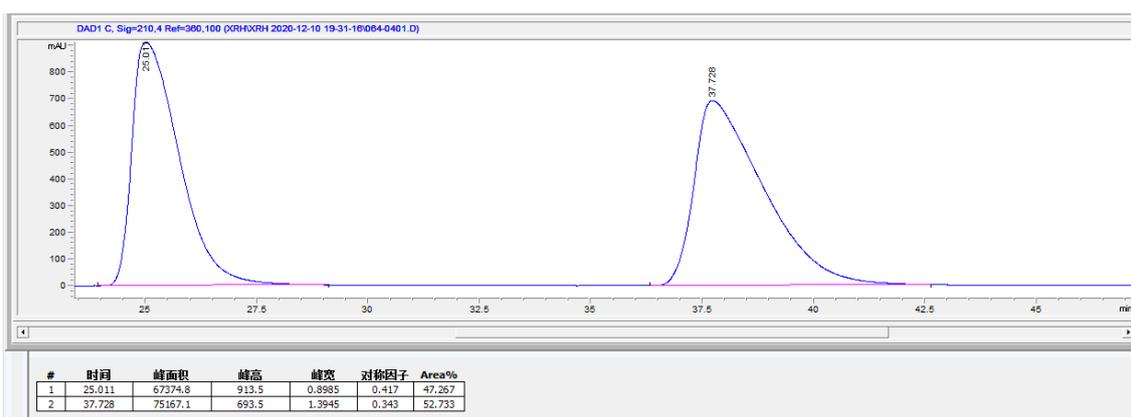
**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** 38.18

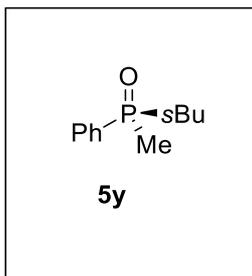
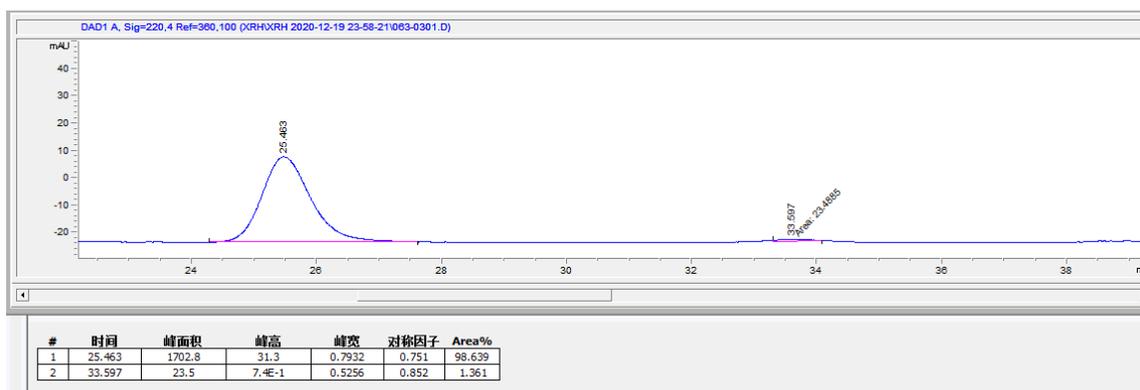
**ESI-MS:** *m/z* 197.05 [M+H]<sup>+</sup>, 219.05 [M+Na]<sup>+</sup>

**HRMS (ESI)** calculated for [M+H, C<sub>11</sub>H<sub>18</sub>OP]<sup>+</sup>: 197.1090 found 197.1091; calculated for [M+Na, C<sub>11</sub>H<sub>17</sub>OPNa]<sup>+</sup>: 219.0909 found: 219.0912.

[α]<sub>D</sub><sup>25</sup>: -0.0197 (c = 1.1200g/100ml, CHCl<sub>3</sub>).

Chiral HPLC conditions: Cellulose-2, *i*-PrOH-hexane 10/90, flow rate 1.00 mL/min, 220 nm. *t*<sub>1</sub> = 25.011 min, *t*<sub>2</sub> = 37.728 min. 97% ee





**Name:** (S)-(methyl)(phenyl)(sec-butyl)phosphine oxide

**Physical States:** colorless oil,

**Yield:** 70% yield,

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 0.91 (t, *J* = 7.4 Hz, 1H), 0.96 – 1.10 (m, 3H), 1.17 (dd, *J* = 16.9, 7.1 Hz, 2H), 1.22 – 1.38 (m, 1H), 1.66 – 1.72 (m, 3H), 1.73 – 1.93 (m, 2H), 7.44 – 7.55 (m, 3H), 7.69 (dddt, *J* = 9.7, 6.7, 2.9, 1.5 Hz, 2H).

**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 11.72 (d, *J* = 11.5 Hz, 1C), 12.21 (d, *J* = 5.5 Hz, 1C), 12.31 (d, *J* = 4.6 Hz, 1C), 22.20 (d, *J* = 19.2 Hz, 1C), 36.10 (d, *J* = 3.6 Hz, 1C), 36.67 (d, *J* = 3.5 Hz, 1C), 128.21 – 129.78 (m, 1C), 130.06 – 130.92 (m, 1C), 131.52, 132.54 (d, *J* = 21.6 Hz, 1C), 133.27 (d, *J* = 21.8 Hz, 1C).

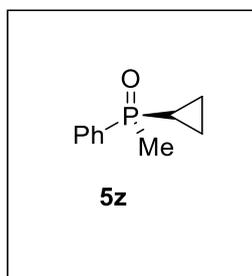
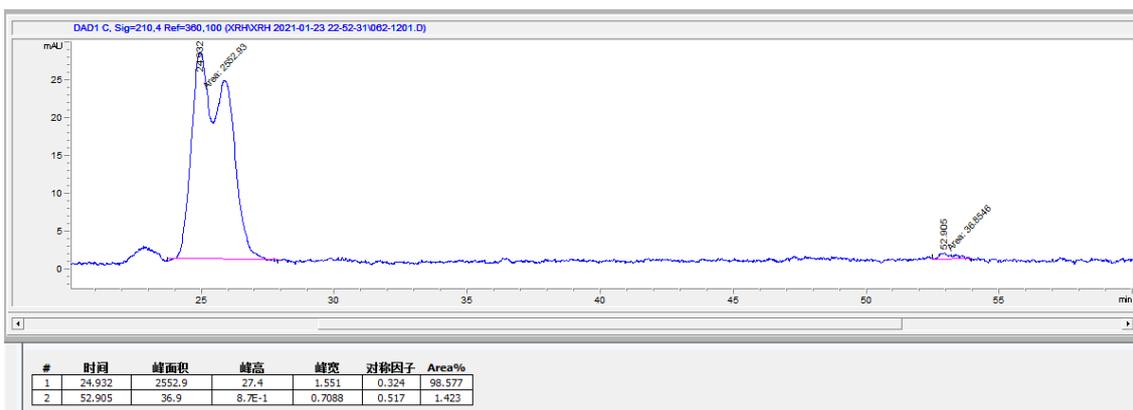
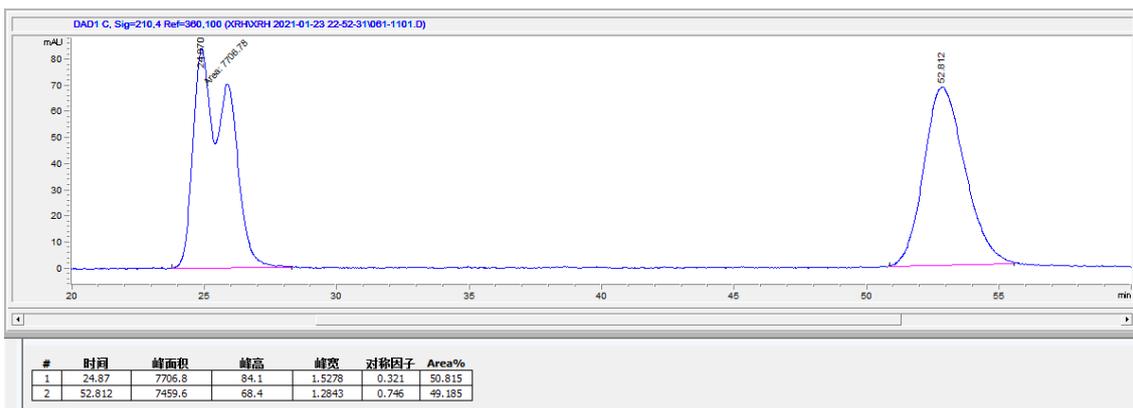
**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** 43.61

**ESI-MS:** *m/z* 196.90 [M+H]<sup>+</sup>,

**HRMS (ESI)** calculated for [M+H, C<sub>11</sub>H<sub>18</sub>OP]<sup>+</sup>: 197.1090 found 197.1091; calculated for [M+Na, C<sub>11</sub>H<sub>17</sub>OPNa]<sup>+</sup>: 219.0909 found: 219.0914.

[α]<sub>D</sub><sup>25</sup>: -3.2184 (c = 0.4480g/100ml, CHCl<sub>3</sub>).

Chiral HPLC conditions: Cellulose-2, *i*-PrOH-hexane 10/90, flow rate 1.00 mL/min, 220 nm. *t*<sub>1</sub> = 24.870 min, *t*<sub>2</sub> = 52.812 min. 97% ee



**Name:** (S)-cyclopropyl(methyl)(phenyl)phosphine oxide

**Physical States:** colorless oil,

**Yield:** 70% yield,

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 0.70 – 0.78 (m, 1H), 0.79 – 0.88 (m, 2H), 0.88 – 0.98 (m, 2H), 1.66 (d, *J* = 13.0 Hz, 3H), 7.38 – 7.48 (m, 3H), 7.65 – 7.72 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 2.55 (d, *J* = 4.5 Hz, 1C), 2.76 (d, *J* = 3.4 Hz, 1C), 8.47 (d, *J* = 101.6 Hz, 1C), 16.19 (d, *J* = 73.8 Hz, 1C), 128.58 (d, *J* = 11.4 Hz, 1C), 129.89 (d, *J* = 9.0 Hz, 1C), 131.58 (d, *J* = 3.2 Hz, 1C), 134.22 (d, *J* = 100.6 Hz, 1C).

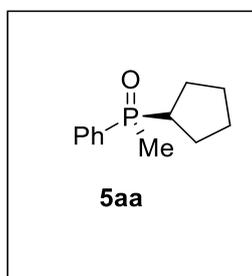
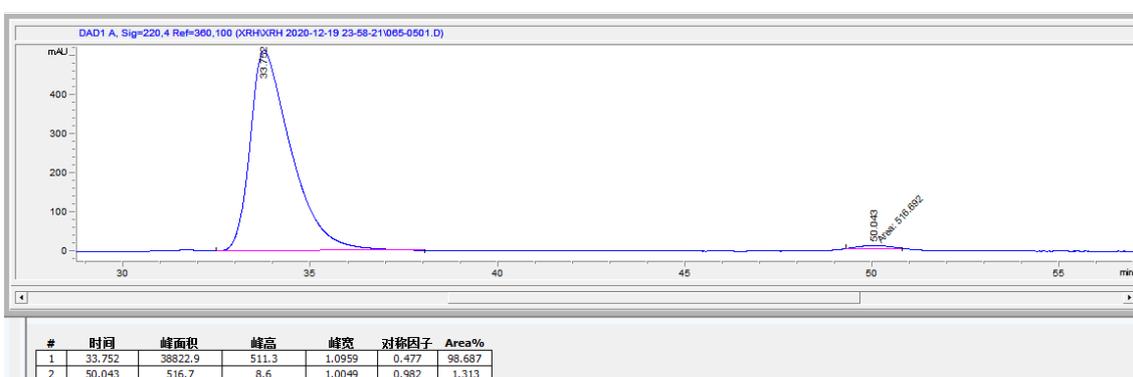
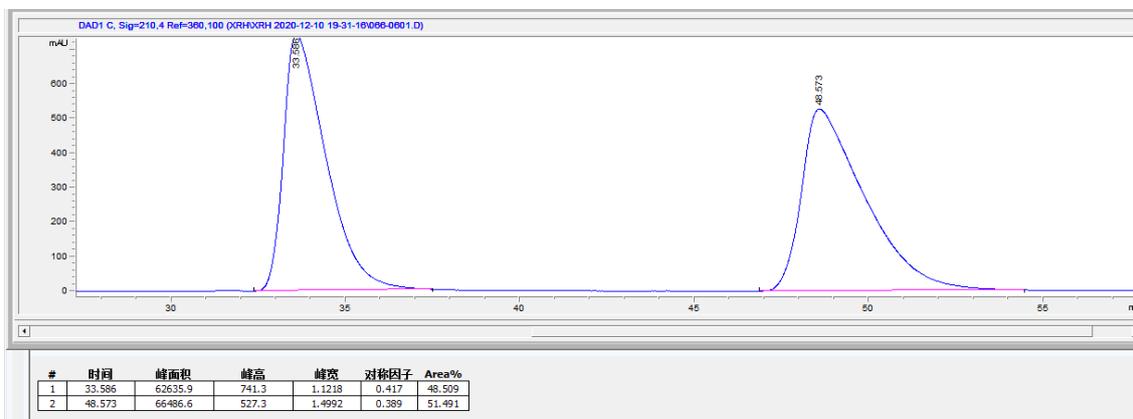
**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** 36.71

**ESI-MS:** *m/z* 180.95 [M+H]<sup>+</sup>, 203.00 [M+Na]<sup>+</sup>

**HRMS (ESI)** calculated for [M+H, C<sub>10</sub>H<sub>14</sub>OP]<sup>+</sup>: 181.0777 found 181.0782; calculated for [M+Na, C<sub>10</sub>H<sub>13</sub>OPNa]<sup>+</sup>: 203.0596 found: 203.0600.

$[\alpha]_D^{25}$ : -46.5436 (c = 0.9520g/100ml, CHCl<sub>3</sub>).

Chiral HPLC conditions: Cellulose-2, *i*-PrOH-hexane 10/90, flow rate 1.00 mL/min, 220 nm.  $t_1 = 33.752$  min,  $t_2 = 50.043$  min. 97% ee



**Name:** (*S*)-cyclopentyl(methyl)(phenyl)phosphine oxide

**Physical States:** colorless oil

**Yield:** 70% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 1.50 – 1.64 (m, 4H), 1.67 (d, *J* = 12.4 Hz, 4H), 1.70 – 1.73 (m, 1H), 1.76 – 1.99 (m, 2H), 2.21 (pt, *J* = 8.8, 5.2 Hz, 2H), 7.43 – 7.53 (m, 3H), 7.70 (ddd, *J* = 10.9, 8.1, 1.6 Hz, 2H)

**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 14.78 (d, *J* = 69.0 Hz, 1C), 26.30 (d, *J* = 9.0 Hz, 1C), 26.48 (d, *J* = 9.1 Hz, 1C), 26.72 (d, *J* = 10.9 Hz, 1C), 39.59 (d, *J* = 74.6 Hz, 1C), 128.53 (d, *J* = 11.2 Hz, 1C), 130.28 (d, *J* = 9.0 Hz, 1C), 131.43 (d, *J* = 3.2 Hz, 1C), 133.73 (d, *J* = 93.9 Hz, 1C).

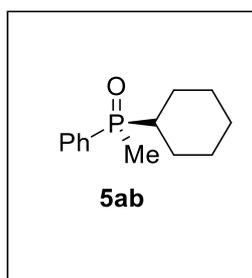
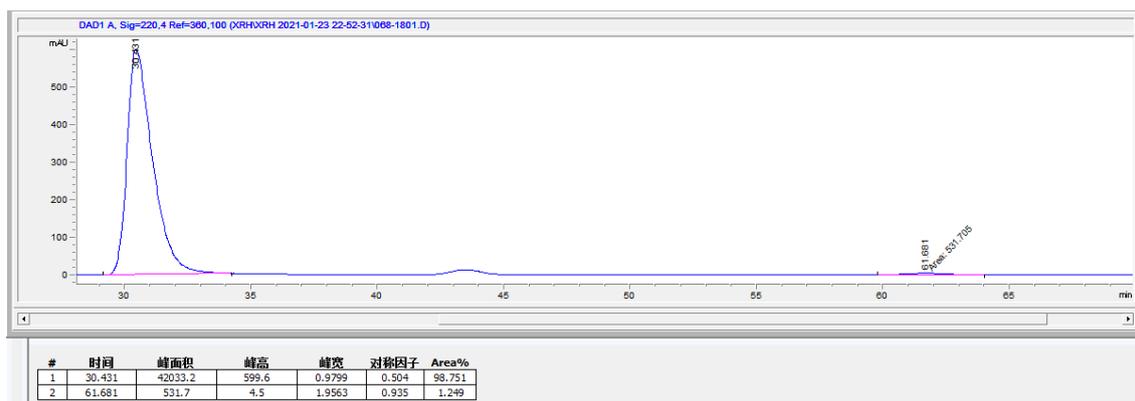
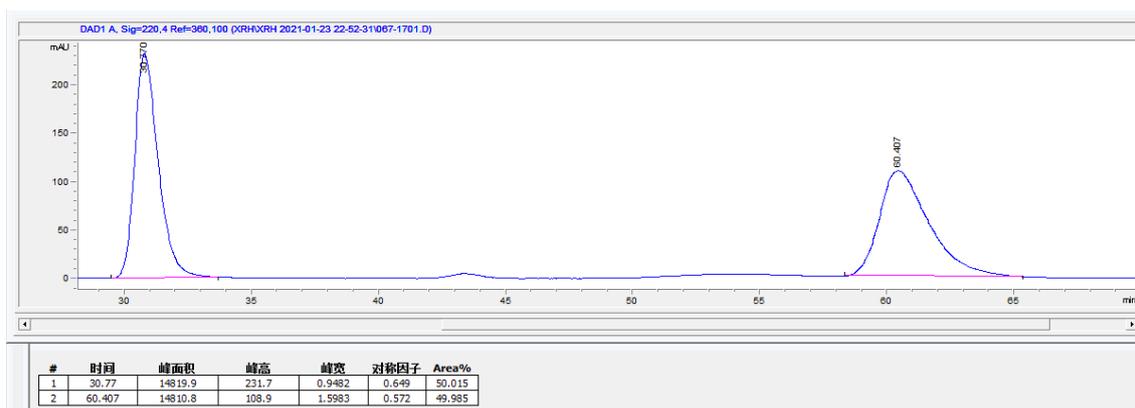
**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** δ 40.69..

ESI-MSm/z 197.00 [M+H]<sup>+</sup>, 205.00 [M+Na]<sup>+</sup>;

HRMS (ESI) calculated for [M+H, C<sub>10</sub>H<sub>16</sub>OP]<sup>+</sup>: 183.0933 found 183.0937; calculated for [M+Na, C<sub>10</sub>H<sub>15</sub>OPNa]<sup>+</sup>: 205.0753 found: 205.0757.

[α]<sub>D</sub><sup>25</sup>: -15.3021 (c = 0.8960g/100ml, CHCl<sub>3</sub>)..

Chiral HPLC conditions: Cellulose-2, *i*-PrOH-hexane 10/90, flow rate 1.00 mL/min, 220 nm. *t*<sub>1</sub> = 30.401 min, *t*<sub>2</sub> = 50.407 min. 97% ee



**Name:** (*S*)-cyclohexyl(methyl)(phenyl)phosphine oxide (**5ap**):

**Physical States:** colorless oil

**Yield:** 70% yield

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 1.09 – 1.41 (m, 6H), 1.63 – 1.70 (m, 5H), 1.74 (tp, J = 9.2, 3.1 Hz, 2H), 1.80 (s, 1H), 1.89 – 1.97 (m, 1H), 7.43 – 7.53 (m, 3H), 7.66 (ddt, J = 10.8, 6.7, 1.5 Hz, 2H).

$^{13}\text{C}$  NMR (126 MHz, Chloroform- $d$ )  $\delta$  12.93 (d,  $J = 67.7$  Hz, 1C), 25.02, 25.74, 26.19 (d,  $J = 3.4$  Hz, 1C), 26.30 (d,  $J = 3.5$  Hz, 1C), 39.69 (d,  $J = 72.2$  Hz, 1C), 128.49 (d,  $J = 11.3$  Hz, 1C), 130.49 (d,  $J = 9.0$  Hz, 1C), 131.48, 132.67 (d,  $J = 92.8$  Hz, 1C).

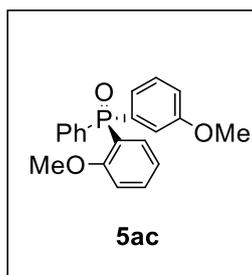
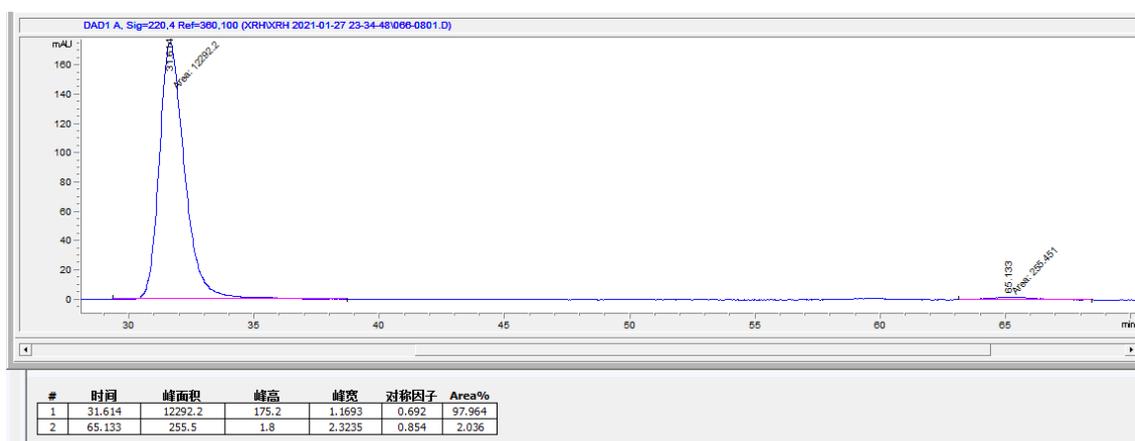
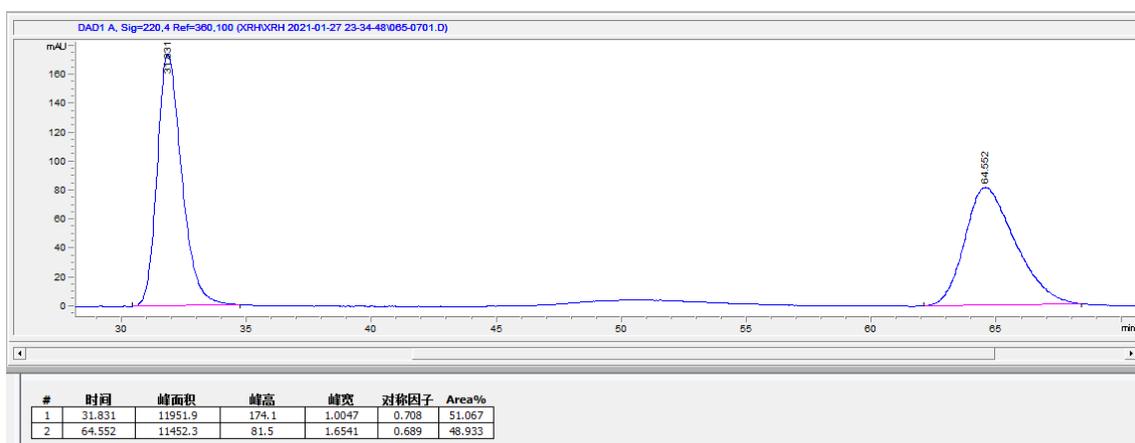
$^{31}\text{P}$  NMR (202 MHz, Chloroform- $d$ )  $\delta$  41.31.

ESI-MS:  $m/z$  223.05  $[\text{M}+\text{H}]^+$ ,

HRMS (ESI) calculated for  $[\text{M}+\text{H}, \text{C}_{13}\text{H}_{20}\text{OP}]^+$ : 223.1246 found 223.1247; calculated for  $[\text{M}+\text{Na}, \text{C}_{13}\text{H}_{19}\text{OPNa}]^+$ : 245.1066 found: 245.1067.

$[\alpha]_{\text{D}}^{25}$ :  $-10.8112$  ( $c = 0.6533\text{g}/100\text{ml}$ ,  $\text{CHCl}_3$ ).

Chiral HPLC conditions: Cellulose-2,  $i$ -PrOH-hexane 10/90, flow rate 1.00 mL/min, 220 nm.  $t_1 = 31.031$  min,  $t_2 = 64.552$  min. 97% ee



Name: (S)-(2-methoxyphenyl)(3-methoxyphenyl)(phenyl)phosphine oxide

**Physical States:** colorless oil

**Yield:** 70% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 3.57 (s, 3H), 3.78 (s, 3H), 6.91 (dd, *J* = 8.3, 5.2 Hz, 1H), 7.00 – 7.08 (m, 2H), 7.21 (ddt, *J* = 12.1, 7.5, 1.2 Hz, 1H), 7.29 – 7.36 (m, 2H), 7.42 (ddd, *J* = 8.5, 6.8, 3.0 Hz, 2H), 7.47 – 7.56 (m, 2H), 7.66 – 7.72 (m, 3H)

**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 55.34, 55.42, 111.46 (d, *J* = 6.7 Hz, 1C), 116.58 (d, *J* = 11.3 Hz, 1C), 117.71 (d, *J* = 3.2 Hz, 1C), 120.91 (d, *J* = 12.2 Hz, 1C), 124.15 (d, *J* = 10.2 Hz, 1C), 128.14 (d, *J* = 12.4 Hz, 1C), 129.30 (d, *J* = 14.0 Hz, 1C), 131.48 (d, *J* = 3.2 Hz, 1C), 131.78 (d, *J* = 10.2 Hz, 1C), 133.17 (d, *J* = 107.4 Hz, 1C), 134.09, 134.32, 134.98 (d, *J* = 7.9 Hz, 1C), 159.31 (d, *J* = 14.8 Hz, 1C), 161.01 (d, *J* = 3.4 Hz, 1C).

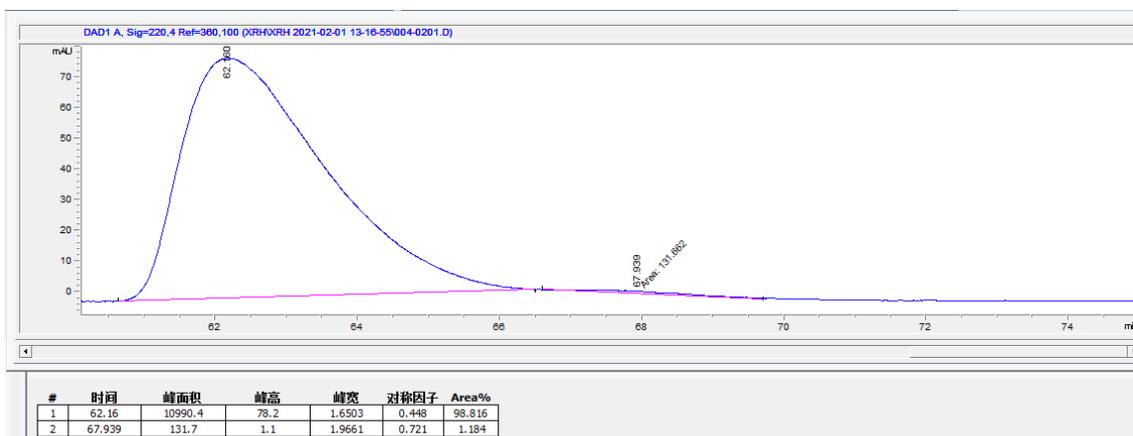
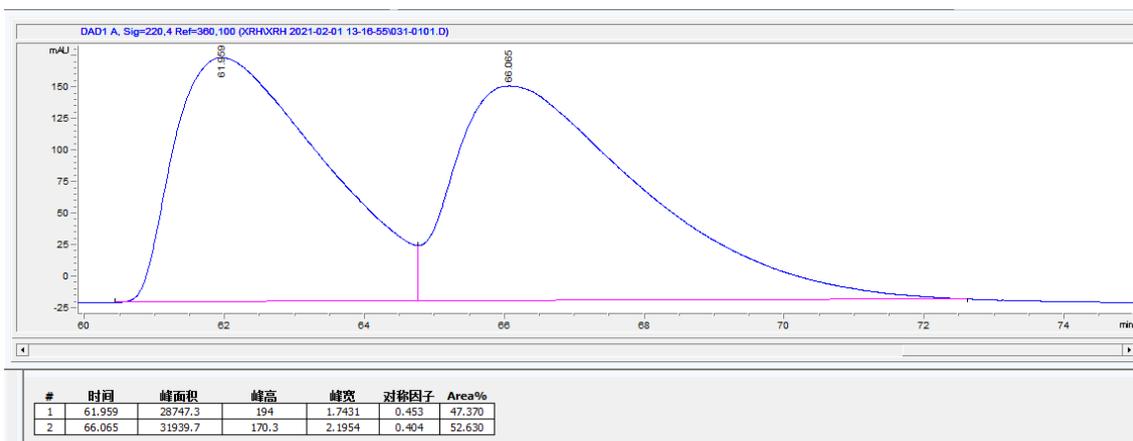
**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** δ 26.59..

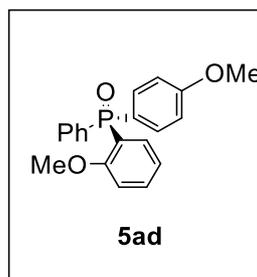
**ESI-MS:** *m/z* 339.10 [M+H]<sup>+</sup>, 360.70 [M+Na]<sup>+</sup>

**HRMS (ESI)** calculated for [M+H, C<sub>20</sub>H<sub>20</sub>O<sub>3</sub>P]<sup>+</sup>: 339.1145 found 339.1148; calculated for [M+Na, C<sub>20</sub>H<sub>19</sub>O<sub>3</sub>PNa]<sup>+</sup>: 361.0964 found: 361.0968.

[α]<sub>D</sub><sup>25</sup>: -10.1390 (c = 0.3333g/100ml, CHCl<sub>3</sub>)

Chiral HPLC conditions: OD-3, *i*-PrOH-hexane 3/97, flow rate 1.00 mL/min, 220 nm. *t*<sub>1</sub> = 61.959 min (*S*), *t*<sub>2</sub> = 66.065 min (*R*). 97% ee





**Name:** (S)-(2-methoxyphenyl)(4-methoxyphenyl)(phenyl)phosphine oxide

**Physical States:** colorless oil

**Yield:** 70% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 3.59 (s, 3H), 3.86 (s, 3H), 6.91 – 6.98 (m, 3H), 7.09 (tdd, *J* = 7.5, 2.0, 0.9 Hz, 1H), 7.43 (tdd, *J* = 8.2, 2.9, 1.3 Hz, 2H), 7.49 – 7.58 (m, 2H), 7.68 (dddd, *J* = 18.6, 11.9, 7.5, 1.6 Hz, 4H), 7.79 (ddd, *J* = 13.4, 7.5, 1.8 Hz, 1H).

**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 55.31, 111.35 (d, *J* = 6.3 Hz, 1C), 113.68 (d, *J* = 13.4 Hz, 1C), 120.23, 120.54 – 121.42 (m, 1C), 124.23 (d, *J* = 114.0 Hz, 1C), 128.08 (d, *J* = 12.5 Hz, 1C), 131.32, 131.75 (d, *J* = 10.7 Hz, 1C), 133.35, 133.78 (d, *J* = 12.2 Hz, 1C), 133.94 (d, *J* = 11.2 Hz, 1C), 134.15, 134.20, 134.98 (d, *J* = 7.0 Hz, 1C), 160.82 (d, *J* = 3.4 Hz, 1C), 162.13

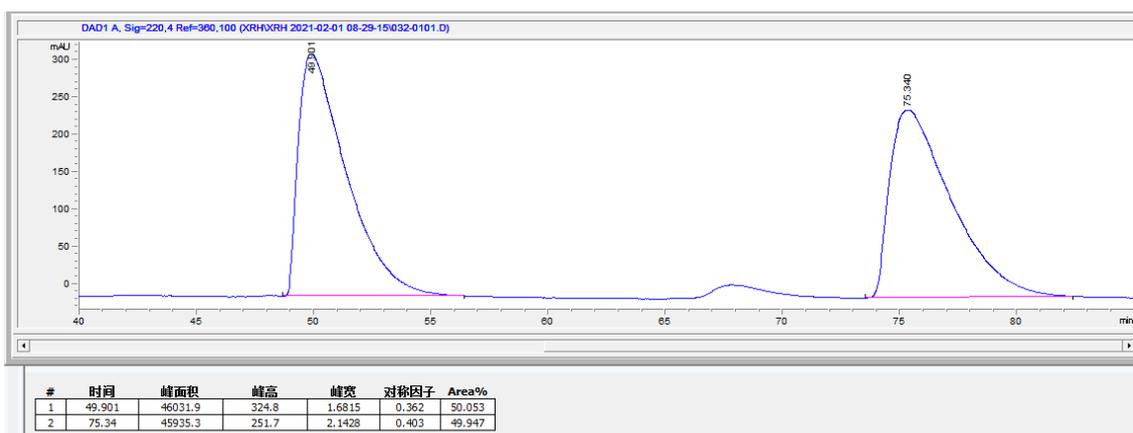
**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** δ 26.07.

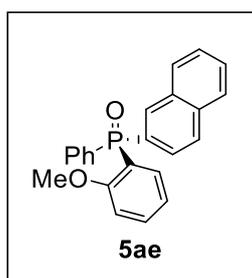
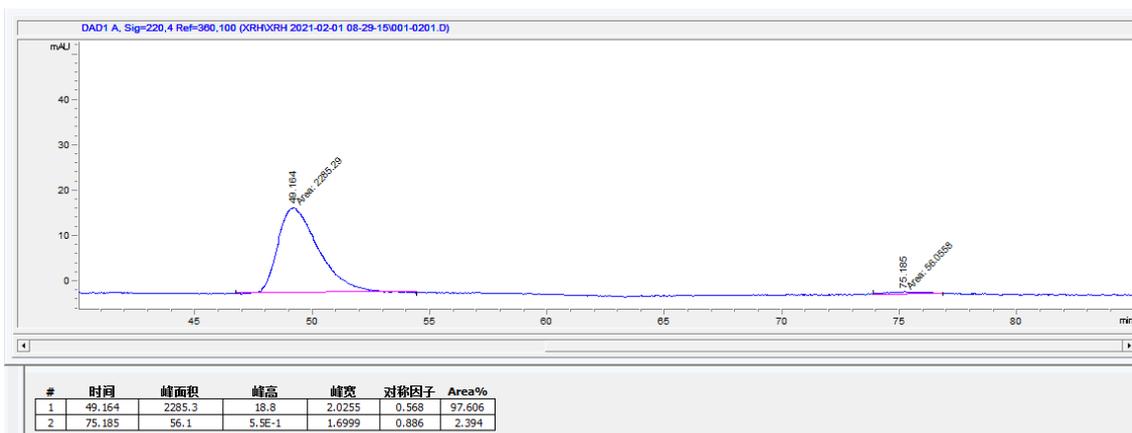
**ESI-MS:** *m/z* 339.15 [M+H]<sup>+</sup>, 361.10 [M+Na]<sup>+</sup>

**HRMS (ESI)** calculated for [M+H, C<sub>10</sub>H<sub>16</sub>OP]<sup>+</sup>: 339.1145 found 339.1152;.

[α]<sub>D</sub><sup>25</sup>: 1.5619 (c = 0.1933g/100ml, CHCl<sub>3</sub>).

Chiral HPLC conditions: OD-3, *i*-PrOH-hexane 5/95, flow rate 0.8 mL/min, 220 nm. *t*<sub>1</sub> = 49.901 min, *t*<sub>2</sub> = 75.34 min. 95% ee





**Name:** (S)-(2-methoxyphenyl)(naphthalen-2-yl)(phenyl)phosphine oxide

**Physical States:** colorless oil

**Yield:** 70% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)** δ 3.59 (s, 3H), 6.94 (dd, *J* = 8.3, 5.3 Hz, 1H), 7.10 (tdd, *J* = 7.5, 2.1, 0.9 Hz, 1H), 7.35 – 7.41 (m, 1H), 7.42 – 7.48 (m, 4H), 7.49 – 7.58 (m, 2H), 7.59 – 7.63 (m, 2H), 7.66 (dd, *J* = 8.4, 2.6 Hz, 2H), 7.71 – 7.85 (m, 5H).

**<sup>13</sup>C NMR (126 MHz, Chloroform-d)** δ 55.32, 111.42 (d, *J* = 6.7 Hz, 1C), 120.68, 121.02 (d, *J* = 12.0 Hz, 1C), 126.82 (d, *J* = 12.5 Hz, 1C), 127.27, 127.93 – 128.39 (m, 1C), 128.94, 131.51 (d, *J* = 3.3 Hz, 1C), 131.83 (d, *J* = 10.4 Hz, 1C), 132.39 (d, *J* = 10.3 Hz, 1C), 134.34, 135.04 (d, *J* = 6.8 Hz, 1C), 140.16, 144.15, 160.87

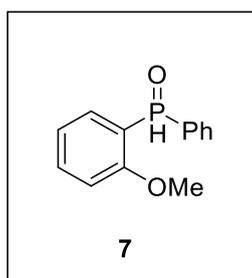
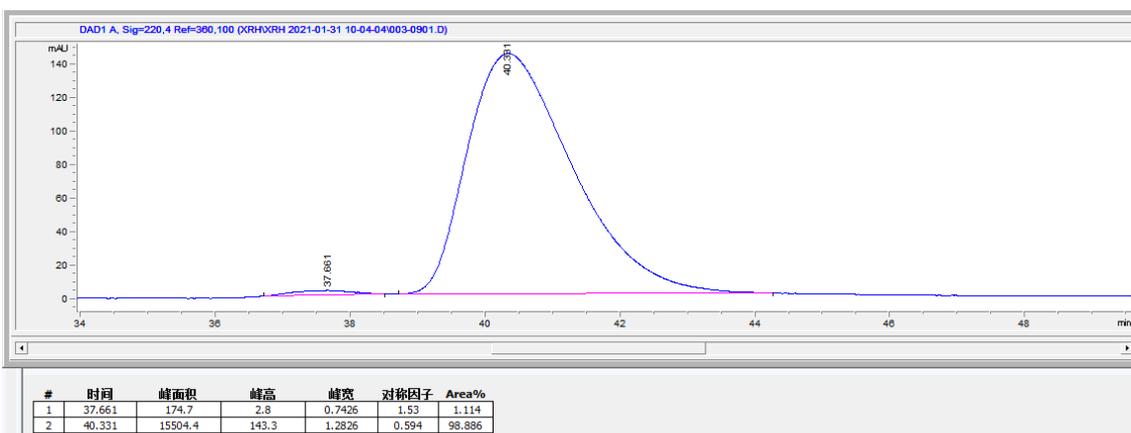
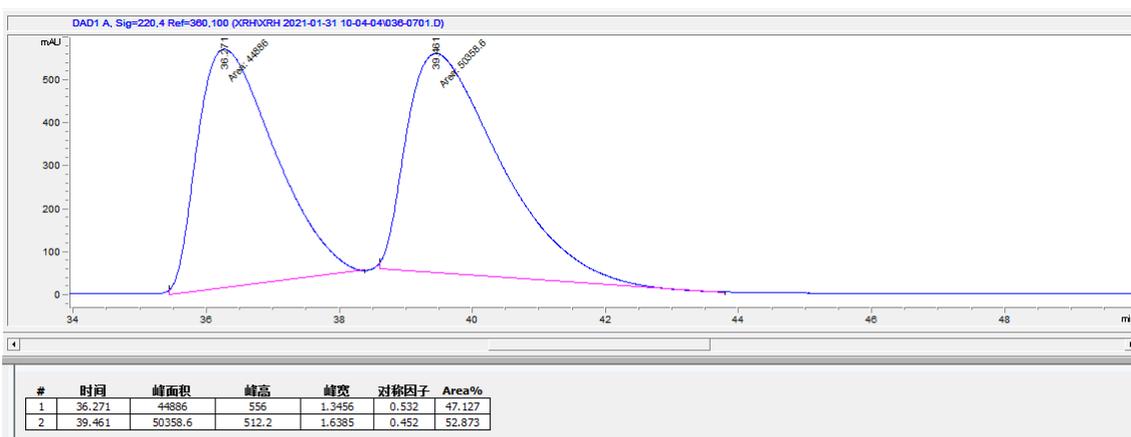
**<sup>31</sup>P NMR (202 MHz, Chloroform-d)** δ 26.22.

**ESI-MS:** *m/z* 359.15 [M+H]<sup>+</sup>, 381.15 [M+Na]<sup>+</sup>

**HRMS (ESI)** calculated for [M+H, C<sub>23</sub>H<sub>20</sub>O<sub>2</sub>P]<sup>+</sup>: 359.1195 found 359.1200; calculated for [M+Na, C<sub>23</sub>H<sub>19</sub>O<sub>2</sub>PNa]<sup>+</sup>: 381.1015 found:381.1021.

[α]<sub>D</sub><sup>25</sup>: -9.7485 (c = 0.0667g/100ml, CHCl<sub>3</sub>).

Chiral HPLC conditions: OD-3, *i*-PrOH-hexane 5/95, flow rate 1.00 mL/min, 220 nm. *t*<sub>1</sub> = 36.271 min, *t*<sub>2</sub> = 39.461 min. 97% ee



**Name:** (2-methoxyphenyl)(phenyl)phosphine oxide

**Physical State:** colorless oil

**Yield:** 70% yield

**<sup>1</sup>H NMR (500 MHz, Chloroform-d)**  $\delta$  3.76 (s, 3H), 6.90 (dd,  $J$  = 8.4, 5.6 Hz, 1H), 7.06 – 7.12 (m, 1H), 7.44 (ddd,  $J$  = 8.5, 6.7, 3.0 Hz, 2H), 7.49 – 7.56 (m, 2H), 7.66 (s, 0H), 7.69 – 7.84 (m, 3H), 8.66 (s, 0H).

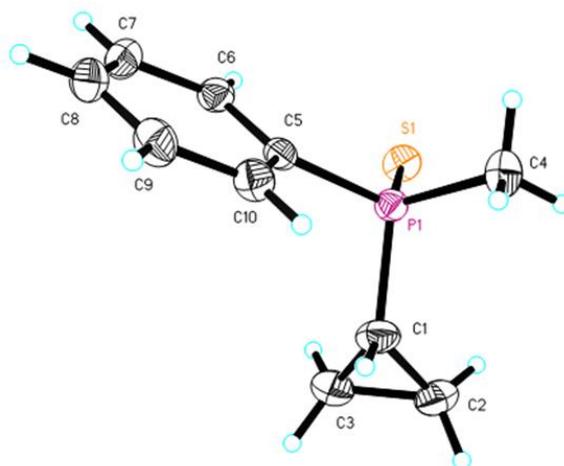
**<sup>13</sup>C NMR (126 MHz, Chloroform-d)**  $\delta$  55.56, 110.80 (d,  $J$  = 6.6 Hz, 1C), 119.33 (d,  $J$  = 101.8 Hz, 1C), 121.15 (d,  $J$  = 12.4 Hz, 1C), 128.54 (d,  $J$  = 13.5 Hz, 1C), 130.47 (d,  $J$  = 11.3 Hz), 1C, 131.68, 132.06 (d,  $J$  = 2.7 Hz, 1C), 132.51, 133.04 (d,  $J$  = 6.8 Hz, 1C), 134.46

**<sup>31</sup>P NMR (202 MHz, Chloroform-d)**  $\delta$  13.43.

**ESI-MS:** m/z 233.00 [M+H]<sup>+</sup>, 255.05 [M+Na]<sup>+</sup>

**HRMS (ESI)** calculated for [M+Na, C<sub>13</sub>H<sub>13</sub>O<sub>2</sub>PNa]<sup>+</sup>: 255.0545 found:255.0553.

## 12. X-ray structural data of 6 am



Crystal data and structure refinement for mo\_d8v20731\_0m.

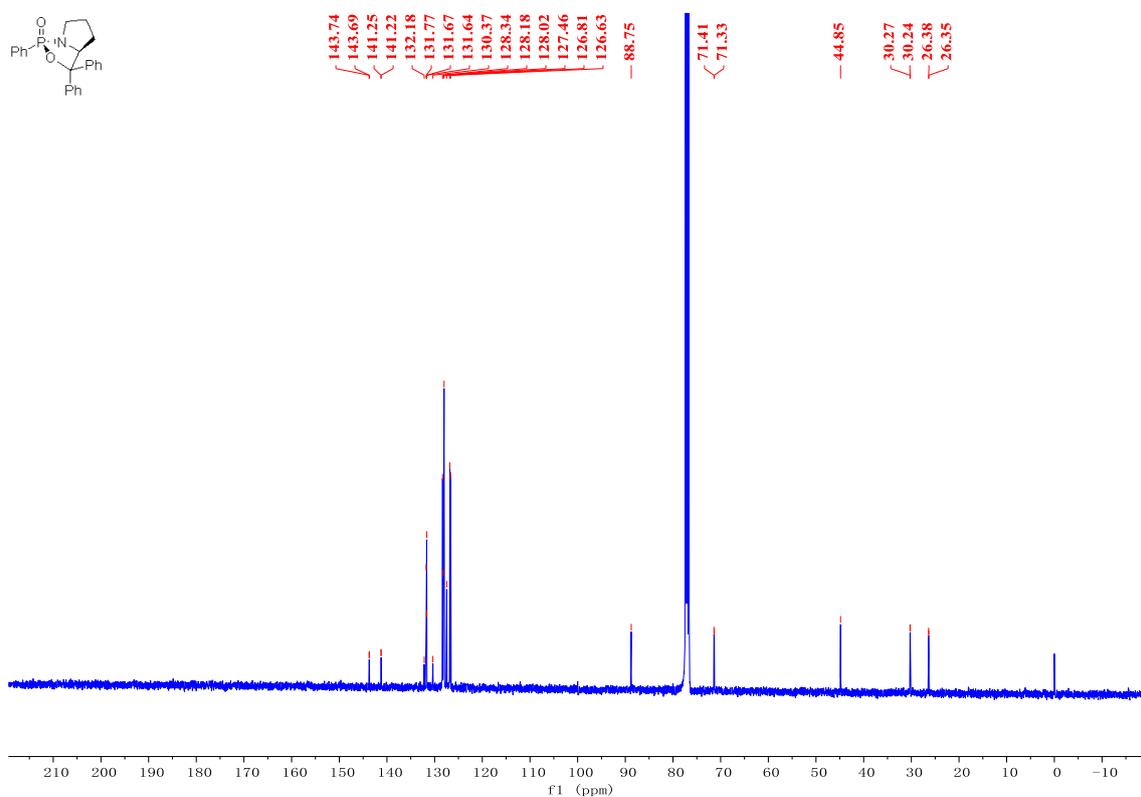
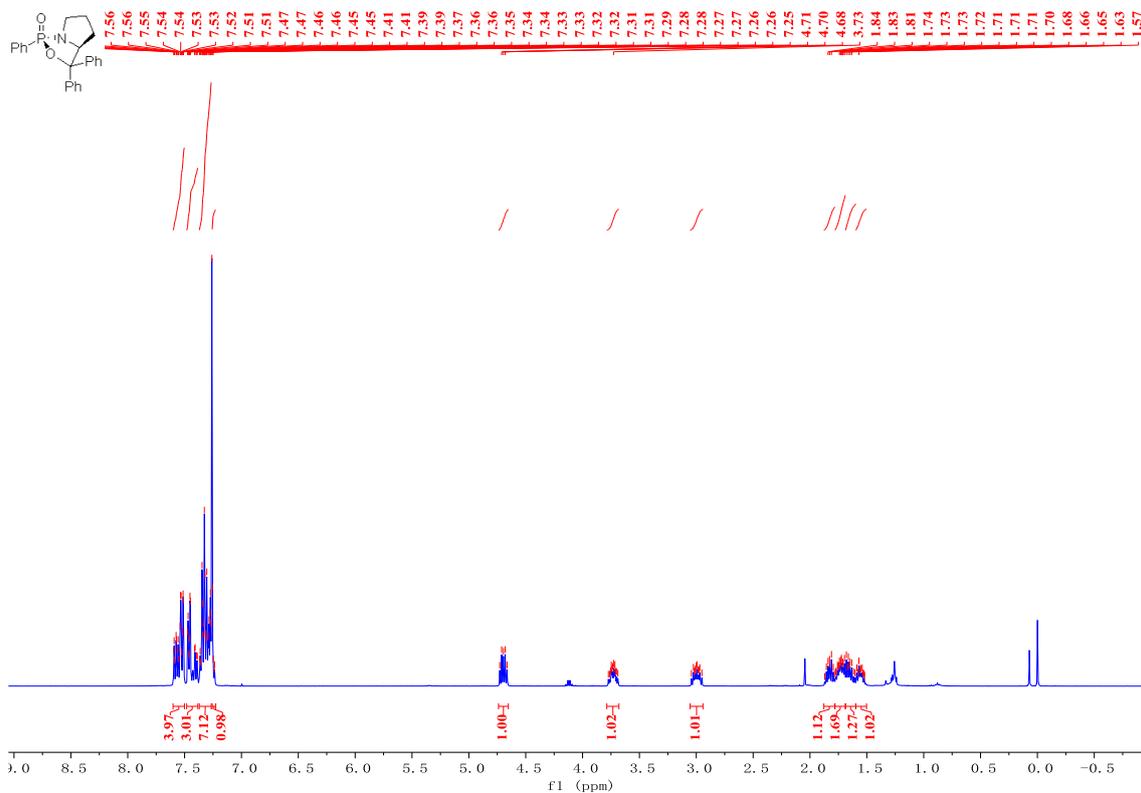
Identification code	mo_d8v20731_0m	
Empirical formula	C <sub>10</sub> H <sub>13</sub> P S	
Formula weight	196.23	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 9.1461(3) Å	α = 90 °
	b = 9.6810(3) Å	β = 90 °
	c = 11.8702(3) Å	γ = 90 °
Volume	1051.03(5) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.240 Mg/m <sup>3</sup>	
Absorption coefficient	0.405 mm <sup>-1</sup>	
F(000)	416	
Crystal size	0.170 x 0.140 x 0.120 mm <sup>3</sup>	
Theta range for data collection	2.715 to 25.995 °	
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -14 ≤ l ≤ 14	
Reflections collected	9523	
Independent reflections	2054 [R(int) = 0.0318]	
Completeness to theta = 25.242 °	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6532	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	2054 / 0 / 111	
Goodness-of-fit on F <sup>2</sup>	1.054	

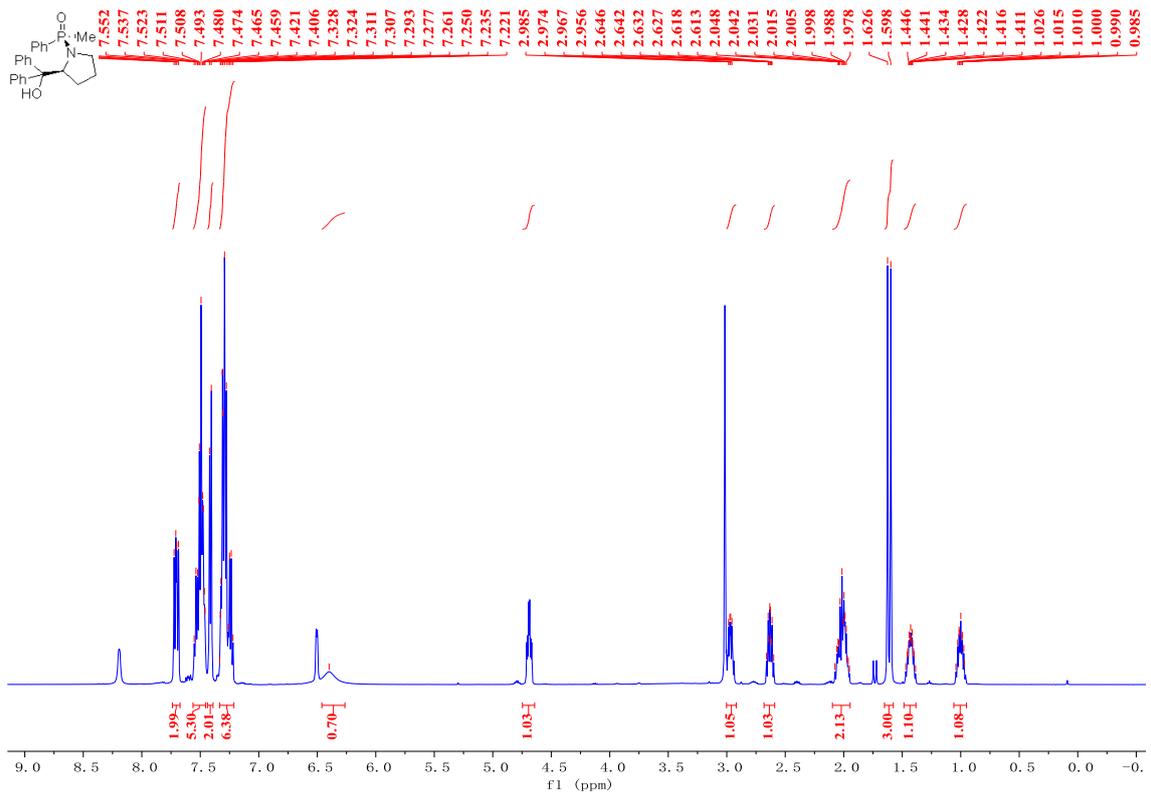
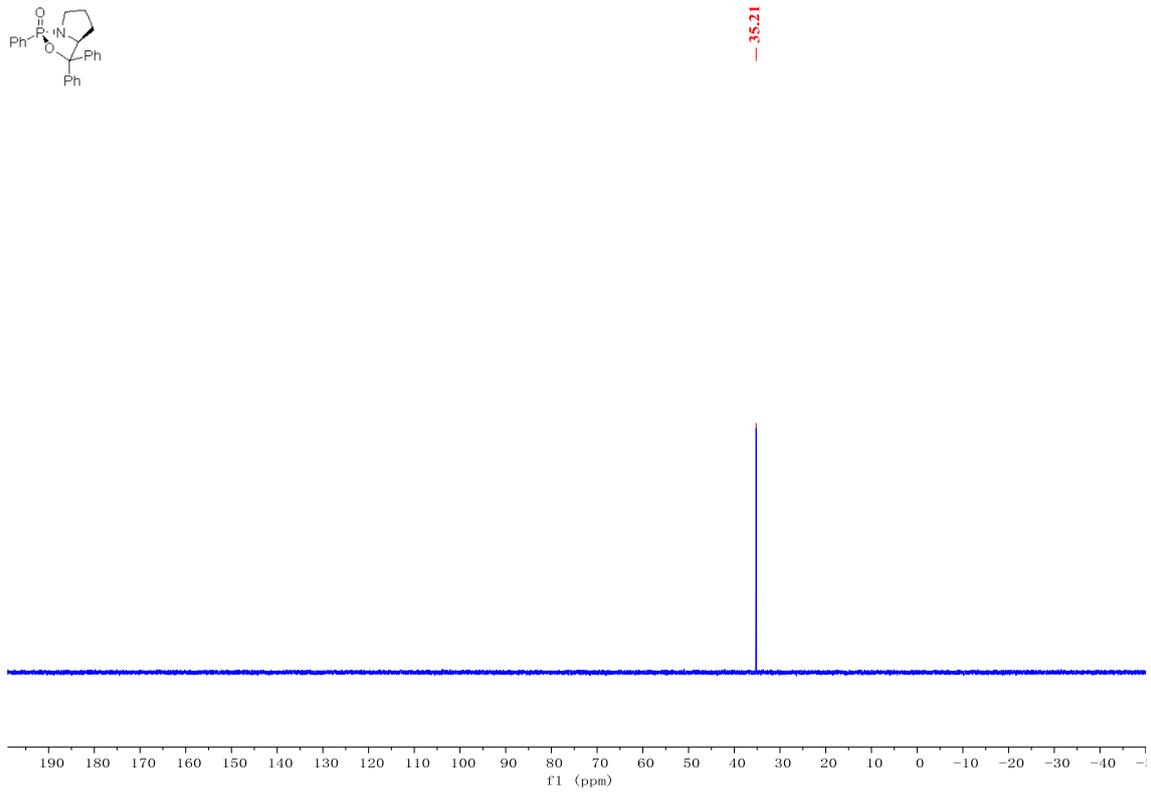
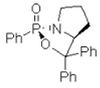
Final R indices [ $I > 2\sigma(I)$ ]	R1 = 0.0238, wR2 = 0.0656
R indices (all data)	R1 = 0.0247, wR2 = 0.0668
Absolute structure parameter	0.00(3)
Extinction coefficient	0.188(15)
Largest diff. peak and hole	0.253 and -0.170 e. $\text{\AA}^{-3}$

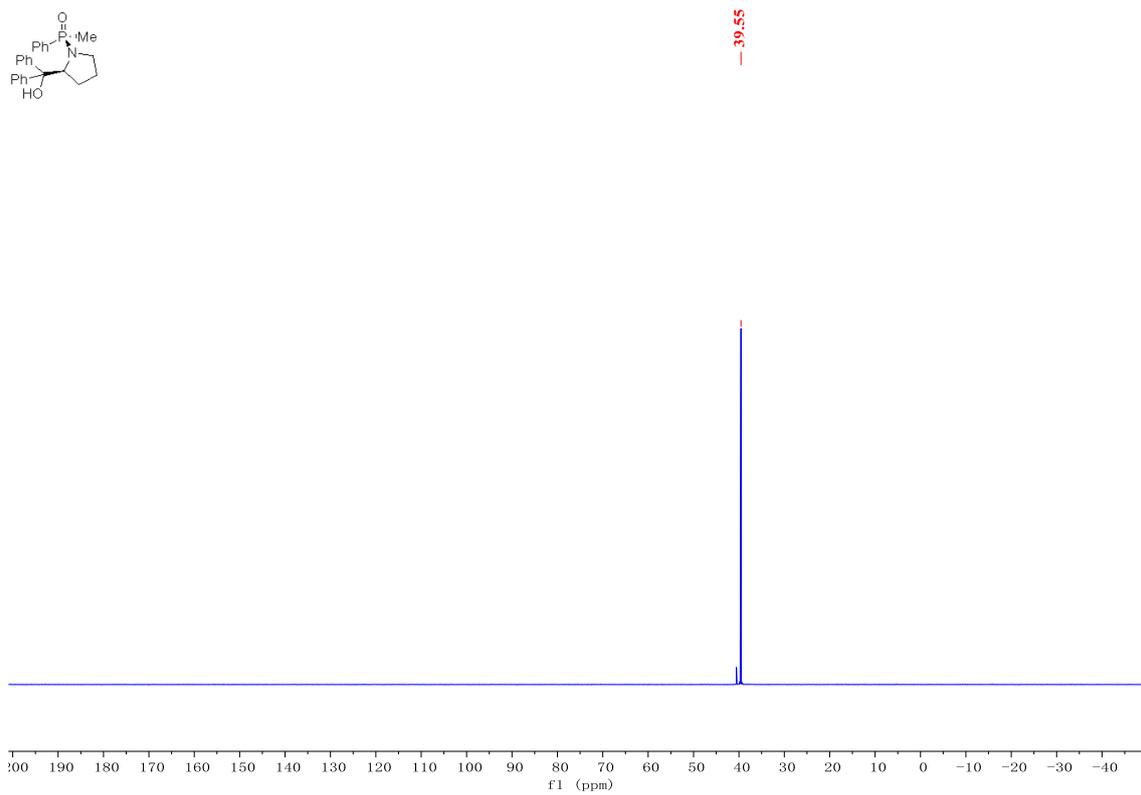
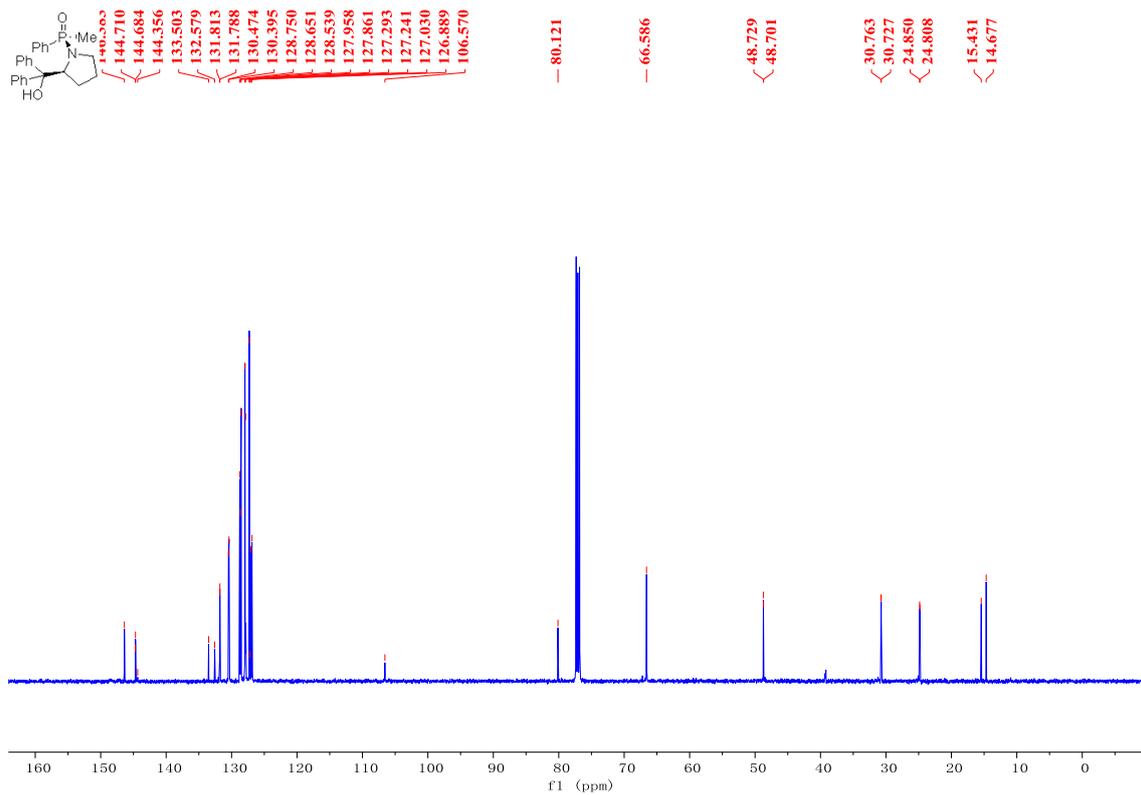
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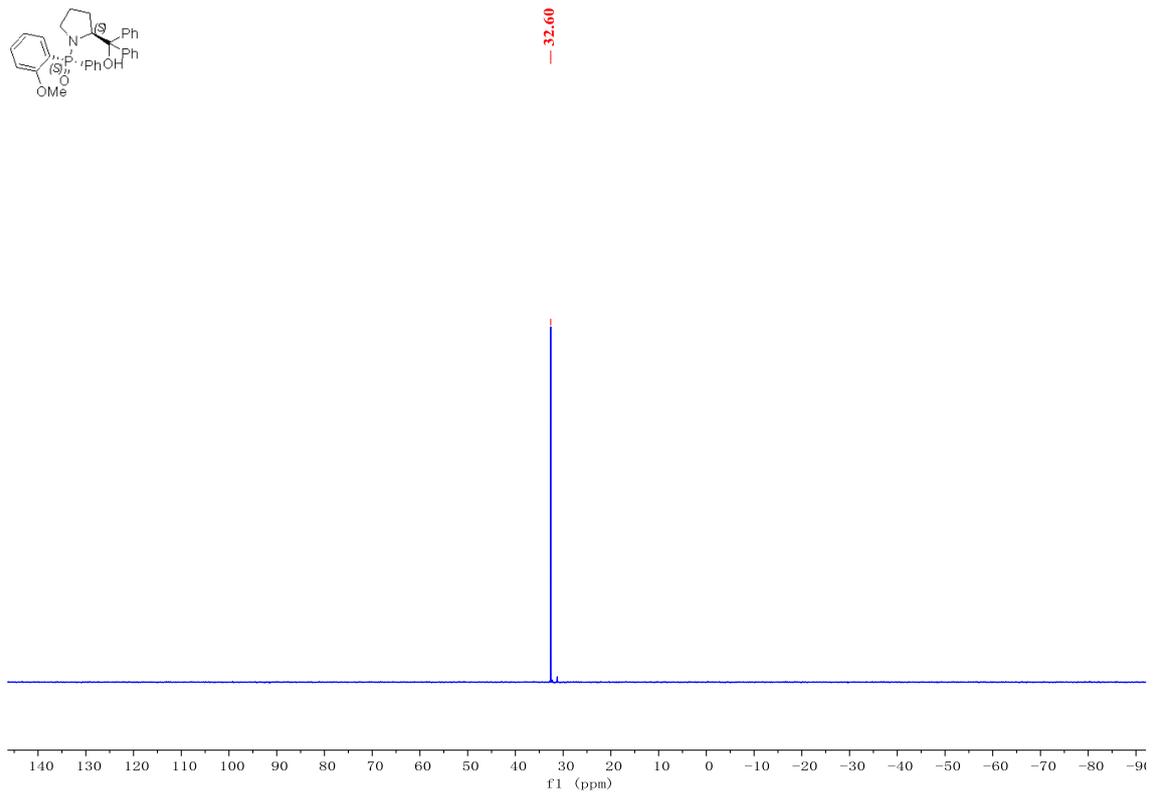
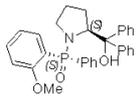
**14. NMR spectra (Note: The order of the spectrum of each compound is  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR,  $^{19}\text{F}$  NMR (if the compound contains fluorine) )**



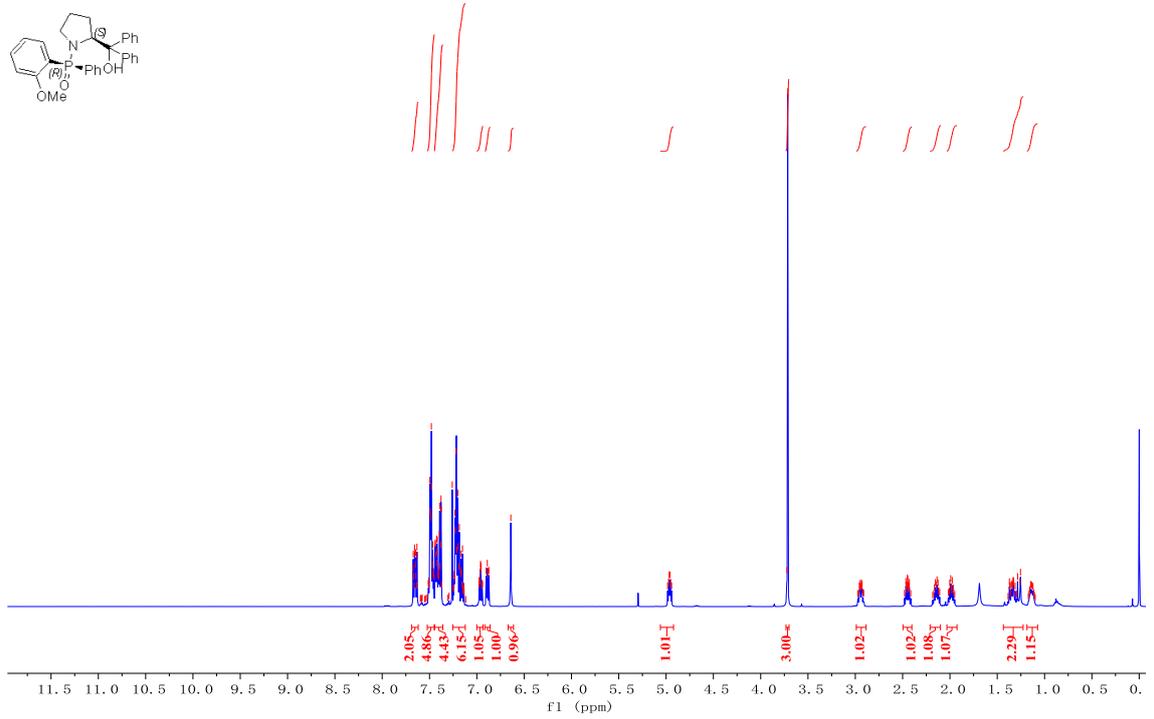
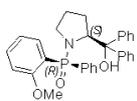


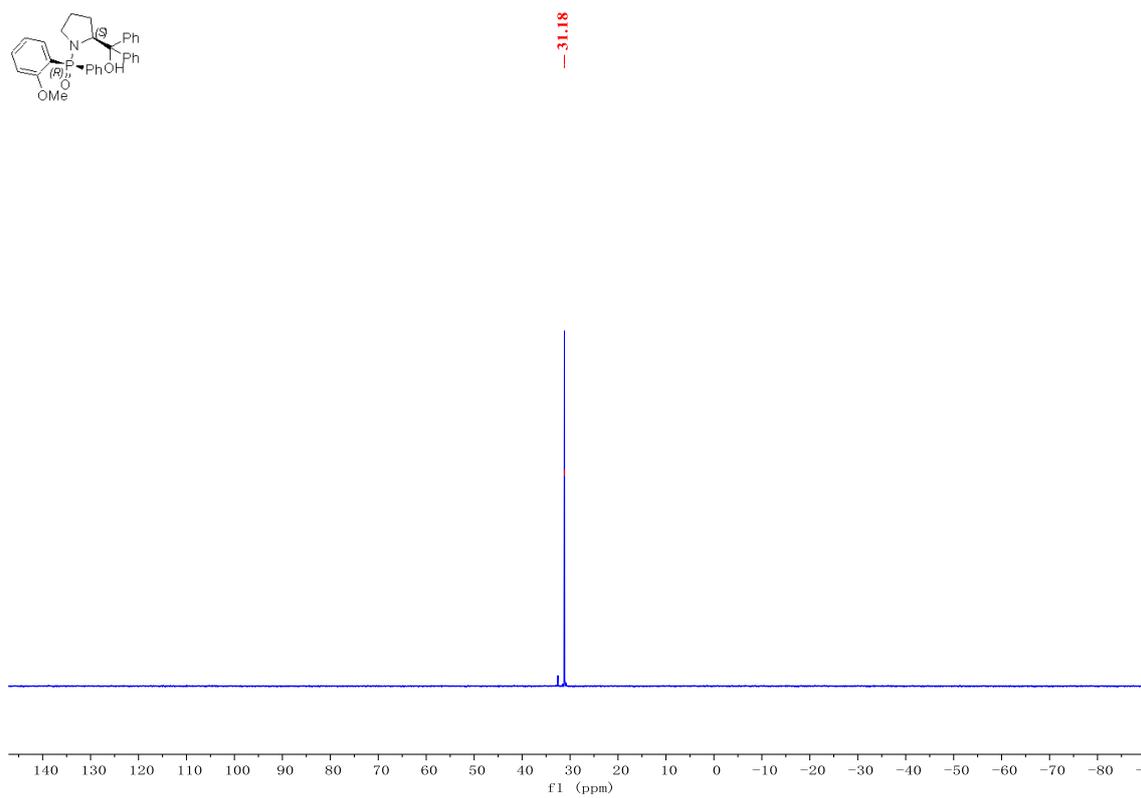
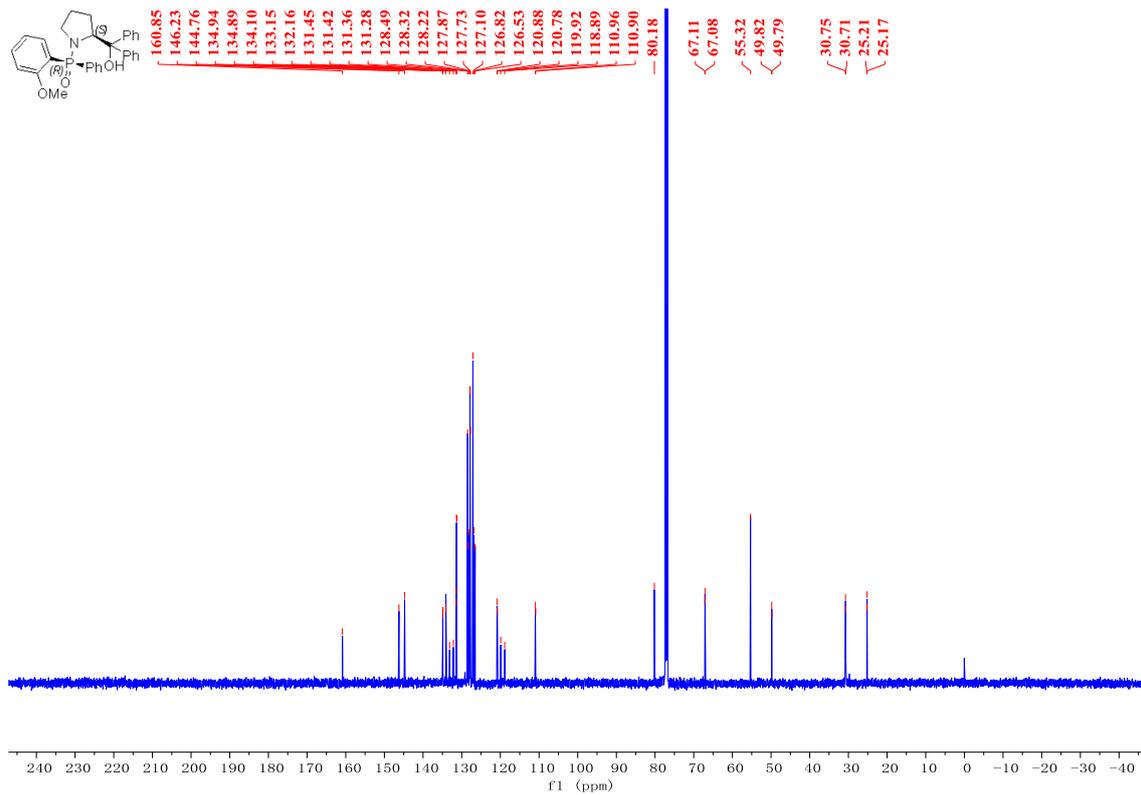


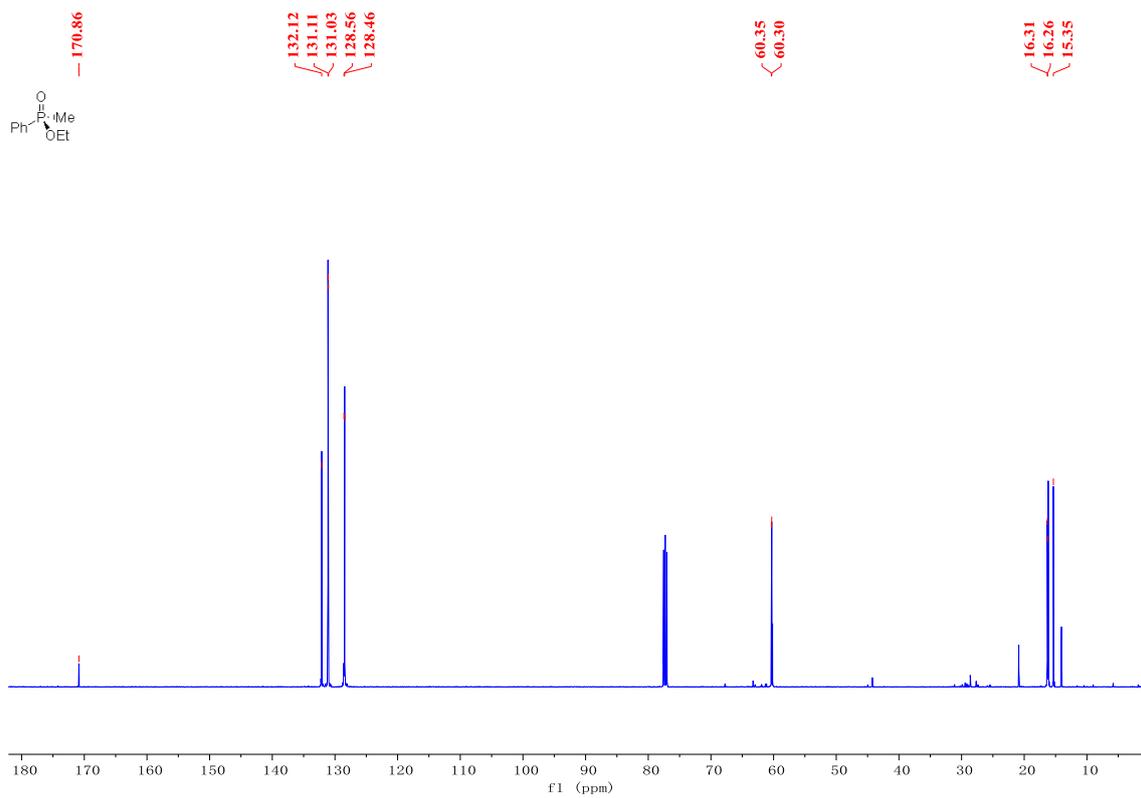
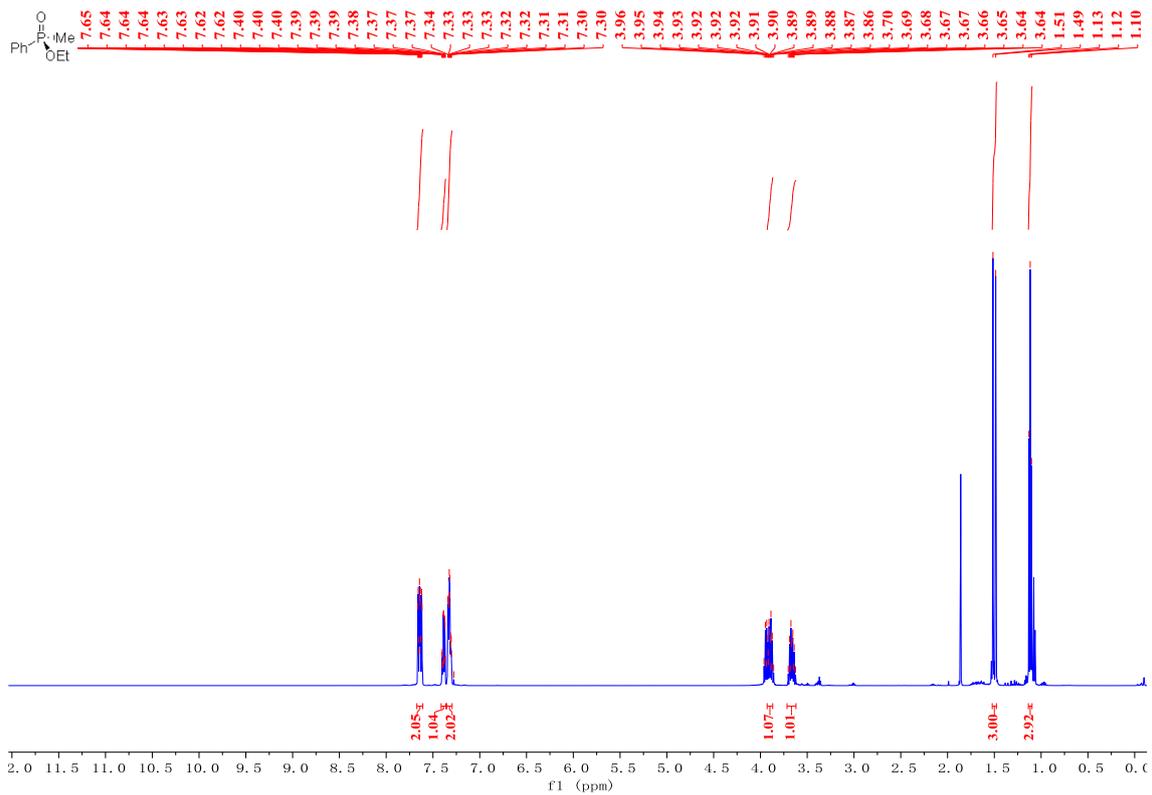


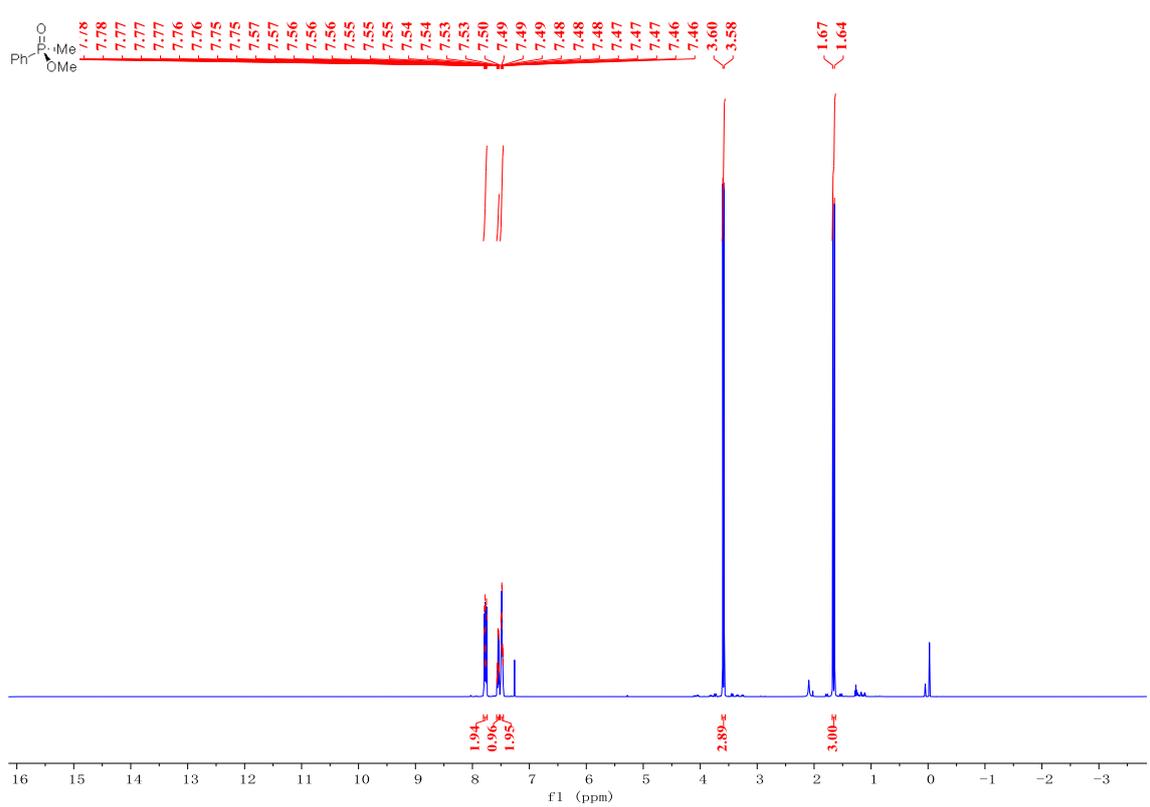
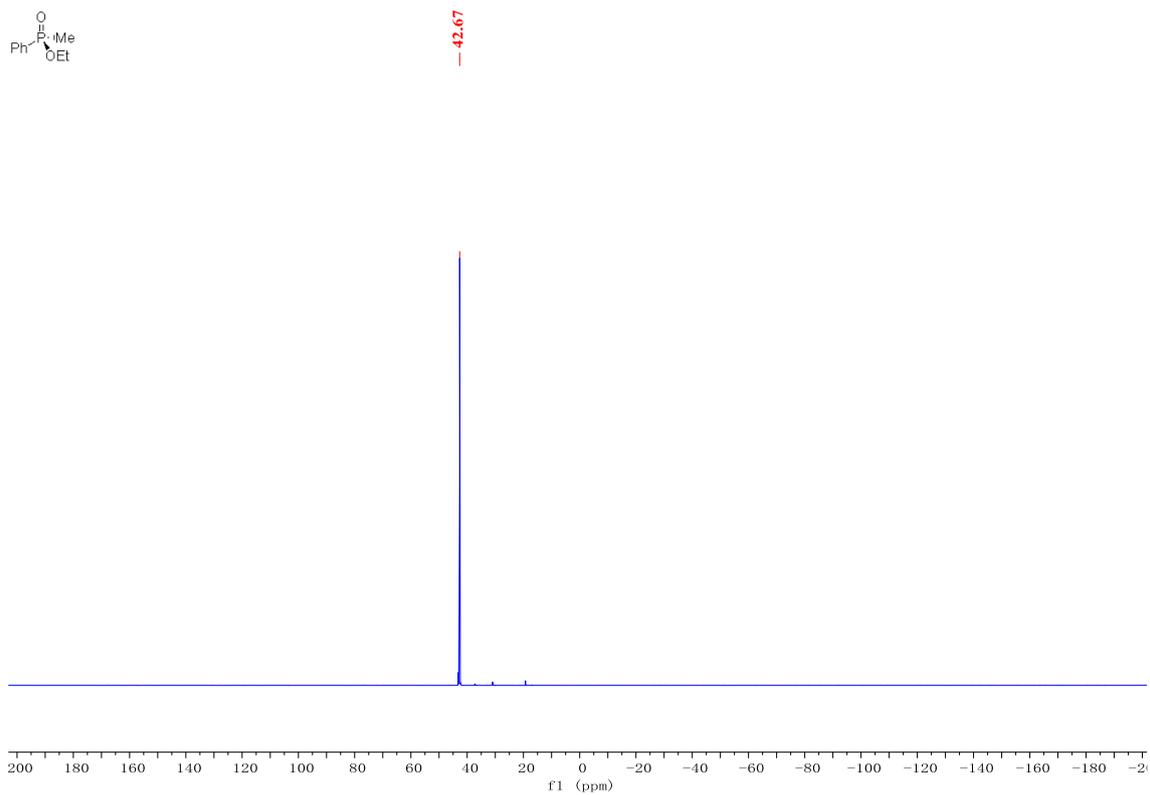


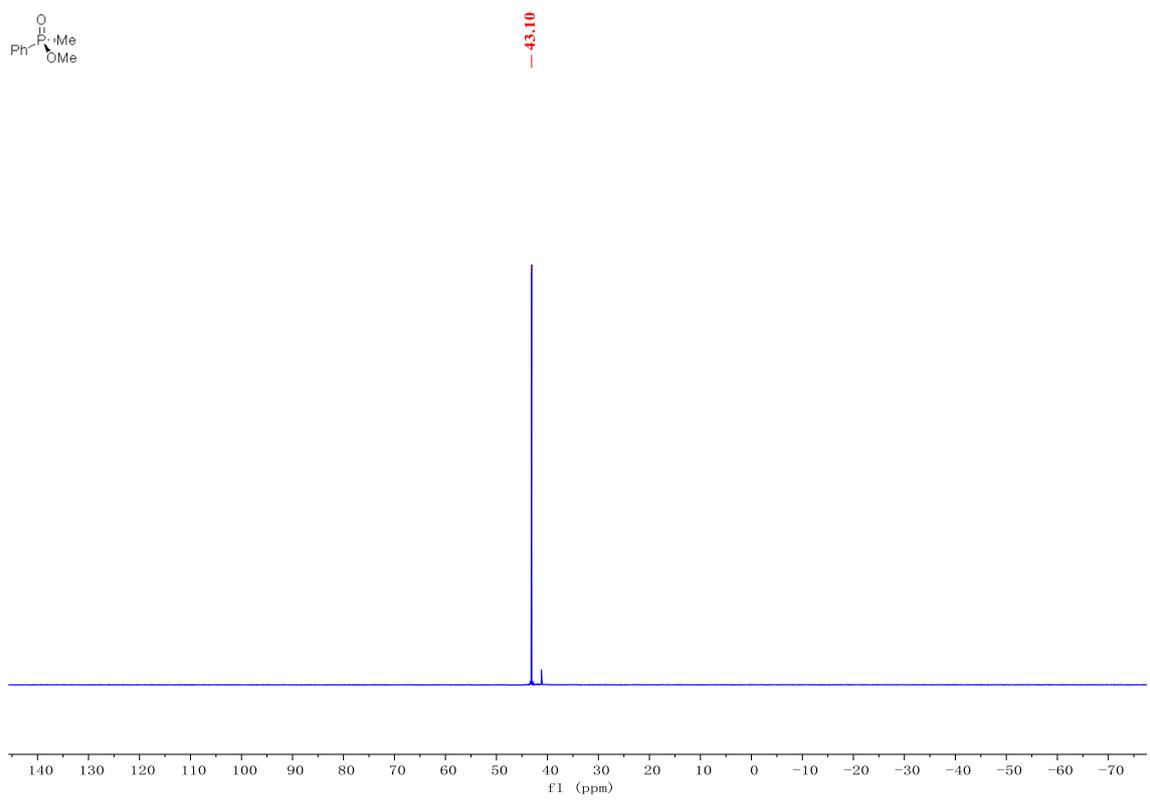
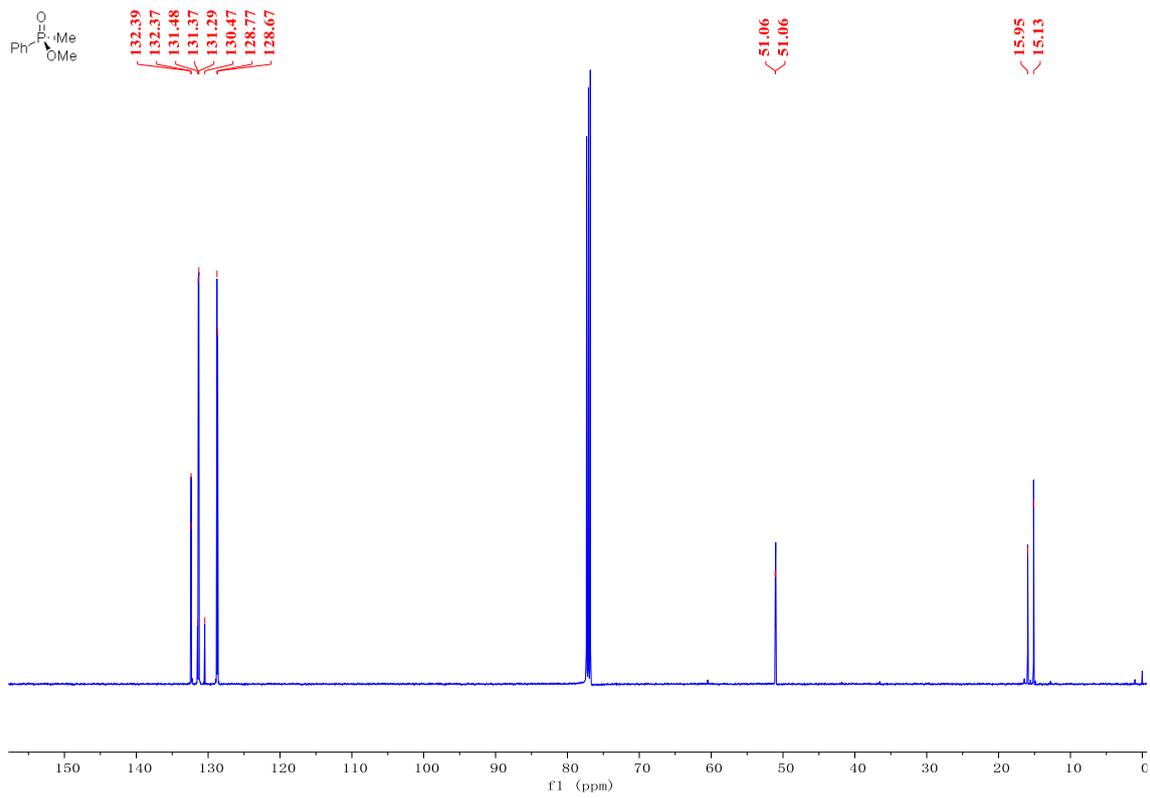
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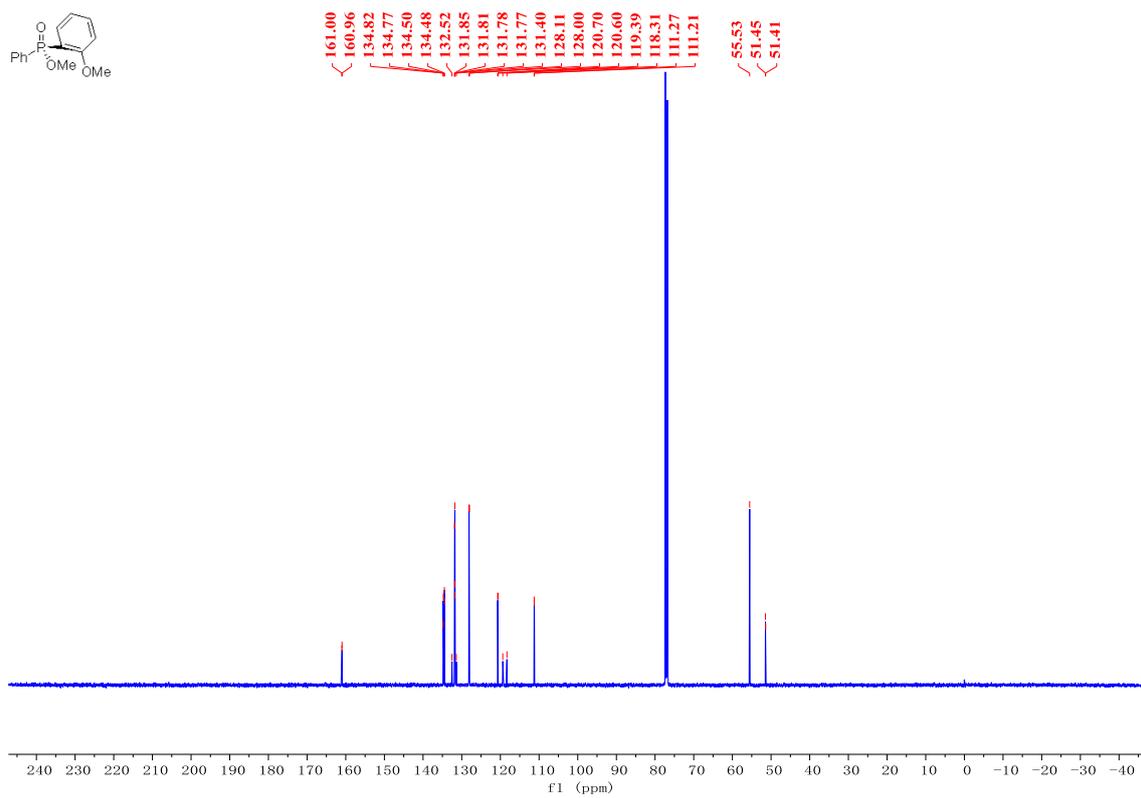
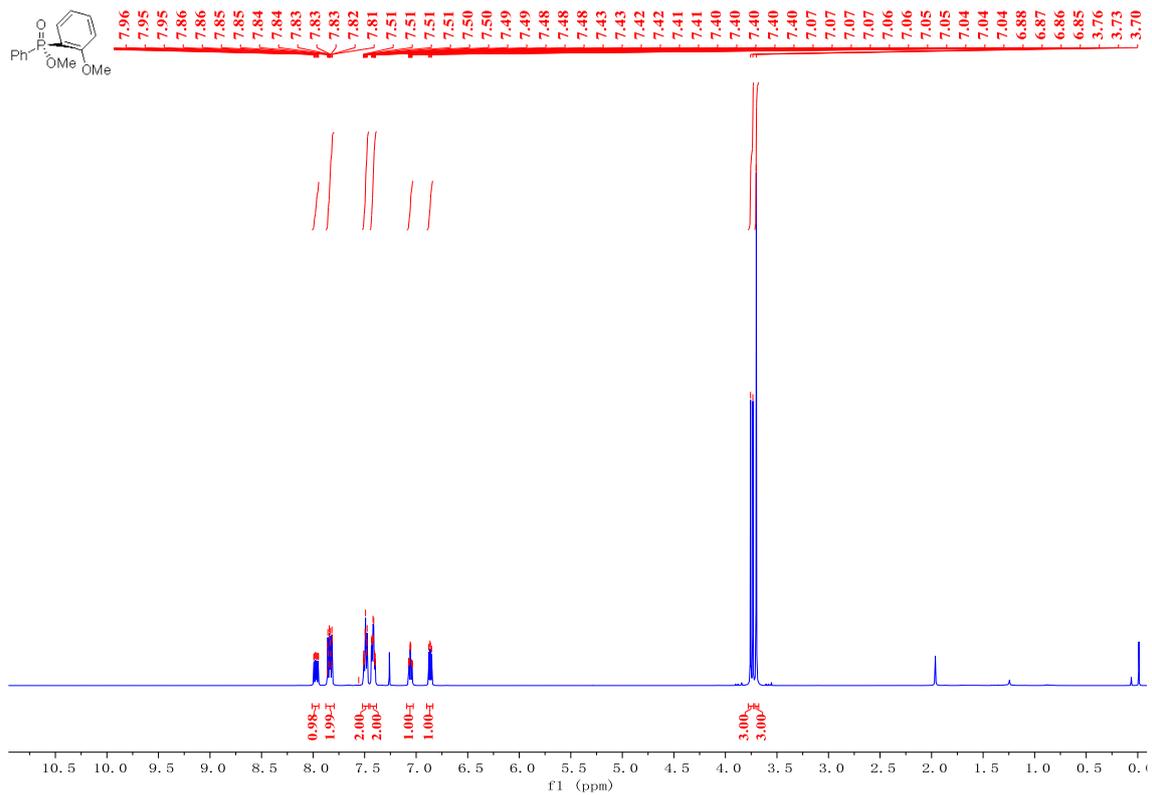


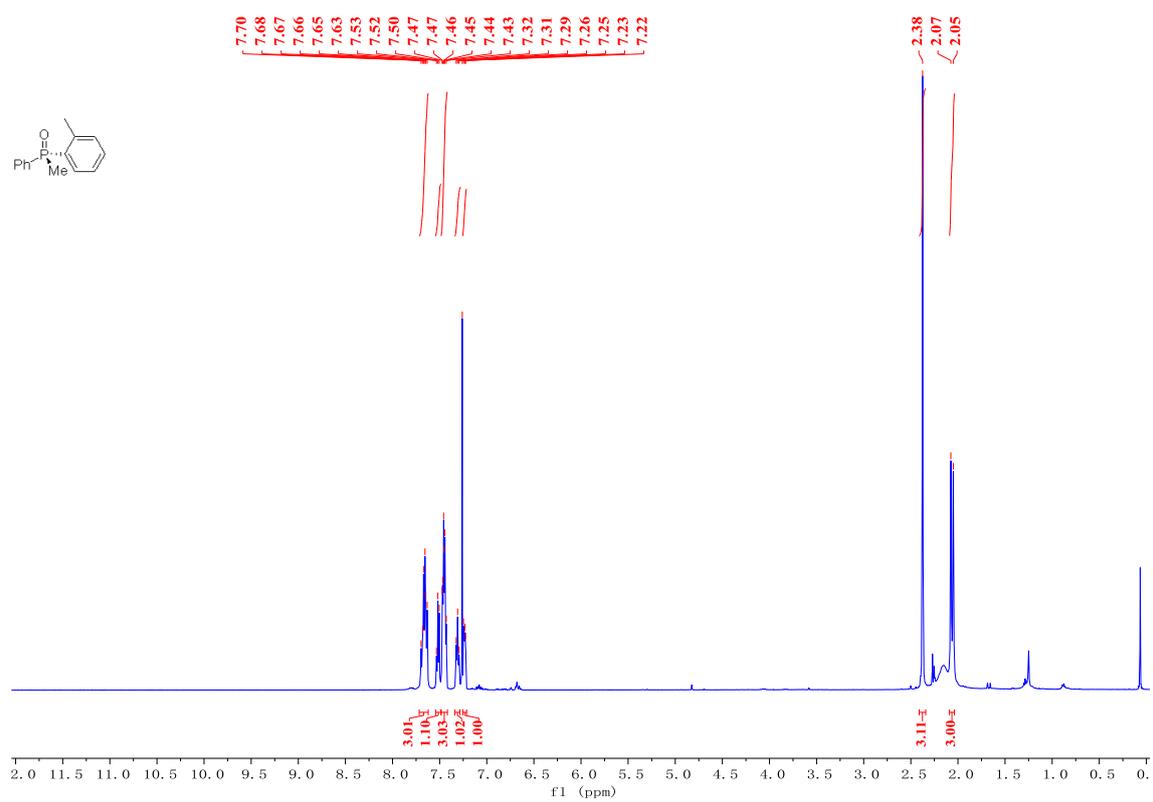
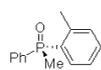
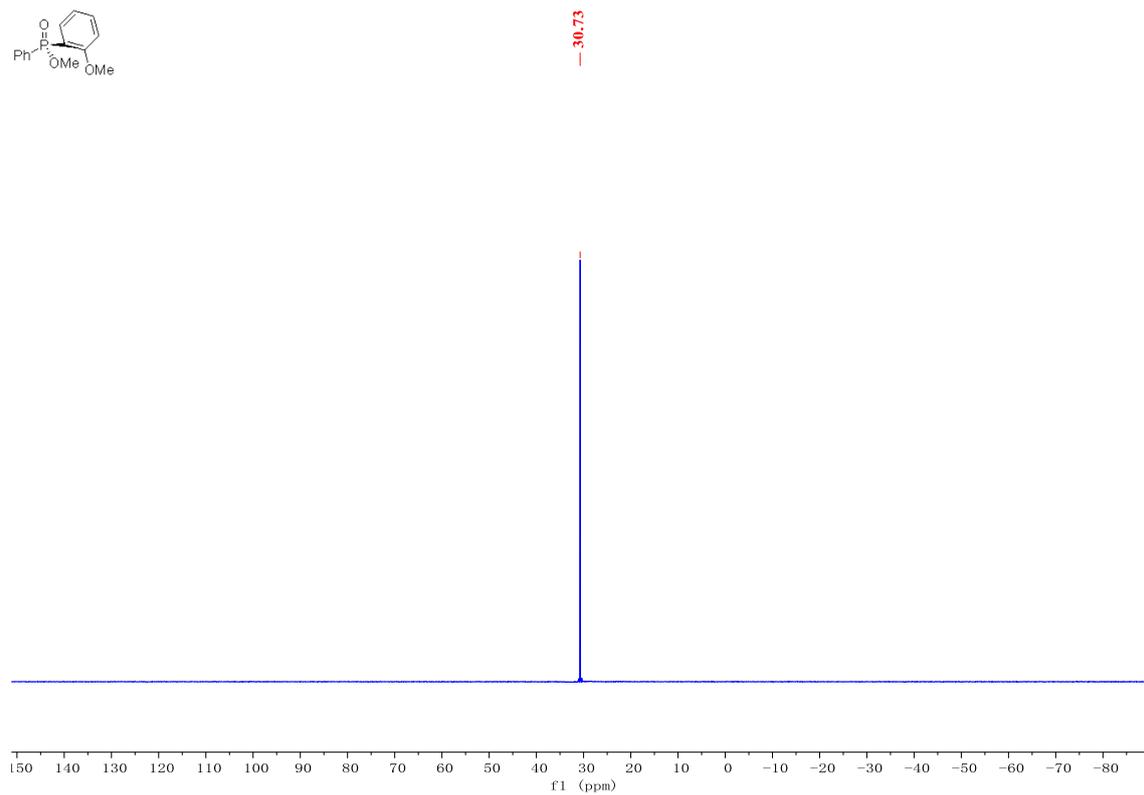
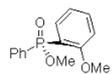


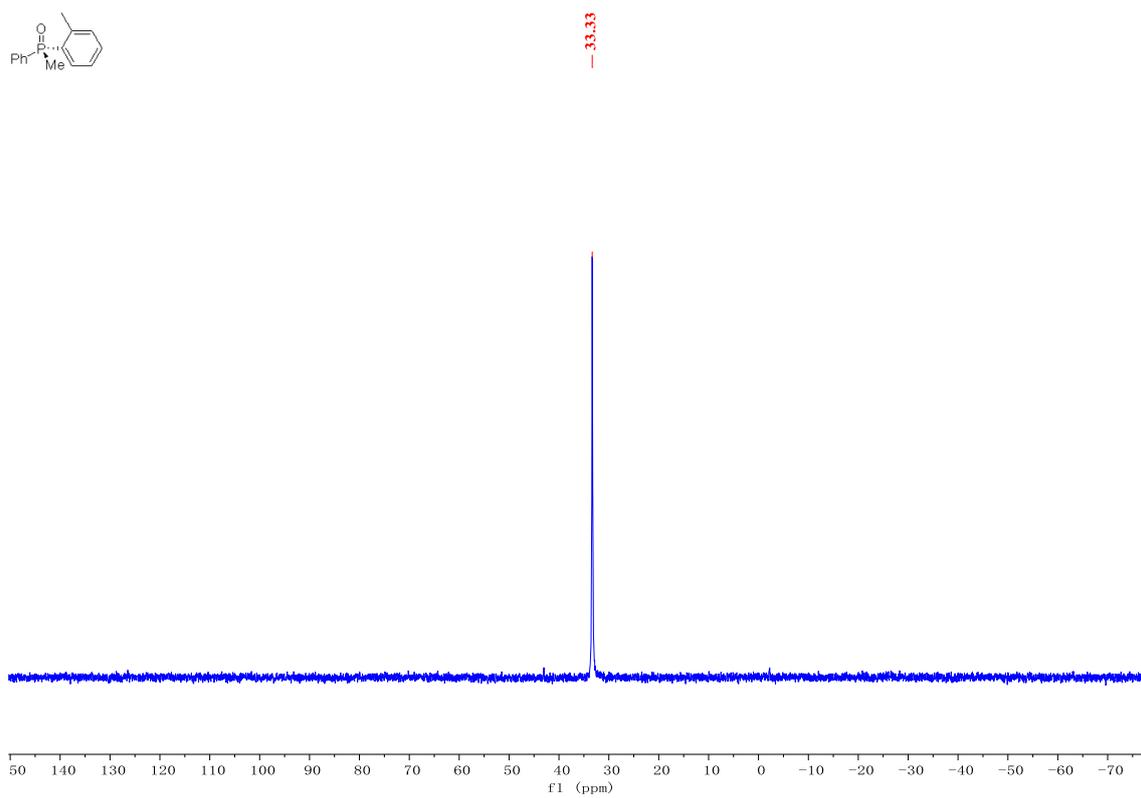
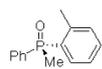
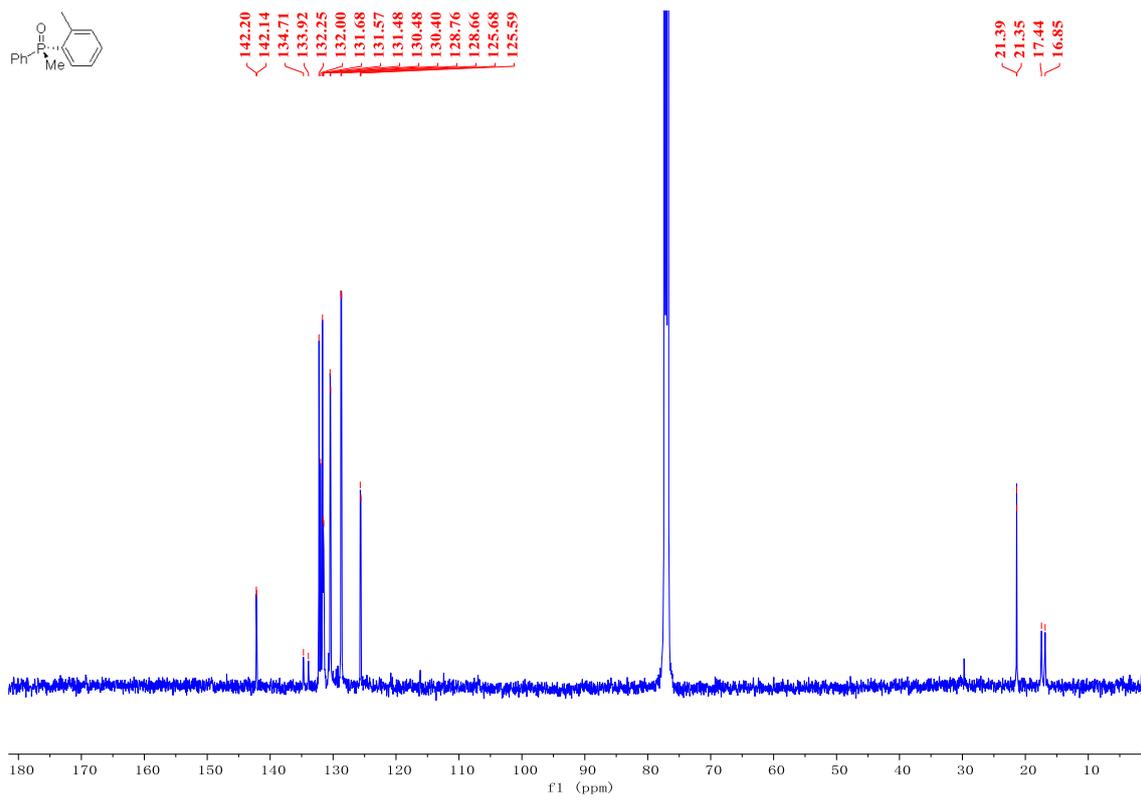
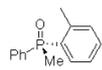


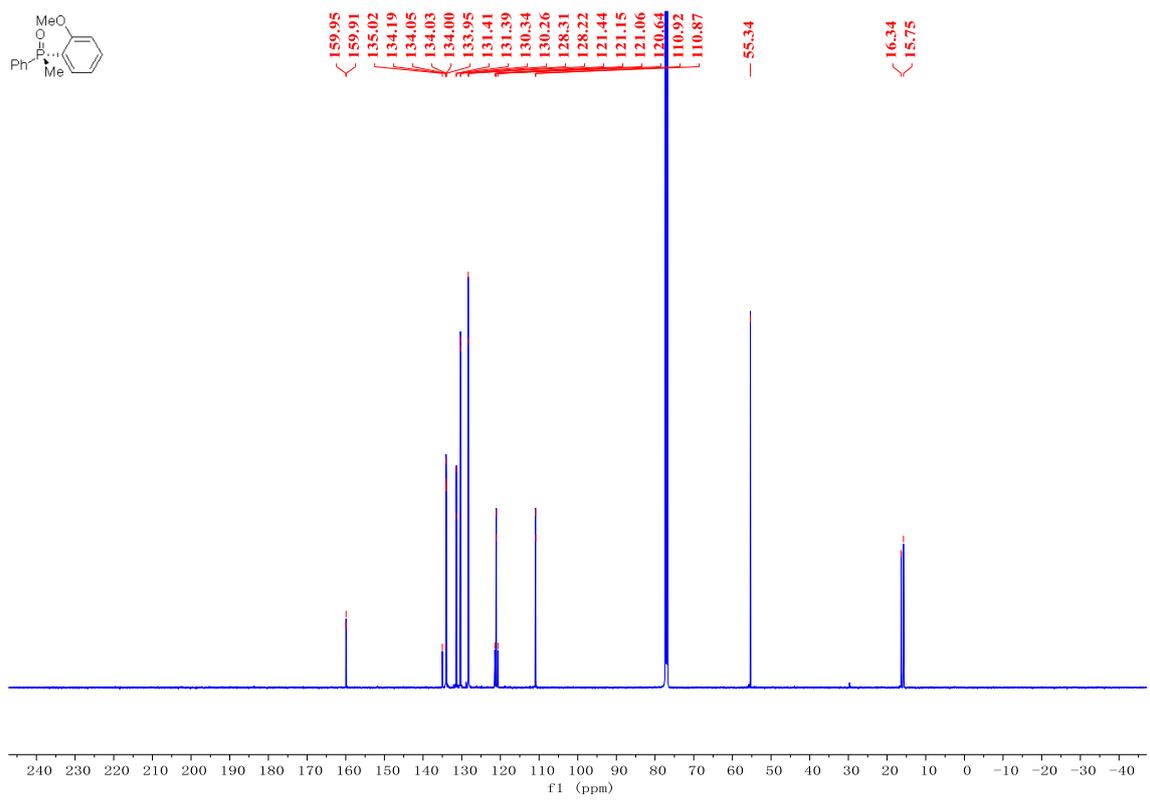
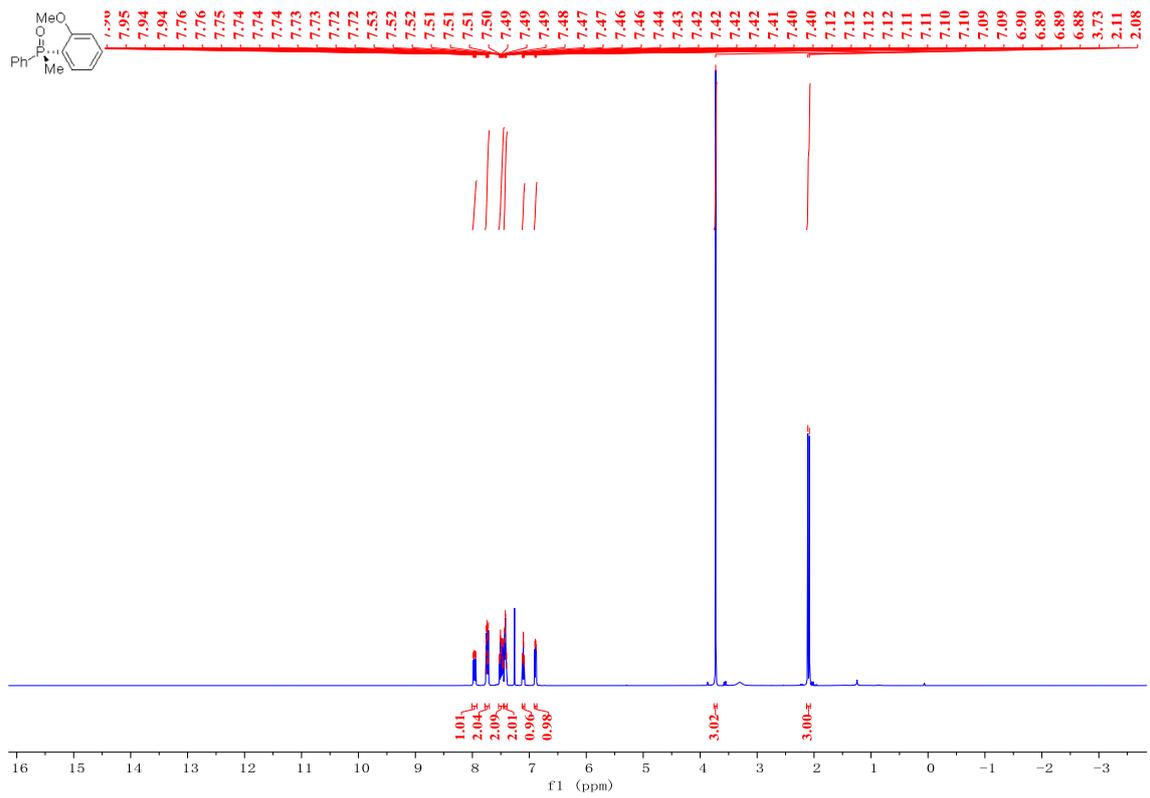


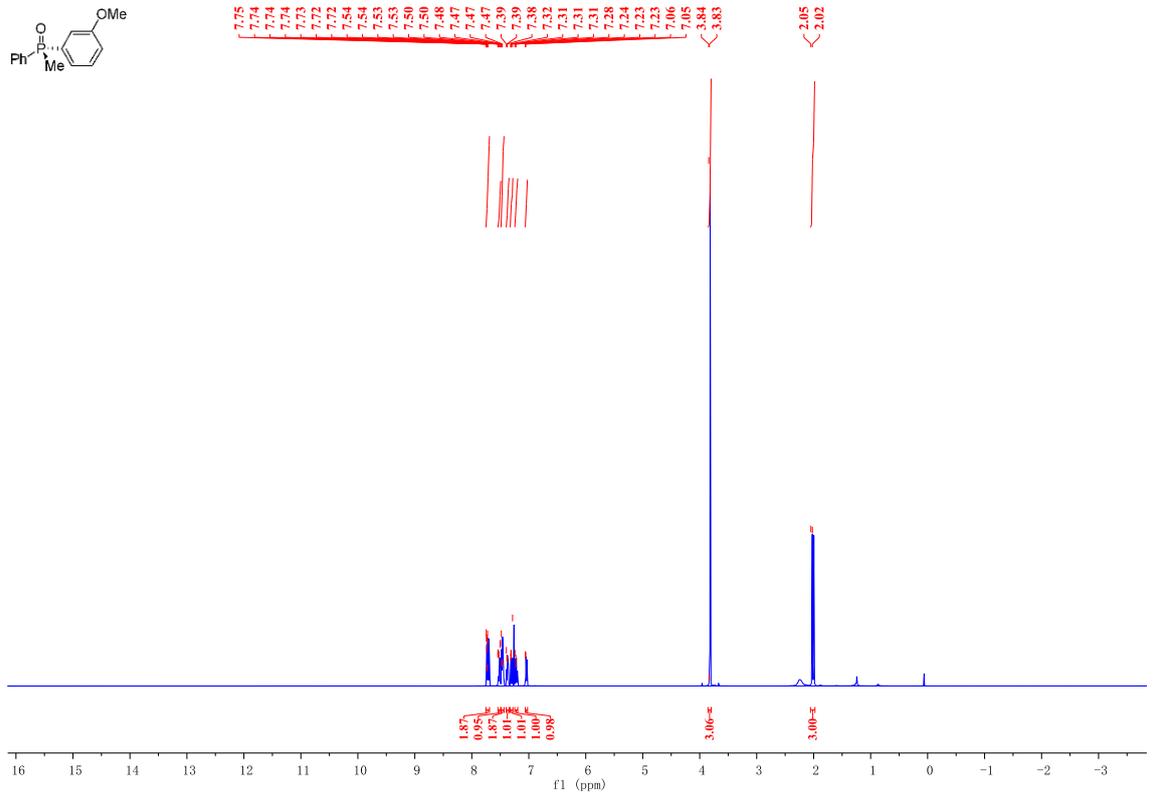
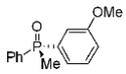
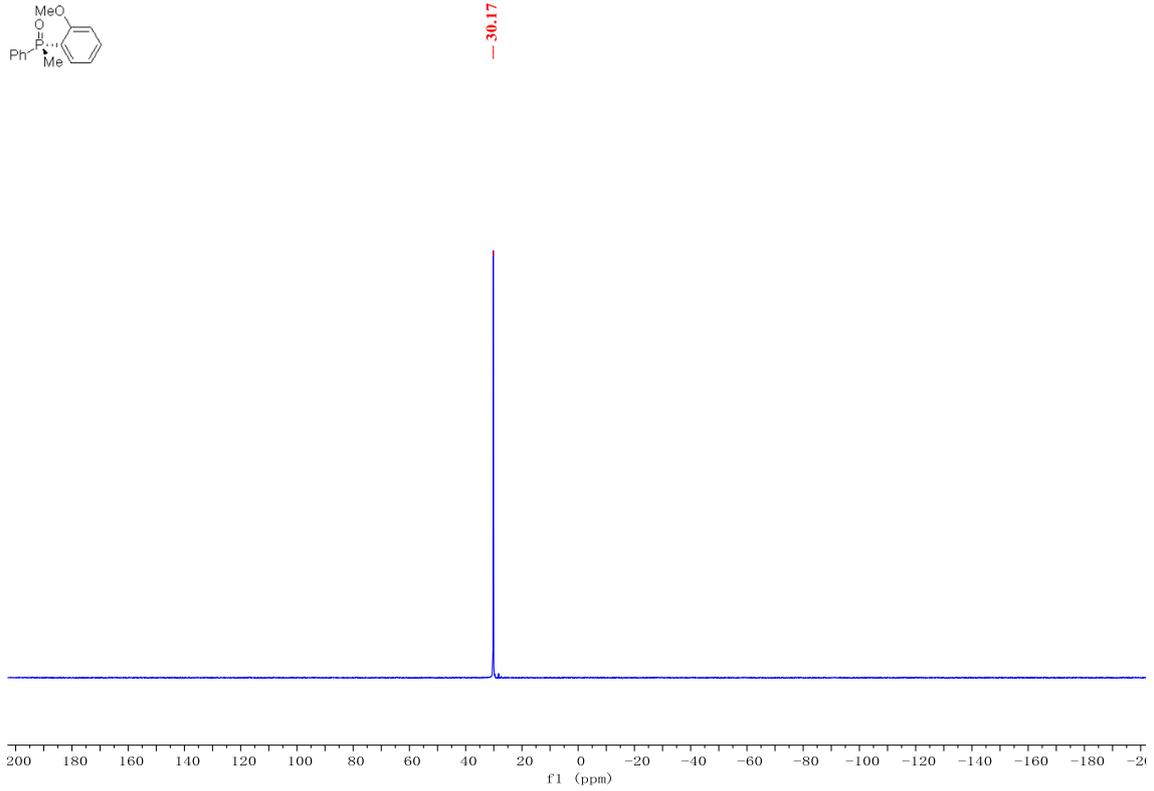
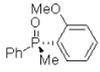


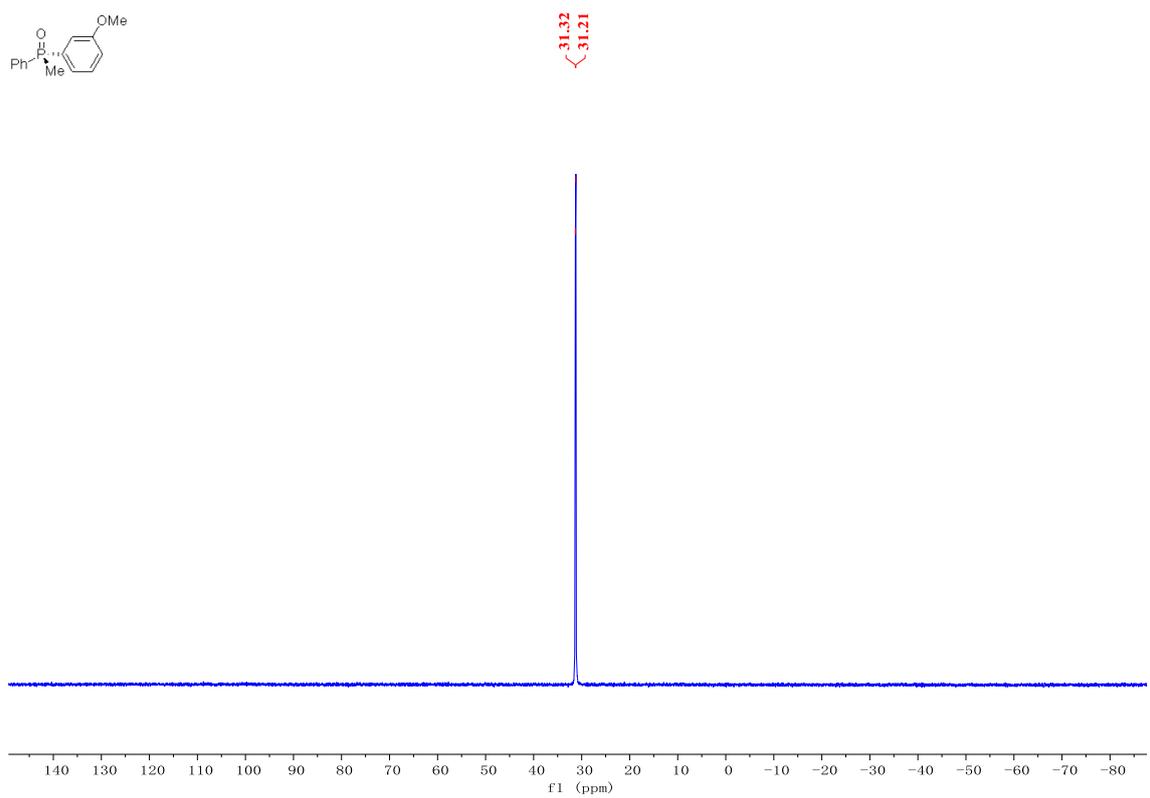
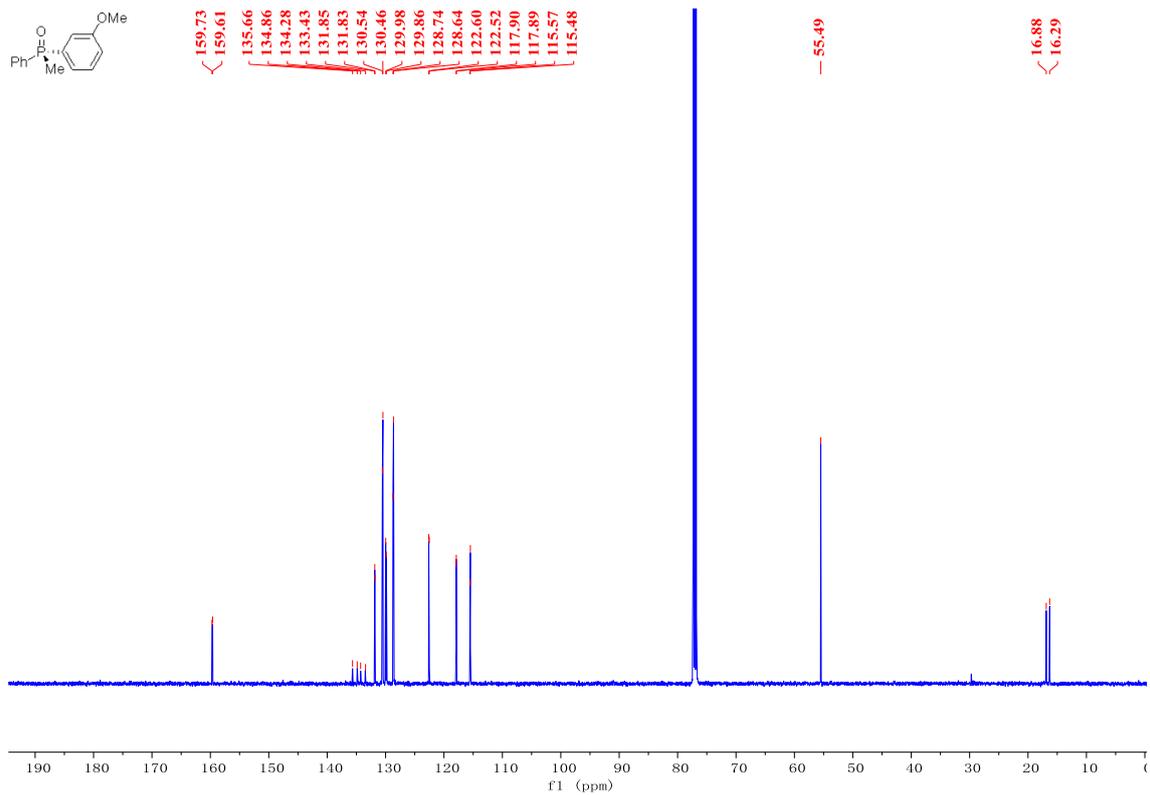


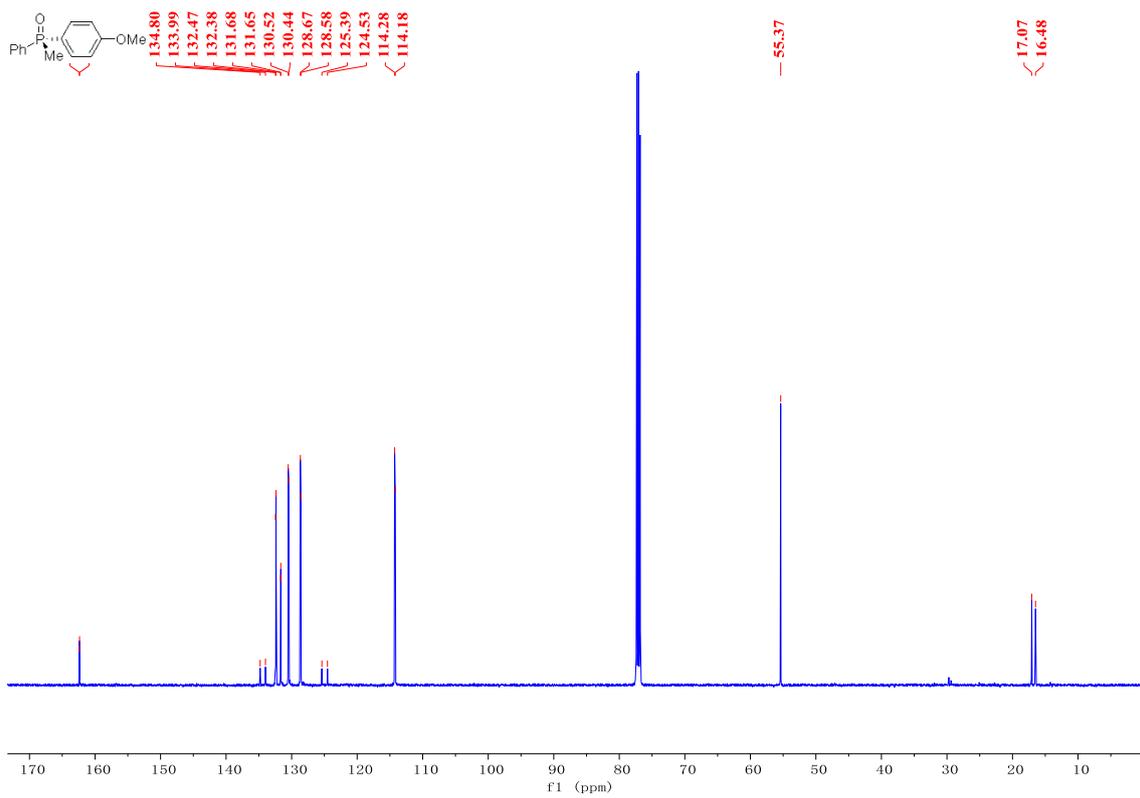
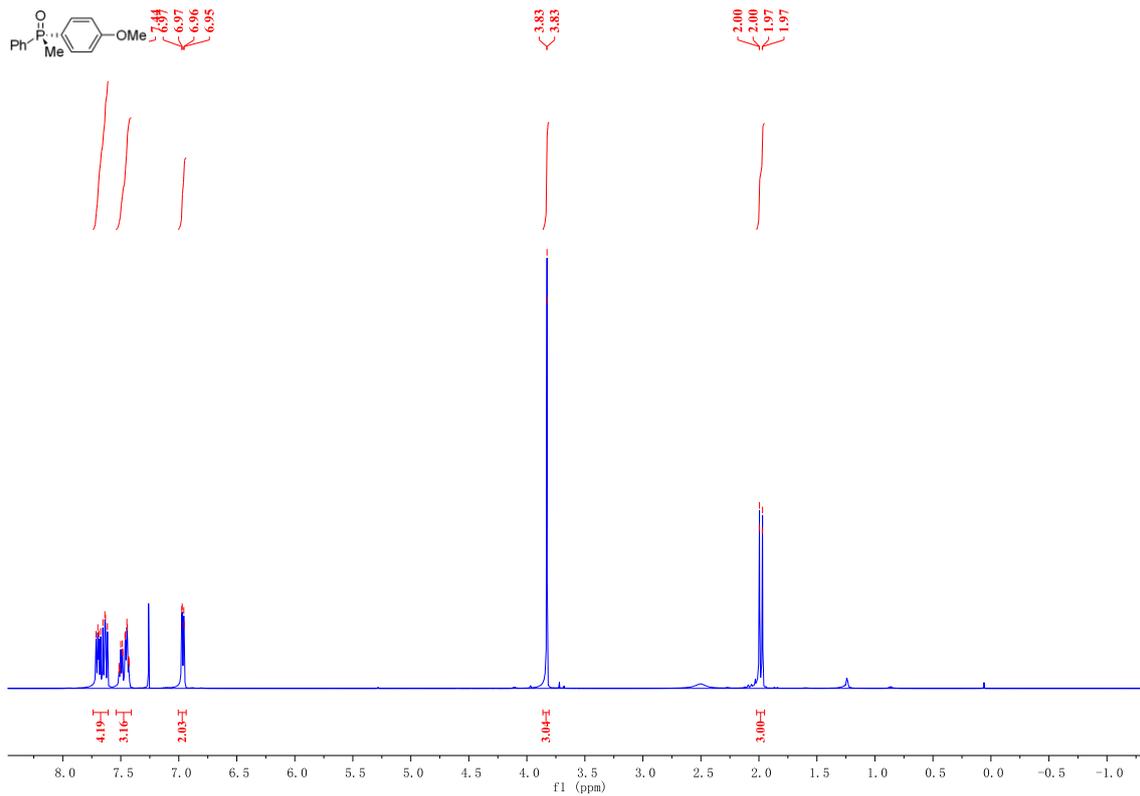


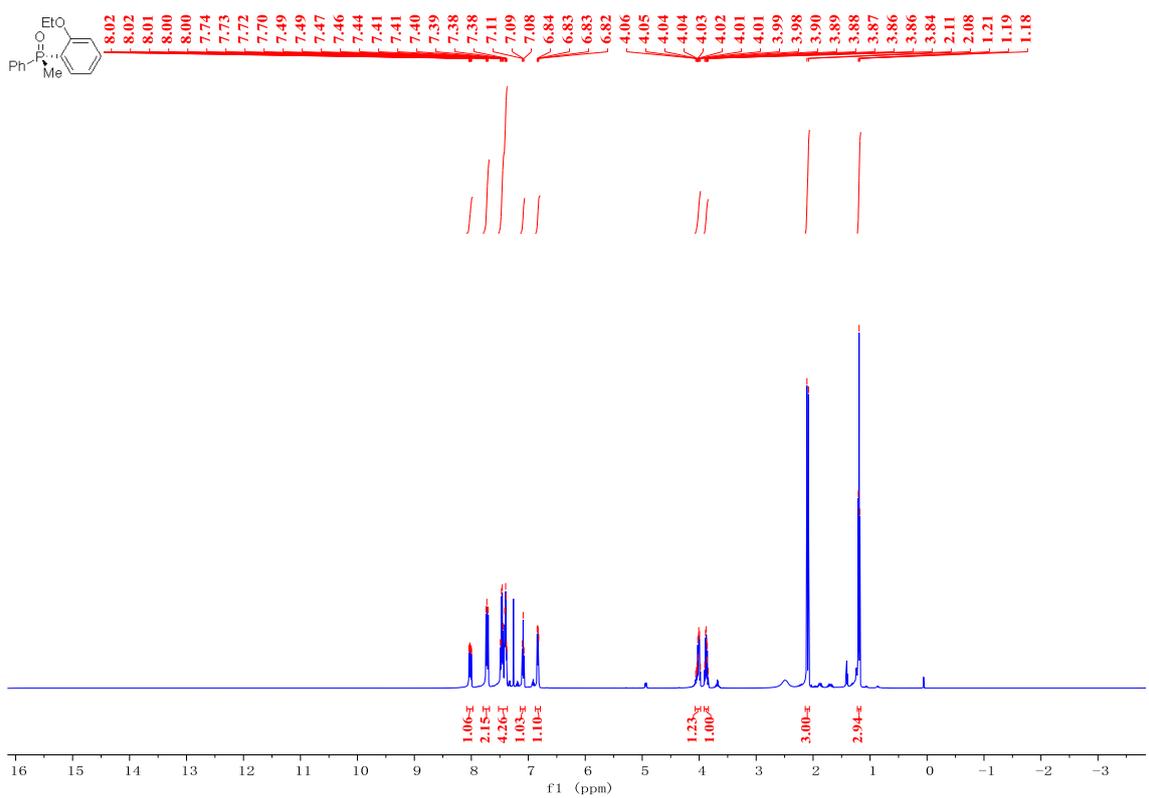
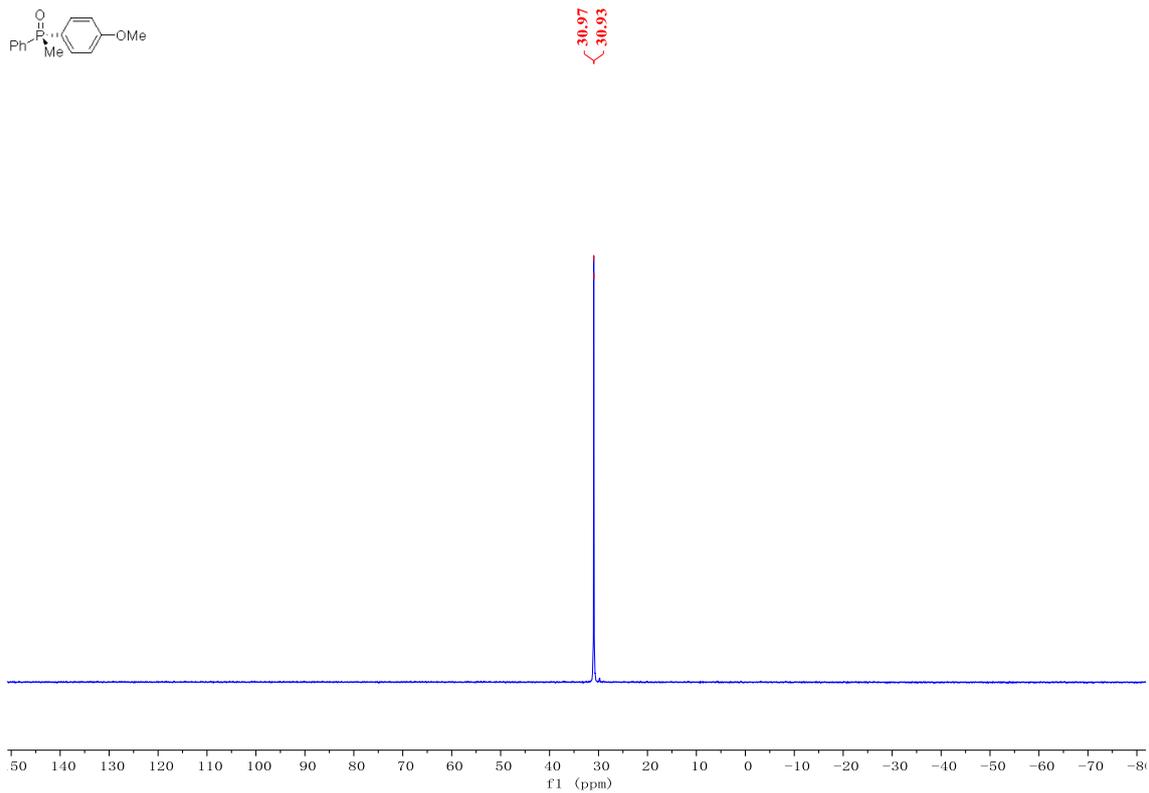
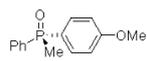


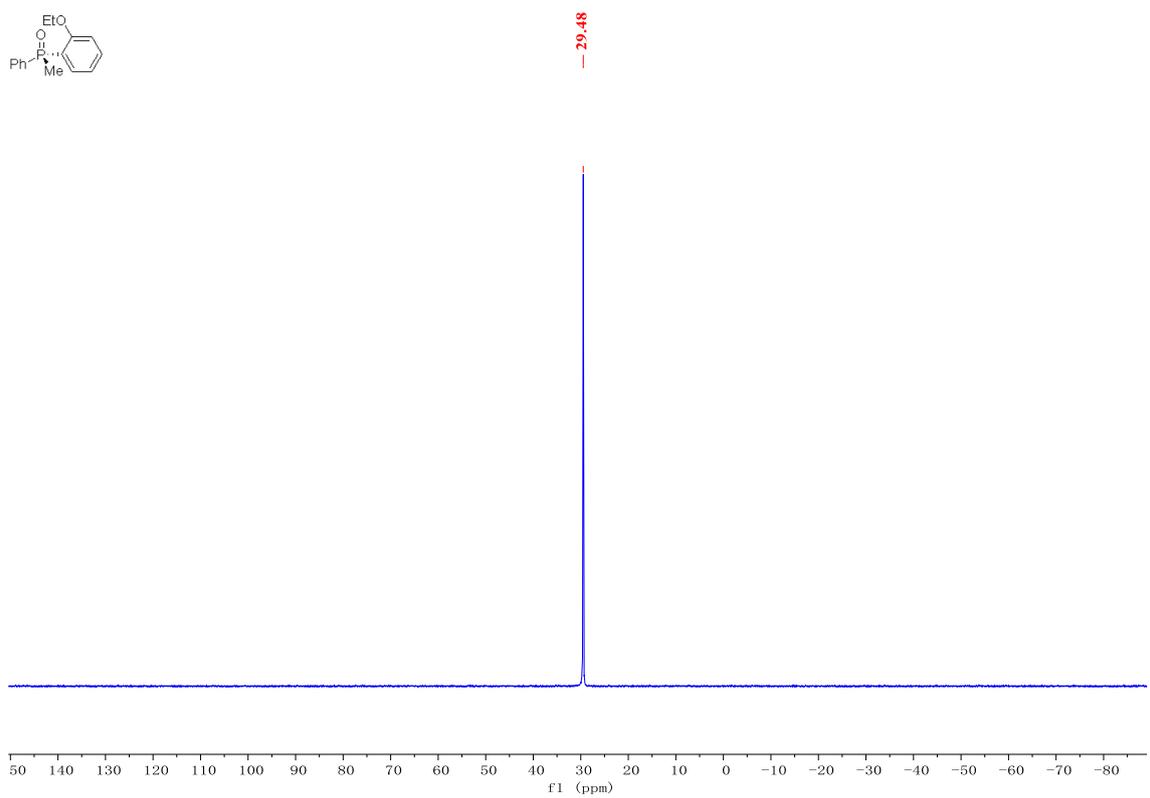
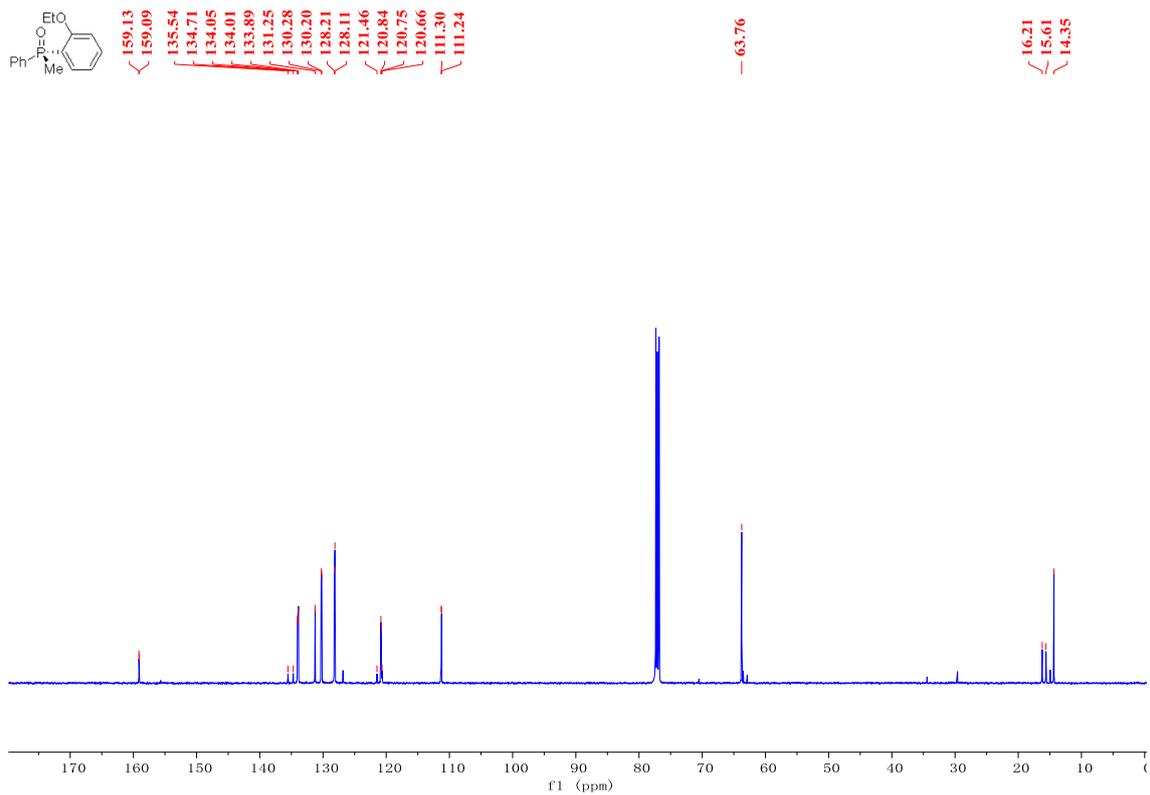


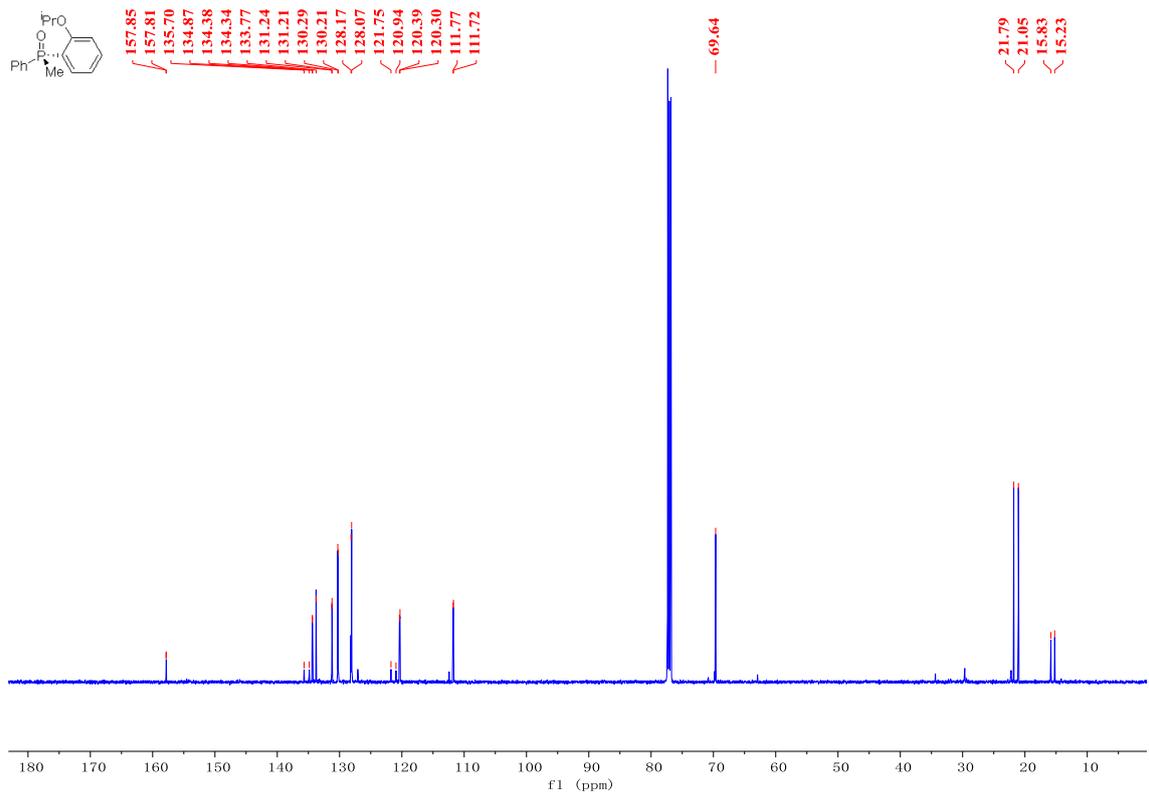
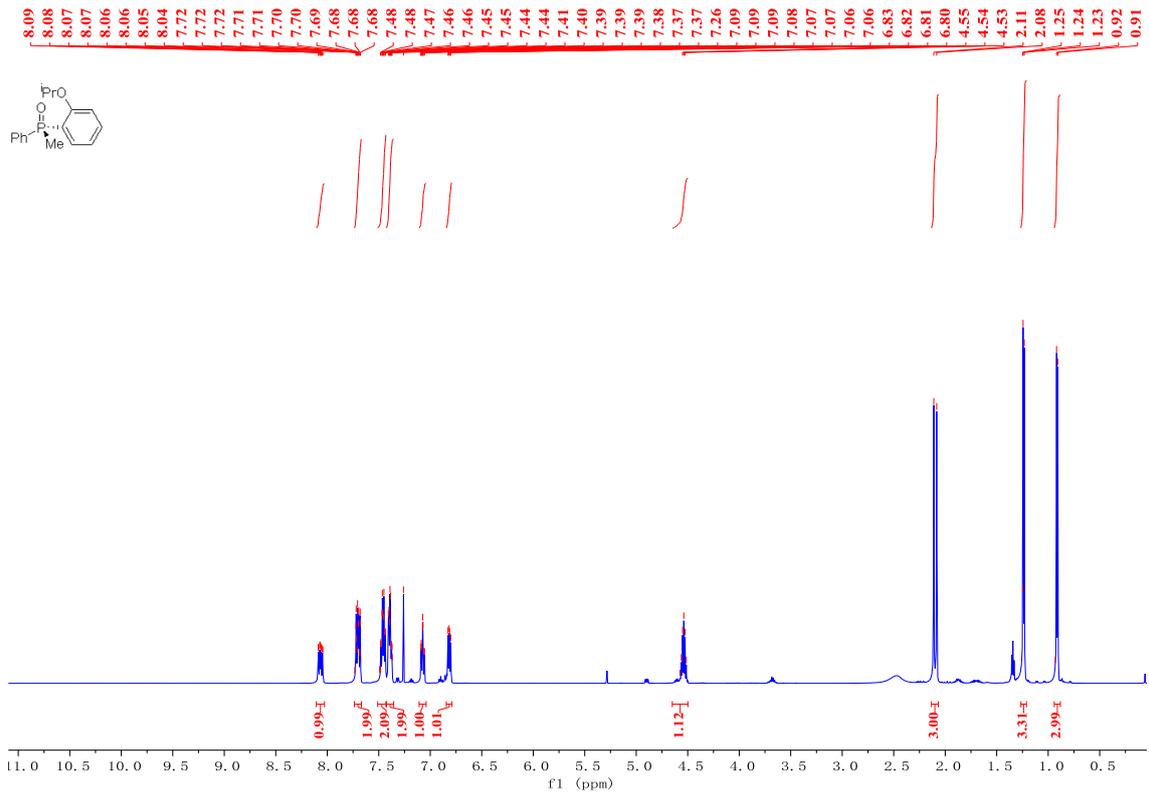


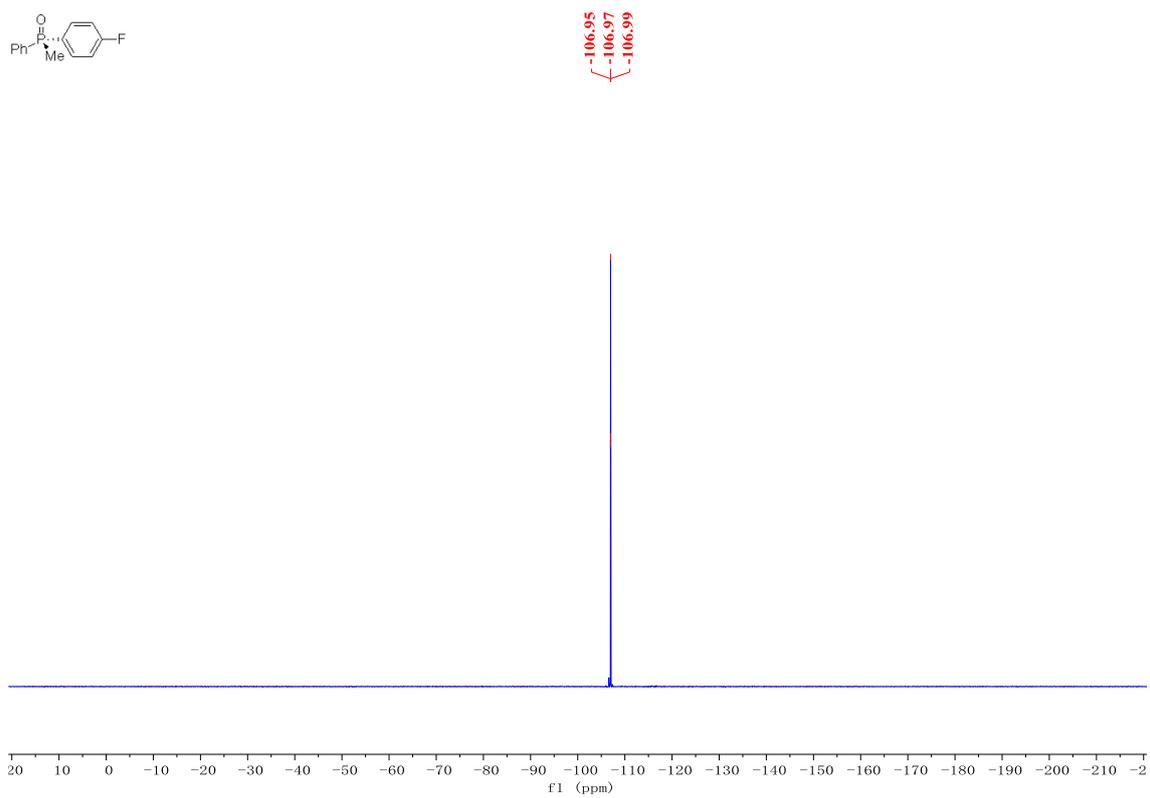
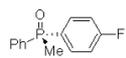
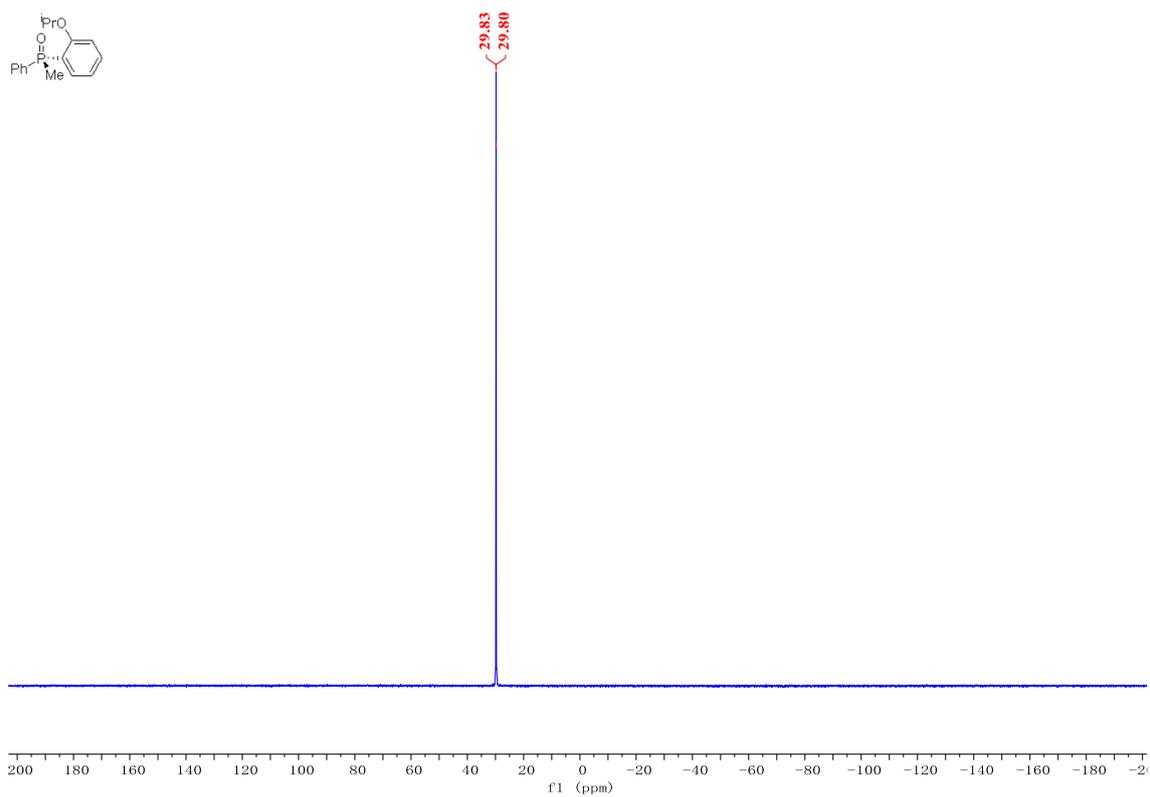
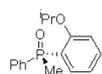




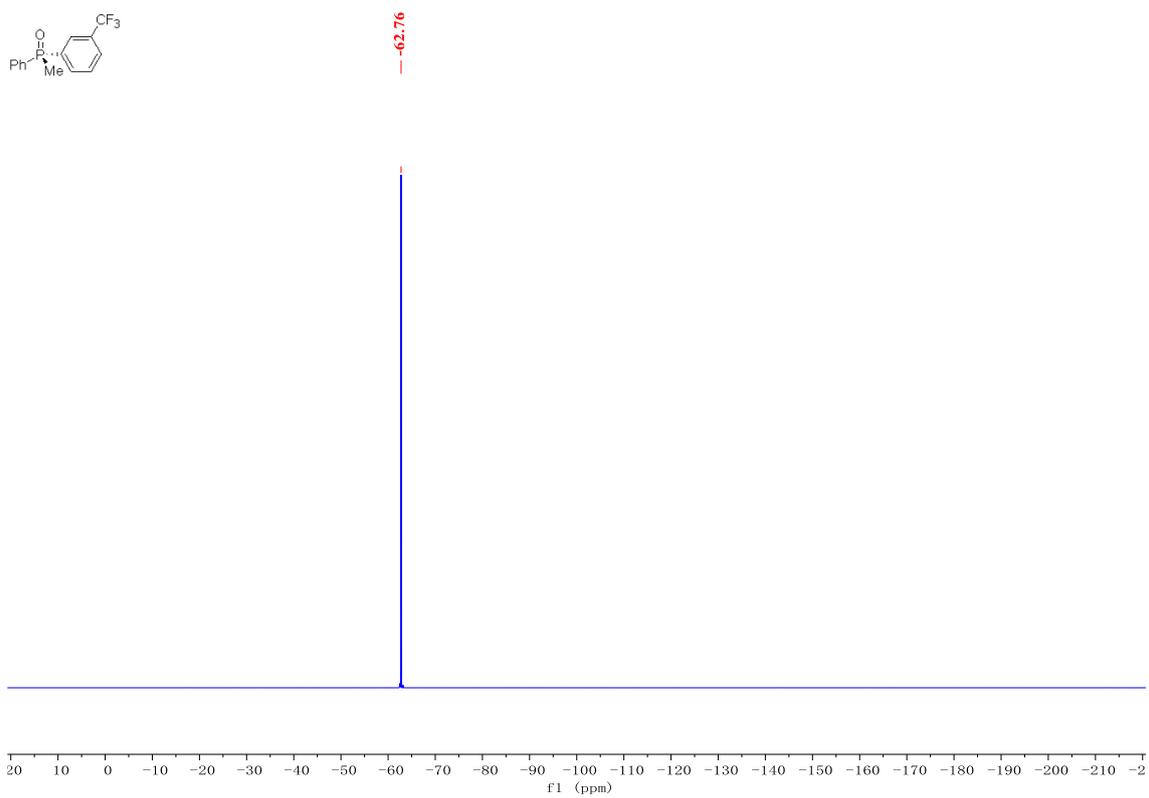
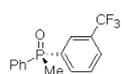
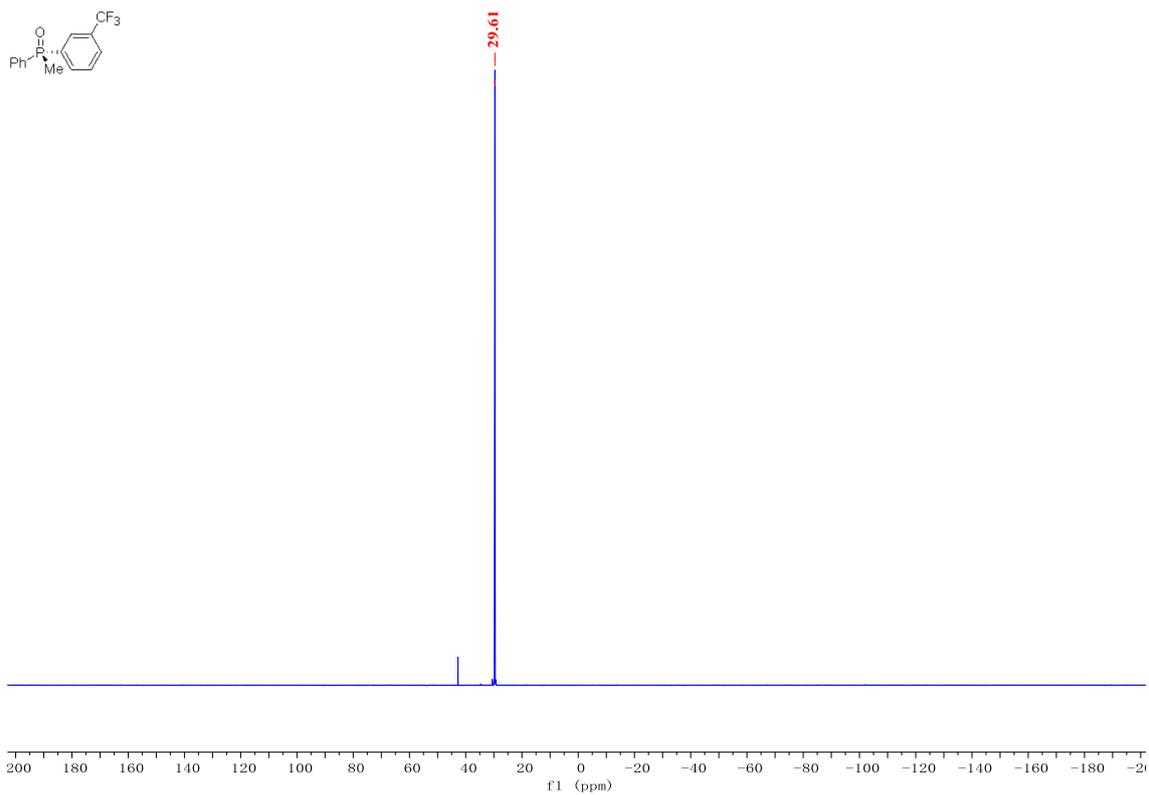
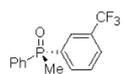


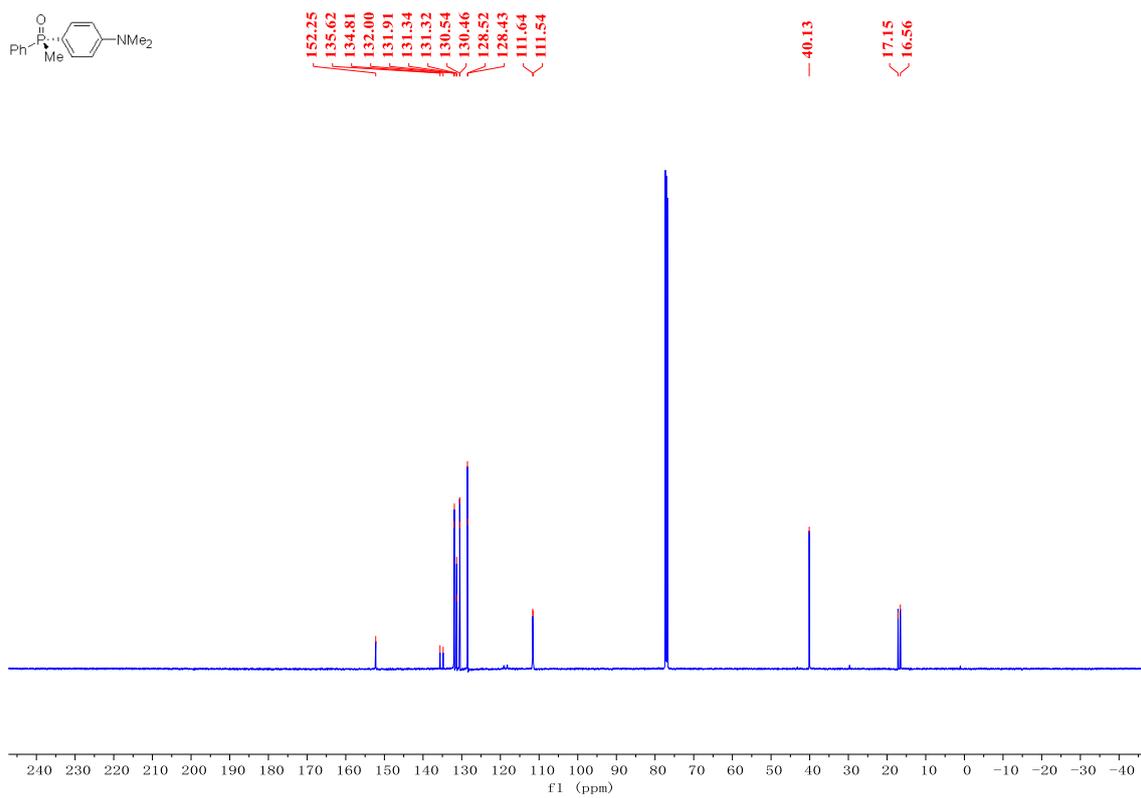
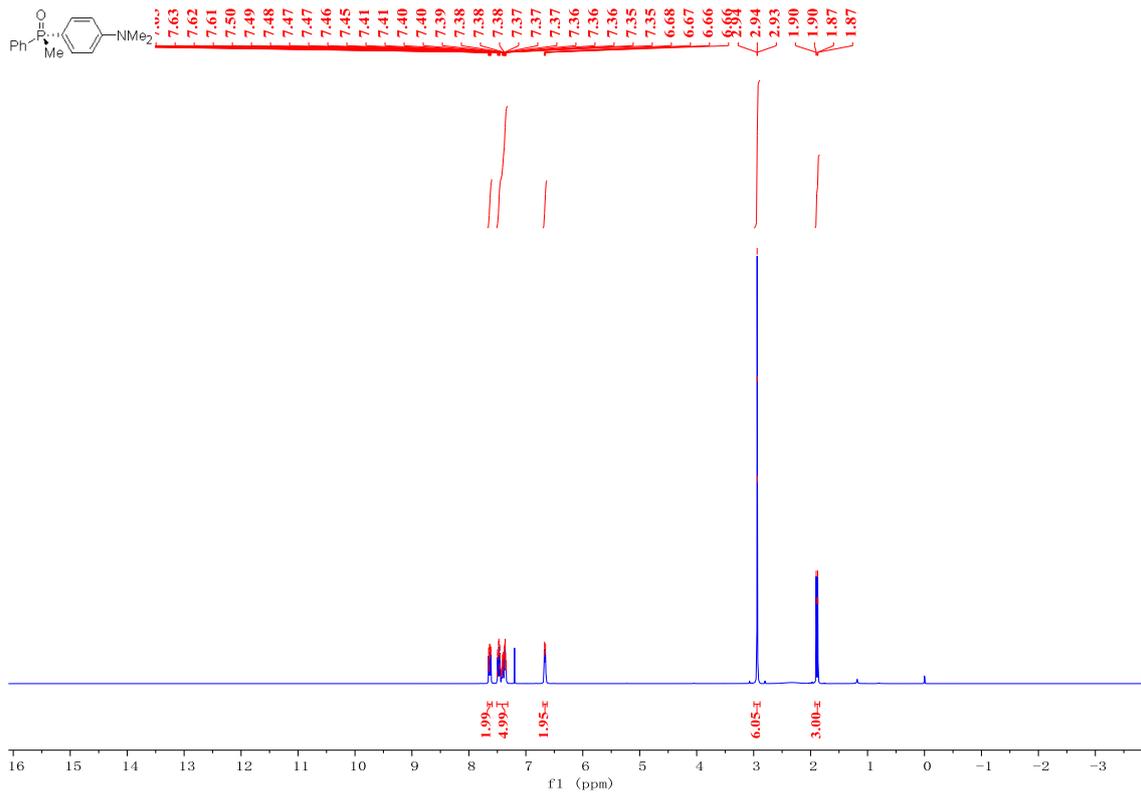


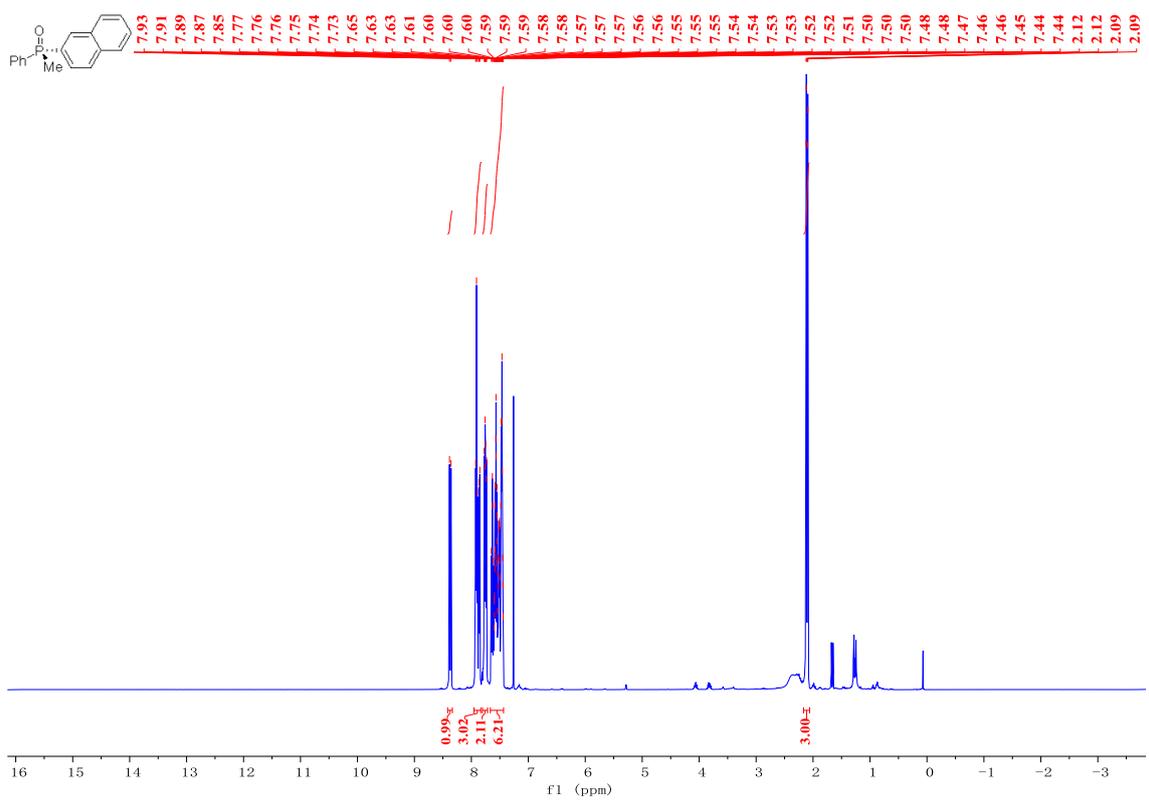
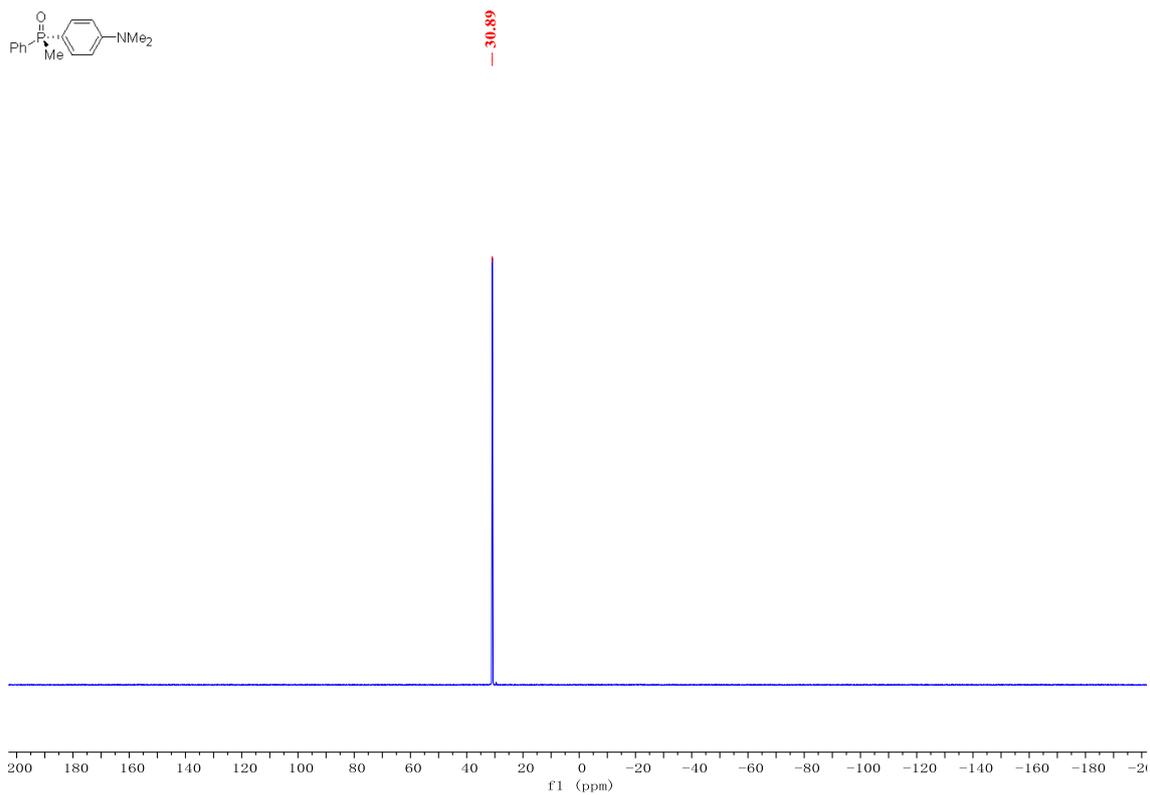
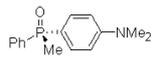


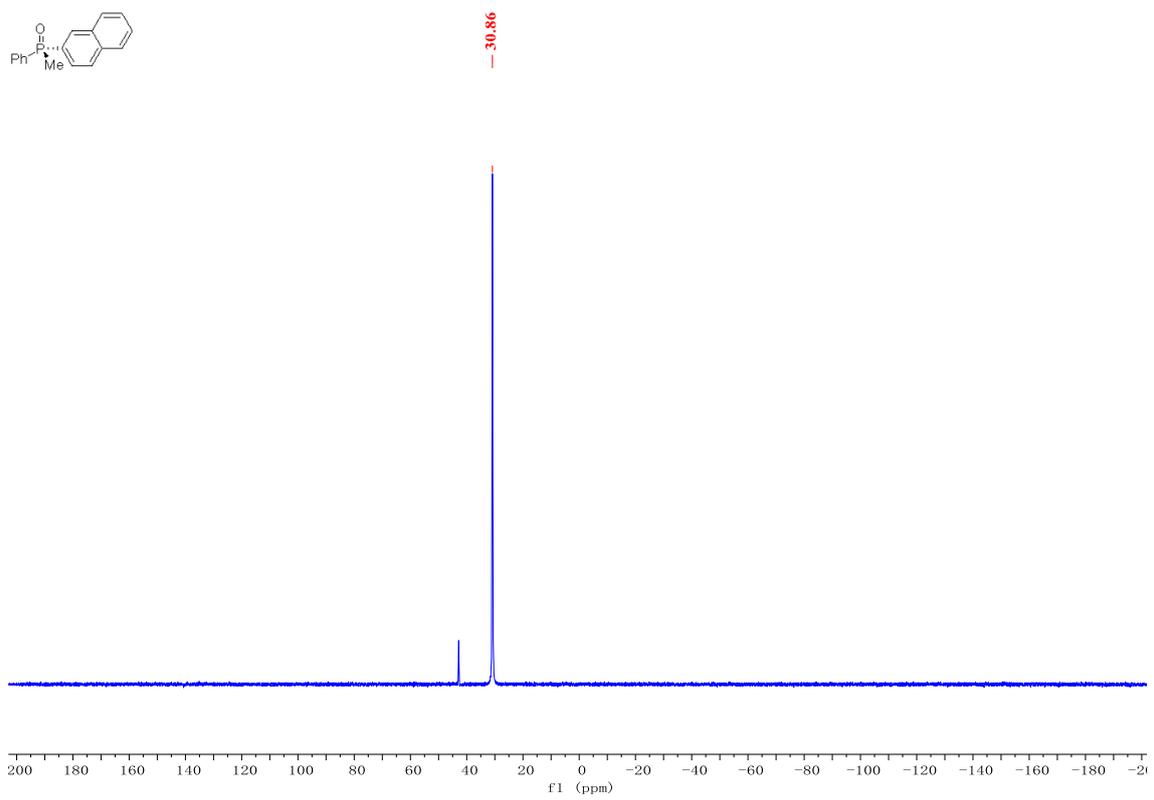
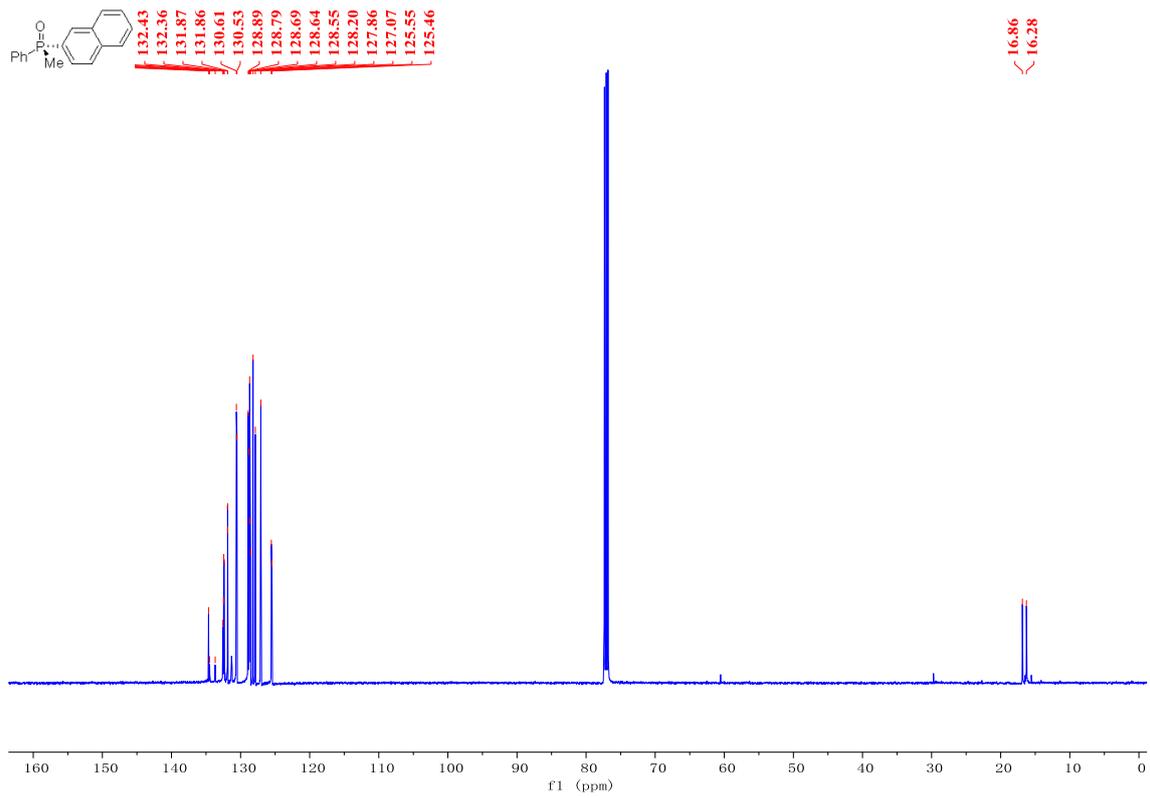


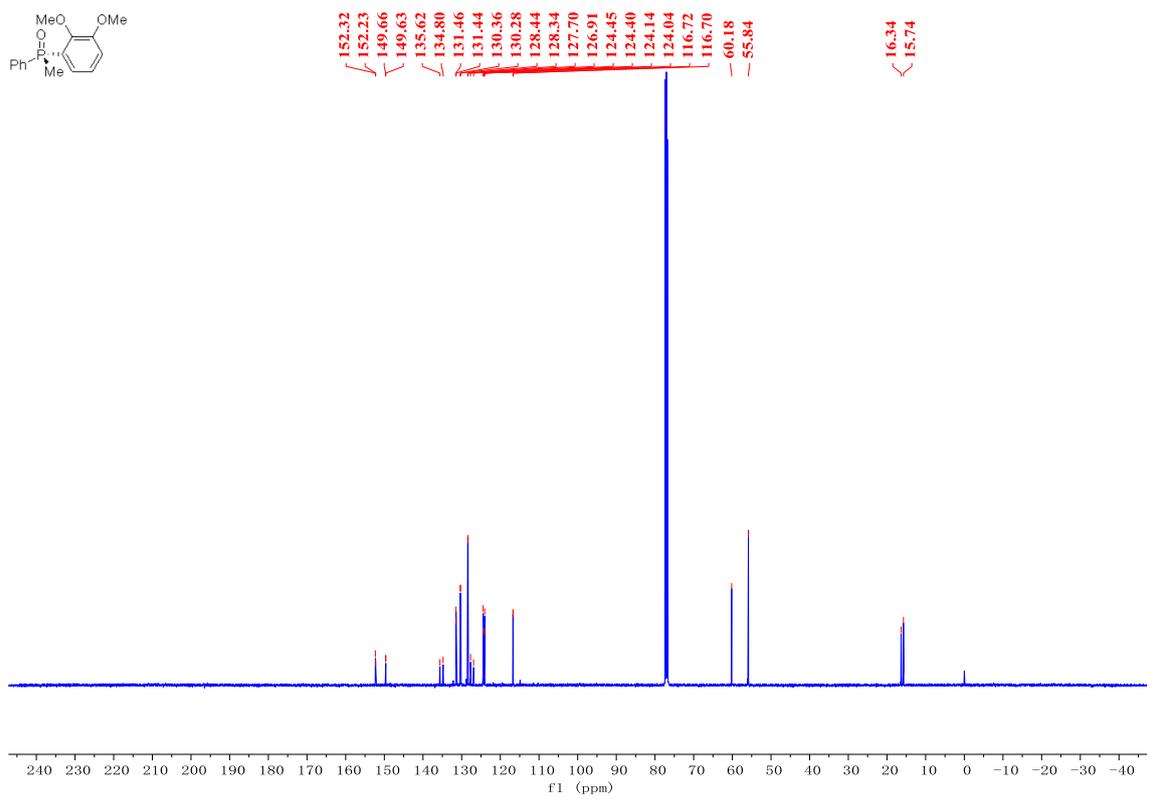
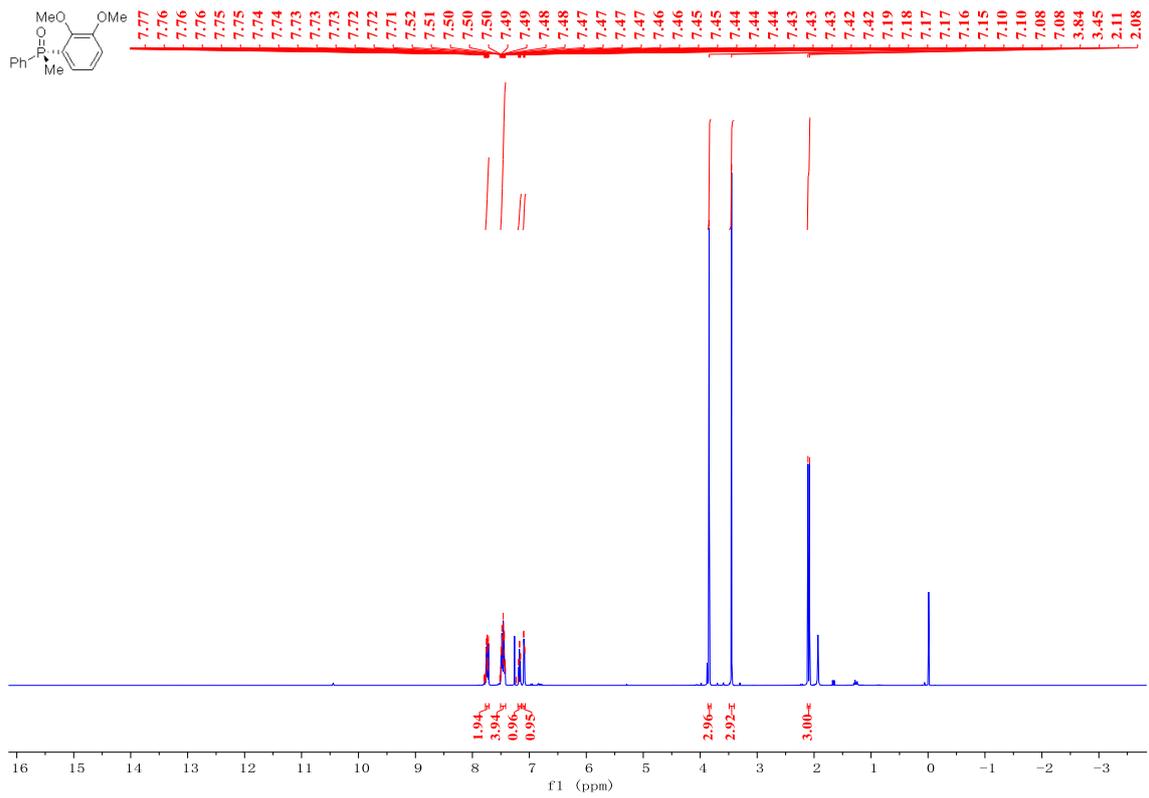


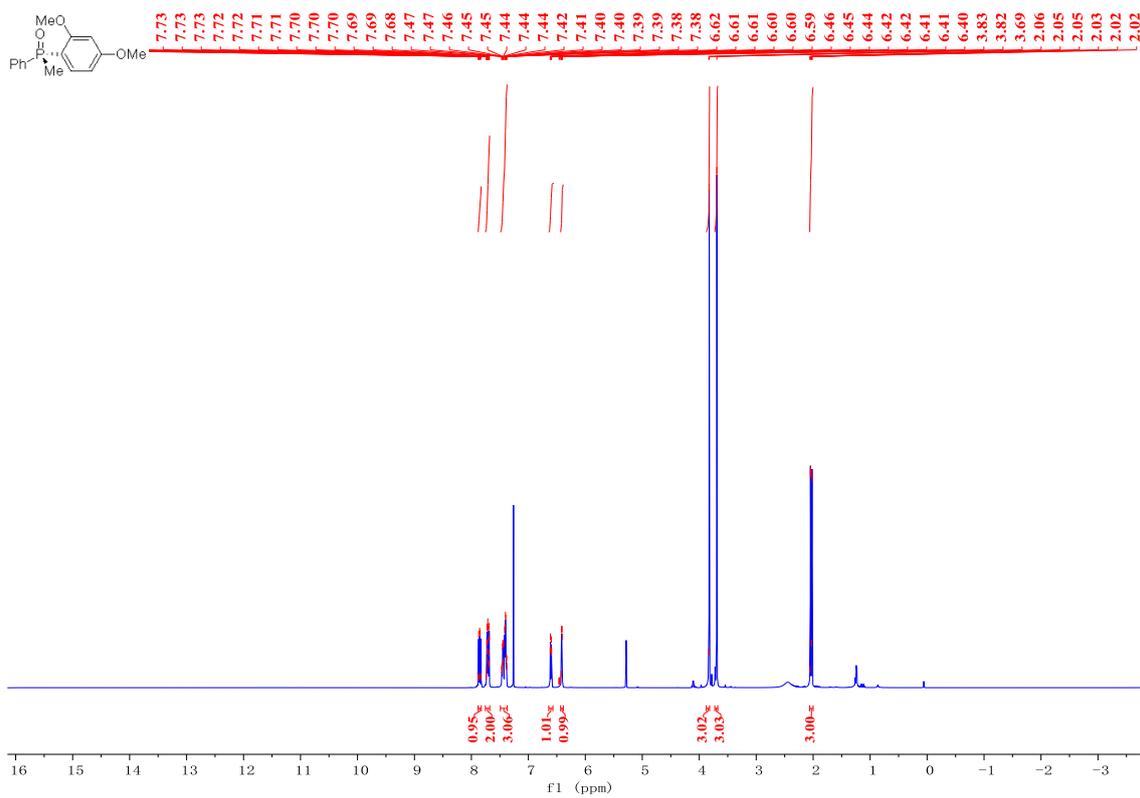
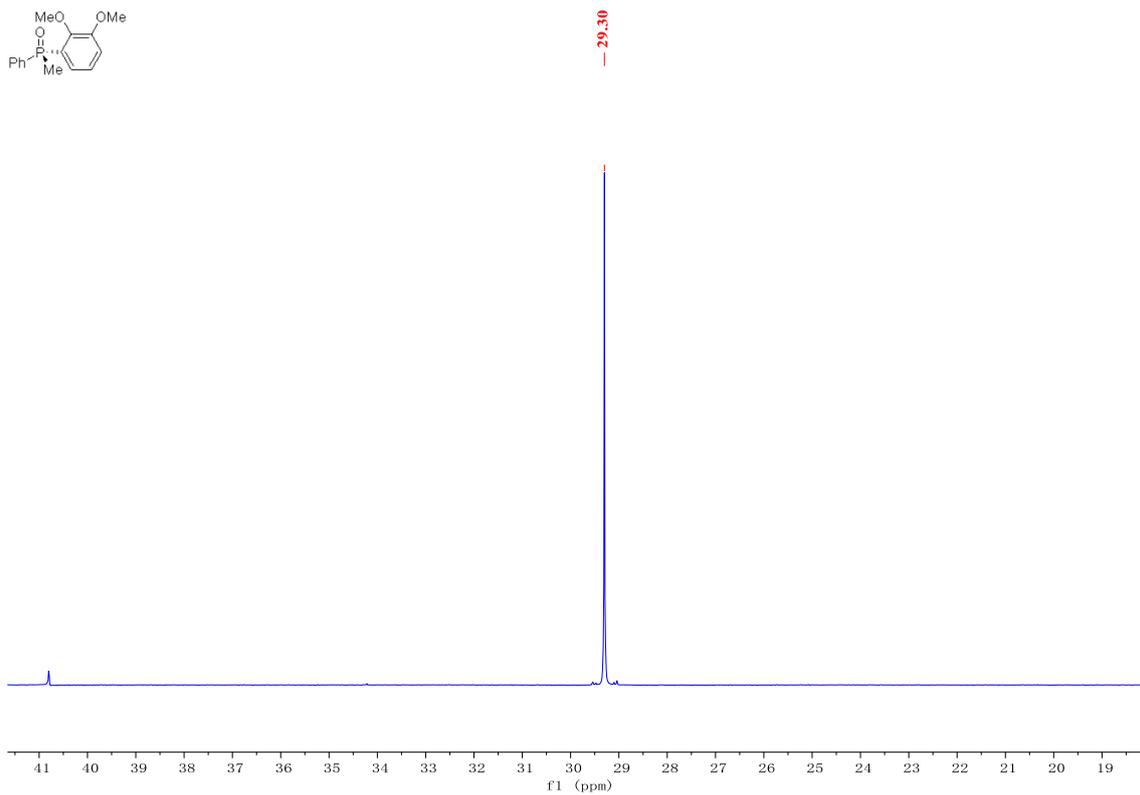
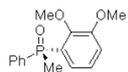


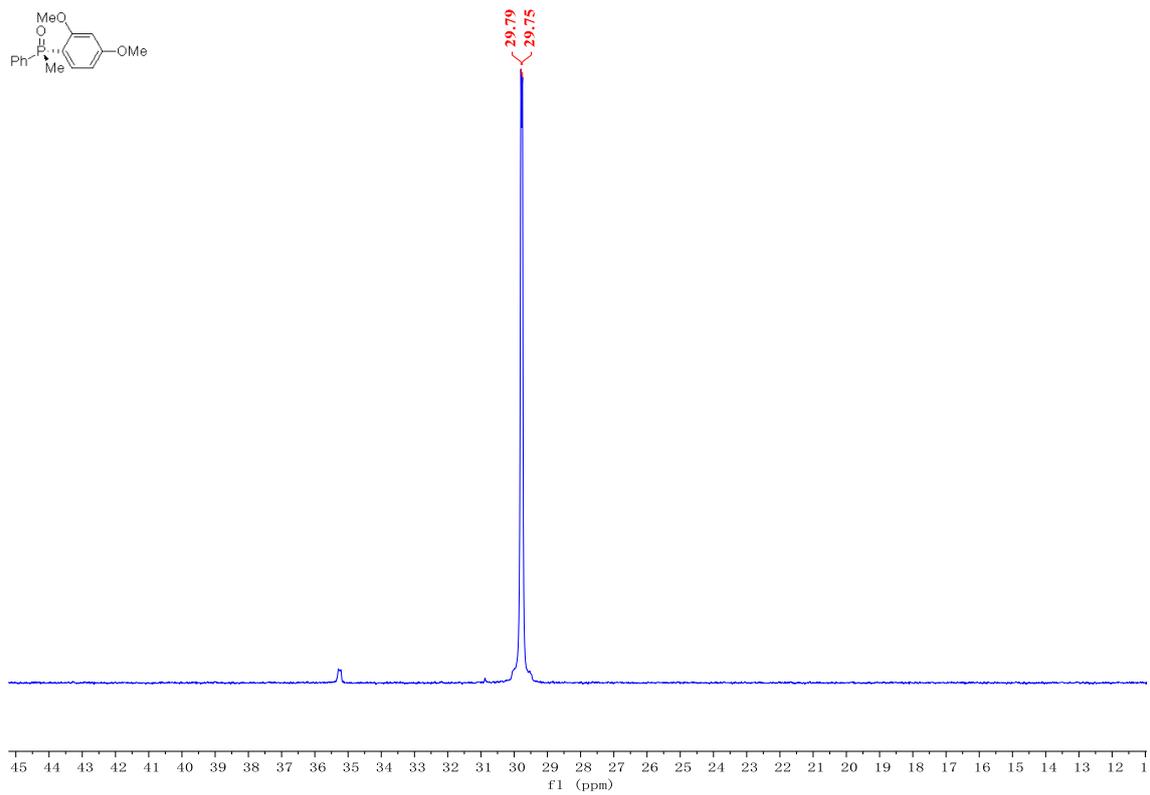
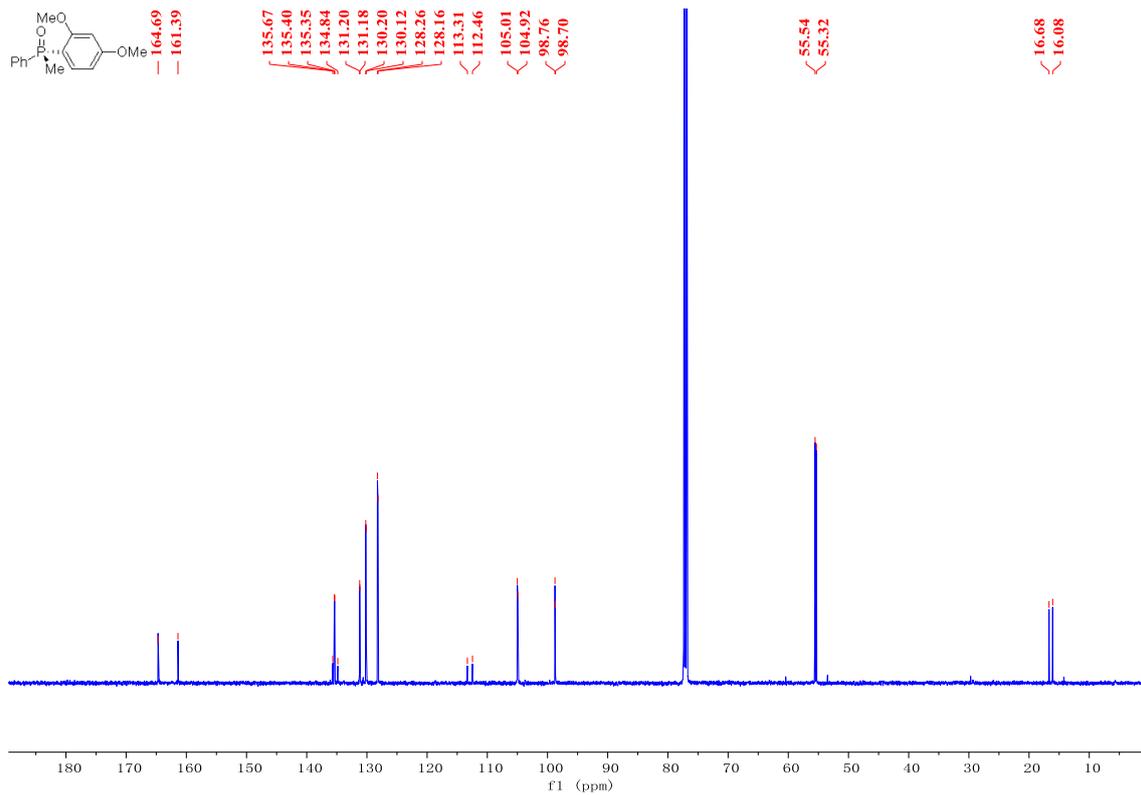


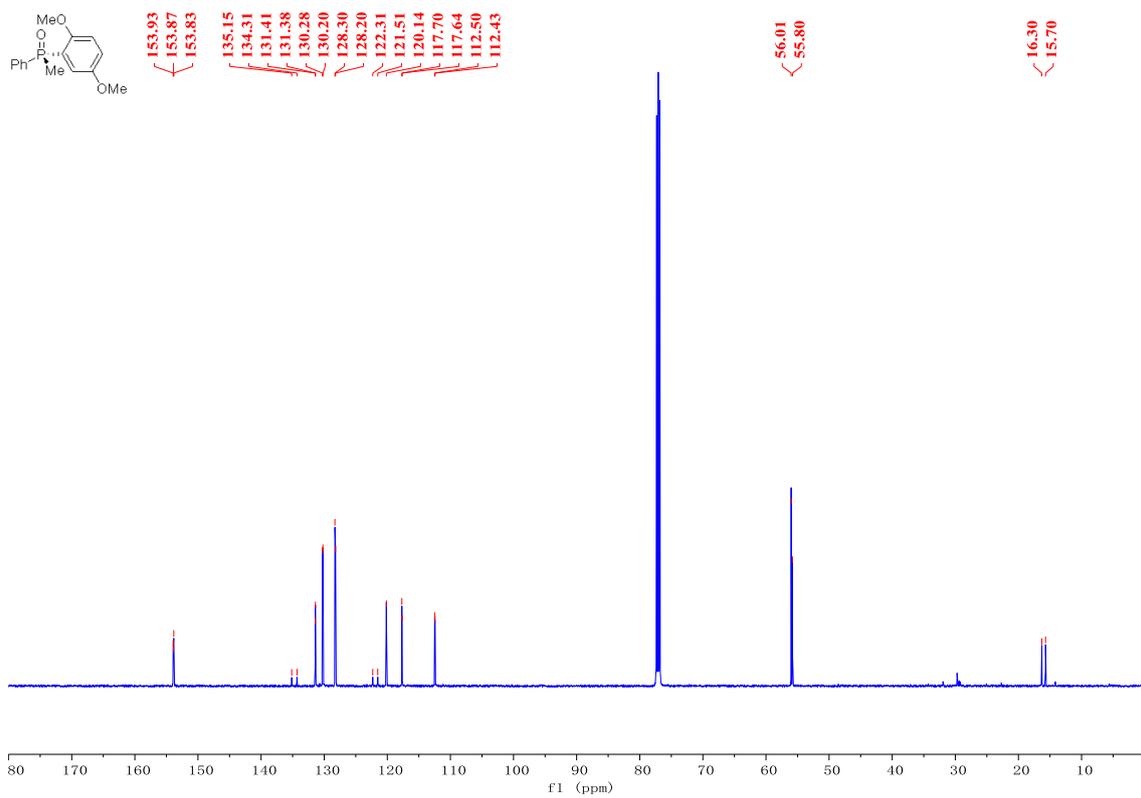
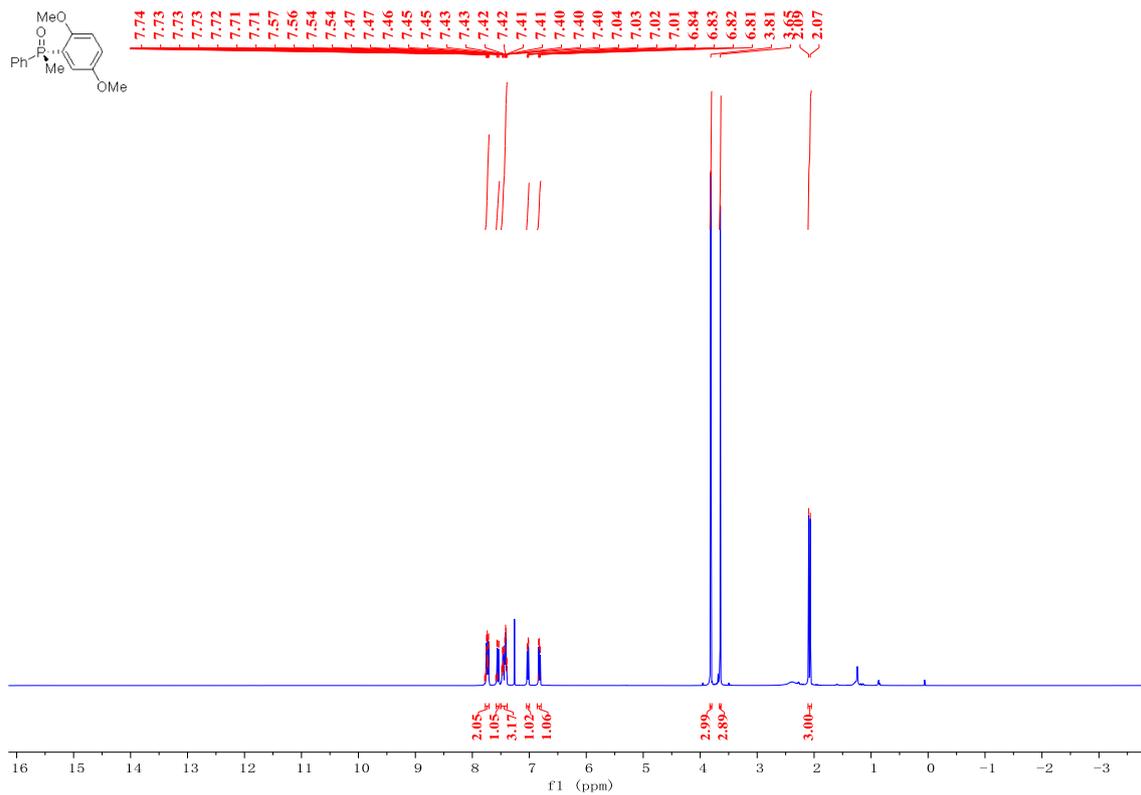


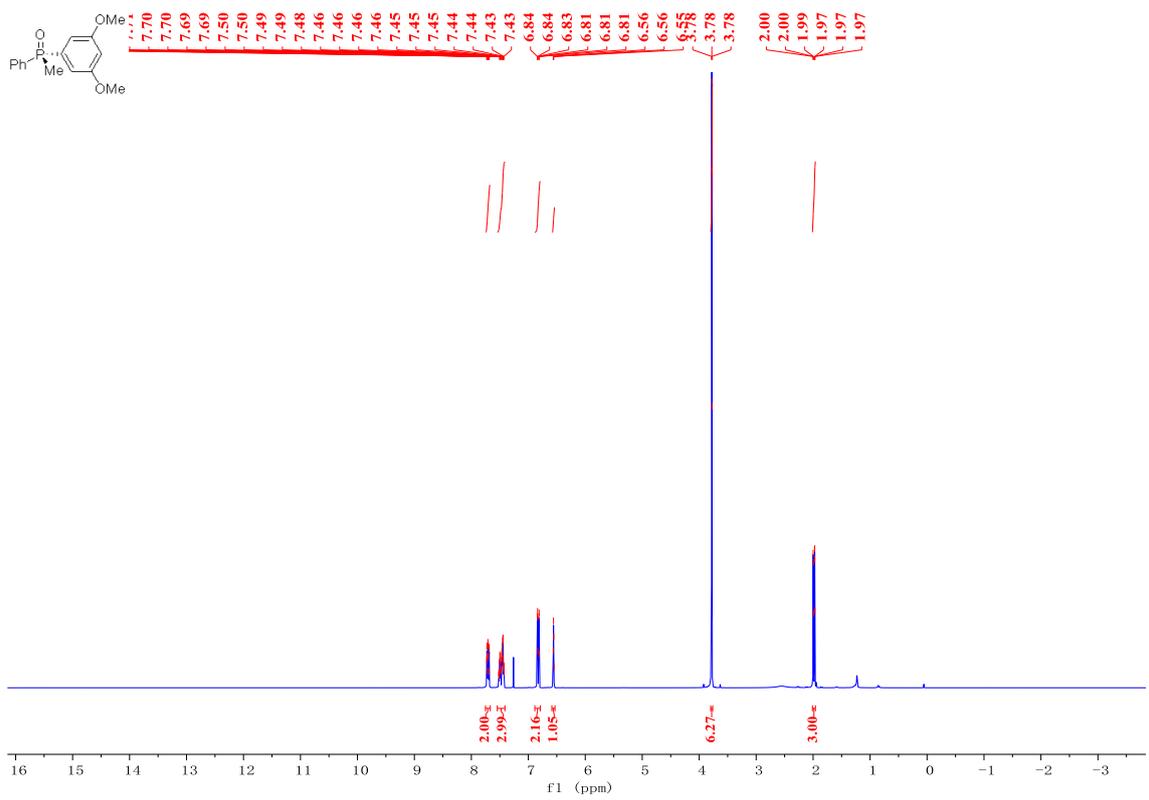
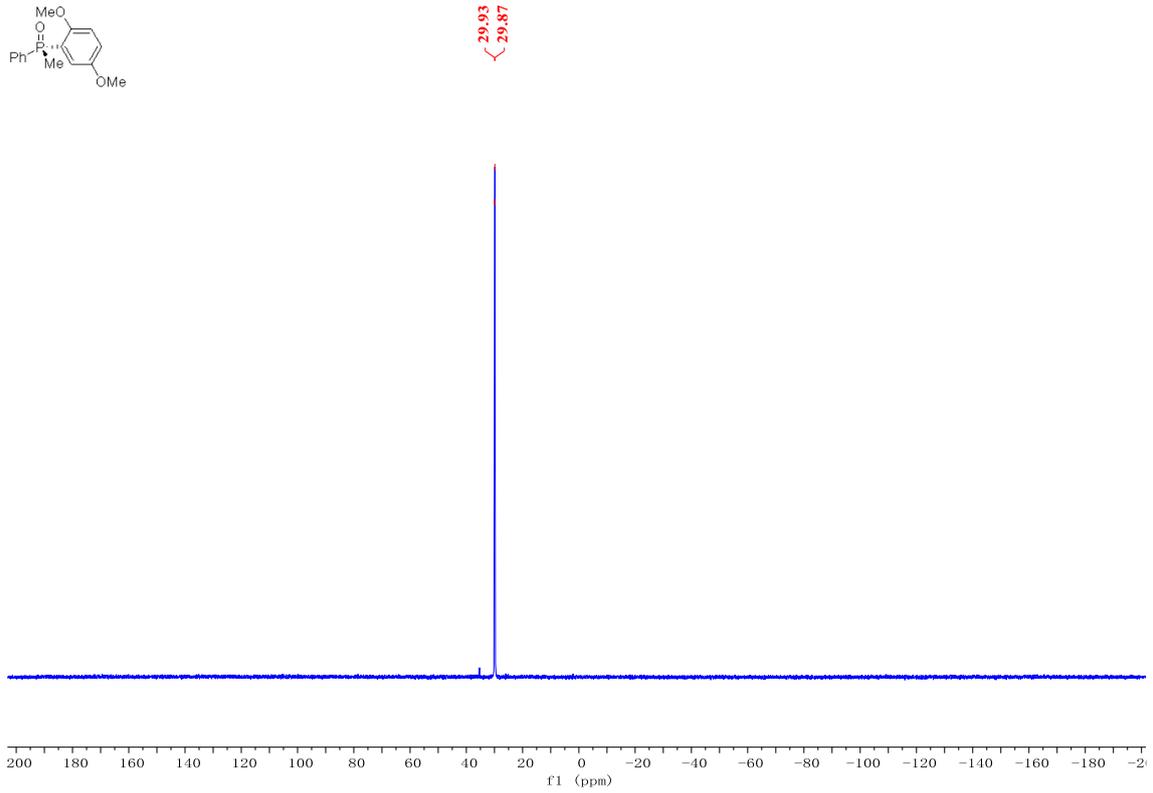
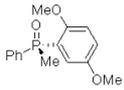


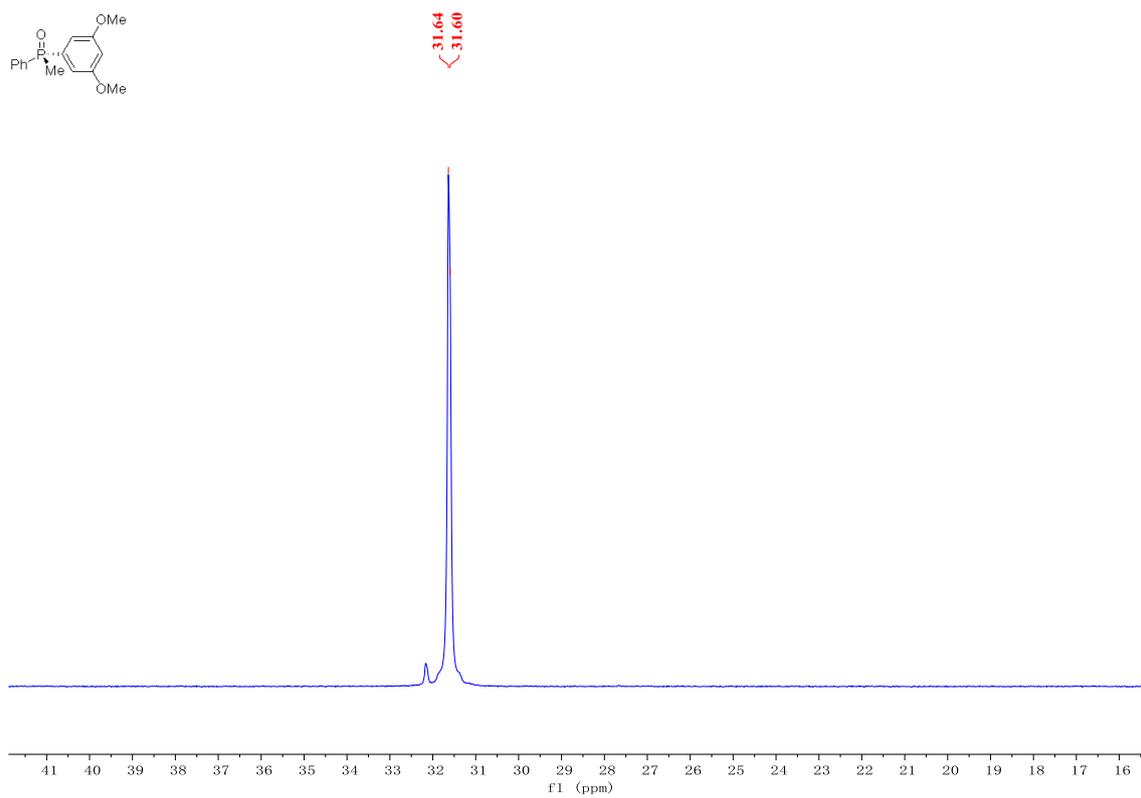
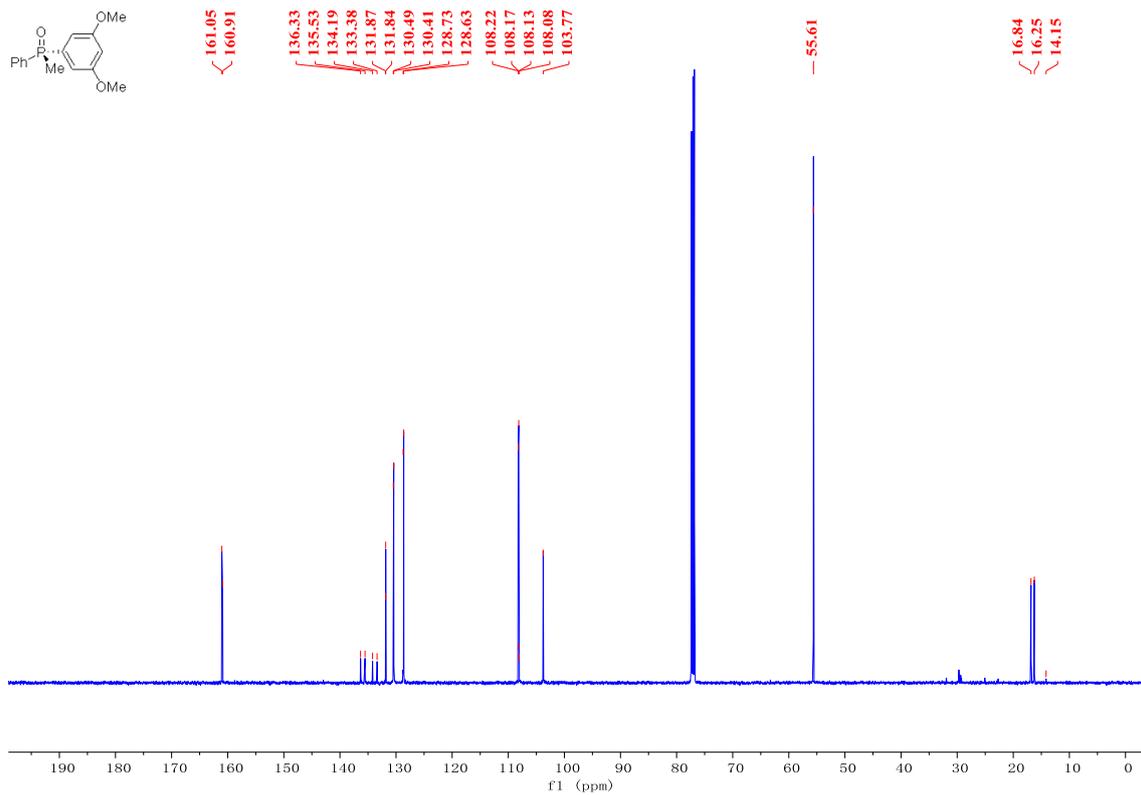


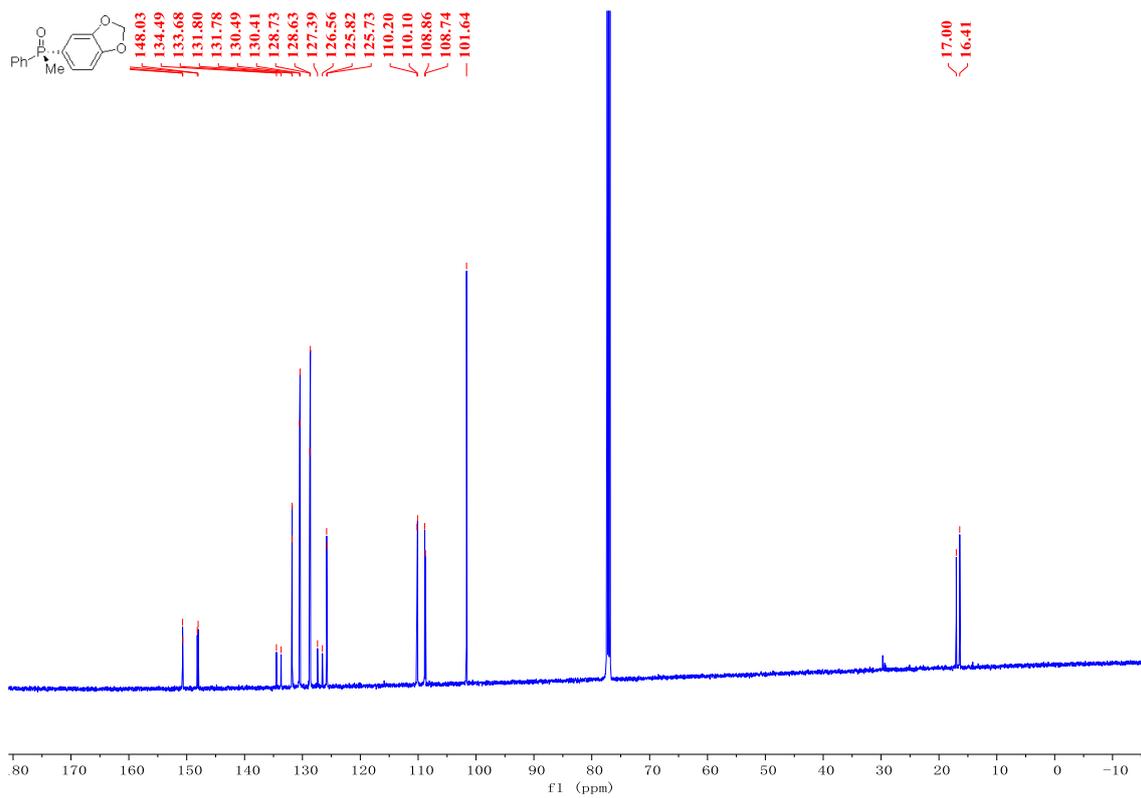
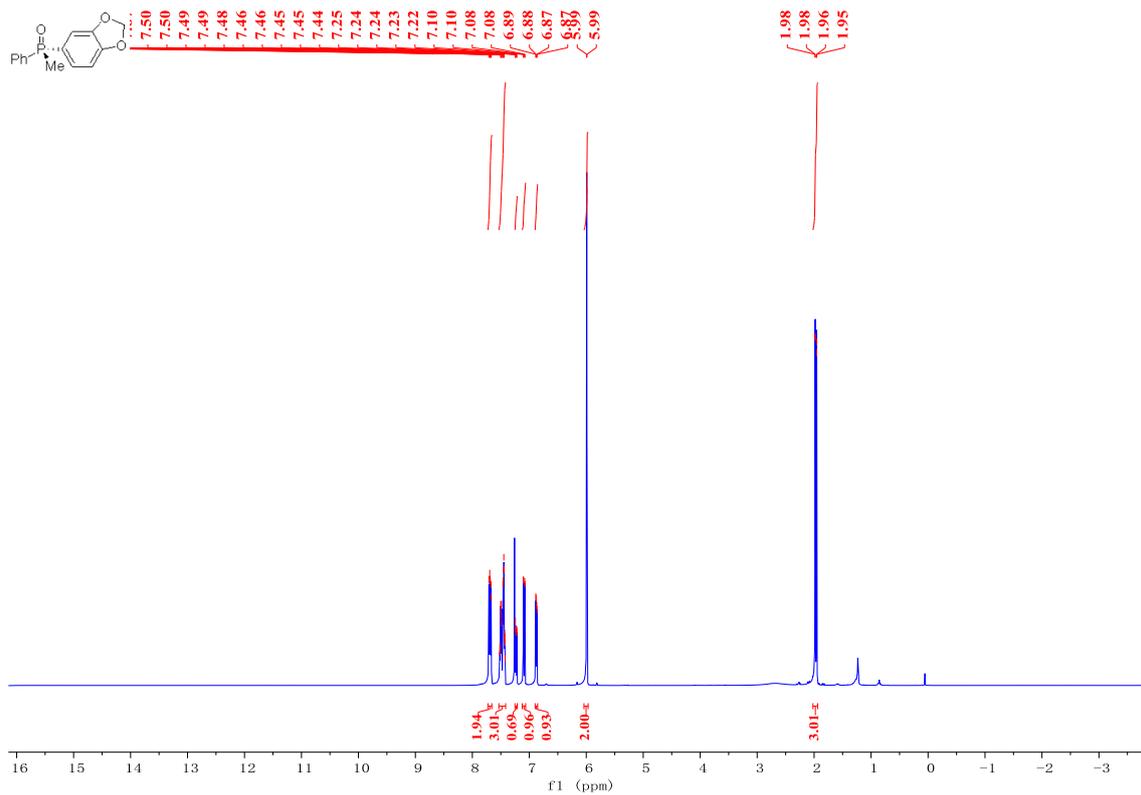


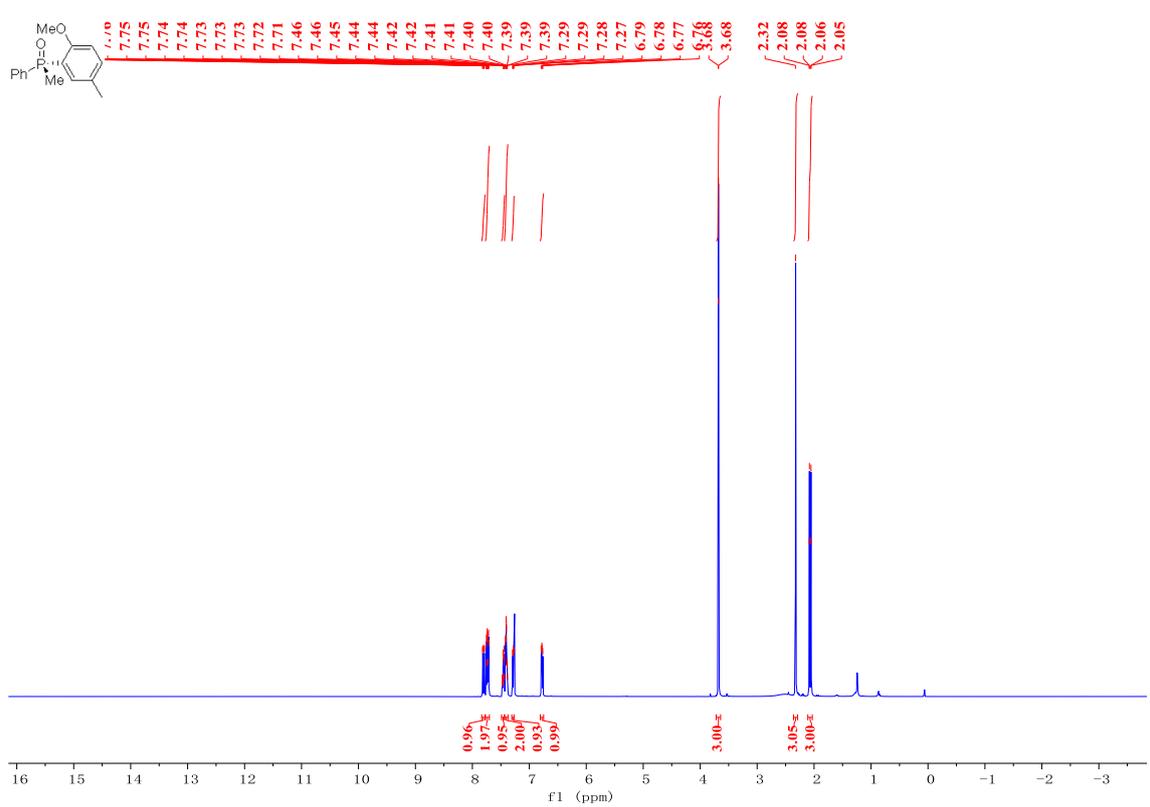
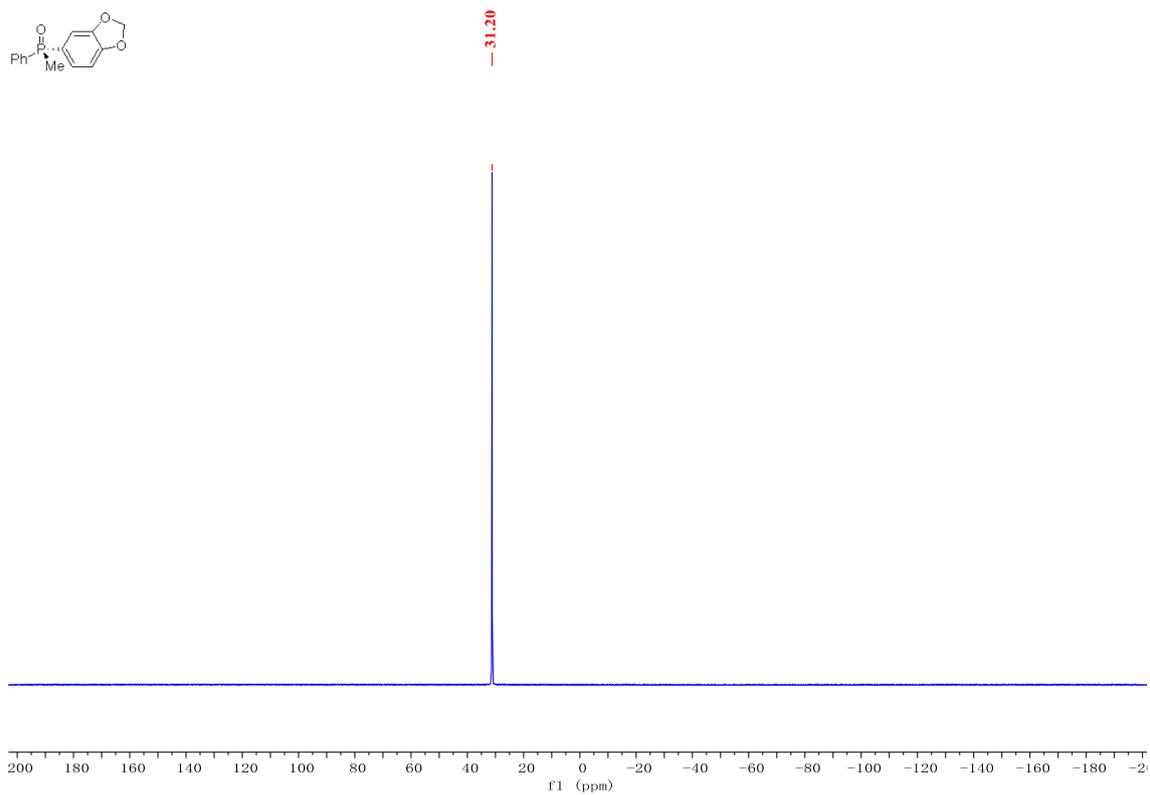
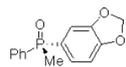


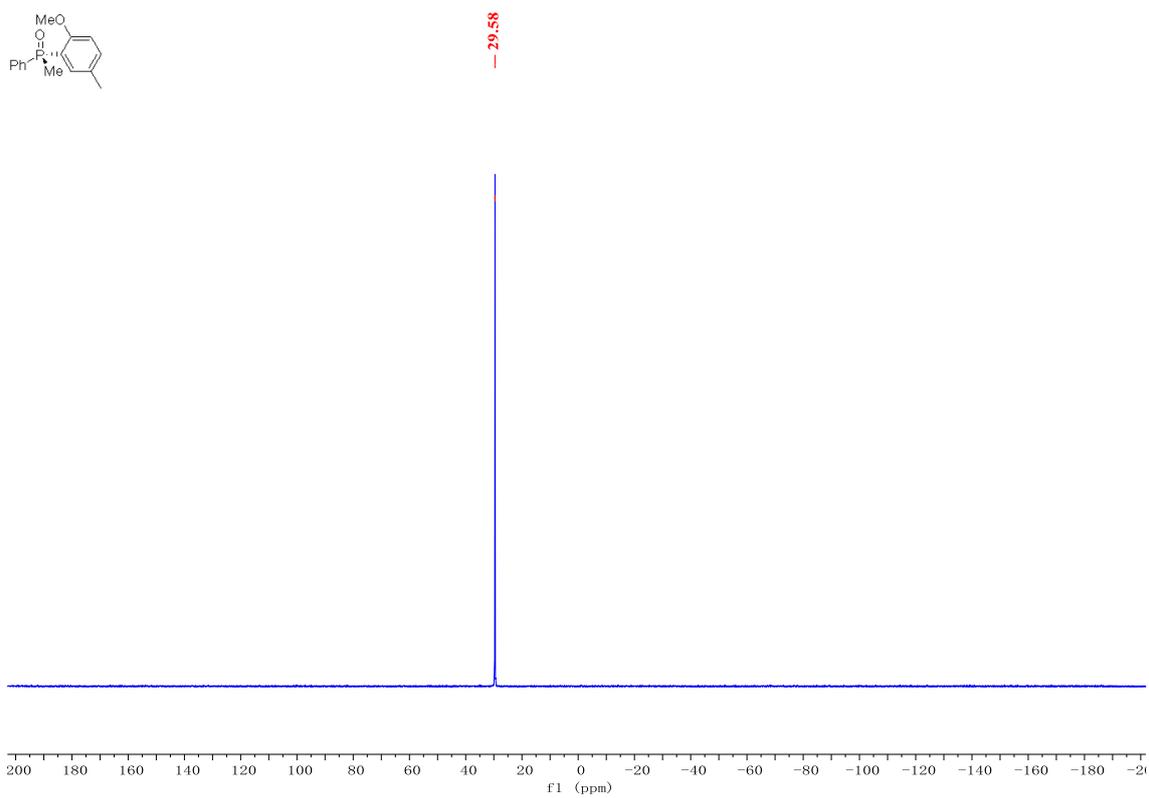
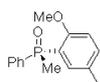
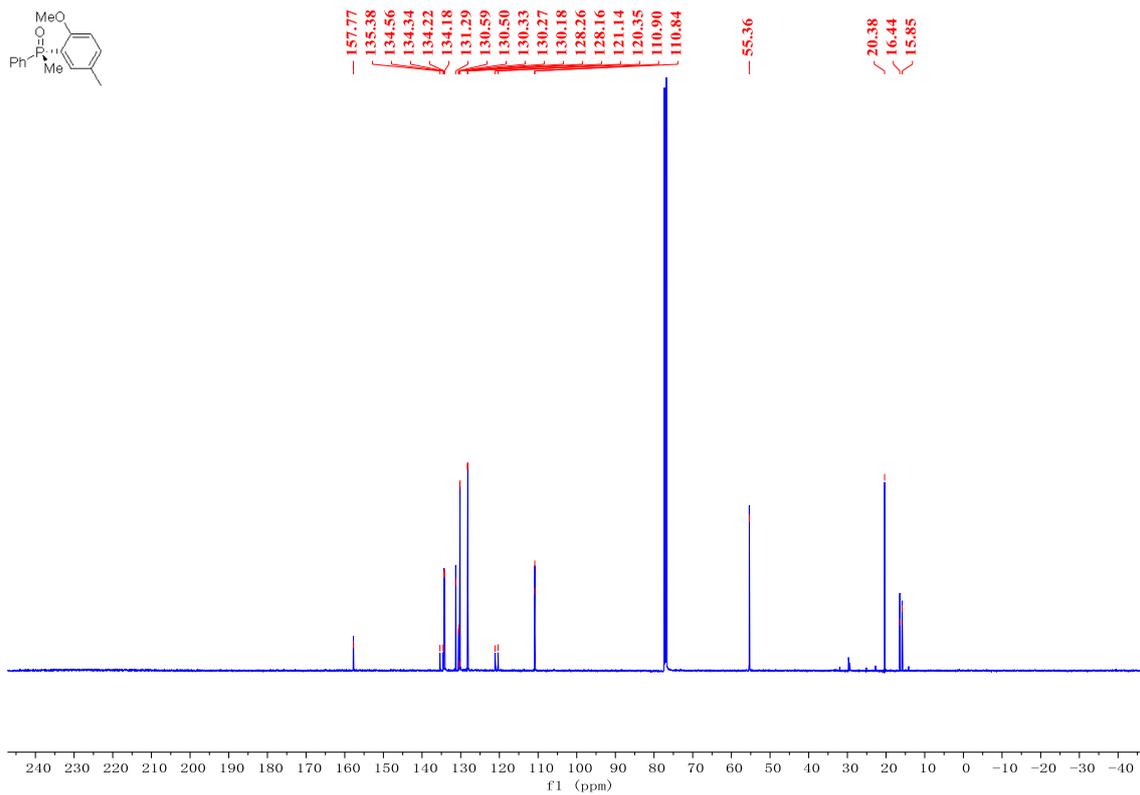
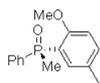


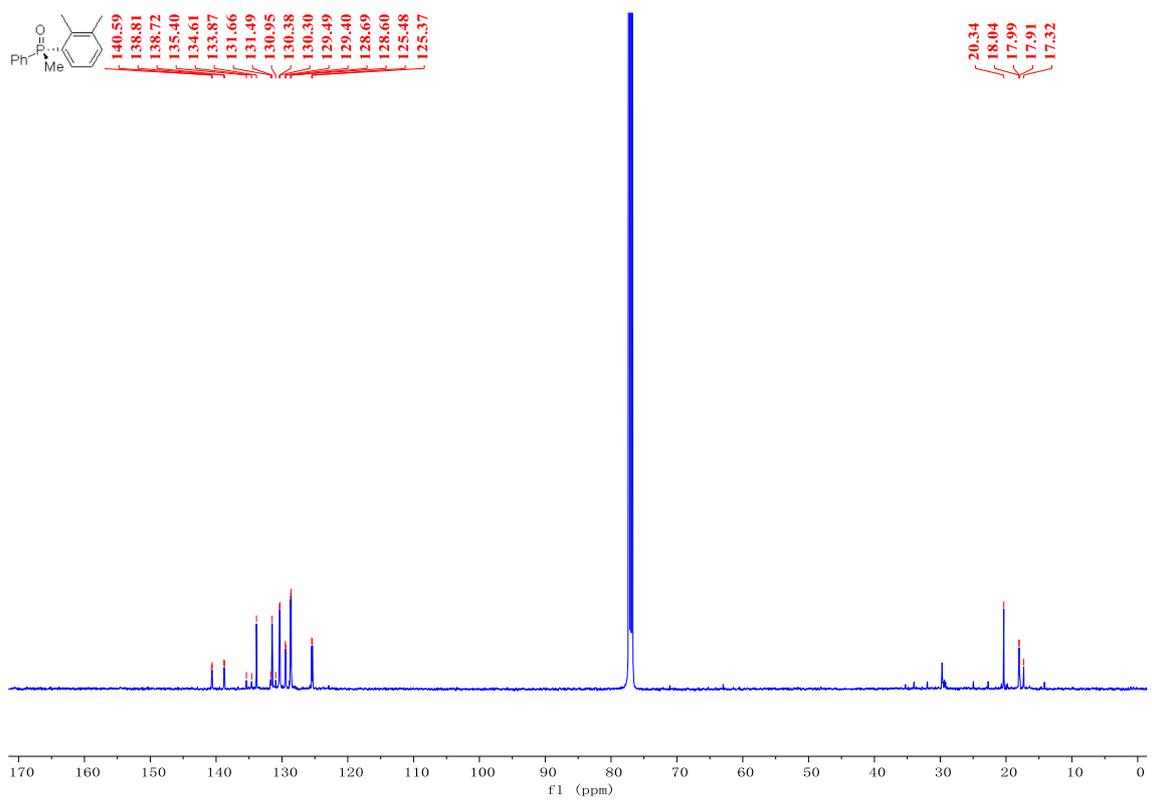
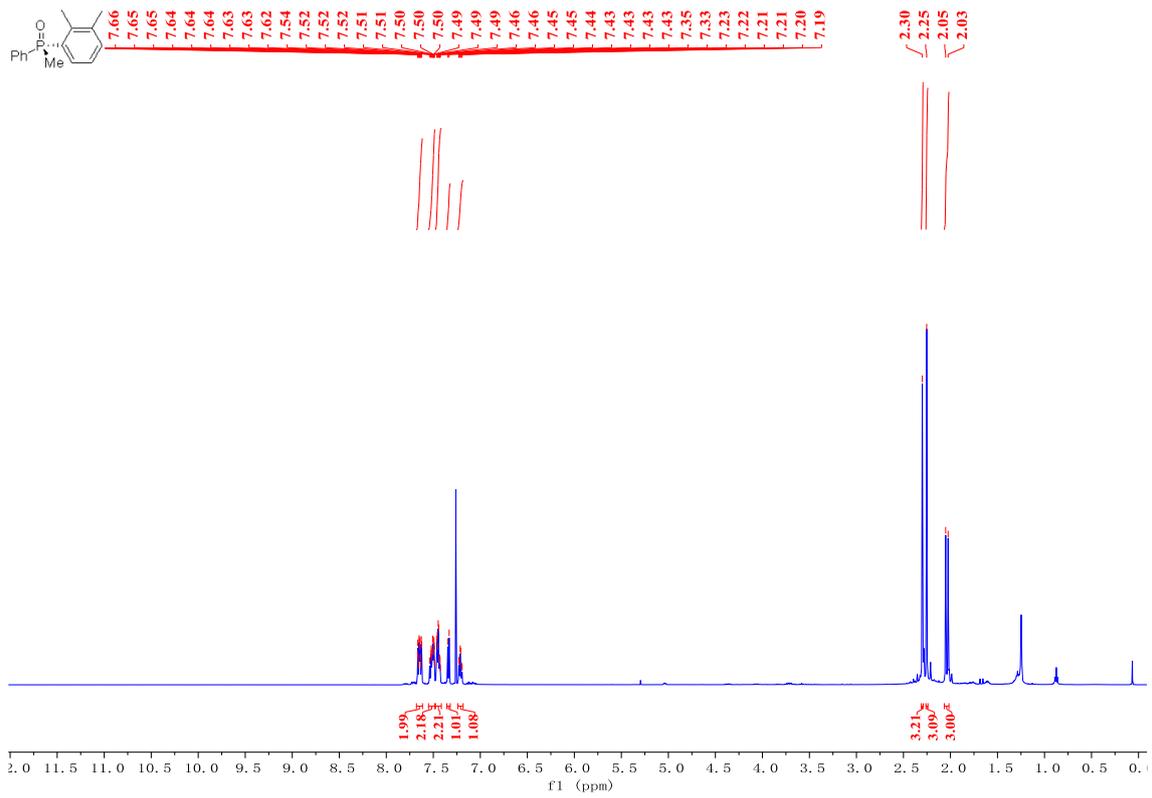


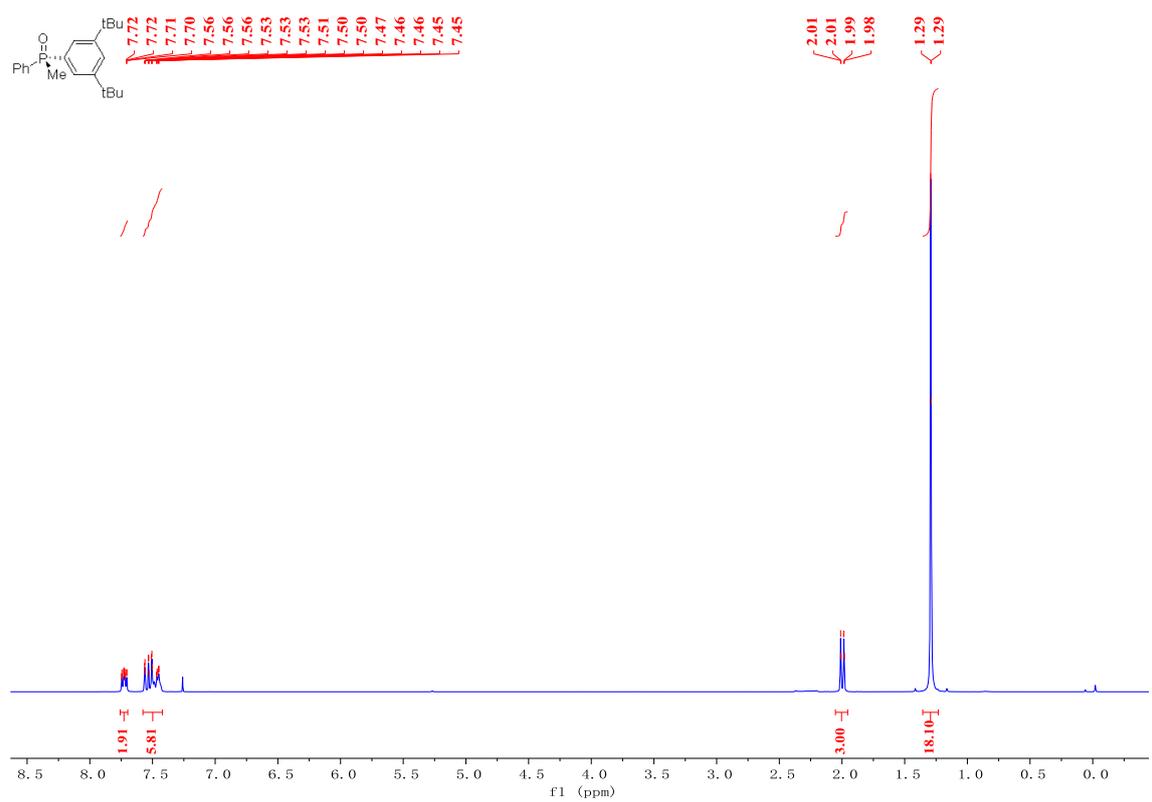
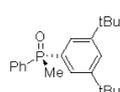
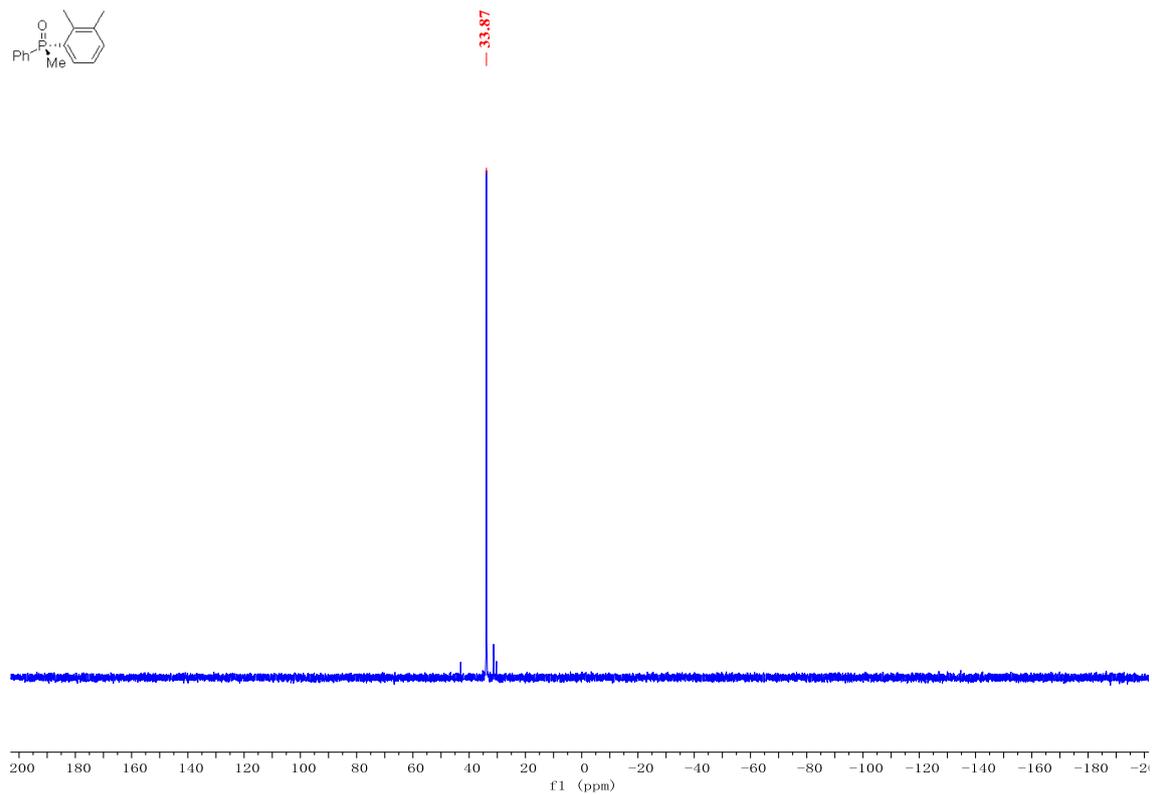
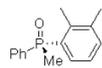


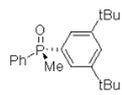






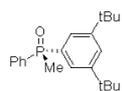
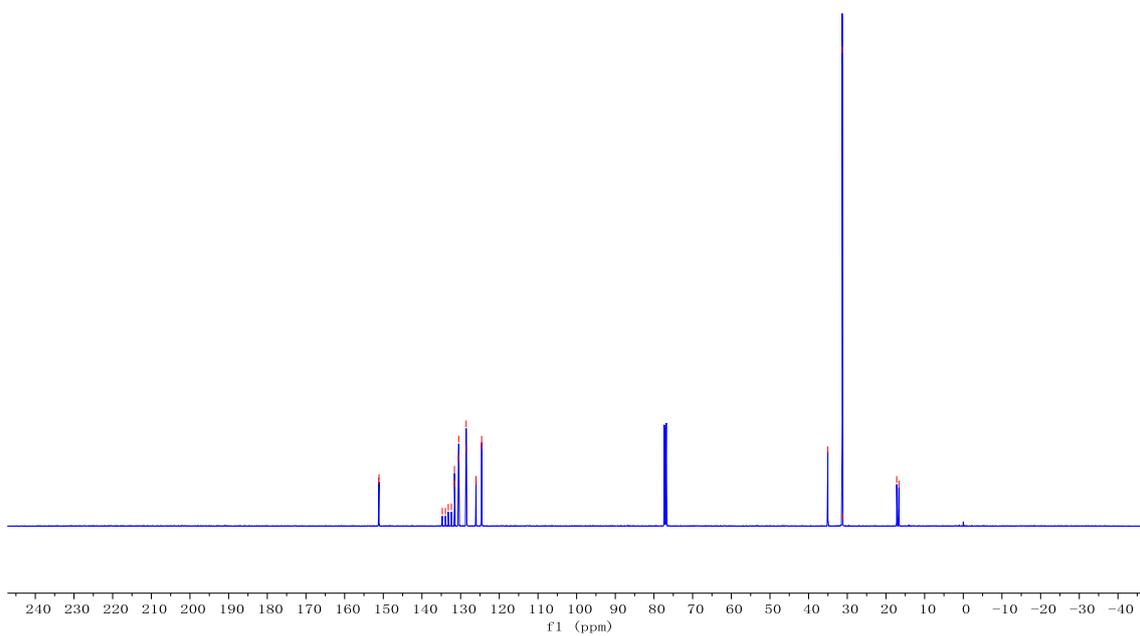




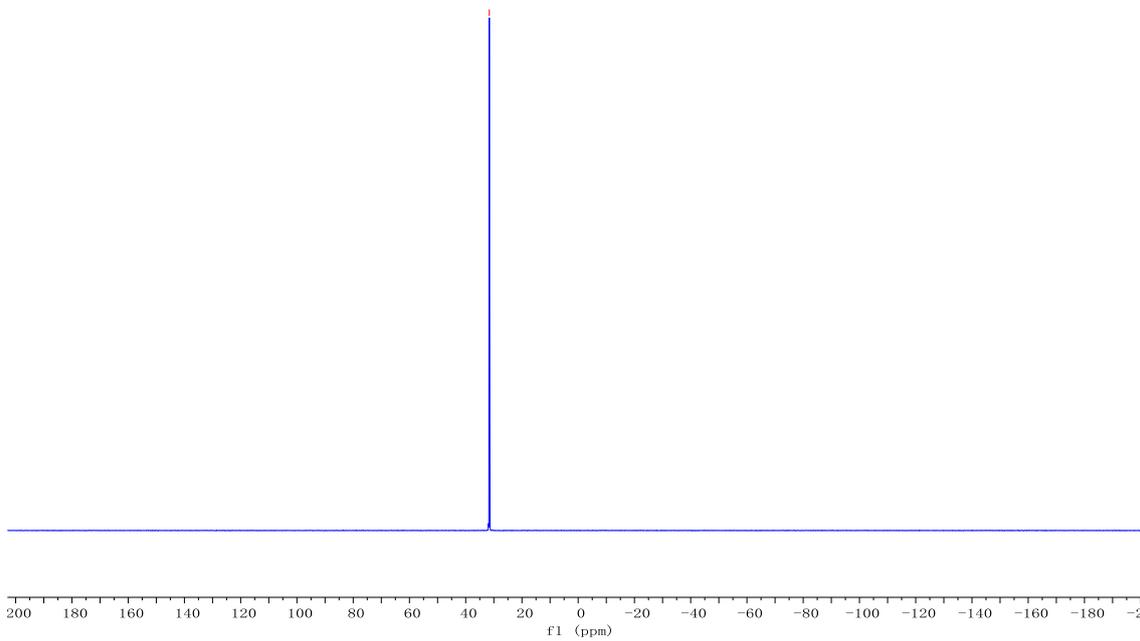


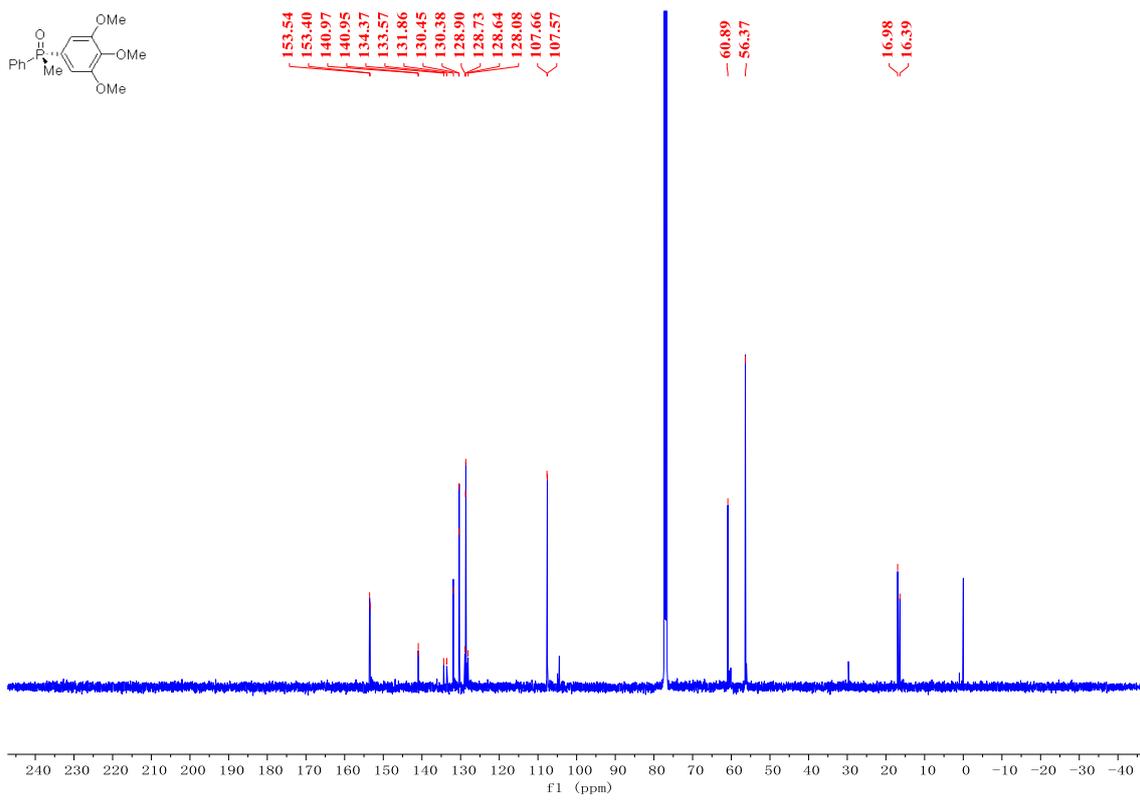
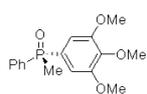
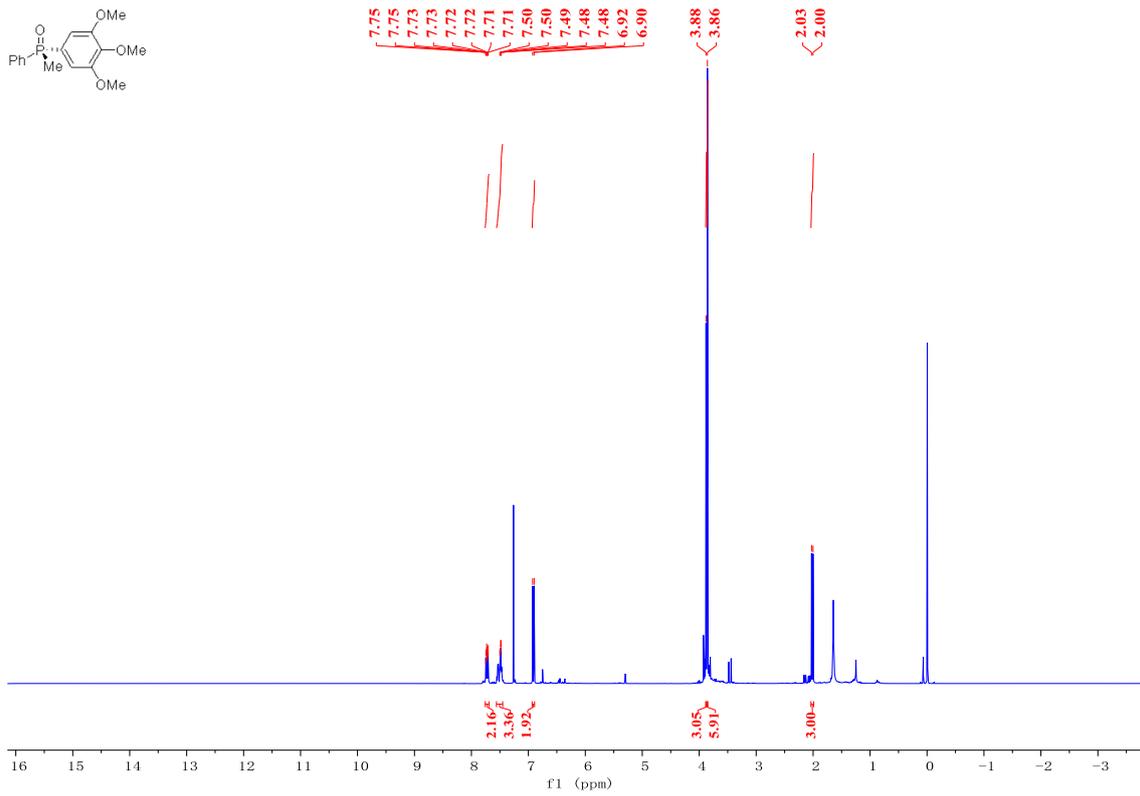
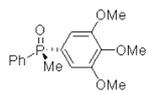
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124.64  
124.56

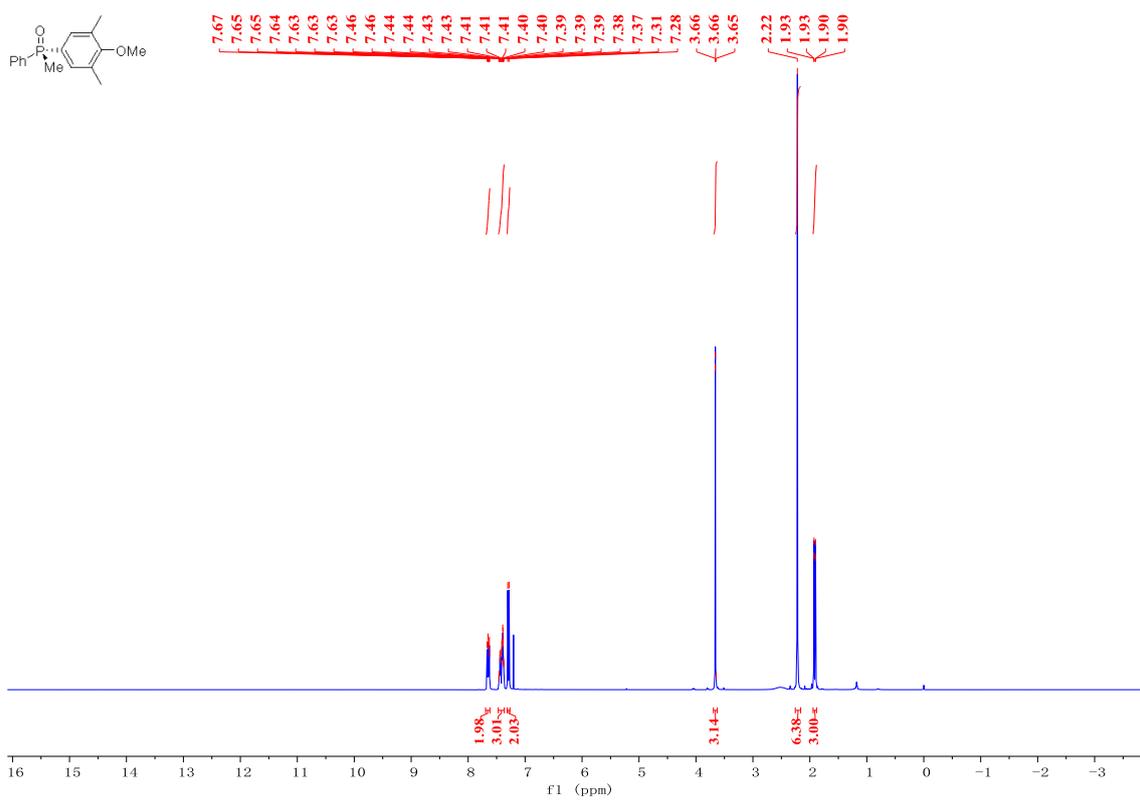
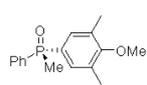
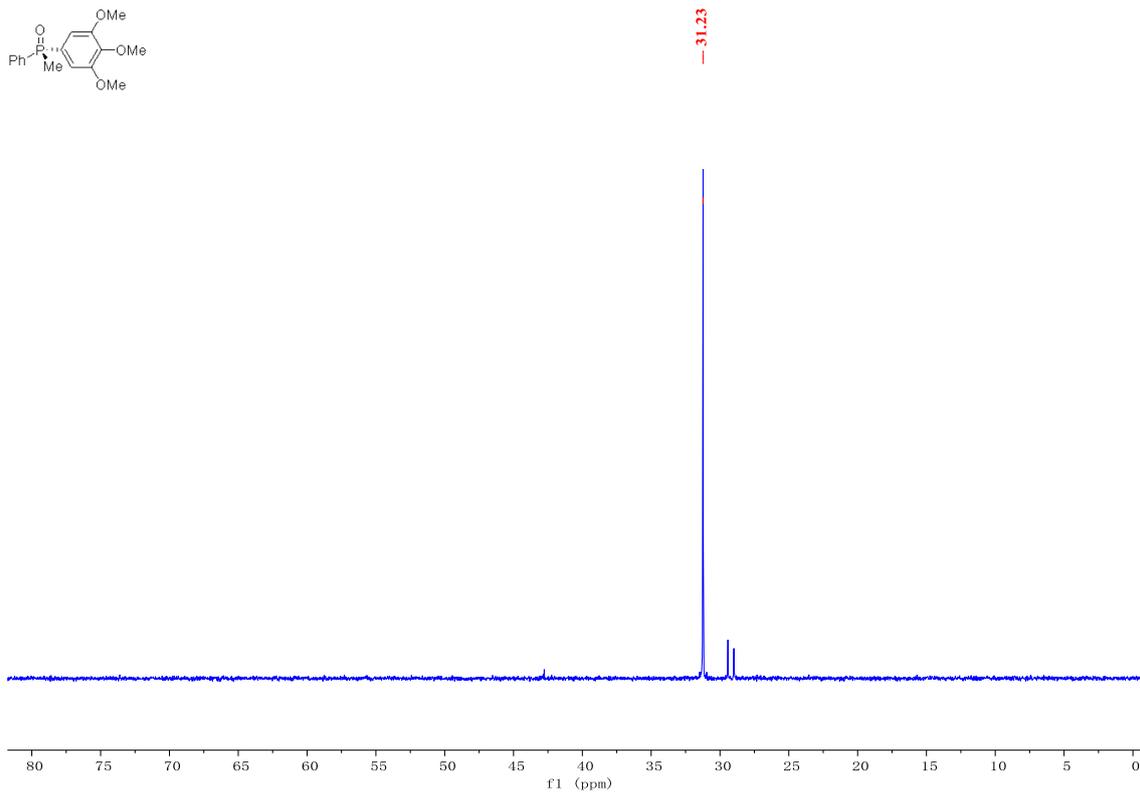
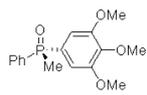
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16.64

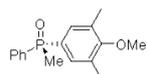


31.60





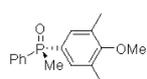
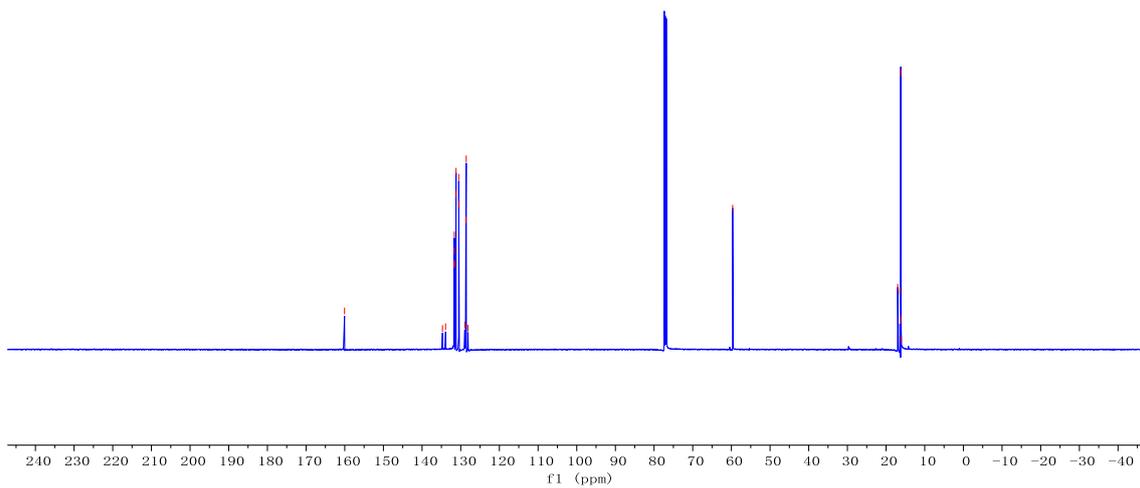




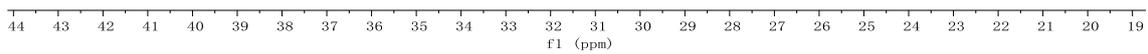
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128.13

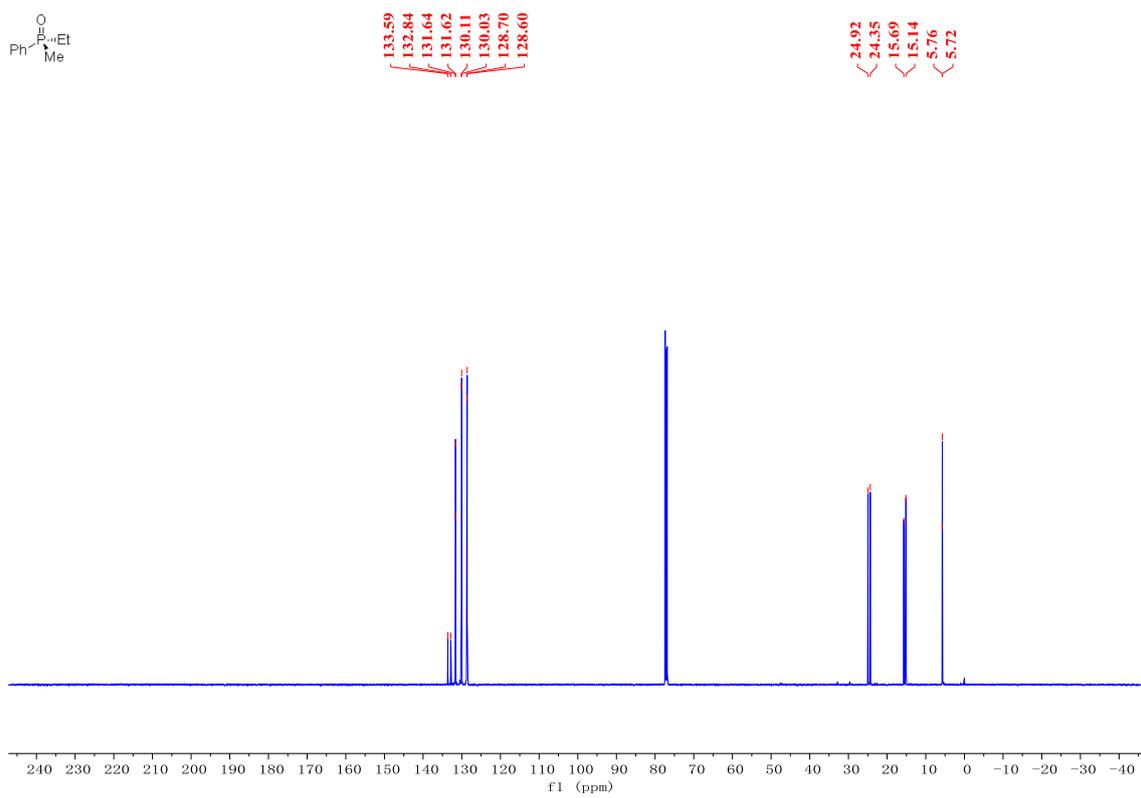
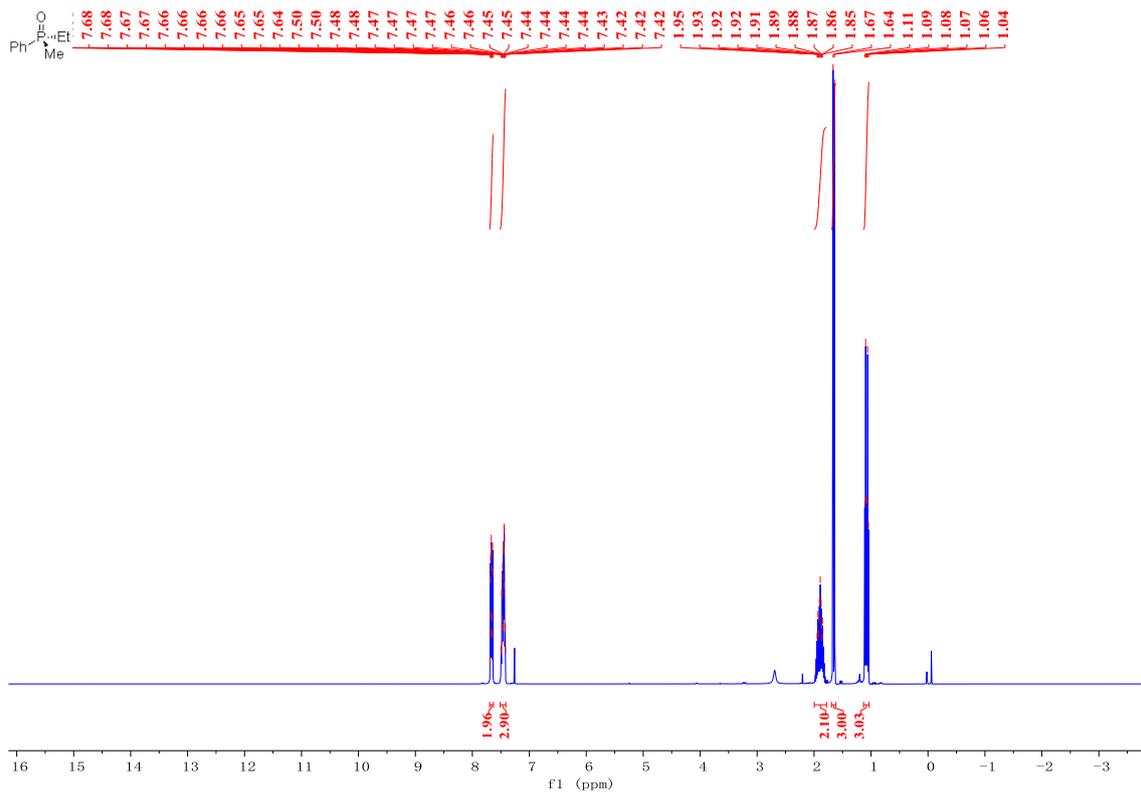
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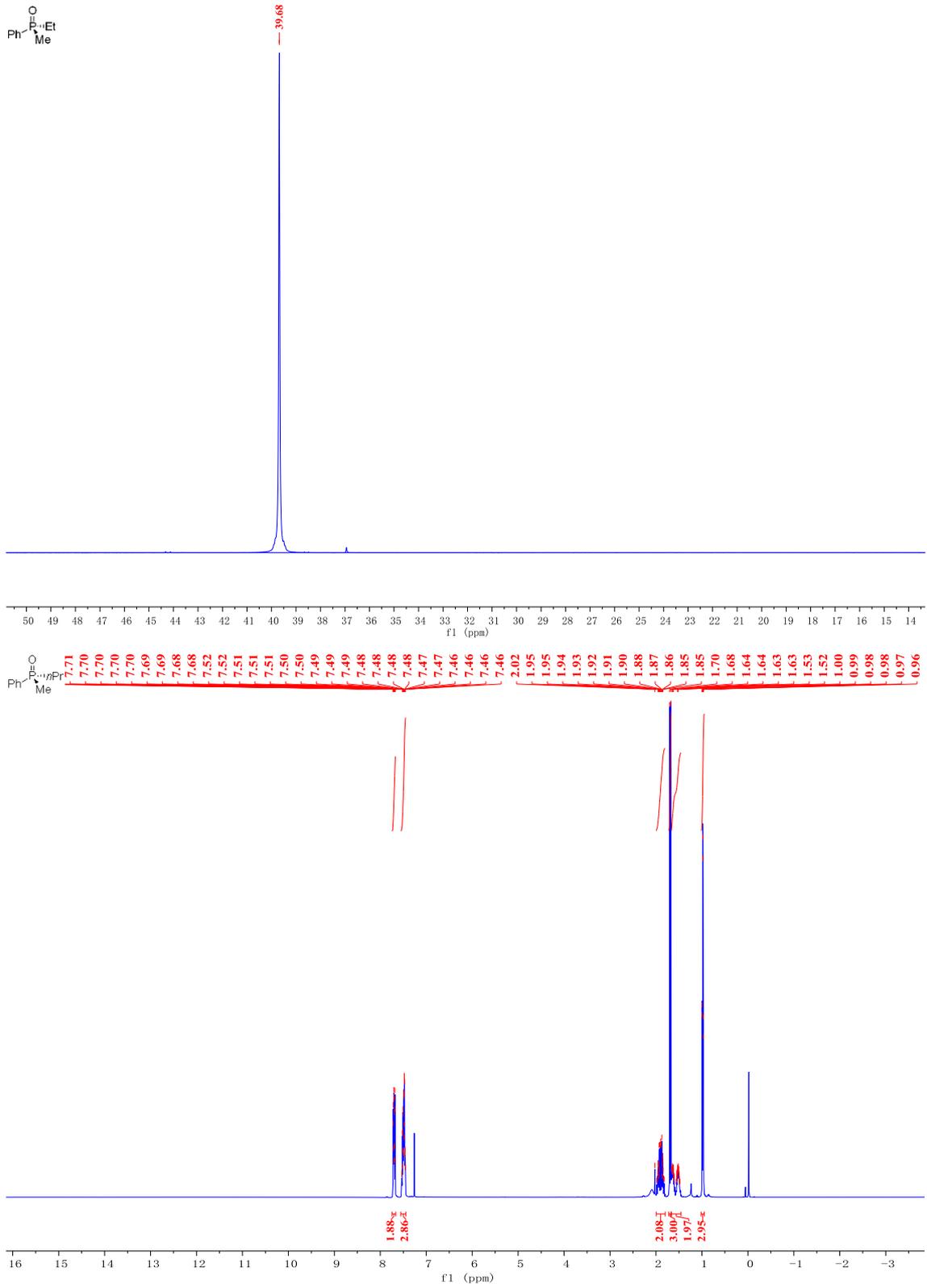
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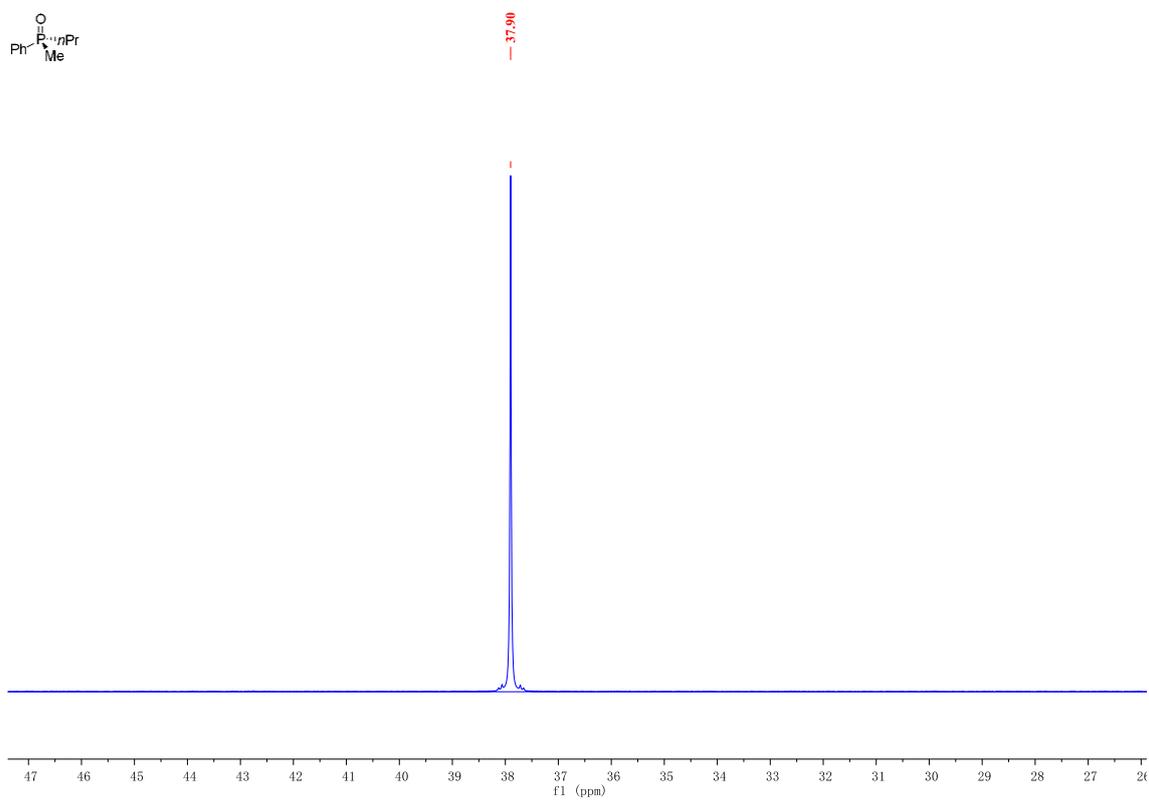
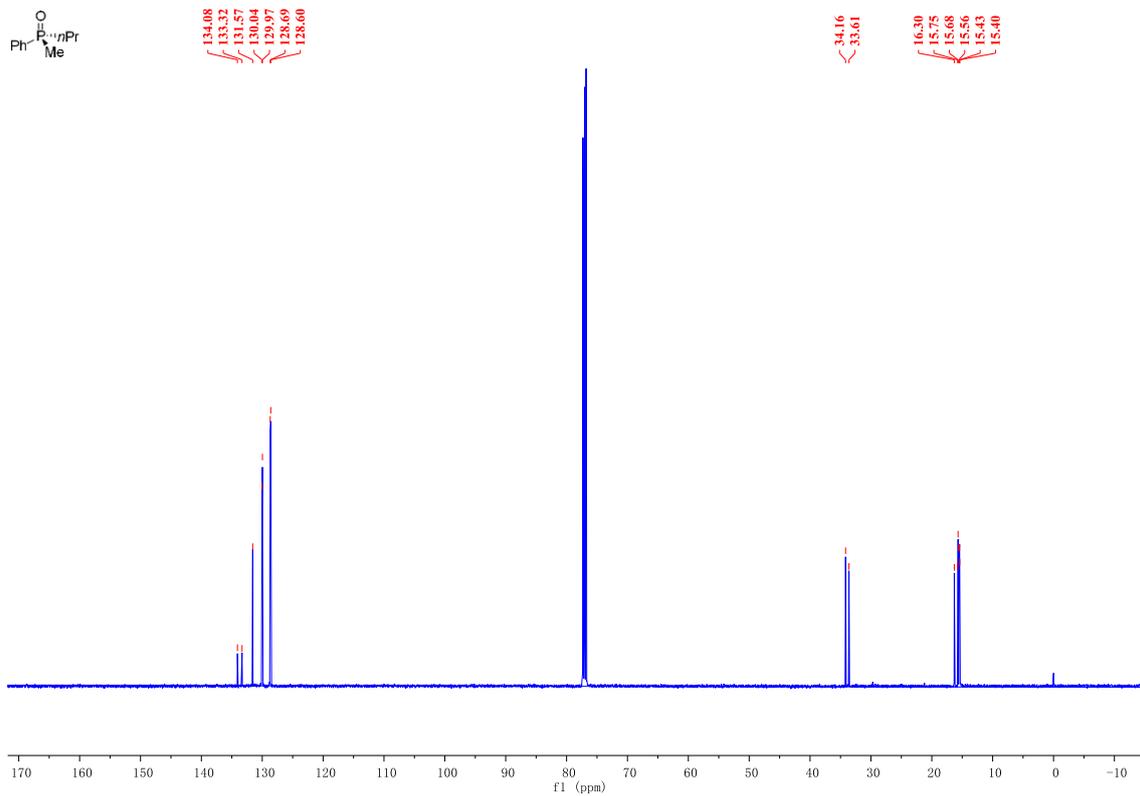


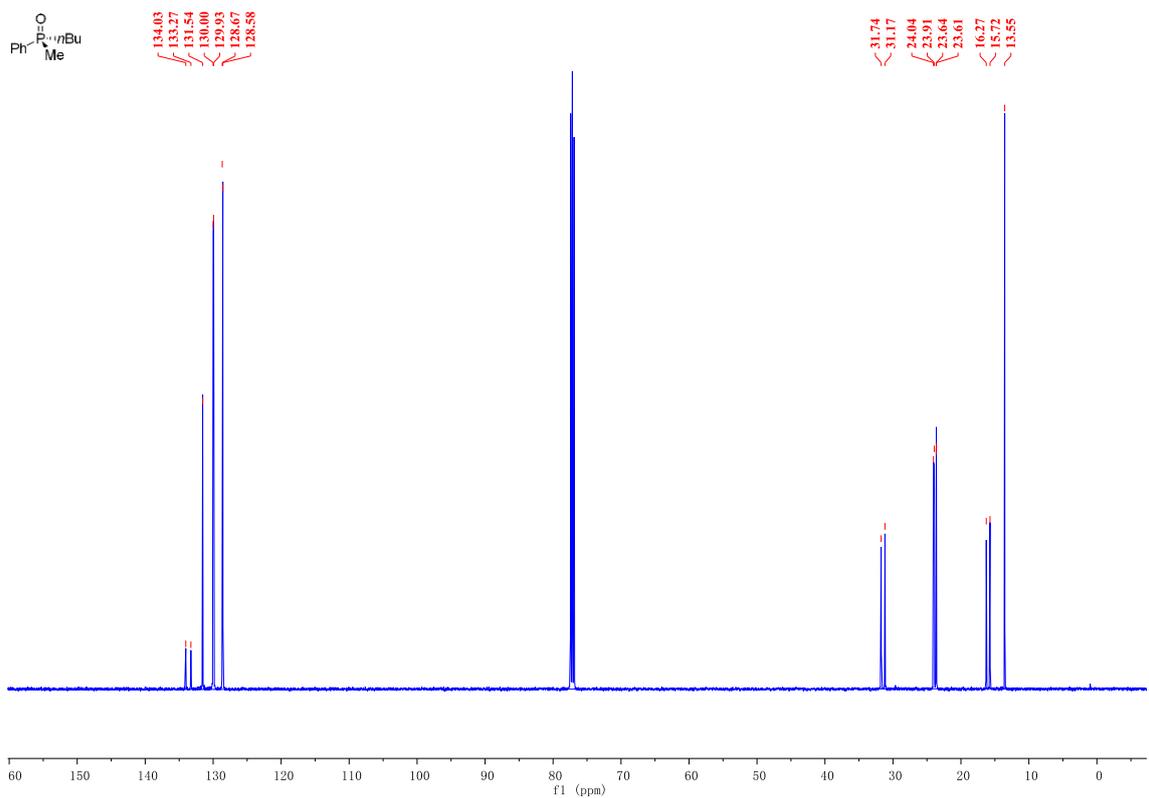
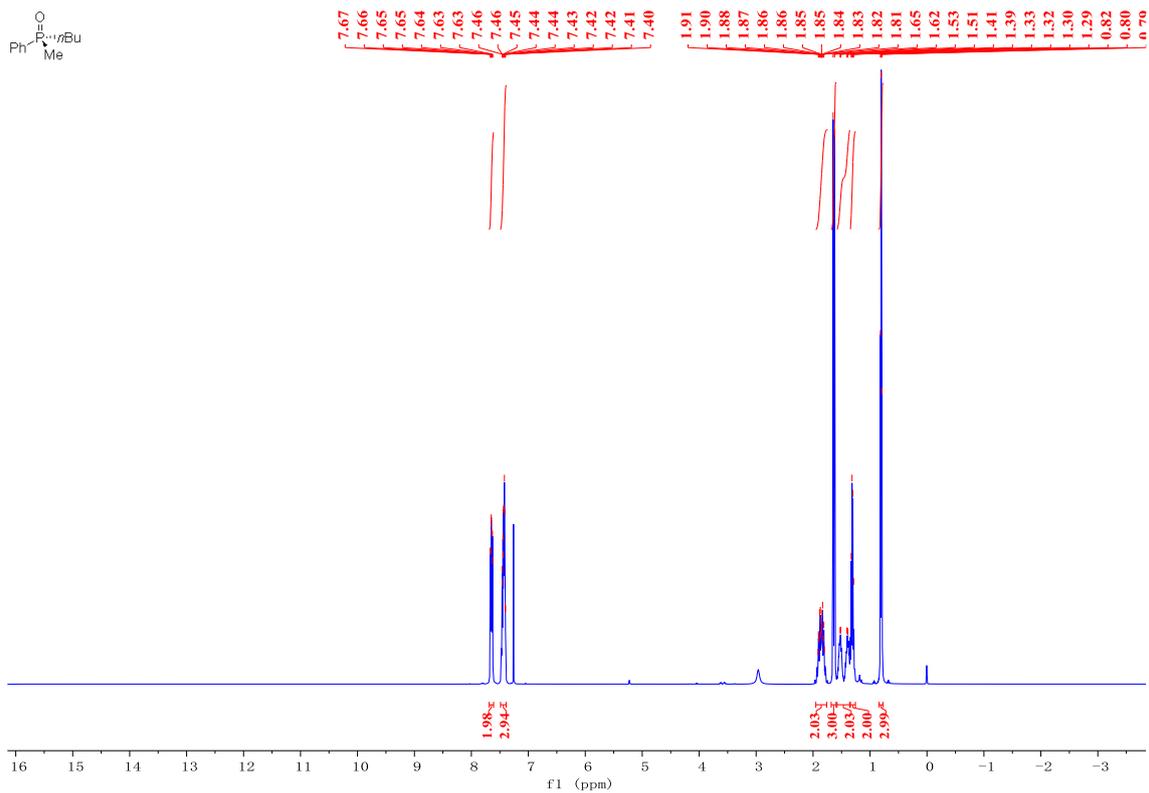
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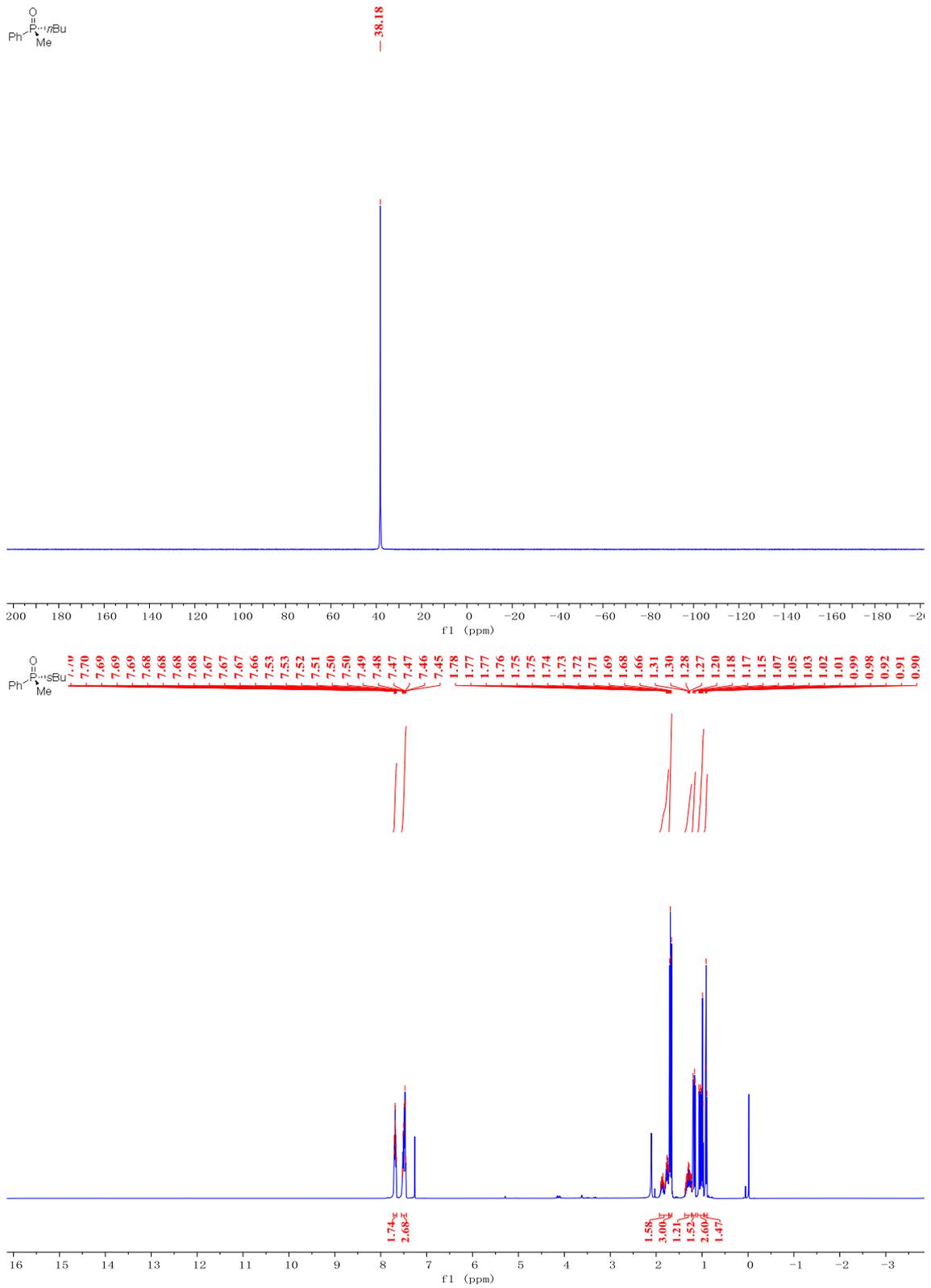








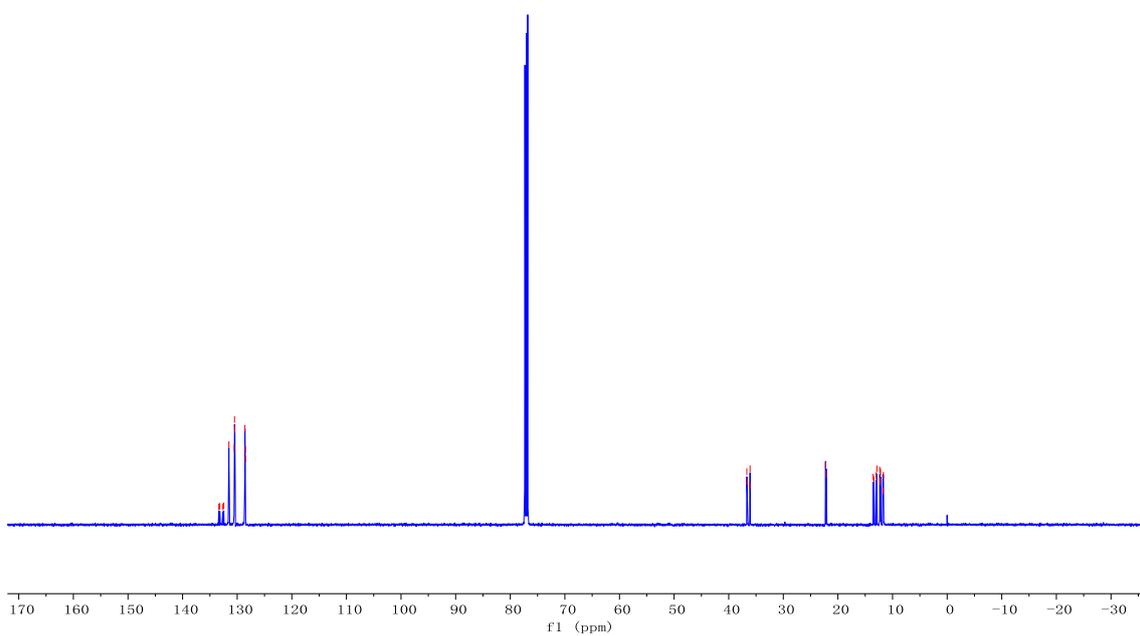




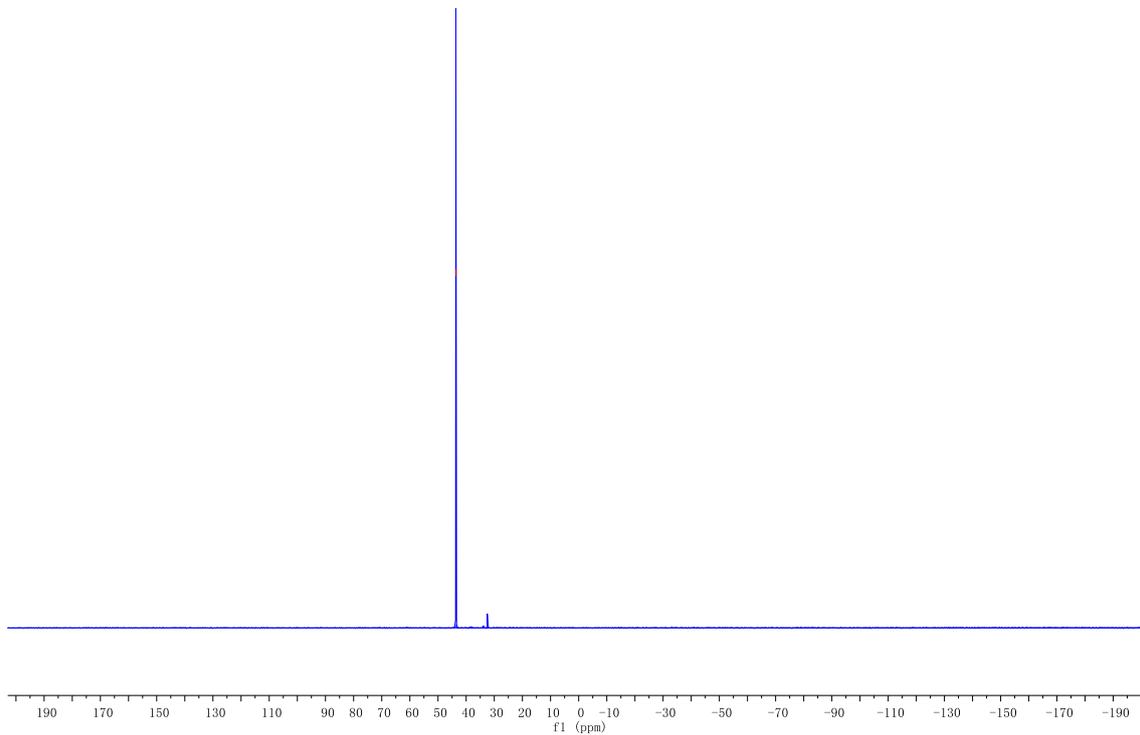


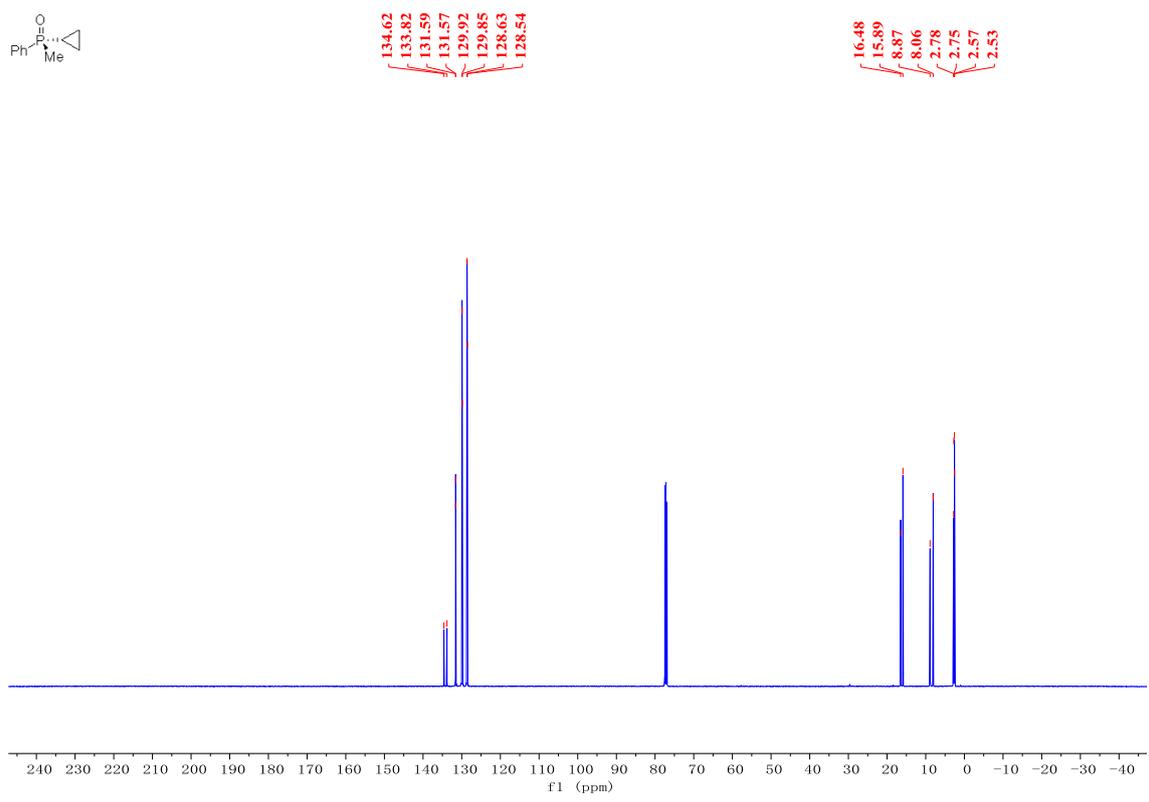
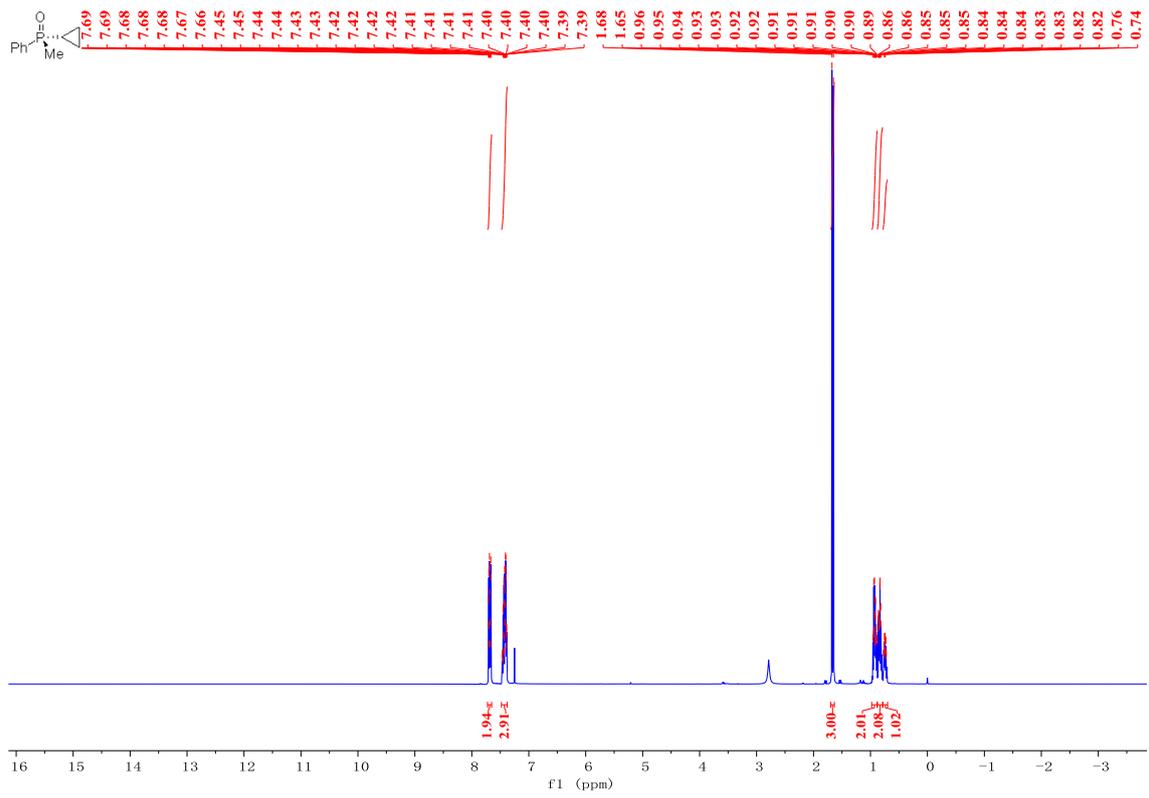
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128.48

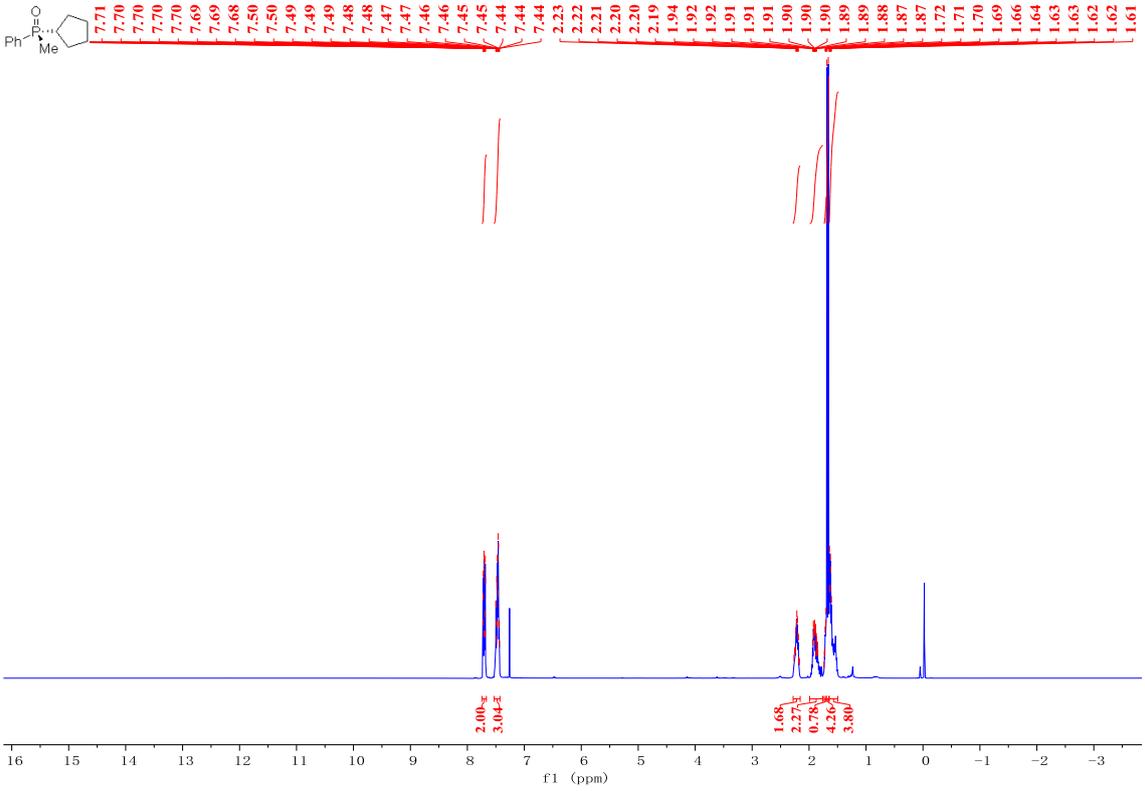
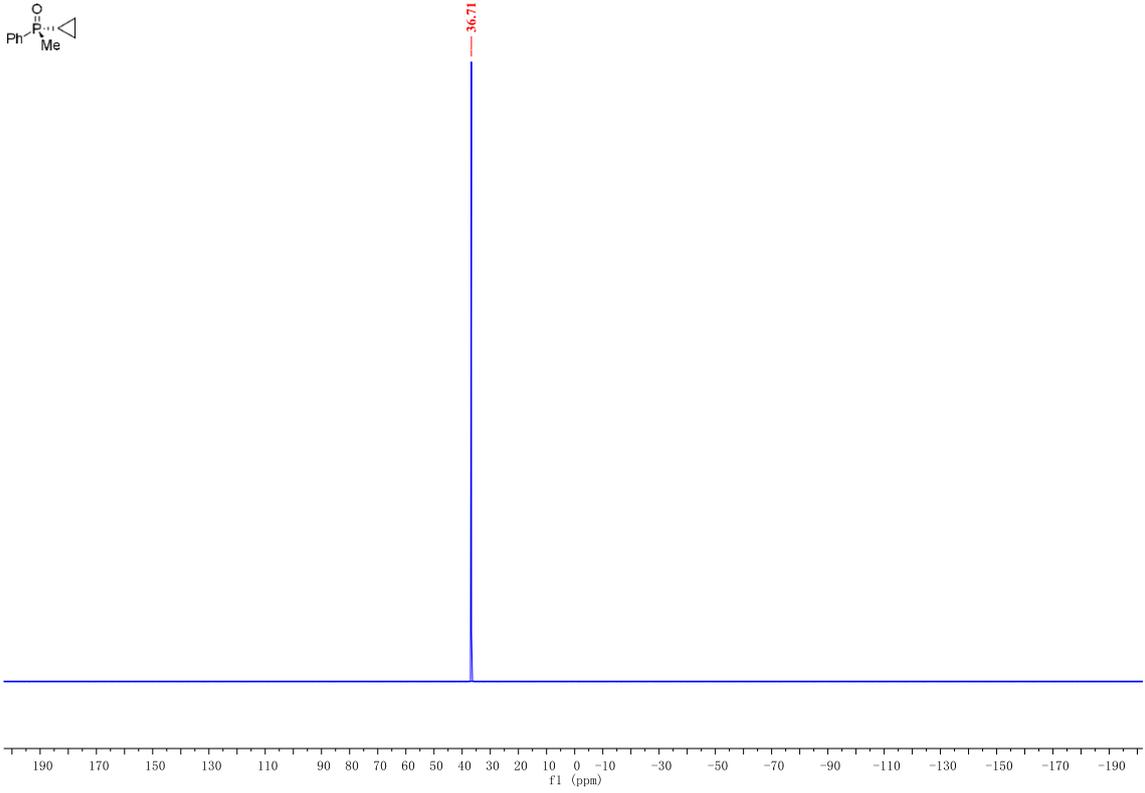
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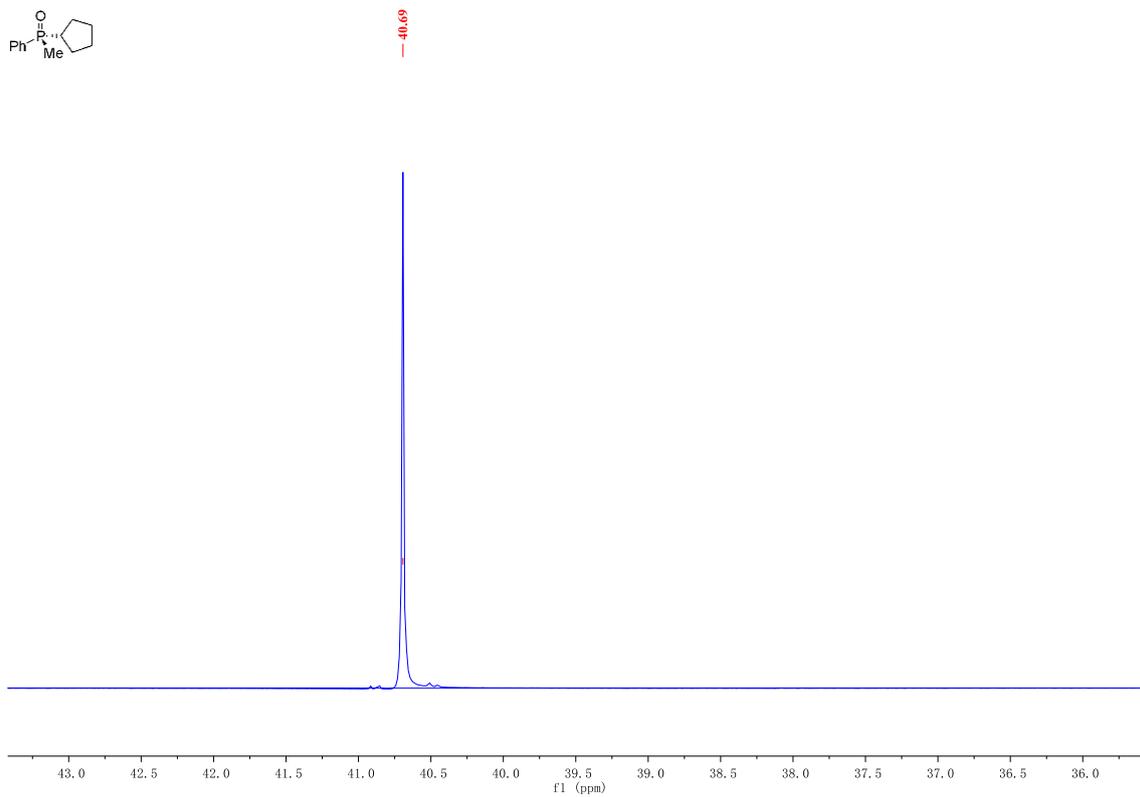
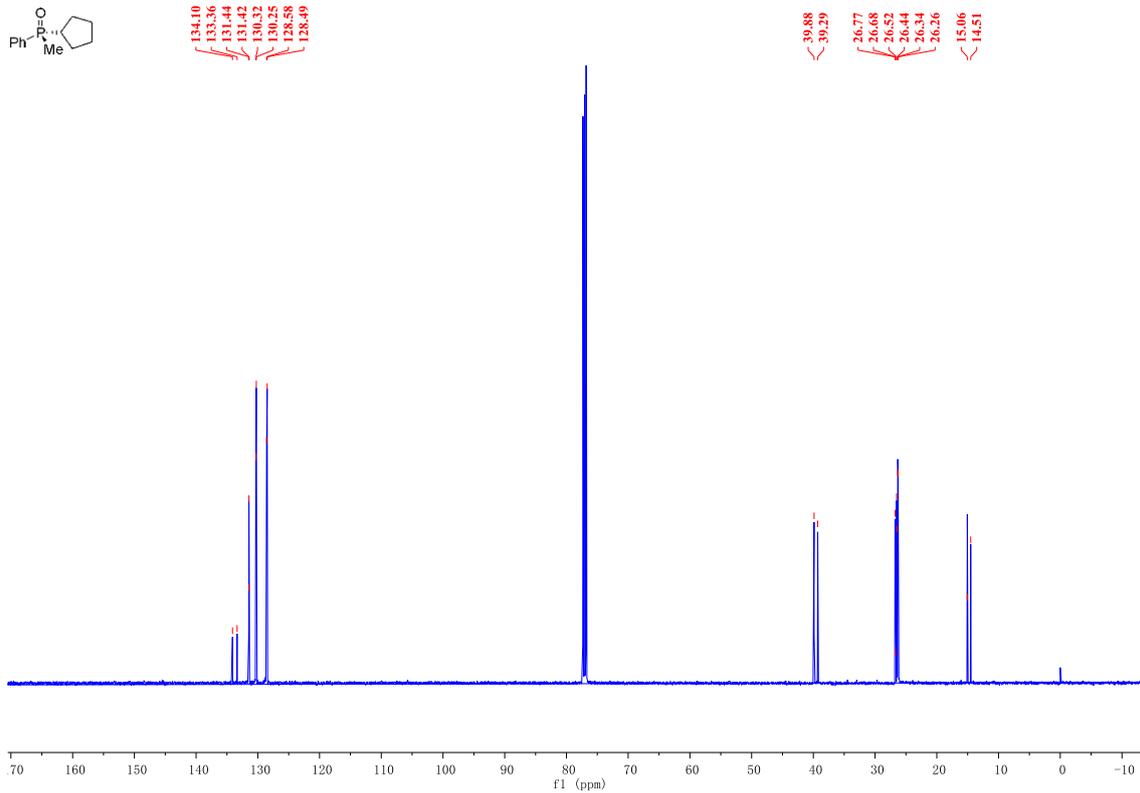


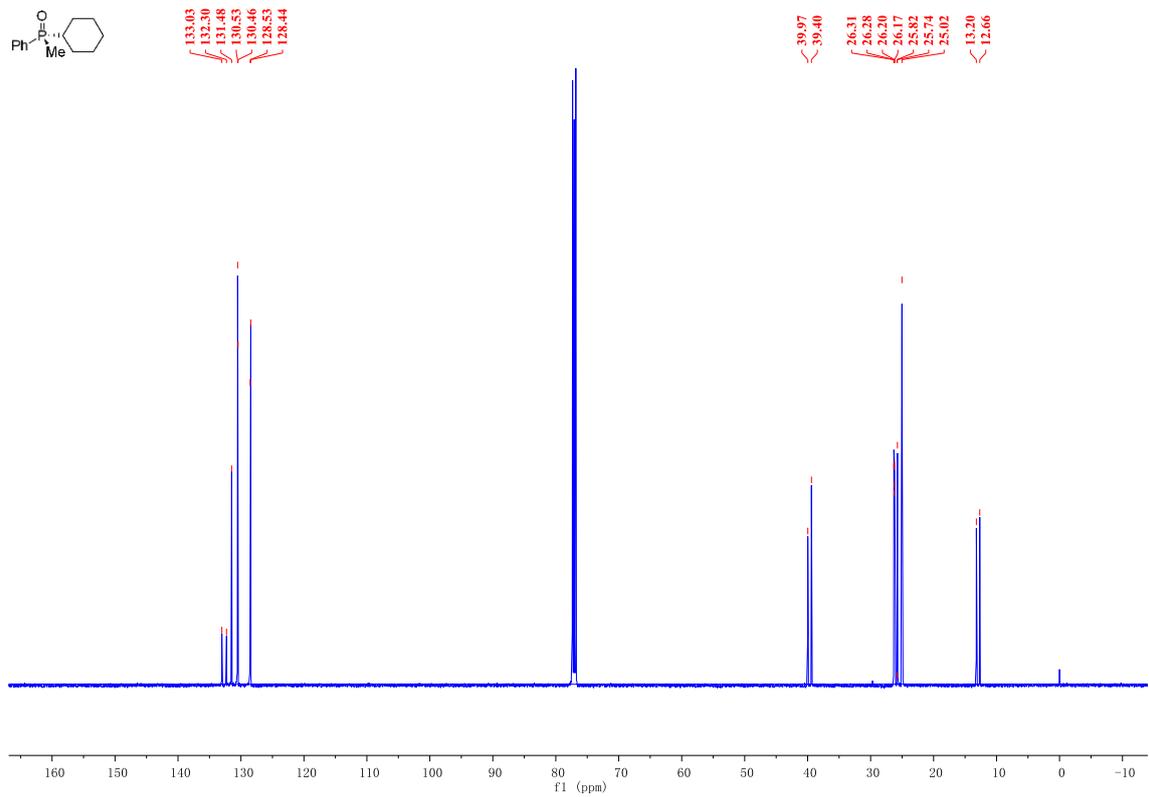
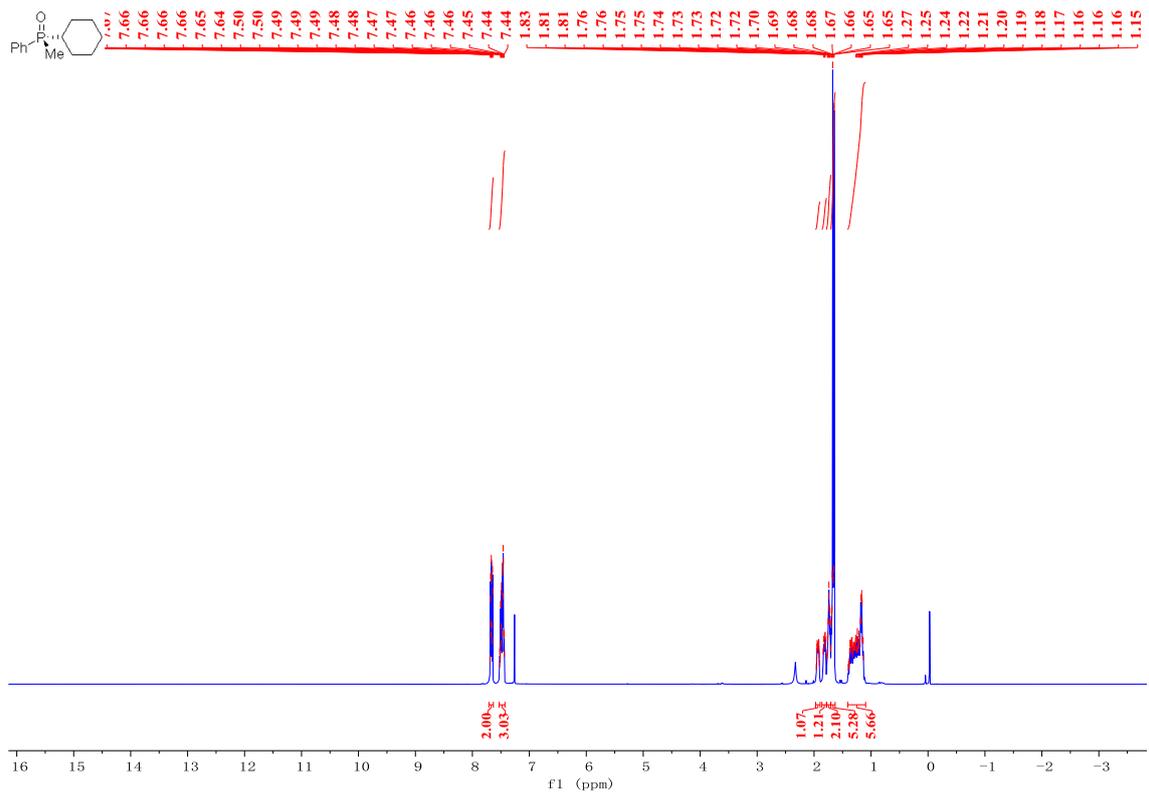
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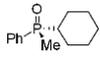












41.31

