Electronic Supplementary Material (ESI) for RSC Advances.

Tandem Addition of Nucleophilic and Electrophilic Reagents to Vinyl Phosphinates: The Stereoselective Formation of Organophosphorus Having Congested Tertiary Carbon

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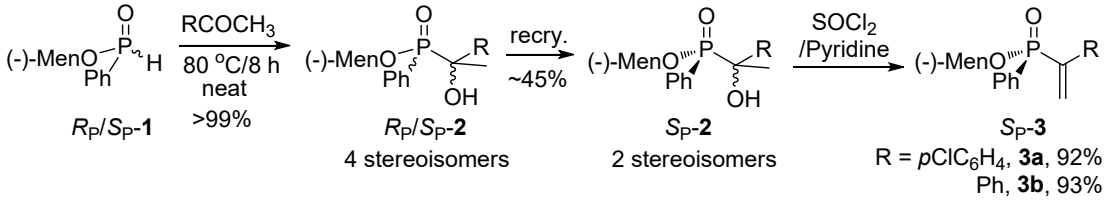
General Chemistry:

^{1}H NMR spectrum were recorded on a 500 MHz spectrometer. Chemical shift for ^{1}H NMR spectrum (in parts per million) relative to internal tetramethylsilane (Me_4Si, δ = 0.00 ppm) with $CDCl_3$. ^{13}C NMR spectrum were recorded at 126 MHz. Chemical shifts for ^{13}C NMR spectrum are reported (in parts per million) relative to $CDCl_3$ (δ = 77.0 ppm). ^{31}P NMR spectrum were recorded at 202 MHz, and chemical shifts reported (in parts per million) relative to external 85% phosphoric acid (δ = 0.0 ppm). TLC plates were visualized by UV. All products were further characterized by HRMS (high resolution mass spectrum) or Elemental Analysis. Copies of their ^{1}H, ^{31}P and ^{13}C NMR spectrum were provided. Melting points were determined on a Reichert Thermovar melting point apparatus and are uncorrected.

Reagent and solvents:

All the solvents used were dried and freshly distilled prior to use. Toluene, chloroform and dichloromethane distilled under calcium hydride. THF, ether and hexane were distilled under sodium and benzophenone. Unless otherwise stated, the commercially available reagents were used without further purification. Some of the Grignard reagent was prepared according standard procedure in ca. 1 M solution in ether or THF. All reactions were carried out under N_2 atmosphere in dry glassware using Schlenk-line techniques. Air and moisture sensitive liquids and solutions were transferred via syringe.

Part 1. The preparation of optically pure S_P-3.



R_P/S_P-**1** R_P/S_P-**2** (4 stereoisomers) S_P-**2** (2 stereoisomers) S_P-**3**

R = pClC$_6$H$_4$, **3a**, 92%; Ph, **3b**, 93%

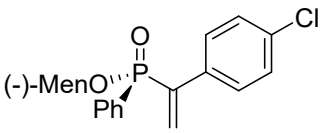
The preparation of S_P-3 via addition, chlorination and elemination

Typical Procedure, the preparation of S_P-3a:

To the solution of R_P/S_P-**1** (1.00 g, 3.57 mmol) and *p*-chloroacetophenone (0.55 mL, 4.28 mmol) in DMF (3.00 mL), was added potassium carbonate (123 mg, 0.89 mmol). The resulted suspension was stirred at room temperature for 24 hours. After the reaction was completed, as monitored with TLC, water (9 - 12 ml) was added and the mixture was stirred for 30 min. The solid was collected by filtration, washed with water (30 mL), and dried under air, affording R_P/S_P-**2a** as a while solid (1.55 g, >99%). ^{31}P NMR spectrum indicated the solid contained four components (38.5, 37.9, 37.6 and 37.1 ppm). After recrystallized with isopropyl ether (30 mL), the residue was analyzed with NMR spectrum. The peaks at 37.9 and 37.2 ppm were observed on ^{31}P NMR spectrum, S_P-**2a** was obtained as a white solid (0.70 g, 45%, 46:54 dr).

To an ice-cooled solution of S_P-**2a** (0.70 g, 1.61 mmol) and pyridine (0.34 ml, 4.20 mmol) in toluene (3.50 ml), thionyl chloride (0.18 ml, 2.42 mmol) was added dropwise with stirring. The mixture was stirred and gradually warmed to room temperature within 3 h. After the reaction was completed, as monitored by TLC, the reaction was quenched with saturated aq. ammonium chloride. The mixture was extracted with dichloromethane (3 × 10 mL), washed with water (3 × 10 mL), and dried over anhydrous magnesium sulfate. After removing solvents, the residue was analyzed with NMR spectrum. S_P-**3a** was obtained as yellow oil (0.62 g, yield 92%).

(S_P)-Menthyl (1-*p*-chlorophenyl-1- vinyl -1-yl)(phenyl)phosphinate (3a)



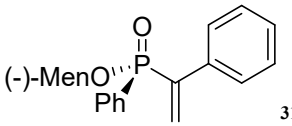
^{31}P NMR (202 MHz, $CDCl_3$): δ 34.6 (s, 8%), 28.8 (s, 92%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.79 – 7.71 (m, 2H), 7.70 – 7.58 (m, 0H), 7.54 – 7.48 (m, 1H), 7.45 – 7.35 (m, 4H), 7.29 – 7.21 (m, 2H), 6.09 – 6.03 (m, 1H), 5.97 (d, J = 1.2 Hz,1H), 4.40 – 4.29 (m, 1H), 2.10 (d, J = 13.6 Hz, 0H), 2.01 (d, J = 14.3 Hz, 0H), 1.97 – 1.87 (m, 1H), 1.85 – 1.79 (m, 1H),

1.75 (s, 0H), 1.69 – 1.54 (m, 2H), 1.43 – 1.34 (m, 1H), 1.34 – 1.26 (m, 1H), 1.25 (s, 0H), 1.12 – 1.02 (m, 1H), 1.01 – 0.91 (m, 2H), 0.87 (d, *J* = 7.1 Hz, 0H), 0.82 (d, *J* = 7.0 Hz, 3H), 0.80 – 0.74 (m, 3H), 0.74 – 0.64 (m, 3H). (L.-B. Han, C.-Q. Zhao, S.-y. Onozawa, M. Goto, and M. Tanaka, *J. Am. Chem. Soc.* **2002, *124*,** 3842-3843)

The preparation of S_P-3b:

Similarly to the above procedure, R_P/S_P-**2b** was obtained as white solid (1.43 g, >99%), ^{31}P NMR spectrum indicated the solid contained four components (39.4, 38.9, 38.8 and 38.3 ppm). After washed with isopropyl ether (30 mL), the residue was analyzed with NMR spectrum. The peaks at 38.5 and 38.2 ppm were observed on ^{31}P NMR spectrum. S_P-**2b** was obtained as a white solid (0.64 g, 45%, 54:46 dr). Then S_P-**3b** was obtained as yellow oil (0.57 g, yield 93%).

(S_P)-Menthyl (1-phenyl-1-vinyl-1-yl)(phenyl)phosphinate (3b)

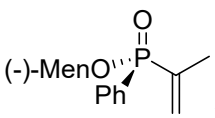


^{31}P NMR (202 MHz, $CDCl_3$): δ 34.9 (s, 5%), 34.8 (s, 2%), 29.1 (s, 93%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.68 (dd, *J* = 12.0, 7.8 Hz, 2H), 7.41 – 7.25 (m, 5H), 7.15 (s, 3H), 5.99 (d, *J* = 19.4 Hz, 2H), 5.89 (s, 0H), 4.34 – 4.19 (m, 1H), 1.91 – 1.82 (m, 1H), 1.77 (d, *J* = 11.9 Hz, 1H), 1.52 (t, *J* = 12.7 Hz, 2H), 1.34 – 1.25 (m, 1H), 1.01 – 0.94 (m, 1H), 0.87 (q, *J* = 14.7, 13.6 Hz, 2H), 0.80 – 0.74 (m, 1H), 0.71 (d, *J* = 7.0 Hz, 3H), 0.67 (d, *J* = 6.4 Hz, 3H), 0.60 (d, *J* = 6.8 Hz, 3H). (L.-B. Han, C.-Q. Zhao, S.-y. Onozawa, M. Goto, and M. Tanaka, *J. Am. Chem. Soc.* **2002, *124*,** 3842-3843)

The preparation of S_P-3d:

Similarly to the above procedure, except for optically pure ***R*$_P$-1** was used to react with acetone. The residue was analyzed with NMR spectrum. The peaks at 40.7 and 40.2 ppm were observed on ^{31}P NMR spectrum, S_P-**2d** was obtained as a white solid (1.21 g, >99% 46:54 dr), S_P-**3d** was obtained as yellow oil (1.09 g, yield 95%).

(S_P)-Menthyl (1-methyl-1-vinyl-1-yl)(phenyl)phosphinate (3d)



^{31}P NMR (202 MHz, $CDCl_3$): δ 37.2 (s, 5%), 30.7 (s, 95%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.84 – 7.74 (m, 2H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.49 – 7.39 (m, 2H), 5.88 (d, *J* = 20.2 Hz, 1H), 5.79 – 5.67 (m, 1H), 4.36 – 4.25 (m, 1H), 2.29 – 2.16 (m, 1H), 2.00 – 1.94 (m, 1H),

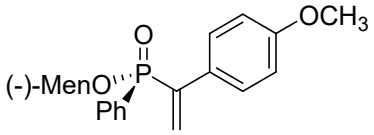
1.86 (d, *J* = 13.1 Hz, 3H), 1.76 – 1.57 (m, 3H), 1.51 – 1.40 (m, 2H), 1.15 – 1.06 (m, 1H), 1.04 – 1.00 (m, 1H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.84 (d, *J* = 6.9 Hz, 4H), 0.79 (d, *J* = 6.5 Hz, 2H).

The preparation of 3c:

Similarly to the above procedure, R_P/S_P-**2c** was obtained as white solid (1.54 g, >99%). ^{31}P NMR spectrum indicated the solid contained four components (39.1, 38.5, 38.4 and 37.9 ppm). After washed with isopropyl ether (30 mL), the residue was analyzed with NMR spectrum. The peaks at 38.3 ppm were observed on ^{31}P NMR spectrum, S_P-**2c** was obtained as a white solid (0.46 g, 30%, >99%:1 dr),

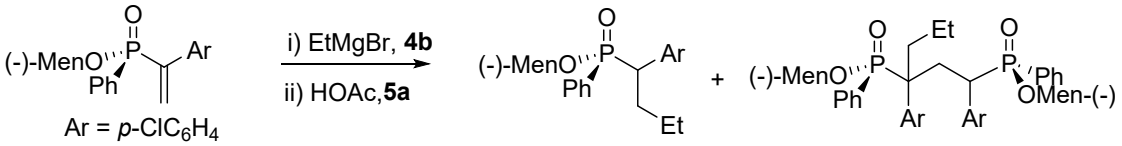
S_P-**2c** (0.46 g) was treated with thionyl chloride and pyridine under similar procedure to the above. The peaks at 34.6 (s, 20 %), 34.4 (s, 44%) and 28.6 ppm (s, 36%) were observed on ^{31}P NMR spectrum of crude product. The peak at 28.6 ppm was assigned S_P-**3c**, and the two other peaks were assigned as α-chlorinated compound. The crude product (0.46 g) was placed in a schlenk tube under the N_2 atmosphere, and LiH-DMSO (2.80 mL, 4.28 mmol, 12.0 g/L) was added slowly. After the mixture was stirred at room temperature for 12 h, diluted hydrochloric acid (4:1) was added with cooling of ice bath. The mixture was extracted with dichloromethane (3 × 10 mL), washed with water (3 × 10 mL), and dried over anhydrous magnesium sulfate. After removing the solvents, the residue was analyzed with NMR spectrum. The peaks at 29.3 ppm were observed on ^{31}P NMR spectrum, then the residue was purified by preparative TLC (silica gel, petroleum ether/ethyl acetate = 3:1 as eluent) to afford yellow oily S_P-**3c** (0.38 g, 87%).

(S_P)-Menthyl (1-*p*-methoxyphenyl-1- vinyl -1-yl)(phenyl)phosphinate (3c)



^{31}P NMR (202 MHz, $CDCl_3$): δ 41.3 (s, 3%), 40.2 (s, 6%), 38.9 (s, 2%), 36.8 (s, 2%), 29.3 (s, 87%), 28.7 (s, 2%).**^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.68 (dd, J = 11.8, 7.7 Hz, 2H), 7.38 (d, J = 7.0 Hz, 1H), 7.31 (d, J = 7.6 Hz, 4H), 6.72 (s, 2H), 6.01 – 5.92 (m, 2H), 5.87 (s, 0H), 4.32 – 4.22 (m, 1H), 3.68 (s, 3H), 1.96 – 1.86 (m, 1H), 1.78 (d, J = 11.8 Hz, 1H), 1.53 (t, J = 12.7 Hz, 2H), 1.31 (d, J = 10.3 Hz, 2H), 0.99 (t, J = 11.8 Hz, 1H), 0.89 (d, J = 11.9 Hz, 1H), 0.74 (d, J = 6.9 Hz, 4H), 0.69 (d, J = 6.3 Hz, 3H), 0.63 (d, J = 6.8 Hz, 3H). (L.-B. Han, C.-Q. Zhao, S.-y. Onozawa, M. Goto, and M. Tanaka, *J. Am. Chem. Soc.* **2002, *124*,** 3842-3843)

Part 2. The examination of the addition of ethyl magnesium bromide to S_P-3a.

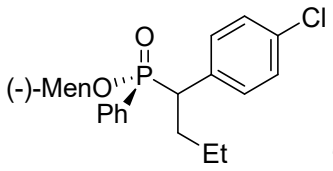


rt/5 h	85% (38:62)	0
-80 °C to rt/17 h	73% (38:62)	15%
-60 °C/8 h	10% (30:70)	61%

Typical Procedure:

To the solution of S_P-**3a** (80.0 mg, 0.19 mmol) in toluene (1 mL), was added ethyl magnesium bromide **4b** (0.38 mL, 0.38 mmol, 1 M solution in THF) slowly, and the solution was stirred at room temperature for 3 hours. The reaction was quenched with a mixture of acetic acid and THF, and the solvent was removed in vacuo. The mixture was extracted with dichloromethane (3 × 5 mL), washed with water (3 × 5 mL), and dried over anhydrous magnesium sulfate. After removing solvents, the residue was analyzed with NMR spectrum. The peaks at 40.0 and 38.6 ppm were observed on ^{31}P NMR spectrum, which were assigned as the two stereoisomers of **6ba**.

(S_P)-Menthyl (1-*p*-chlorophenylbutyl -1-yl)(phenyl)phosphinate (6ba)



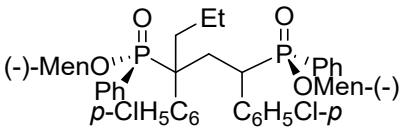
The crude **6ba** was formed in a ratio of 38:62 (estimated by ^{31}P-NMR spectrum), the pure compound **6ba** was obtained as white solid (28.2 mg, 33%, 97:3 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 3:1 as eluent); m.p. 178.0-179.1 °C. **^{31}P NMR (202 MHz, $CDCl_3$):** δ 40.0 (s, 97%), 38.6 (s, 3%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.51 – 7.44 (m, 2H), 7.44 – 7.38 (m, 1H), 7.29 (td, *J* = 7.6, 3.4 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.93 (dd, *J* = 8.5, 2.2 Hz, 2H), 4.31 (tdd, *J* = 10.9, 7.0, 4.5 Hz, 1H), 3.07 (ddd, *J* = 18.3, 11.8, 3.3 Hz, 1H), 2.36 (dtd, *J* = 13.8, 7.0, 2.5 Hz, 1H), 2.12 (dddt, *J* = 13.8, 10.1, 7.0, 3.4 Hz, 1H), 1.90 (dddd, *J* = 16.7, 12.2, 7.3, 2.7 Hz, 1H), 1.71 – 1.63 (m, 3H), 1.63 – 1.56 (m, 1H), 1.45 – 1.36 (m, 1H), 1.13 (ddd, *J* = 13.9, 9.5, 7.0 Hz, 1H), 1.00 (dd, *J* = 17.8, 5.1 Hz, 4H), 0.90 (d, *J* = 6.9 Hz, 4H), 0.85 (t, *J* = 7.3 Hz, 4H), 0.78 (dd, *J* = 12.2, 3.2 Hz, 1H), 0.70 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 134.7 (d, *J* = 3.6 Hz), 132.4 (d, *J* = 4.2 Hz), 132.1, 132.2, 131.7 (d, *J* = 2.5 Hz), 131.2, 130.8, 130.8, 128.1, 128.1, 127.8, 127.8, 49.0 (d, *J* = 5.6 Hz), 48.0, 47.3, 43.1, 34.0, 31.4, 30.1 (d, *J* = 2.9 Hz), 25.6, 22.7, 21.9, 21.2, 20.8 (d, *J* = 13.8 Hz), 15.6, 13.7. **HRMS (ESI+)** Calcd.

for $C_{26}H_{36}ClO_2P$ [M+Na$^+$]: 469.2039, Found: 469.2049.

Run2: 4b was added at -80 °C, then the mixture was warmed to room temperature and stirred for 17 h. The peaks at 40.0 (s, 28%) and 38.6 ppm (s, 45%) were observed on ^{31}P NMR spectrum. Meanwhile, multi signals around 43 to 39 ppm (15%) were observed on ^{31}P NMR spectrum, which indicated the formation **7a**.

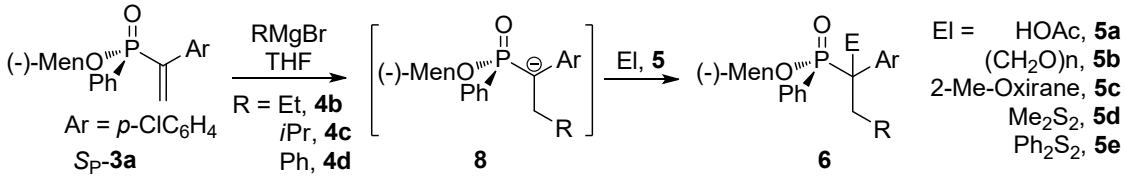
Run3: 4b was added at -60 °C and the mixture was stirred at the same temperature for 8 h. The peaks at 40.0 (s, 3.0%) and 38.6 ppm (s, 7.0%) were observed on ^{31}P NMR spectrum. Meanwhile, multi signals around 43 to 39 ppm (61%) were observed on ^{31}P NMR spectrum.

(S_P,S_P)-Menthyl 1,3-bis(4-chlorophenyl)-1-(menthoxyphenylphosphoryl)hexan-3-yl phenyl phosphinate (7a)



Crude **7a** was obtained in 61% yield (estimated by ^{31}P NMR spectrum), and the **7a** was obtained as a white solid (30.0 mg, 50%), from preparative TLC (silica gel, petroleum ether/ethyl acetate = 3:1 as eluent); m.p. 99.6-103.4 °C. **^{31}P NMR (202 MHz, CDCl3)** δ: 43.1 (s, 24%), 43.0 (s, 11%), 42.7 (s, 13%), 39.8 (s, 14%), 39.5 (s, 25%), 39.1 (s, 13%). **^{1}H NMR (500 MHz, CDCl3)** δ: 7.92 – 7.83 (m, 0H), 7.75 – 7.67 (m, 1H), 7.57 – 7.52 (m, 0H), 7.50 – 7.39 (m, 3H), 7.39 – 7.34 (m, 2H), 7.33 – 7.25 (m, 4H), 7.25 – 7.20 (m, 2H), 7.20 – 7.14 (m, 1H), 7.13 – 7.05 (m, 1H), 7.01 – 6.84 (m, 4H), 4.38 – 4.24 (m, 1H), 4.23 – 4.09 (m, 1H), 4.06 – 3.91 (m, 0H), 3.80 (t, J = 5.9 Hz, 0H), 3.61 – 3.46 (m, 0H), 3.37 – 3.15 (m, 1H), 2.96 (d, J = 20.4 Hz, 1H), 2.79 – 2.57 (m, 1H), 2.51 – 2.44 (m, 0H), 2.43 – 2.30 (m, 1H), 2.28 – 2.15 (m, 1H), 1.72 – 1.55 (m, 7H), 1.54 – 1.35 (m, 4H), 1.08 – 0.93 (m, 9H), 0.90 (dd, J = 13.2, 6.8 Hz, 4H), 0.87 – 0.81 (m, 5H), 0.78 – 0.70 (m, 4H), 0.69 – 0.60 (m, 4H), 0.51 (d, J = 6.9 Hz, 1H), 0.33 – 0.24 (m, 1H), 0.19 (t, J = 7.1 Hz, 2H). **HRMS (ESI+)** Calcd. for $C_{50}H_{66}Cl_2O_4P_2$ [M+H$^+$]: 863.3891, Found: 863.3892.

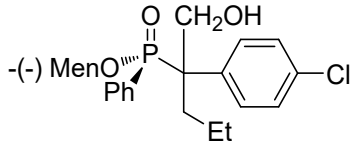
Part 3. The addition of Grignard reagents to S_P-3a and subsequent modification with El reagents.



General procedure:

To the solution of S_P-**3a** (80.0 mg, 0.19 mmol) in THF (1 mL), was added the solution of Grignard reagent (0.38 ml, 0.38 mmol, 1 M solution in THF) After stirring at room temperature for 30 min, El reagent (1.5 eq. to S_P-**3a**) was added and the mixture was stirred at rt for 3 h. The reaction was quenched with saturated aq. ammonium chloride and the solvent was removed in vacuo. The mixture was extracted with dichloromethane (3 × 5 mL), washed with water (3 × 5 mL), and dried over anhydrous magnesium sulfate. After removing the solvents, the yield and dr were estimated by $^{31}P\{^{1}H\}$ NMR spectrum.

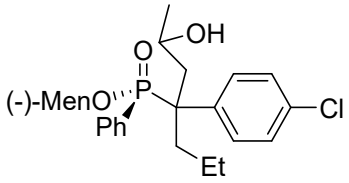
(S_P)-Menthyl (2-*p*-chlorophenyl-1-hydroxypentan-2-yl)(phenyl)phosphinate (6bb)



The crude **6bb** was formed in a ratio of 56:44 (estimated by ^{31}P-NMR spectrum), the pure compound **6bb** was obtained as colorless oil (49.7mg, 55%, 64:36 dr) from preparative TLC (silica gel, dichloromethane /ethyl acetate = 6:1 as eluent). **^{31}P NMR (202 MHz, $CDCl_3$):** δ 45.6 (s, 64%), 44.4 (s, 36%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.57 – 7.50 (m, 1H), 7.47 – 7.41 (m, 1H), 7.41 – 7.34 (m, 2H), 7.25 – 7.15 (m, 3H), 6.96 (dt, *J* = 8.7, 4.2 Hz, 2H), 4.73 (t, *J* = 11.7 Hz, 1H), 4.36 (tt, *J* = 10.5, 4.9 Hz, 1H), 4.12 (t, *J* = 13.0 Hz, 1H), 3.90 – 3.69 (m, 1H), 2.54 – 2.41 (m, 1H), 2.41 – 2.26 (m, 2H), 2.18 (s, 0H), 1.73 – 1.62 (m, 1H), 1.57 (q, *J* = 17.0, 14.2 Hz, 3H), 1.47 (d, *J* = 11.2 Hz, 0H), 1.35 (qt, *J* = 12.4, 4.7 Hz, 2H), 1.28 – 1.17 (m, 1H), 1.01 (d, *J* = 7.1 Hz, 2H), 0.97 (d, *J* = 7.0 Hz, 3H), 0.91 (td, *J* = 10.4, 6.1 Hz, 4H), 0.84 (t, *J* = 7.1 Hz, 2H), 0.80 – 0.71 (m, 2H), 0.66 (dd, *J* = 10.4, 6.5 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 135.1 (d, *J* = 4.1 Hz), 134.2 (d, *J* = 4.8 Hz), 132.4 (d, *J* = 9.3 Hz), 131.8 (t, *J* = 4.3 Hz), 131.5 (d, *J* = 2.7 Hz), 131.29, 139.3, 128.6 (d, *J* = 4.6 Hz), 128.3 (d, *J* = 4.9 Hz), 127.6, 127.2 (d, *J* = 2.8 Hz), 126.9 (d, *J* = 3.0 Hz), 126.6 (dd, *J* = 19.7, 12.3 Hz), 62.0(d, *J* = 5.5 Hz), 60.6, 52.4, 48.3 – 48.0 (m), 48.0, 47.4, 42.0 , 32.9 (d, *J* = 7.4 Hz), 30.4 (d, *J* = 2.7 Hz), 29.3– 28.7 (m), 24.6(d, *J* = 9.7 Hz), 21.5 (d,

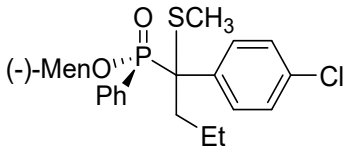
J = 2.8 Hz), 20.8 (d, J = 5.2 Hz), 20.2 (d, J = 13.6 Hz). **HRMS (ESI+)** Calcd. for $C_{27}H_{38}ClO_3P$ [M+Na^+]: 499.2145, Found: 499.2148.

(S_P)-Menthyl (4-*p*-chlorophenyl-2- hydroxyheptan-4-yl)(phenyl)phosphinate (6bc)



The crude **6bc** was formed in a ratio of 23:31:26:20 (estimated by ^{31}P-NMR spectrum), the pure compound **6bc** was obtained as white solid (16.5 mg, 17%, >99:1 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 3:2 as eluent); m.p. 144.1-150.5 ^{o}C. **^{31}P NMR (202 MHz, $CDCl_3$):** δ 45.9 (s). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.44 – 7.38 (m, 1H), 7.31 – 7.24 (m, 3H), 7.23 – 7.18 (m, 3H), 7.16 (d, J = 8.7 Hz, 2H), 4.28 – 4.20 (m, 1H), 4.07 (s, 1H), 3.32 (s, 1H), 2.18 – 2.04 (m, 3H), 2.02 – 1.90 (m, 1H), 1.54 – 1.46 (m, 1H), 1.37 – 1.23 (m, 3H), 1.18 (s, 3H), 1.12 (d, J = 6.2 Hz, 3H), 0.92 (td, J = 13.0, 3.1 Hz, 1H), 0.86 (d, J = 7.0 Hz, 3H), 0.81 (t, J = 7.2 Hz, 3H), 0.74 (d, J = 6.8 Hz, 4H), 0.68 (d, J = 11.9 Hz, 2H), 0.58 (d, J = 6.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 137.9, 137.9, 133.4, 133.3, 132.6 (d, J = 3.2 Hz), 132.1 (d, J = 2.7 Hz), 130.6 (d, J = 5.4 Hz), 130.5, 129.6, 127.8 (d, J = 2.2 Hz), 127.6, 127.5, 78.1 (d, J = 8.4 Hz), 64.9 (d, J = 6.6 Hz), 49.1 (d, J = 6.4 Hz), 48.7, 48.0, 43.2, 35.4, 33.9, 31.4, 29.7, 25.3, 24.7, 22.6, 21.8, 21.3, 17.2 (d, J = 6.4 Hz), 15.7, 14.8, 1.0. **HRMS (ESI+)** Calcd. for $C_{29}H_{42}ClO_3P$ [M+H^+]: 505.2638, Found: 505.2638.

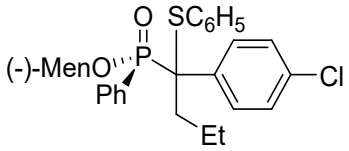
(S_P)-Menthyl (1-*p*-chlorophenyl-1-methylthiobutyl-1-yl)(phenyl)phosphinate (6bd)



The crude **6bd** was formed in a ratio of 54:46 (estimated by ^{31}P-NMR spectrum), **6bd** was obtained as colorless oil (58.6 mg, 62%, 48:52 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 2:1 as eluent). **^{31}P NMR (202 MHz, $CDCl_3$):** δ 39.5 (s, 48%), 37.5 (s, 52%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.37 (q, J = 7.1 Hz, 1H), 7.29 (dt, J = 11.0, 6.7 Hz, 2H), 7.23 – 7.16 (m, 2H), 7.16 – 7.09 (m, 3H), 7.07 (d, J = 8.7 Hz, 1H), 4.30 (qd, J = 6.4, 2.2 Hz, 0.5H), 4.27 – 4.17 (m, 0.5H), 2.59 – 2.48 (m, 0.5H), 2.42 – 2.30 (m, 0.5H), 2.20 (d, J = 26.0 Hz, 4H), 2.17 – 2.07 (m, 1H), 1.64 – 1.54 (m, 2H), 1.55 – 1.43 (m, 1H), 1.43 – 1.26 (m, 2H), 1.11 – 1.00 (m, 1H), 0.96 – 0.84 (m, 7H), 0.80 (dd, J = 12.9, 6.8 Hz, 4H), 0.76 – 0.65 (m, 2H), 0.60 (dd, J = 13.4, 6.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 134.5 (d, J = 2.8 Hz), 134.0

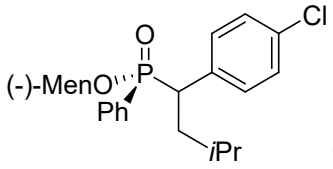
(d, *J* = 2.4 Hz), 133.0 (d, *J* = 8.4 Hz), 132.7 (d, *J* = 8.4 Hz), 131.9 (t, *J* = 3.8 Hz), 130.9 (d, *J* = 2.0 Hz), 129.7 (d, *J* = 4.7 Hz), 129.5 (d, *J* = 4.3 Hz), 129.0, 128.5, 126.6 (dd, *J* = 5.8, 2.5 Hz), 126.0 (dd, *J* = 30.4, 12.2 Hz), 76.9 (dd, *J* = 8.3, 3.6 Hz), 53.7 (d, *J* = 31.0 Hz), 52.9 (d, *J* = 33.2 Hz), 48.0 (dd, *J* = 26.4, 5.8 Hz), 42.2 (d, *J* = 18.0 Hz), 32.9, 30.5 (d, *J* = 25.7 Hz), 28.7, 24.4 (d, *J* = 40.6 Hz), 21.6 (d, *J* = 5.3 Hz), 20.9 (d, *J* = 7.3 Hz), 20.2 (d, *J* = 6.4 Hz), 15.3 (dd, *J* = 9.3, 3.6 Hz), 14.6 (d, *J* = 13.0 Hz), 13.2 (d, *J* = 6.0 Hz), 12.2 (d, *J* = 30.2 Hz). **HRMS (ESI+)** Calcd. for $C_{27}H_{38}ClO_2PS$ [M+Na$^+$]: 515.1917, Found: 515.1918.

(S_P)-Menthyl (1-*p*-chlorophenyl-1-phenylthiobutyl -1-yl)(phenyl)phosphinate (6be)



The crude **6be** was formed in a ratio of 55:45 (estimated by ^{31}P-NMR spectrum), **6be** was obtained as colorless oil (59.6 mg, 56%, 54:46 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 3:1 as eluent). **^{31}P NMR (202 MHz, $CDCl_3$):** δ 38.5 (s, 54%), 37.9 (s, 46%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.58 – 7.54 (m, 1H), 7.53 – 7.47 (m, 1H), 7.44 – 7.32 (m, 3H), 7.29 – 7.20 (m, 4H), 7.17 (d, *J* = 7.3 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 1H), 7.07 (d, *J* = 8.6 Hz, 2H), 4.36 – 4.20 (m, 1H), 2.28 – 2.11 (m, 2H), 2.11 – 1.97 (m, 1H), 1.97 – 1.86 (m, 1H), 1.67 – 1.44 (m, 4H), 1.44 – 1.22 (m, 3H), 0.94 – 0.80 (m, 3H), 0.75 (dd, *J* = 13.4, 6.9 Hz, 3H), 0.70 (d, *J* = 4.2 Hz, 1H), 0.65 (t, *J* = 7.3 Hz, 2H), 0.62 (d, *J* = 6.5 Hz, 2H), 0.60 – 0.57 (m, 2H), 0.55 (d, *J* = 7.3 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 135.5, 135.2 (dd, *J* = 9.6, 1.2 Hz), 134.8, 133.2 (d, *J* = 8.7 Hz), 132.8 (d, *J* = 8.6 Hz), 132.0(d, *J* = 3.5 Hz), 131.0 (dd, *J* = 5.7, 2.6 Hz), 130.4 – 130.2 (m), 130.1 (d, *J* = 3.2 Hz), 130.0 (d, *J* = 3.3 Hz), 129.5 (d, *J* = 6.6 Hz), 128.5 (d, *J* = 4.1 Hz), 127.7 (d, *J* = 14.0 Hz), 127.4 (d, *J* = 12.8 Hz), 126.4 (t, *J* = 2.6 Hz), 126.2 (d, *J* = 2.8 Hz), 126.0, 77.6 (d, *J* = 8.3 Hz), 77.1 (d, *J* = 8.2 Hz), 67.0, 58.9 (d, *J* = 2.1 Hz), 58.1, 52.4, 47.8 (d, *J* = 6.1 Hz), 42.2 (d, *J* = 14.8 Hz), 32.9 (d, *J* = 5.5 Hz), 32.4 (d, *J* = 4.1 Hz), 30.5, 24.7 – 23.9 (m), 21.7 – 20.1 (m), 16.2 (dd, *J* = 7.4, 5.1 Hz), 14.5 (d, *J* = 1.9 Hz), 13.0 (d, *J* = 3.2 Hz). **HRMS (ESI+)** Calcd. for $C_{32}H_{40}ClO_2PS$ [M+Na$^+$]: 577.2073, Found: 577.2064.

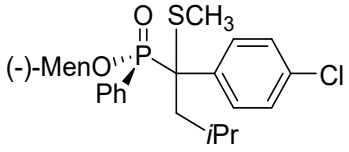
(S_P, S_C)-Menthyl (1-*p*-chlorophenyl-3-methylbutyl-1-yl)(phenyl)phosphinate (6ca)



The crude **6ca** was formed in a ratio of 49:51 (estimated by ^{31}P-

NMR spectrum), the pure compound **6ca** was obtained as white solid (18.6 mg, 21%, 56:44 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 3:1 as eluent); m.p. 173.5-185.5 °C. **^{31}P NMR (202 MHz, $CDCl_3$):** δ 40.5 (s, 56%), 38.9 (s, 44%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.70 – 7.62 (m, 1H), 7.45 (t, *J* = 7.1 Hz, 0H), 7.42 – 7.28 (m, 3H), 7.19 (p, *J* = 8.8 Hz, 3H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 6.6 Hz, 1H), 4.30 – 4.19 (m, 0.5H), 4.12 – 4.02 (m, 0.5H), 3.12 – 3.00 (m, 1H), 2.35 – 2.25 (m, 0H), 1.99 – 1.86 (m, 1H), 1.88 – 1.73 (m, 1H), 1.68 – 1.56 (m, 1H), 1.52 (d, *J* = 12.6 Hz, 1H), 1.44 (t, *J* = 10.5 Hz, 1H), 1.34 (t, *J* = 11.4 Hz, 1H), 1.30 – 1.21 (m, 2H), 1.13 – 1.01 (m, 1H), 0.93 (dd, *J* = 19.3, 4.8 Hz, 2H), 0.84 (q, *J* = 8.1, 5.8 Hz, 2H), 0.80 – 0.69 (m, 5H), 0.64 (dt, *J* = 15.3, 7.2 Hz, 5H), 0.57 (dd, *J* = 9.3, 6.7 Hz, 3H), 0.45 (d, *J* = 6.8 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 134.1 (d, *J* = 8.2 Hz), 133.7 (d, *J* = 3.5 Hz), 132.0, 131.7 (d, *J* = 3.2 Hz), 131.3, 131.1 – 130.9 (m), 130.7 (d, *J* = 2.6 Hz), 130.3, 130.1 (d, *J* = 6.1 Hz), 129.8 (d, *J* = 6.3 Hz), 127.2 (d, *J* = 7.2 Hz), 127.1 (d, *J* = 3.0 Hz), 126.8 (d, *J* = 12.3 Hz), 75.2 (d, *J* = 7.8 Hz), 47.9 (dd, *J* = 20.0, 5.7 Hz), 45.3, 44.5 (d, *J* = 1.6 Hz), 42.0 (d, *J* = 24.0 Hz), 36.2, 35.6 (d, *J* = 3.4 Hz), 33.0 (d, *J* = 7.5 Hz), 30.4 (d, *J* = 13.5 Hz), 24.6 – 24.0 (m), 23.6, 22.6 (d, *J* = 20.5 Hz), 21.6 (d, *J* = 37.0 Hz), 20.9, 20.2 – 19.3 (m), 14.4 (d, *J* = 60.6 Hz). **HRMS (ESI+)** Calcd. for $C_{27}H_{38}ClO_2P$ [M+Na^+]: 483.2196, Found: 483.2196.

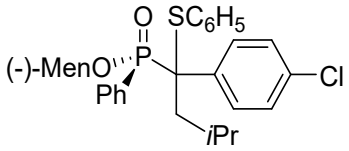
(S_P)-Menthyl (1-*p*-chlorophenyl-3-methyl-1-methylthiobutyl-1-yl)(phenyl)phosphinate (6cd)



The crude **6cd** was formed in a ratio of 61:39 (estimated by ^{31}P-NMR spectrum), the pure compound **6cd** was obtained as colorless oil (48.6 mg, 50%, 48:52 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 2:1 as eluent). **^{31}P NMR (202 MHz, $CDCl_3$):** δ 40.9 (s, 48%), 37.1 (s, 52%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.38 – 7.32 (m, 2H), 7.31 – 7.25 (m, 1H), 7.25 – 7.20 (m, 2H), 7.17 (dq, *J* = 7.4, 4.0, 3.5 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 4.38 – 4.28 (m, 0.5H), 4.28 – 4.18 (m, 0.5H), 2.55 – 2.46 (m, 0.5H), 2.35 (s, 2H), 2.33 – 2.29 (m, 1H), 2.26 (d, *J* = 4.9 Hz, 2H), 2.22 – 2.11 (m, 0.5H), 1.92 – 1.74 (m, 1H), 1.70 – 1.56 (m, 2H), 1.57 – 1.46 (m, 2H), 1.44 – 1.31 (m, 1H), 0.99 – 0.88 (m, 6H), 0.86 (dd, *J* = 11.5, 5.4 Hz, 2H), 0.80 (d, *J* = 6.9 Hz, 2H), 0.78 – 0.65 (m, 2H), 0.63 (d, *J* = 6.5 Hz, 2H), 0.58 (d, *J* = 6.5 Hz, 2H), 0.54 (d, *J* = 6.7 Hz, 1H), 0.49 (d, *J* = 6.7 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 135.0 (d, *J* = 3.7 Hz), 134.2, 132.8 (dd, *J* = 8.2, 4.7 Hz), 131.9 (d, *J* = 3.7 Hz),

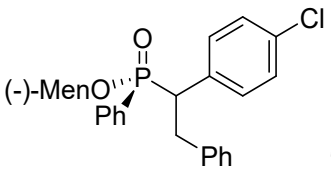
130.8, 129.9 (d, J = 5.2 Hz), 129.7 (d, J = 4.6 Hz), 129.1 (d, J = 25.8 Hz), 128.1 (d, J = 29.6 Hz), 126.4 (d, J = 2.6 Hz), 126.2 (d, J = 2.7 Hz), 126.0 – 125.7 (m), 76.9 (dd, J = 23.8, 8.5 Hz), 54.12, 53.5 (d, J = 19.2 Hz), 52.8, 48.0 (dd, J = 18.8, 5.9 Hz), 42.2 (d, J = 33.2 Hz), 36.6 (d, J = 5.1 Hz), 32.9, 30.4 (d, J = 5.5 Hz), 24.5 (d, J = 45.2 Hz), 23.9 (dd, J = 10.4, 6.7 Hz), 23.4 (d, J = 10.2 Hz), 23.2 (d, J = 13.1 Hz), 21.6 (d, J = 6.6 Hz), 20.8 (d, J = 7.2 Hz), 20.2 (d, J = 1.7 Hz), 14.6 (d, J = 8.9 Hz), 12.8 (d, J = 5.9 Hz). **HRMS (ESI+)** Calcd. for $C_{28}H_{40}ClO_2PS$ [M+Na$^+$]: 529.2073, Found: 529.2073.

(S_P)-Menthyl (1-*p*-chlorophenyl-3-methyl-1-phenylthiobutyl-1-yl)(phenyl)phosphinate (6ce)



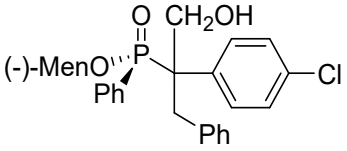
The crude **6ce** was formed in a ratio of 65:35 (estimated by ^{31}P-NMR spectrum), **6ce** was obtained as colorless oil (57.8 mg, 53%, 71:29 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 3:1 as eluent). **^{31}P NMR (202 MHz, CDCl$_3$):** δ 39.4 (s, 71%), 38.8 (s, 29%). **^{1}H NMR (500 MHz, CDCl$_3$):** δ 7.72 – 7.62 (m, 1H), 7.57 (dd, J = 8.0, 1.7 Hz, 2H), 7.54 – 7.51 (m, 1H), 7.51 – 7.46 (m, 2H), 7.47 – 7.39 (m, 1H), 7.31 – 7.20 (m, 5H), 7.10 (d, J = 8.6 Hz, 2H), 4.42 – 4.31 (m, 1H), 2.37 – 2.12 (m, 4H), 1.90 – 1.82 (m, 0H), 1.74 (dd, J = 14.8, 12.1 Hz, 1H), 1.67 – 1.51 (m, 2H), 1.35 (ddd, J = 13.0, 10.4, 3.1 Hz, 2H), 1.31 – 1.18 (m, 3H), 1.02 – 0.87 (m, 4H), 0.85 – 0.79 (m, 2H), 0.77 (d, J = 6.4 Hz, 2H), 0.69 (d, J = 6.6 Hz, 2H), 0.64 (d, J = 6.5 Hz, 1H), 0.60 (d, J = 6.4 Hz, 2H), 0.49 (dd, J = 9.6, 6.7 Hz, 2H). **^{13}C NMR (126 MHz, CDCl$_3$):** δ 135.3, 135.2, 134.7, 134.3 (d, J = 8.6 Hz), 134.0 (d, J = 8.4 Hz), 133.1 (d, J = 3.5 Hz), 132.6, 132.4 (d, J = 2.6 Hz), 132.0 – 131.8 (m), 131.5 (dd, J = 12.6, 5.0 Hz), 130.5, 129.5, 128.4 (d, J = 9.2 Hz), 128.1, 127.9, 127.4 (d, J = 1.8 Hz), 127.3 – 127.1 (m), 127.1 (d, J = 11.2 Hz), 78.5 (dd, J = 14.6, 8.3 Hz), 60.5 (d, J = 18.5 Hz), 59.7 (d, J = 21.2 Hz), 48.9 – 48.7 (m), 43.2 (d, J = 17.0 Hz), 40.6, 34.0 (d, J = 8.1 Hz), 31.5 (d, J = 8.6 Hz), 25.5, 25.2 (d, J = 7.8 Hz), 25.0 – 24.8 (m), 24.6 (d, J = 6.2 Hz), 24.4 (d, J = 5.1 Hz), 22.6, 21.9 (d, J = 8.4 Hz), 21.2 (d, J = 4.5 Hz), 15.6 (d, J = 12.3 Hz). **HRMS (ESI+)** Calcd. for $C_{33}H_{42}ClO_2PS$ [M+H$^+$]: 569.2410, Found: 569.2402.

(S_P)-Menthyl (1-*p*-chlorophenyl-2-phenylethyl-1-yl)(phenyl)phosphinate (6da)



The crude **6da** was formed in a ratio of 52:48 (estimated by ^{31}P-NMR spectrum), the pure compound **6da** was obtained as white solid (36.1 mg, 38%, 98:2 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 3:1 as eluent); m.p. 146.9-151.6 ^{o}C. **^{31}P NMR (202 MHz, $CDCl_3$):** δ 39.4 (s, 98%) 38.0 (s, 2%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.49 – 7.41 (m, 2H), 7.33 (td, *J* = 7.5, 1.5 Hz, 1H), 7.22 (td, *J* = 7.6, 3.4 Hz, 2H), 7.12 (s, 0H), 7.09 – 6.99 (m, 3H), 6.92 (d, *J* = 8.1 Hz, 2H), 6.89 – 6.85 (m, 2H), 6.84 – 6.79 (m, 2H), 4.36 – 4.26 (m,1H), 3.57 – 3.48 (m, 1H), 3.32 – 3.22 (m, 1H), 3.16 – 3.06 (m, 1H), 2.44 – 2.34 (m, 1H), 1.68 – 1.60 (m, 3H), 1.59 – 1.50 (m, 1H), 1.45 – 1.34 (m, 1H), 0.99 (dd, *J* = 13.1, 3.5 Hz, 4H), 0.93 (d, *J* = 7.0 Hz, 4H), 0.87 (d, *J* = 7.0 Hz, 1H), 0.74 (dd, *J* = 12.3, 3.4 Hz, 0H), 0.65 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 139.2, 139.1, 133.8, 132.5 (d, *J* = 4.0 Hz), 132.1, 132.0, 131.9, 131.9 (d, *J* = 1.8 Hz), 131.1 (d, *J* = 4.4 Hz), 131.0, 128.8, 128.2, 128.1 (d, *J* = 2.3 Hz), 128.0, 127.9, 126.2 50.1, 49.3, 49.0 (d, *J* = 5.7 Hz), 43.1, 34.6, 34.0, 31.5, 29.7, 25.7, 22.7, 21.9, 21.2, 15.6, 1.0. **HRMS (ESI+)** Calcd. for $C_{30}H_{36}ClO_2P$ [M+Na^+]: 517.2039, Found: 517.2036.

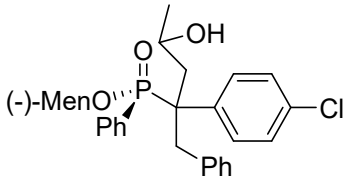
(S_P,S_C)-Menthyl (2-*p*-chlorophenyl-1-hydroxy-3-phenylpropan-2-yl)(phenyl)phosphinate (6db)



The crude **6db** was formed in a ratio of 42:58 (estimated by ^{31}P-NMR spectrum), the pure compound **6db** was obtained as white solid (70.5 mg, 70%, 36:64 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 2:1 as eluent); m.p. 192.5-195.6 ^{o}C. **^{31}P NMR (202 MHz, $CDCl_3$):** δ 46.4 (s, 36%), 44.4 (s, 64%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.45 (q, *J* = 10.4, 8.5 Hz, 1H), 7.38 – 7.28 (m, 1H), 7.15 (dd, *J* = 22.1, 9.4 Hz, 4H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.06 – 6.97 (m, 4H), 6.94 (d, *J* = 6.1 Hz, 3H), 4.66 (d, *J* = 10.8 Hz, 1H), 4.45 – 4.29 (m, 1H), 4.10 (d, *J* = 11.0 Hz, 0H), 3.84 (t, *J* = 12.4 Hz, 1H), 3.78 – 3.67 (m, 1H), 3.67 – 3.56 (m, 0H), 3.55 – 3.48 (m, 1H), 3.44 (t, *J* = 11.4 Hz, 0H), 3.15 (dd, *J* = 13.7, 6.6 Hz, 0H), 2.48 – 2.36 (m, 1H), 2.29 – 2.17 (m, 0H), 1.75 – 1.58 (m, 2H), 1.58 – 1.46 (m, 2H), 1.38 – 1.30 (m, 1H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.86 (dd, *J* = 16.7, 6.9 Hz, 5H), 0.80 – 0.68 (m, 2H), 0.63 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 135.5, 135.4 (d, *J* = 3.0 Hz), 135.2, 134.6 (d, *J* = 4.0 Hz), 133.5,

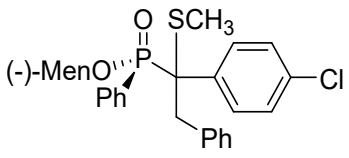
133.4, 133.2 (d, J = 8.7 Hz), 133.0 (d, J = 3.7 Hz), 132.7, 132.4 (d, J = 2.6 Hz), 130.8 (d, J = 4.4 Hz), 123.0 – 129.8 (m), 129.2, 128.2 (d, J = 2.7 Hz), 128.0 – 127.8 (m), 127.7, 126.5 (d, J = 4.1 Hz), 78.9 (d, J = 8.1 Hz), 78.3 (d, J = 8.5 Hz), 62.1 (d, J = 4.5 Hz), 61.1, 49.7, 49.1 (d, J = 5.4 Hz), 49.0 – 48.9 (m), 43.2(d, J = 21.8 Hz), 34.7 (d, J = 31.3 Hz), 33.9, 31.5 (d, J = 6.9 Hz), 25.7 (d, J = 30.5 Hz), 22.6 (d, J = 3.7 Hz), 21.9 (d, J = 5.0 Hz), 21.2 (d, J = 26.0 Hz), 15.4. **HRMS (ESI+)** Calcd. for $C_{31}H_{38}ClO_3P$ [M+Na$^+$]: 547.2145, Found: 547.2139.

(S_P)-Menthyl (2-*p*-chlorophenyl-4-hydroxy-1-phenylpentan -2-yl)(phenyl)phosphinate (6dc)



The crude **6dc** was formed in a ratio of 6:41:42:11 (estimated by ^{31}P-NMR spectrum), the pure compound **6dc** was obtained as white solid (71.0 mg, 67%, 5:81:5:9 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 3:1 as eluent); m.p. 69.5-72.6 ^{o}C. **^{31}P NMR (202 MHz, $CDCl_3$):** δ 47.3 (s, 5%), 45.8 (s, 81%), 39.4 (s, 5%), 38.0 (s, 9%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.83 – 7.78 (m, 0H), 7.57 – 7.45 (m, 1H), 7.39 – 7.29 (m, 2H), 7.19 (s, 1H), 7.15 (d, J = 8.4 Hz, 2H), 7.13 – 7.09 (m, 1H), 7.09 – 6.99 (m, 4H), 6.82 (dd, J = 6.4, 2.9 Hz, 2H), 6.76 – 6.73 (m, 0H), 6.06 (s, 1H), 4.47 – 4.36 (m, 1H), 4.14 (d, J = 7.4 Hz, 1H), 3.77 (dd, J = 16.5, 8.3 Hz, 1H), 3.43 (dd, J = 16.5, 6.2 Hz, 1H), 2.87 – 2.76 (m, 1H), 2.60 – 2.50 (m, 1H), 2.09 (dd, J = 29.2, 15.1 Hz, 1H), 1.69 (ddd, J = 17.0, 13.0, 3.7 Hz, 2H), 1.60 (d, J = 3.3 Hz, 3H), 1.47 – 1.36 (m, 1H), 1.32 – 1.21 (m, 2H), 1.10 – 0.92 (m, 9H), 0.78 – 0.61 (m, 4H), 0.53 (d, J = 6.9 Hz, 0H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 137.9, 137.9, 136.0, 135.9, 133.8, 133.7, 132.9 (d, J = 4.4 Hz), 132.6 (d, J = 2.6 Hz), 130.8, 130.7, 129.6, 129.4, 128.2, 127.6, 127.6, 127.6, 127.5, 79.5, 79.4, 62.5, 49.2, 49.1, 48.8, 48.1, 43.2, 43.0 (d, J = 3.9 Hz), 34.0, 33.9, 31.5, 25.6, 24.3, 22.5, 21.3, 15.7. **HRMS (ESI+)** Calcd. for $C_{33}H_{42}ClO_3P$ [M+H$^+$]: 553.2638, Found: 553.2640.

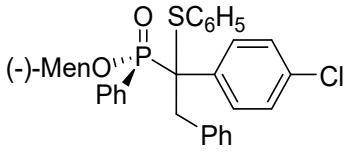
(S_P)-Menthyl (1-*p*-chlorophenyl-1-methylthio- 2-phenylethyl -1-yl)(phenyl)phosphinat (6dd)



The crude **6dd** was formed in a ratio of 81:19 (estimated by 31P-NMR spectrum), **6dd** was obtained as colorless oil (70.5 mg, 68%, 79:21 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 4:1 as eluent). **^{31}P NMR (202 MHz, $CDCl_3$):** δ 39.2 (s, 79%), 38.8 (s, 21%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.54 – 7.47 (m, 2H), 7.47 – 7.41 (m,

1H), 7.35 – 7.26 (m, 4H), 7.19 (d, *J* = 8.4 Hz, 0.5H), 7.15 – 7.05 (m, 6H), 6.93 (d, *J* = 6.6 Hz, 0.5H), 4.48 – 4.34 (m, 1H), 3.97 (dd, *J* = 16.0, 6.0 Hz, 1H), 3.59 (dd, *J* = 16.0, 7.6 Hz, 1H), 3.49 (dd, *J* = 15.8, 7.4 Hz, 0H), 2.62 (pd, *J* = 6.9, 2.3 Hz, 1H), 2.22 (s, 1H), 1.95 (s, 2H), 1.82 – 1.75 (m, 1H), 1.71 (dd, *J* = 13.6, 3.2 Hz, 1H), 1.65 – 1.57 (m, 1H), 1.56 – 1.47 (m, 1H), 1.34 – 1.23 (m, 1H), 1.09 – 0.98 (m, 3H), 0.93 (d, *J* = 6.9 Hz, 3H), 0.89 (d, *J* = 7.1 Hz, 1H), 0.86 – 0.81 (m, 1H), 0.80 (d, *J* = 3.3 Hz, 1H), 0.76 (dd, *J* = 13.4, 3.3 Hz, 0H), 0.72 (d, *J* = 6.5 Hz, 2H), 0.68 (d, *J* = 6.5 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 135.9, 135.8, 135.4 (d, *J* = 14.4 Hz), 134.2 (d, *J* = 8.3 Hz), 133.9 (d, *J* = 8.5 Hz), 133.2 (d, *J* = 3.8 Hz), 132.2 – 132.0 (m), 131.6 (d, *J* = 4.8 Hz), 131.2 (d, *J* = 4.6 Hz), 130.3 (d, *J* = 10.2 Hz), 129.3, 127.9, 127.7 (d, *J* = 4.1 Hz), 127.6 (d, *J* = 2.6 Hz), 127.4 – 127.1 (m), 127.0, 126.5 (d, *J* = 5.6 Hz), 78.5 (d, *J* = 8.4 Hz), 78.3 (d, *J* = 8.4 Hz), 55.8, 55.0 (d, *J* = 9.1 Hz), 49.2 (d, *J* = 5.8 Hz), 49.0 (d, *J* = 6.0 Hz), 43.3 (d, *J* = 8.3 Hz), 35.9, 34.0 (d, *J* = 5.9 Hz), 31.5 (d, *J* = 6.8 Hz), 25.5 (d, *J* = 9.4 Hz), 22.7 (d, *J* = 6.3 Hz), 21.9 (d, *J* = 6.5 Hz), 21.3 (d, *J* = 12.9 Hz), 15.6 (d, *J* = 9.1 Hz), 13.8 (d, *J* = 21.1 Hz). **HRMS (ESI+)** Calcd. for $C_{31}H_{38}ClO_2PS$ [M+H$^+$]: 541.2097, Found: 541.2092.

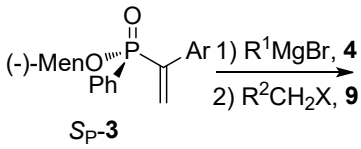
(S_P)-Menthyl (1-*p*-chlorophenyl-2-phenyl-1-phenylthioethyl -1-yl)(phenyl)phosphinat (6de)



The crude **6de** was formed in a ratio of 73:27 (estimated by ^{31}P-NMR spectrum), the pure compound **6de** was obtained as colorless oil (78.6 mg, 68%, 75:25 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 4:1 as eluent). **^{31}P NMR (202 MHz, $CDCl_3$):** δ 38.5 (s, 75%), 38.4 (s, 25%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.53 – 7.48 (m, 1H), 7.47 – 7.42 (m, 3H), 7.36 (d, *J* = 7.2 Hz, 2H), 7.34 – 7.29 (m, 1H), 7.27 (dt, *J* = 8.2, 4.2 Hz, 2H), 7.23 – 7.14 (m, 3H), 7.14 (s, 0H), 7.11 – 7.04 (m, 7H), 7.01 (d, *J* = 6.7 Hz, 0H), 6.88 (dd, *J* = 12.1, 7.8 Hz, 0H), 4.49 – 4.35 (m, 1H), 4.00 (ddd, *J* = 36.3, 17.4, 7.6 Hz, 1H), 3.52 (dd, *J* = 17.5, 6.8 Hz, 1H), 2.32 – 2.23 (m, 0H), 2.22 – 2.13 (m, 1H), 1.77 – 1.69 (m, 1H), 1.69 – 1.52 (m, 2H), 1.39 – 1.32 (m, 0H), 1.03 – 1.00 (m, 0H), 0.99 (d, *J* = 2.8 Hz, 1H), 0.98 – 0.89 (m, 3H), 0.88 (d, *J* = 7.0 Hz, 3H), 0.82 (d, *J* = 7.0 Hz, 3H), 0.79 (d, *J* = 2.9 Hz, 0H), 0.77 (d, *J* = 2.9 Hz, 0H), 0.75 – 0.66 (m, 3H), 0.64 (d, *J* = 6.5 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 136.7, 136.2 – 135.8 (m), 135.7 – 135.5 (m), 134.8 (d, *J* = 8.3 Hz), 134.4 (d, *J* = 2.3 Hz), 134.1 (d, *J* = 8.4 Hz), 133.2 (d, *J* = 4.1 Hz), 132.3 – 132.0 (m), 131.4 (dd, *J* = 11.2, 4.6 Hz), 130.8 (d, *J* = 11.3 Hz), 130.3, 130.2,

120.0, 129.0, 128.8, 128.5, 128.0 (d, J = 3.3 Hz), 127.7 (d, J = 11.9 Hz), 127.5 (dd, J = 14.3, 2.6 Hz), 127.2 (d, J = 12.3 Hz), 127.1 (d, J = 12.6 Hz), 126.0 (d, J = 6.5 Hz), 115.7, 79.0 (d, J = 8.3 Hz), 78.7 (d, J = 8.1 Hz), 58.4 (d, J = 16.8 Hz), 57.6 (d, J = 19.5 Hz), 48.8 (dd, J = 10.8, 6.1 Hz), 43.2 (d, J = 27.5 Hz), 35.6, 34.8, 34.0 (d, J = 11.6 Hz), 31.5 (d, J = 2.6 Hz), 25.4 (d, J = 74.5 Hz), 22.6, 21.9 (d, J = 13.4 Hz), 21.2 (d, J = 12.5 Hz), 15.5 (d, J = 5.6 Hz). **HRMS (ESI+)** Calcd. for $C_{36}H_{40}ClO_2PS$ [M+Na^+]: 625.2073, Found: 625.2055.

Part 4. The tandem addition of Grignard reagents and alkyl halides to S_P-3.



S_P-**3** **10**

Ar = pRC$_6$H$_4$	R^{1}MgBr, **4**	R^{2}CH$_2$X, **9**
R = Cl, **3a**	R^1 = Me, **4a**	R^2, X = H, I, **9a**
H, **3b**	Et, **4b**	Me, Br, **9b**
MeO, **3c**	*i*Pr, **4c**	Et, Br, **9c**
	Ph, **4d**	*n*Pr, Br, **9d**
		Ph, Cl, **9e**

Typical procedure (Entry 1 of Table 2):

To an ice-bath cooled solution of S_P-**3a** (80.0 mg, 0.19 mmol) and bromoethane (28.4 μL, 41.4 mg, 0.38 mmol) in THF (1mL), was added the solution of methyl magnesium bromide (0.76 ml, 0.76 mmol, 1 M solution in THF), and the mixture was stirred and warmed gradually to room temperature within 3 h. The reaction was quenched with aq. ammonium chloride, and the solvent was removed in vacuo. The mixture was extracted with dichloromethane (3 × 5 mL), washed with water (3 × 5 mL), and dried over anhydrous magnesium sulfate. After removing the solvents, the yield and dr were estimated by $^{31}P\{^1H\}$ NMR spectrum.

Entry 2 , 5 , 6 , 7 , 8 of Table 2: To the solution of S_P-**3a** (80.0 mg, 0.19 mmol) in THF (1 mL), was added Grignard reagent (0.36 ml, 0.36 mmol, 1 M solution in THF). After stirring at room temperature for 30 min, El reagent (1.5 eq. to S_P-**3a**) was added. The subsequent treatment was similar to entry 1.

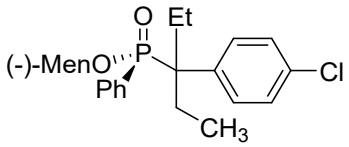
Entry 3 of Table 2: Similar to entry 1, Grignard reagent (0.76 ml, 0.76 mmol, 1 M solution in THF) was added at room temperature.

Entry 10 of Table 2: To the solution of S_P-**3a** (80.0 mg, 0.19 mmol) in THF (1 mL), was added phenyl magnesium bromide (0.36 ml, 0.36 mmol, 1 M solution in THF) at 0 °C. The mixture was stirred and warmed gradually to room temperature, Benzyl chloride (33.4 μL, 36.7 mg, 0.29 mmol) was added. The subsequent treatment was similar to entry 1.

Entry 17 of Table 2: To the solution of ethyl magnesium bromide (0.38 ml, 0.38 mmol, 1 M solution in THF) and bromoethane (28.4 μL, 41.4 mg, 0.38 mmol) in THF (1mL). was added the solution of S_P-**3c** (80.0 mg, 0.19 mmol) in THF (1 mL). The subsequent treatment was similar to entry 1.

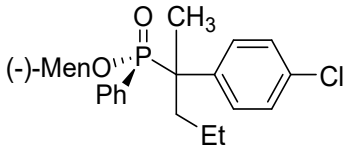
The reactions of other entries were carried out similarly to entry 1.

(S_P)-Menthyl (3-*p*-chlorophenylpentan-3-yl)(phenyl)phosphinate (10aab)



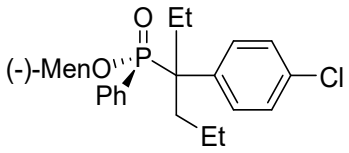
Crude **10aab** was obtained in 63% yield (estimated by ^{31}P-NMR spectrum), the pure compound **10aab** was obtained as colorless oil (44.2 mg, 50%) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 7:2 as eluent). **^{31}P NMR (202 MHz, $CDCl_3$):** δ 43.3 (s). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.45 – 7.38 (m, 1H), 7.28 – 7.20 (m, 4H), 7.16 (d, *J* = 8.7 Hz, 2H), 7.07 (dd, *J* = 8.8, 2.4 Hz, 2H), 4.31 – 4.19 (m, 1H), 2.45 – 2.29 (m, 2H), 2.17 – 1.86 (m, 4H), 1.61 (dddd, *J* = 30.1, 12.5, 6.5, 2.9 Hz, 3H), 1.43 – 1.34 (m, 1H), 1.03 – 0.89 (m, 10H), 0.85 (d, *J* = 6.9 Hz, 3H), 0.80 (d, *J* = 11.4 Hz, 1H), 0.75 (dd, *J* = 12.4, 3.4 Hz, 1H), 0.73 – 0.70 (m, 0H), 0.66 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 137.0 (d, *J* = 3.8 Hz), 132.3, 132.2, 131.2 (d, *J* = 4.0 Hz), 130.6 (d, *J* = 2.7 Hz), 130.1, 129.9, 129.8, 129.2, 126.4 (d, *J* = 2.9 Hz), 126.3, 126.2, 48.1, 48.0，47.5, 46.7, 42.1, 32.9, 30.4, 24.4, 22.2 (d, *J* = 2.1 Hz), 21.6, 21.4, 20.3, 14.4, 7.5 (d, *J* = 7.0 Hz), 7.1 (d, *J* = 8.1 Hz). **HRMS (ESI+)** Calcd. for $C_{27}H_{38}ClO_2P$ [M+Na^+]: 483.2196, Found: 483.2195.

(S_P)-Menthyl (2-*p*-chlorophenylpentan-2-yl)(phenyl)phosphinate (10aba)



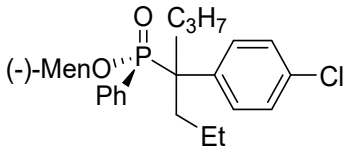
The crude **10aba** was formed in a ratio of 60:40 (estimated by ^{31}P-NMR spectrum), the pure compound **10aba** was obtained as colorless oil (51.3 mg, 58%, 99:1 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 3:1 as eluent). **^{31}P NMR (202 MHz, $CDCl_3$):** δ 43.4 (s, 99%), 40.0 (s, 1%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.45 – 7.38 (m, 1H), 7.36 – 7.29 (m, 2H), 7.28 – 7.23 (m, 3H), 7.16 (d, *J* = 8.8 Hz, 2H), 7.12 (dd, *J* = 8.9, 2.3 Hz, 1H), 4.36 – 4.27 (m, 1H), 2.37 – 2.28 (m, 1H), 2.28 – 2.22 (m, 1H), 1.88 – 1.76 (m, 2H), 1.73 – 1.67 (m, 3H), 1.65 (q, *J* = 3.3 Hz, 1H), 1.63 – 1.56 (m, 1H), 1.49 (d, *J* = 16.0 Hz, 3H), 1.46 – 1.40 (m, 1H), 1.04 – 0.97 (m, 1H), 0.95 (d, *J* = 7.0 Hz, 3H), 0.94 – 0.89 (m, 2H), 0.86 (dd, *J* = 12.2, 6.7 Hz, 6H), 0.70 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 136.7 (d, *J* = 2.7 Hz), 132.2, 132.1, 131.3 (d, *J* = 4.4 Hz), 130.6, 129.8, 129.1, 129.1, 128.9, 126.64 (d, *J* = 2.9 Hz), 126.4, 126.3, 48.1 (d, *J* = 5.8 Hz), 44.4, 43.6, 42.3, 34.9, 33.1, 30.5, 28.7, 24.3, 21.6, 20.9, 20.2, 17.8, 15.1 (d, *J* = 11.8 Hz), 14.4, 13.5. **HRMS (ESI+)** Calcd. for $C_{27}H_{38}ClO_2P$ [M+Na^+]: 483.2196, Found: 483.2200.

(S_P)-Menthyl (3-(*p*-chlorophenyl)hexan-3-yl)(phenyl)phosphinate (10abb)



The crude **10abb** was formed in a ratio of 56:44 (estimated by ^{31}P-NMR spectrum), the pure compound **10abb** was obtained as colorless oil (52.8 mg, 58%, >99:1 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 3:1 as eluent). **^{31}P NMR (202 MHz, $CDCl_3$):** δ 43.3 (s). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.46 – 7.38 (m, 1H), 7.29 – 7.19 (m, 4H), 7.16 (d, *J* = 8.6 Hz, 2H), 7.07 (dd, *J* = 8.9, 2.5 Hz, 2H), 4.32 – 4.20 (m, 1H), 2.40 – 2.30 (m, 2H), 2.11 – 1.94 (m, 3H), 1.94 – 1.80 (m, 1H), 1.71 – 1.48 (m, 4H), 1.40 (d, *J* = 3.0 Hz, 1H), 1.02 – 0.94 (m, 6H), 0.94 – 0.88 (m, 4H), 0.86 (d, *J* = 6.9 Hz, 3H), 0.84 – 0.79 (m, 2H), 0.78 – 0.73 (m, 1H), 0.66 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 137.2 (d, *J* = 3.8 Hz), 132.3, 132.2, 131.2, 131.2, 130.6 (d, *J* = 2.7 Hz), 130.1, 129.7, 129.7, 129.1, 126.0 (d, *J* = 2.9 Hz), 126.3, 126.2, 48.1 (d, *J* = 5.6 Hz), 47.5, 46.7, 42.1, 33.0, 31.1, 30.4, 24.4, 22.8 (d, *J* = 2.1 Hz), 21.6, 20.9, 20.3, 15.7 (d, *J* = 7.7 Hz), 14.5, 13.8, 7.6 (d, *J* = 7.0 Hz). **HRMS (ESI+)** Calcd. for $C_{28}H_{40}ClO_2P$ [M+Na^+]: 497.2352, Found: 497.2355.

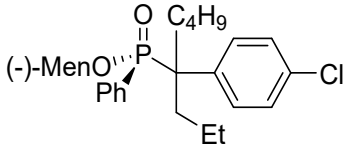
(S_P)-Menthyl (4-*p*-chlorophenylheptan-4-yl)(phenyl)phosphinate (10abc)



Crude **10abc** was obtained in 66% yield (estimated by ^{31}P-NMR spectrum), the pure compound **10abc** was obtained as colorless oil (46.7 mg, 50%) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 6:1 as eluent). **^{31}P NMR (202 MHz, $CDCl_3$):** δ 43.0 (s). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.45 – 7.39 (m, 1H), 7.29 – 7.22 (m, 3H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 2H), 7.06 (dd, *J* = 8.8, 2.4 Hz, 2H), 4.31 – 4.20 (m, 1H), 2.40 – 2.31 (m, 1H), 2.32 – 2.21 (m, 1H), 2.08 – 1.96 (m, 2H), 1.97 – 1.89 (m, 1H), 1.89 – 1.76 (m, 1H), 1.70 – 1.60 (m, 2H), 1.61 – 1.56 (m, 1H), 1.45 – 1.35 (m, 1H), 1.30 – 1.14 (m, 4H), 0.98 (d, *J* = 7.1 Hz, 4H), 0.94 (d, *J* = 7.3 Hz, 2H), 0.91 (d, *J* = 7.9 Hz, 3H), 0.89 – 0.84 (m, 4H), 0.83 – 0.71 (m, 2H), 0.66 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 137.4 (d, *J* = 4.0 Hz), 132.3, 132.3, 131.2, 131.2, 130.6 (d, *J* = 2.6 Hz), 130.0, 129.6, 129.6, 129.0, 126.4 (d, *J* = 3.0 Hz), 126.3, 126.2, 48.1 (d, *J* = 5.5 Hz), 47.4, 46.7, 42.1, 33.0, 32.6 (d, *J* = 2.5 Hz), 31.6, 30.4, 28.7, 24.4, 21.6, 20.9, 20.3, 16.2, 15.7 (d, *J* = 7.9 Hz), 14.5, 13.8 (d, *J* = 6.9 Hz). **HRMS (ESI+)** Calcd.

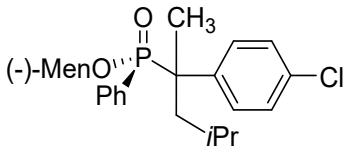
for $C_{29}H_{42}ClO_2P$ [M+Na$^+$]: 511.2509, Found: 511.2510.

(S_P)-Menthyl (4-*p*-chlorophenyloctan-4-yl)(phenyl)phosphinate (10abd)



The crude **10abd** was formed in a ratio of 47:53 (estimated by ^{31}P-NMR spectrum), the pure compound **10abd** was obtained as colorless oil (33.8 mg, 35%, 49:51 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 4:1 as eluent). **^{31}P NMR (202 MHz, $CDCl_3$):** δ 43.2 (s, 49%), 42.9 (s, 51%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.42 (t, *J* = 7.3 Hz, 1H), 7.24 (dd, *J* = 7.4, 3.2 Hz, 2H), 7.22 – 7.13 (m, 4H), 7.05 (d, *J* = 8.6 Hz, 2H), 4.32 – 4.20 (m, 1H), 2.42 – 2.33 (m, 1H), 2.31 – 2.21 (m, 1H), 2.07 – 1.91 (m, 2H), 1.89 – 1.75 (m, 1H), 1.70 – 1.53 (m, 4H), 1.51 – 1.34 (m, 3H), 1.34 – 1.25 (m, 2H), 1.17 – 1.09 (m, 1H), 0.98 (d, *J* = 7.0 Hz, 4H), 0.96 – 0.92 (m, 3H), 0.91 – 0.88 (m, 4H), 0.87 (d, *J* = 6.5 Hz, 3H), 0.85 – 0.71 (m, 2H), 0.66 (d, *J* = 5.9 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 137.5 (d, *J* = 4.2 Hz), 132.3, 132.3, 131.2, 131.2, 130.6, 129.9, 129.6, 129.6, 129.0, 126.4 (d, *J* = 2.4 Hz), 126.3, 126.2, 48.2 – 48.0 (m), 42.3 – 41.9 (m), 32.9, 32.8 – 32.3 (m), 31.7, 30.4, 30.0 – 29.5 (m), 28.9, 24.9 (d, *J* = 6.7 Hz), 24.5 – 24.3 (m), 22.5 (d, *J* = 5.4 Hz), 21.6, 20.9, 20.3, 16.2 (d, *J* = 6.1 Hz), 15.8 (d, *J* = 7.5 Hz), 14.5, 13.8 (d, *J* = 5.3 Hz), 13.0. **HRMS (ESI+)** Calcd. for $C_{30}H_{44}ClO_2P$ [M+Na$^+$]: 525.2665, Found: 525.2666.

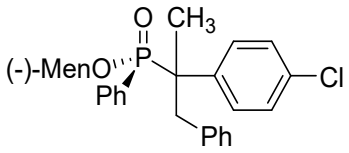
(S_P)-Menthyl (2-*p*-chlorophenyl-4-methylpentan-2-yl)(phenyl)phosphinate (10aca)



The crude **10aca** was formed in a ratio of 62:38 (estimated by ^{31}P-NMR spectrum), the pure compound **10aca** was obtained as white solid (11.8 mg, 13%, 99:1 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 2:1 as eluent); m.p. 75.1-78.9 °C. **^{31}P NMR (202 MHz, $CDCl_3$):** δ 43.4 (s, 99%), 40.5 (s, 1%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.41 – 7.36 (m, 1H), 7.31 – 7.27 (m, 0H), 7.26 (d, *J* = 1.6 Hz, 1H), 7.25 – 7.21 (m, 3H), 7.19 (dd, *J* = 8.9, 2.5 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 4.40 – 4.30 (m, 1H), 2.43 – 2.32 (m, 2H), 1.95 – 1.86 (m, 1H), 1.88 – 1.80 (m, 1H), 1.70 (d, *J* = 3.4 Hz, 1H), 1.69 – 1.64 (m, 1H), 1.65 – 1.57 (m, 1H), 1.52 (d, *J* = 16.2 Hz, 4H), 1.48 – 1.43 (m, 1H), 1.05 (dd, *J* = 13.1, 3.5 Hz, 1H), 0.98 (d, *J* = 7.0 Hz, 4H), 0.94 (s, 0H), 0.89 (dd, *J* = 6.8, 3.4 Hz, 6H), 0.84 (d, *J* = 3.1 Hz, 0H), 0.83 – 0.78 (m, 1H),

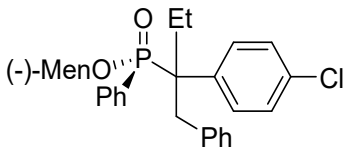
0.71 (d, *J* = 6.6 Hz, 3H), 0.55 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 138.3, 133.1, 133.0, 132.4, 131.5 (d, *J* = 2.6 Hz), 130.8, 130.2, 130.1, 129.8, 127.6, 127.5, 127.3, 127.3, 77.7 (d, *J* = 8.2 Hz), 53.4, 49.1 (d, *J* = 6.9 Hz), 45.7, 45.0, 43.4, 34.1, 31.5, 25.5, 25.1, 24.5 (d, *J* = 12.8 Hz), 24.3, 22.7, 21.9, 21.3, 18.8, 15.6. **HRMS (ESI+)** Calcd. for $C_{28}H_{40}ClO_2P$ [M+Na^+]:497.2352, Found: 497.2352.

(S_P)-Menthyl (2-*p*-chlorophenyl-1-phenylpropan-2-yl)(phenyl)phosphinate (10ada)



The crude **10ada** was formed in a ratio of 62:38 (estimated by ^{31}P-NMR spectrum), the pure compound **10ada** was obtained as colorless oil (58.5 mg, 60%, >99:1 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 4:1 as eluent). **^{31}P NMR (202 MHz, $CDCl_3$):** δ 43.2 (s). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.40 – 7.31 (m, 3H), 7.28 (d, *J* = 6.6 Hz, 2H), 7.26 – 7.19 (m, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.07 (q, *J* = 6.5, 6.0 Hz, 3H), 6.76 – 6.71 (m, 2H), 4.53 – 4.43 (m, 1H), 3.87 (dd, *J* = 13.8, 5.7 Hz, 1H), 3.19 (dd, *J* = 13.8, 7.5 Hz, 1H), 2.61 – 2.51 (m, 1H), 1.90 (d, *J* = 11.5 Hz, 1H), 1.73 – 1.70 (m, 1H), 1.68 – 1.60 (m, 2H), 1.60 – 1.53 (m, 1H), 1.33 (d, *J* = 15.6 Hz, 3H), 1.06 (d, *J* = 7.0 Hz, 4H), 0.99 (t, *J* = 8.0 Hz, 4H), 0.89 – 0.81 (m, 1H), 0.74 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 136.2, 135.6, 135.5, 131.9, 131.8, 131.7, 131.6, 130.6 (d, *J* = 2.5 Hz), 129.9, 129.4, 129.4, 128.9, 126.7, 126.7, 126.5, 126.4, 125.4, 77.0, 76.9, 48.2, 48.1, 45.3, 42.4, 39.1 (d, *J* = 2.4 Hz), 33.1, 30.5, 24.8, 21.7, 20.9, 20.3, 17.4, 14.6. **HRMS (ESI+)** Calcd. for $C_{31}H_{38}ClO_2P$ [M+Na^+]: 531.2196, Found:531.2195.

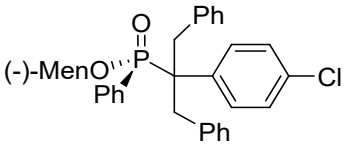
(S_P)-Menthyl (2-*p*-chlorophenyl-1-phenylbutan-2-yl)(phenyl)phosphinate (10adb)



The crude **10adb** was formed in a ratio of 72:28 (estimated by ^{31}P-NMR spectrum), the pure compound **10adb** was obtained as colorless oil (40.1 mg, 40%, 84:16 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 3:1 as eluent). **^{31}P NMR (202 MHz, $CDCl_3$):** δ 44.2 (s, 84%), 42.4 (s, 16%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.39 – 7.32 (m, 1H), 7.31 – 7.24 (m, 1H), 7.24 – 7.21 (m, 1H), 7.21 – 7.14 (m, 4H), 7.08 (d, *J* = 8.7 Hz, 2H), 7.04 – 6.99 (m, 3H), 6.86 (dd, *J* = 6.4, 2.8 Hz, 2H), 6.80 – 6.76 (m, 0H), 4.36 – 4.26 (m, 1H),

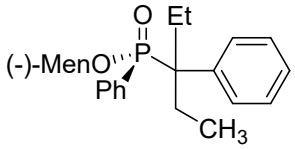
4.27 – 4.18 (m, 0H), 3.68 (dd, *J* = 15.2, 8.6 Hz, 1H), 3.43 (dd, *J* = 15.3, 8.2 Hz, 1H), 2.45 – 2.36 (m, 1H), 2.16 – 2.03 (m, 1H), 1.91 – 1.73 (m, 1H), 1.73 – 1.67 (m, 1H), 1.66 – 1.57 (m, 1H), 1.57 – 1.48 (m, 1H), 1.46 – 1.38 (m, 1H), 1.36 – 1.28 (m, 0H), 1.26 – 1.19 (m, 1H), 1.16 – 1.04 (m, 1H), 1.02 – 0.92 (m, 6H), 0.84 (q, *J* = 6.1 Hz, 4H), 0.78 – 0.73 (m, 1H), 0.73 – 0.67 (m, 1H), 0.63 (d, *J* = 6.5 Hz, 2H), 0.59 (d, *J* = 6.5 Hz, 0H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 138.0, 137.5 (d, *J* = 3.4 Hz), 137.2, 137.1, 133.3 (d, *J* = 8.6 Hz), 133.1 (d, *J* = 8.5 Hz), 132.6 (d, *J* = 3.9 Hz), 131.9, 131.8 (d, *J* = 2.5 Hz), 131.0, 130.3, 130.2, 130.0, 127.9, 127.8, 127.8 – 127.6 (m), 127.4 (d, *J* = 11.9 Hz), 126.3 (d, *J* = 11.7 Hz), 78.0 (d, *J* = 8.5 Hz), 65.9, 53.5, 49.2, 49.1 (d, *J* = 5.7 Hz), 43.3, 43.2, 35.2, 34.0 (d, *J* = 7.8 Hz), 31.5 (d, *J* = 11.0 Hz), 25.5 (d, *J* = 18.4 Hz), 24.4 (d, *J* = 33.8 Hz), 22.7, 21.9, 15.5 (d, *J* = 6.2 Hz), 9.8 (d, *J* = 3.6 Hz). **HRMS (ESI+)** Calcd. for $C_{32}H_{40}ClO_2P$ [M+H$^+$]: 523.2532, Found: 523.2531.

(S_P)-Menthyl (2-*p*-chlorophenyl-1,3-diphenylpropan-2-yl)(phenyl)phosphinate (10ade)



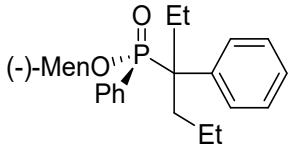
Crude **10ade** was obtained in 79% yield (estimated by ^{31}P-NMR spectrum), the pure compound **10ade** was obtained as white solid (70.7 mg, 63%) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 5:1 as eluent); m.p. 50.9-52.2 °C. **^{31}P NMR (202 MHz, $CDCl_3$):** δ 43.1 (s). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.45 – 7.38 (m, 1H), 7.37 (dd, *J* = 8.8, 2.5 Hz, 2H), 7.28 (d, *J* = 1.6 Hz, 1H), 7.27 – 7.21 (m, 3H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.09 – 6.97 (m, 6H), 6.93 – 6.88 (m, 2H), 6.86 – 6.80 (m, 2H), 4.36 – 4.26 (m, 1H), 3.67 (t, *J* = 15.3 Hz, 1H), 3.59 – 3.44 (m, 3H), 2.10 – 2.01 (m, 1H), 1.69 (d, *J* = 11.8 Hz, 1H), 1.66 – 1.59 (m, 1H), 1.60 – 1.53 (m, 1H), 1.38 – 1.29 (m, 1H), 1.01 – 0.89 (m, 2H), 0.87 (d, *J* = 7.1 Hz, 3H), 0.81 (d, *J* = 6.9 Hz, 4H), 0.77 – 0.70 (m, 1H), 0.67 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 137.7, 137.6, 137.0, 137.0, 136.7, 136.6, 133.5 (d, *J* = 8.8 Hz), 132.8, 132.8, 131.8 (d, *J* = 2.8 Hz), 131.4, 131.3, 130.8 (d, *J* = 4.4 Hz), 130.6, 130.4, 129.9, 127.6, 127.6, 127.5 (d, *J* = 5.3 Hz), 127.5, 127.4, 126.2, 125.9, 78.4, 78.3, 50.6, 49.9, 48.9, 48.9, 43.2, 38.8, 37.0, 34.0, 31.5, 25.3, 22.6, 21.9, 21.3, 15.6. **HRMS (ESI+)** Calcd. for $C_{37}H_{42}ClO_2P$ [M+H$^+$]: 585.2689, Found: 585.2680.

(S_P)-Menthyl (3-phenylpentan-3-yl)(phenyl)phosphinate (10bab)



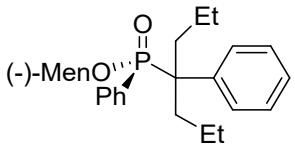
Crude **10bab** was obtained in 43% yield (estimated by ^{31}P-NMR spectrum), the pure compound **10bab** was obtained as colorless oil (29.4 mg, 33%) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 4:1 as eluent). **^{31}P NMR (202 MHz, $CDCl_3$):** δ 43.9 (s). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.41 – 7.36 (m, 1H), 7.20 (dd, *J* = 8.0, 3.5 Hz, 1H), 7.20 – 7.14 (m, 5H), 7.16 – 7.10 (m, 3H), 4.31 – 4.20 (m, 1H), 2.48 – 2.37 (m, 2H), 2.19 – 2.09 (m, 2H), 2.09 – 1.95 (m, 2H), 1.69 – 1.52 (m, 3H), 1.45 – 1.36 (m, 1H), 1.03 – 0.92 (m, 10H), 0.87 (d, *J* = 6.9 Hz, 4H), 0.83 – 0.75 (m, 1H), 0.75 – 0.71 (m, 0H), 0.64 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 138.2, 138.2, 132.3, 132.3, 130.4 (d, *J* = 3.0 Hz), 129.4, 128.5, 128.4, 126.3, 126.3, 126.1, 126.0, 125.2, 125.2, 48.1 (d, *J* = 5.7 Hz), 47.6, 42.1, 33.0, 30.4, 28.7, 24.4, 22.1(d, *J* = 2.6 Hz), 21.6, 21.2, 20.9, 20.3, 14.5, 7.6 (d, *J* = 7.1 Hz), 7.2 (d, *J* = 8.1 Hz). **HRMS (ESI+)** Calcd. for $C_{27}H_{39}O_2P$ [M+H^+]: 427.2766, Found: 427.2776.

(S_P)-Menthyl (3-phenylhexan-3-yl)(phenyl)phosphinate (10bbb)



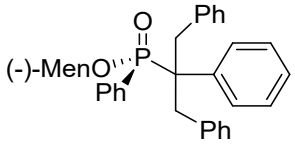
The crude **10bbb** was formed in a ratio of 67:33 (estimated by ^{31}P-NMR spectrum), the pure compound **10bbb** was obtained as colorless oil (21.2 mg, 23%, 88:12 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 5:1 as eluent). **^{31}P NMR (202 MHz, $CDCl_3$):** δ 44.0 (s, 88%), 43.7 (s, 12%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.41 – 7.36 (m, 1H), 7.23 – 7.15 (m, 7H), 7.14 – 7.09 (m, 2H), 4.31 – 4.21 (m, 1H), 2.50 – 2.34 (m, 2H), 2.19 – 2.01 (m, 2H), 2.01 – 1.83 (m, 2H), 1.69 – 1.60 (m, 2H), 1.60 – 1.50 (m, 3H), 1.45 – 1.37 (m, 1H), 0.98 (dt, *J* = 7.3, 3.8 Hz, 7H), 0.92 (t, *J* = 7.3 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H), 0.84 – 0.78 (m, 1H), 0.78 – 0.68 (m, 1H), 0.68 – 0.61 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 138.4 (d, *J* = 3.8 Hz), 132.4, 132.3, 132.2, 130.4 (d, *J* = 2.7 Hz), 130.3, 129.4, 128.3 (d, *J* = 4.6 Hz), 126.3 (d, *J* = 3.0 Hz), 126.1, 126.0, 125.2, 125.2, 48.1 (d, *J* = 5.6 Hz), 47.7, 47.0, 42.1, 33.0, 32.0 (d, *J* = 3.0 Hz), 31.0, 28.7, 22.7 (d, *J* = 2.6 Hz), 21.6, 20.9, 20.3, 16.2 (d, *J* = 6.7 Hz), 15.7 (d, *J* = 7.8 Hz), 14.5, 13.9 (d, *J* = 4.2 Hz), 7.7 (d, *J* = 7.2 Hz), 7.2 (d, *J* = 8.6 Hz). **HRMS (ESI+)** Calcd. for $C_{28}H_{41}O_2P$ [M+Na^+]: 463.2742, Found: 463.2749.

(S_P)-Menthyl (4-phenylheptan-4-yl)(phenyl)phosphinate (10bbc)



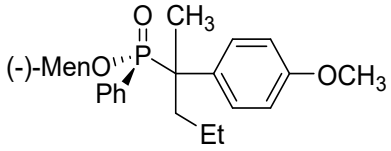
Crude **10bbc** was obtained in 77% yield (estimated by ^{31}P-NMR spectrum), the pure compound **10bbc** was obtained as colorless oil (57.9 mg, 61%) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 6:1 as eluent). **^{31}P NMR (202 MHz, $CDCl_3$):** δ 43.6 (s). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.38 (t, *J* = 7.3 Hz, 1H), 7.20 (dd, *J* = 7.6, 3.3 Hz, 2H), 7.16 (dd, *J* = 5.9, 3.3 Hz, 4H), 7.15 – 7.09 (m, 3H), 4.32 – 4.22 (m, 1H), 2.49 – 2.40 (m, 1H), 2.39 – 2.27 (m, 1H), 2.12 – 1.95 (m, 2H), 1.94 – 1.79 (m, 1H), 1.69 – 1.63 (m, 1H), 1.57 (dd, *J* = 17.8, 10.7 Hz, 4H), 1.46 – 1.38 (m, 2H), 1.26 – 1.15 (m, 2H), 0.99 (d, *J* = 7.0 Hz, 4H), 0.91 (dt, *J* = 23.0, 7.2 Hz, 9H), 0.84 – 0.70 (m, 2H), 0.64 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 139.7, 139.7, 133.4, 133.3, 131.4 (d, *J* = 2.6 Hz), 131.2, 130.3, 129.2, 129.2, 127.3 (d, *J* = 3.0 Hz), 127.1, 127.0, 126.2 (d, *J* = 3.3 Hz), 49.1 (d, *J* = 5.6 Hz), 48.6, 47.9, 43.1, 34.0, 33.6 (d, *J* = 2.8 Hz), 31.4, 25.4, 22.6, 21.9, 21.4, 17.3, 17.2, 16.8, 16.7, 15.5, 14.9, 14.8. **HRMS (ESI+)** Calcd. for $C_{29}H_{43}O_2P$ [M+Na$^+$]: 477.2899, Found: 477.2901.

(*S*$_P$)-Menthyl (2-phenyl-1,3-diphenylpropan-2-yl)(phenyl)phosphinate (10bde)



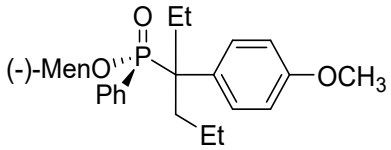
Crude **10bde** was obtained in 68% yield (estimated by ^{31}P-NMR spectrum), the pure compound **10bde** was obtained as white solid (57.5 mg, 50%) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 4:1 as eluent); m.p**.** 63.9-66.1 °C. **^{31}P NMR (202 MHz, $CDCl_3$):** δ 43.5 (s). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.43 (d, *J* = 7.1 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.26 – 7.14 (m, 7H), 7.07 – 6.95 (m, 6H), 6.93 (d, *J* = 7.2 Hz, 2H), 6.84 (d, *J* = 7.5 Hz, 2H), 4.36 – 4.26 (m, 1H), 3.72 (t, *J* = 15.3 Hz, 1H), 3.65 – 3.47 (m, 3H), 2.22 – 2.06 (m, 1H), 1.70 (d, *J* = 12.0 Hz, 1H), 1.66 – 1.58 (m, 1H), 1.55 (d, *J* = 12.6 Hz, 1H), 1.35 (t, *J* = 11.4 Hz, 1H), 0.96 (dd, *J* = 13.0, 3.1 Hz, 1H), 0.87 (d, *J* = 7.0 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 4H), 0.80 – 0.69 (m, 2H), 0.66 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 139.0, 138.9, 137.4, 137.4, 137.1, 137.0, 133.6, 133.5, 131.6 (d, *J* = 2.6 Hz), 131.2, 130.9, 130.8, 130.2, 130.0 (d, *J* = 5.2 Hz), 127.6 (d, *J* = 2.7 Hz), 127.4 (d, *J* = 4.8 Hz), 127.3, 127.2, 126.8, 126.8, 126.0, 125.8, 115.9, 78.2, 78.1, 50.9, 50.2, 49.0, 48.9, 43.2, 38.6, 37.0, 34.0, 31.5, 25.3, 22.7, 21.9, 21.4, 15.6. **HRMS (ESI+)** Calcd. for $C_{37}H_{43}O_2P$ [M+H$^+$]: 551.3079, Found: 551.3071.

(S_P)-Menthyl (2-*p*-methoxyphenylpentan-2-yl)(phenyl)phosphinate (10cba)



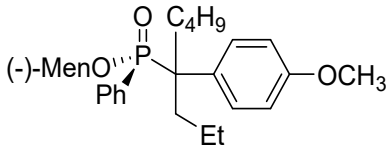
The crude **10cba** was formed in a ratio of >99:1 (estimated by ^{31}P-NMR spectrum), the pure compound **10cba** was obtained as colorless oil (51.3 mg, 58%, >99:1 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 3:1 as eluent). **^{31}P NMR (202 MHz, $CDCl_3$):** δ 41.1 (s). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.51 – 7.41 (m, 3H), 7.32 – 7.24 (m, 2H), 6.85 (s, 2H), 6.57 (s, 2H), 4.07 – 3.93 (m, 1H), 3.70 (s, 3H), 2.90 – 2.83 (m, 1H), 1.64 (s, 1H), 1.57 – 1.40 (m, 5H), 1.37 – 1.21 (m, 2H), 1.13 – 1.04 (m, 2H), 0.87 (d, *J* = 17.2 Hz, 3H), 0.83 – 0.73 (m, 4H), 0.71 (d, *J* = 7.0 Hz, 3H), 0.66 (d, *J* = 15.0 Hz, 1H), 0.59 (d, *J* = 6.5 Hz, 3H), 0.47 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 157.1, 133.0, 132.9, 131.0 (d, *J* = 7.5 Hz), 130.5, 130.2, 129.2, 126.5, 126.4, 111.7, 54.1, 47.9, 47.9, 44.1, 44.0, 43.4, 43.3, 42.1, 34.5, 30.4, 28.7, 23.5, 21.5, 20.9, 18.0, 14.2, 13.1, -0.00. **HRMS (ESI+)** Calcd. for $C_{28}H_{41}O_3P$ [M+Na^+]: 479.2691 Found: 479.2692

(S_P)-Menthyl (3-*p*-methoxyphenylhexan-3-yl)(phenyl)phosphinate (10cbb)



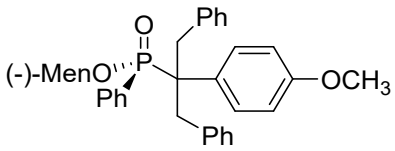
The crude **10cbb** was formed in a ratio of 65:35 (estimated by ^{31}P-NMR spectrum), the pure compound **10cbb** was obtained as colorless oil (4.56 mg, 5%, 96:4 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 2:1 as eluent). **^{31}P NMR (202 MHz, $CDCl_3$):** δ 44.2 (s, 96%), 44.0 (s, 4%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.32 (t, *J* = 7.0 Hz, 1H), 7.18 – 7.06 (m, 4H), 7.00 – 6.94 (m, 2H), 6.66 (d, *J* = 8.6 Hz, 2H), 4.23 – 4.13 (m, 1H), 3.73 (s, 3H), 2.41 – 2.23 (m, 2H), 2.07 – 1.89 (m, 2H), 1.87 – 1.73 (m, 2H), 1.52 (dd, *J* = 27.7, 16.4 Hz, 4H), 0.90 (dt, *J* = 13.9, 6.9 Hz, 7H), 0.86 – 0.78 (m, 7H), 0.76 – 0.66 (m, 3H), 0.60 – 0.56 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 157.0, 156.9, 132.4, 132.4, 132.3, 132.3, 130.3, 129.4, 129.4, 126.1, 126.0 (d, *J* = 4.3 Hz), 111.7, 111.7, 54.2, 48.1 (d, *J* = 5.5 Hz), 46.9, 46.2, 42.1, 33.0, 31.1, 30.4, 28.7, 24.4, 22.8, 21.6, 20.3, 15.7 (d, *J* = 7.8 Hz), 14.5, 13.9 (d, *J* = 4.2 Hz), 7.6 (d, *J* = 7.0 Hz). **HRMS (ESI+)** Calcd. for $C_{29}H_{43}O_3P$ [M+Na^+]: 493.2848, Found: 493.2856.

(S_P)-Menthyl (4-*p*-methoxyphenyloctan-4-yl)(phenyl)phosphinate (10cbd)



The crude **10cbd** was formed in a ratio of 43:57 (estimated by ^{31}P-NMR spectrum), the pure compound **10cbd** was obtained as colorless oil (32.9 mg, 34%, 40:60 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 5:2 as eluent). **^{31}P NMR (202 MHz, $CDCl_3$):** δ 44.1 (s, 40%), 43.9 (s, 60%).**^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.40 (t, J = 7.2 Hz, 1H), 7.25 – 7.12 (m, 4H), 7.03 (d, J = 8.8 Hz, 2H), 6.73 (d, J = 8.5 Hz, 2H), 4.31 – 4.21 (m, 1H), 3.81 (s, 2H), 2.51 – 2.38 (m, 1H), 2.28 (ttt, J = 13.7, 9.2, 4.6 Hz, 1H), 2.10 – 1.89 (m, 2H), 1.73 (s, 1H), 1.62 (ddd, J = 43.4, 16.2, 7.9 Hz, 7H), 1.46 – 1.36 (m, 2H), 1.35 – 1.24 (m, 4H), 0.99 (d, J = 7.0 Hz, 3H), 0.96 – 0.93 (m, 2H), 0.90 (dd, J = 14.3, 6.2 Hz, 7H), 0.84 – 0.73 (m, 2H), 0.65 (d, J = 6.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 158.0 (d, J = 3.1 Hz), 133.4, 133.4, 131.6, 131.6, 131.4, 130.4, 130.3, 130.3, 127.1, 127.0, 112.7, 112.7, 55.2, 49.2 (d, J = 5.5 Hz), 47.7, 47.0, 43.0, 34.0, 33.7, 32.8, 31.4, 30.8, 30.0, 29.7, 25.9 (d, J = 6.8 Hz), 25.4, 23.6 (d, J = 6.1 Hz), 22.6, 21.9, 21.4, 17.2 (d, J = 6.5 Hz), 16.8 (d, J = 7.4 Hz), 15.5, 14.9 (d, J = 4.6 Hz), 14.0. **HRMS (ESI+)** Calcd. for $C_{31}H_{47}O_3P$ [M+Na^+]: 521.3161, Found: 521.3163.

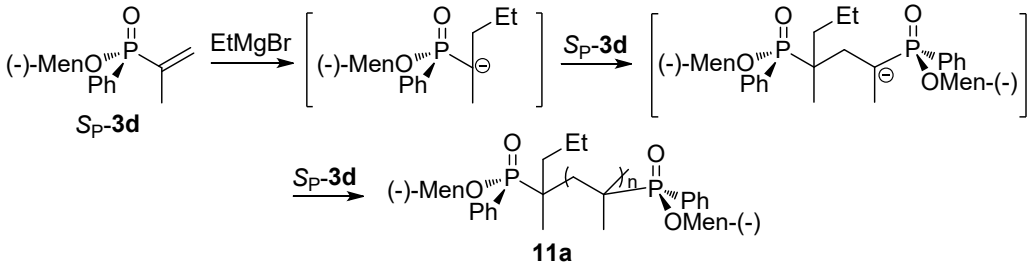
(S_P)-Menthyl (2-*p*-methoxyphenyl-1,3-diphenylpropan-2-yl)(phenyl)phosphinate (10cde)



Crude **10cde** was obtained in 90% yield (estimated by 31P-NMR spectrum), the pure compound **10cde** was obtained as white solid (90.1 mg, 80%) from preparative TLC (silica gel, petroleum ether/ethyl acetate =2:1 as eluent); m.p. 74.2-75.6 °C. **^{31}P NMR (202 MHz, $CDCl_3$):** δ 43.6 (s). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.30 (t, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 7.0 Hz, 2H), 7.21 – 7.15 (m, 2H), 7.15 – 7.08 (m, 2H), 6.98 – 6.88 (m, 6H), 6.85 (d, *J* = 7.1 Hz, 2H), 6.77 (d, *J* = 7.4 Hz, 2H), 6.68 (d, *J* = 8.6 Hz, 2H), 4.26 – 4.18 (m, 1H), 3.73 (s, 3H), 3.59 (t, *J* = 15.5 Hz, 1H), 3.53 – 3.43 (m, 2H), 3.39 (t, *J* = 15.4 Hz, 1H), 2.13 – 2.01 (m, 1H), 1.62 (d, *J* = 11.9 Hz, 1H), 1.58 – 1.52 (m, 1H), 1.48 (d, *J* = 12.4 Hz, 2H), 1.31 – 1.23 (m, 1H), 0.93 – 0.82 (m, 1H), 0.79 (d, *J* = 7.0 Hz, 3H), 0.75 (d, *J* = 6.9 Hz, 3H), 0.72 – 0.63 (m, 2H), 0.58 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 158.4, 158.4, 137.5, 137.4, 137.2, 137.1, 133.6, 133.5, 131.5 (d, *J* = 2.7 Hz), 131.3, 131.1, 131.1, 130.9, 130.8, 130.7, 130.3, 127.4, 127.4, 127.3, 127.2, 126.0, 125.7, 112.9 (d, *J* = 2.7 Hz), 78.0, 77.9, 55.2, 50.1, 49.4, 49.0 (d, *J* = 5.9 Hz), 43.2,

38.5, 37.0 34.0, 31.5, 25.3, 22.6, 21.9, 21.4, 15.6. **HRMS (ESI+)** Calcd. for $C_{38}H_{45}O_3P$ [$M+H^+$]: 581.3184, Found: 581.3174.

The polymerization of 2-propenyl phosphinate S_P-3d with 4b.



To the solution of S_P-**3d** (80.0 mg, 0.25 mmol) in THF (1 mL), was added the solution of ethyl magnesium bromide (0.50 ml, 0.50 mmol, 1 M solution in THF), and the mixture was stirred at room temperature for 3 h. The reaction was quenched with saturated aq. ammonium chloride, and the solvent was removed in vacuo. The mixture was extracted with dichloromethane (3 × 5 mL), washed with water (3 × 5 mL), and dried over anhydrous magnesium sulfate. After removing the solvents, the residue was analyzed with NMR spectrum. The yield and dr were estimated by $^{31}P\{^{1}H\}$ NMR spectrum, then the residue was purified by preparative TLC (silica gel, petroleum ether/ethyl acetate = 3:1 as eluent) to afford **11a** (Figure S1).

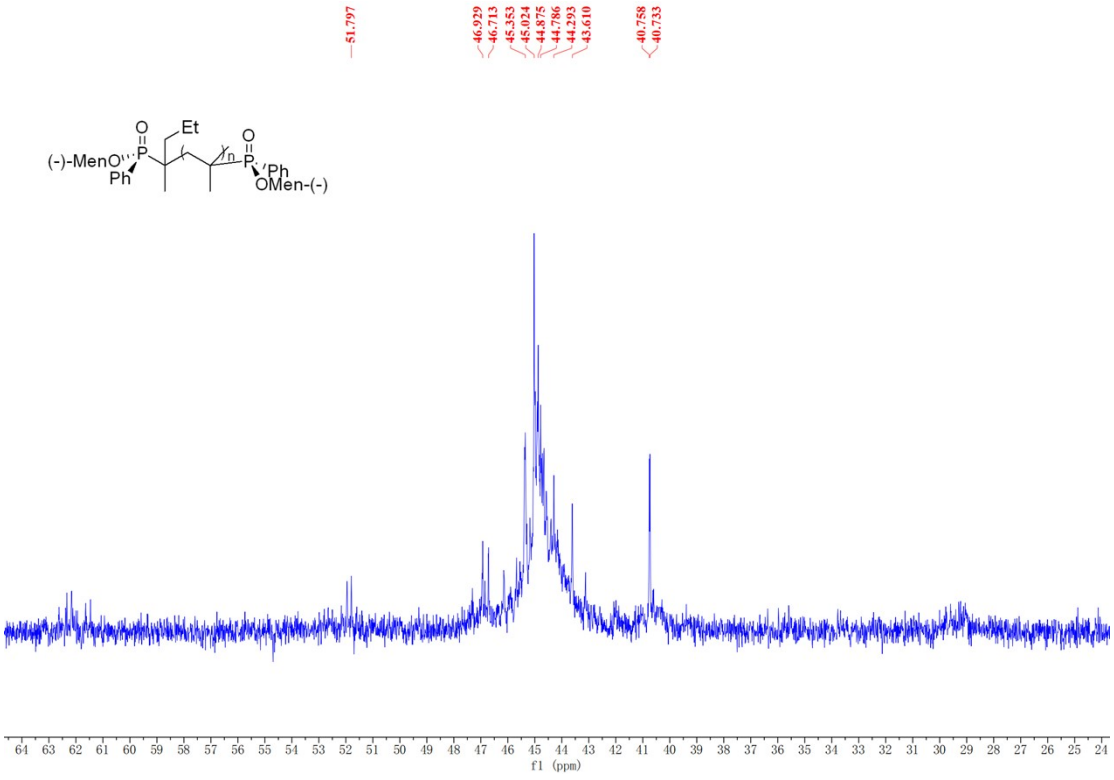
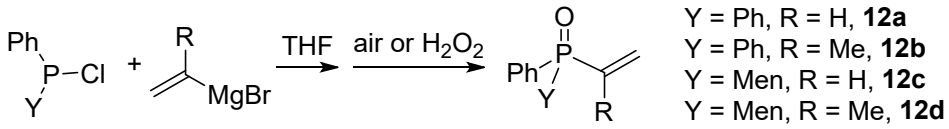


Figure S1. The ^{31}P NMR spectrum of isolated 11a.

Part 5. The preparation of vinyl phosphines 12.



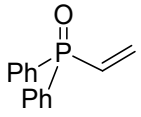
Y = Ph, R = H, **12a**
Y = Ph, R = Me, **12b**
Y = Men, R = H, **12c**
Y = Men, R = Me, **12d**

Typical procedure, the preparation of 12a

To the solution of chlorodiphenyl phosphine (1.00 ml, 5.60 mmol) in THF (3 mL), was added vinyl magnesium bromide (6.72 mL, 6.72 mmol, 1 M solution in THF) slowly at 0 °C, and the mixture was stirred at room temperature for 3 hours. After the reaction was completed, as monitored with TLC, the reaction was quenched with aq. ammonium chloride and the solvent was removed in vacuo. The mixture was extracted with dichloromethane (3 × 10 mL), washed with water (3 × 10 mL), and dried over anhydrous magnesium sulfate.

After removing solvent, the crude residue (1.20 g) was dissolved in THF (2 ml), hydrogen peroxide solution (30%, 0.76 g, 6.72 mmol) was added slowly. After stirring at room temperature for 1 h, the mixture was extracted with dichloromethane (3 × 10 mL), washed with water (3 × 10 mL), and dried over anhydrous magnesium sulfate. After removing solvents, the residue was analyzed with NMR spectrum. The peaks at 24.1 ppm were observed on ^{31}P NMR spectrum. **12a** was obtained by recrystallization from dichlormethane and petroleum ether (60-90°C).

Diphenyl(vinyl)phosphine oxide (12a)

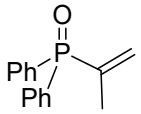


Crude **12a** was obtained in >99% yield (estimated by ^{31}P-NMR spectrum), the pure **12a** was obtained as a white solid (1.15 g, 90%) from recrystallization with dichloromethane-petroleum ether (60-90 °C). **^{31}P NMR (202 MHz, $CDCl_3$):** δ 24.1 (s).**^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.75 – 7.67 (m, 4H), 7.58 – 7.50 (m, 2H), 7.50 – 7.43 (m, 4H), 6.76 – 6.59 (m, 1H), 6.43 – 6.23 (m, 2H). **HRMS (ESI+)** Calcd. for $C_{14}H_{13}OP$ [M+K$^+$]: 267.0341, Found: 267.0349.

The preparation of 12b

Similar to the above procedure, except for vinyl magnesium bromide was replaced with isopropenyl magnesium bromide (13.4 mL, 6.72 mmol, 0.50 M solution in THF). The residue was purified by preparative TLC (silica gel, petroleum ether/ethyl acetate = 1:1 as eluent) to afford **12b.**

Diphenyl(prop-1-en-2-yl)phosphine oxide (12b)

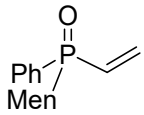


Crude **12b** was obtained in 95% yield (estimated by ^{31}P-NMR spectrum), the pure **12b** was obtained as a white solid (1.22 g, 90%) from recrystallization with dichloromethane-petroleum ether (60-90 °C). **^{31}P NMR (202 MHz, $CDCl_3$):** δ 31.3 (s).**^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.79 – 7.69 (m, 4H), 7.55 (dd, *J* = 9.4, 5.4 Hz, 2H), 7.51 – 7.44 (m, 4H), 6.03 – 5.86 (m, 1H), 5.63 (d, *J* = 19.7 Hz, 1H), 2.00 (d, *J* = 12.2 Hz, 3H). **HRMS (ESI+)** Calcd. for $C_{15}H_{15}OP$ [M+Na^+]: 265.0759, Found: 265.0778.

Typical procedure, the preparation of 12c

To the solution of dichlorophenylphosphine (1.00 ml, 7.40 mmol) in THF (3 mL), was added menthyl magnesium chloride (10.1 mL, 8.14 mmol, 1.0 M solution in THF) slowly at 0 °C, and the mixture was stirred at room temperature for 3 hours. The mixture was cooled with ice-both, and vinyl magnesium bromide (11.1 mL, 11.1 mmol, 1.0 M solution in THF) was added. After the reaction was completed, as monitored with TLC, the reaction was quenched with aq. ammonium chloride and the solvent was removed in vacuo. The residue was extracted with dichloromethane (3 × 10 mL), washed with water (3 × 10 mL), and dried over anhydrous magnesium sulfate. After removing solvent, the residue (2.03 g) was placed in a 50 ml round-bottom flask, and was oxidized by air. After the oxidization was completed, the residue was purified by preparative TLC (silica gel, petroleum ether/ethyl acetate = 1:1 as eluent) to afford R_P-**12c** was obtained by recrystallization from dichlormethane and petroleum ether (60-90 °C).

(R_P)-Menthyl (phenyl)(vinyl)phosphine oxide (12c)

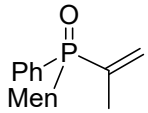


The crude **12c** was formed in a ratio of 51:49 (estimated by ^{31}P-NMR spectrum), optically pure **(R_P)-12c** was obtained as a white solid (0.24 g, 11%, >99:1 dr) from preparative TLC (silica gel, dichloromethane as eluent) and then recrystallization with dichloromethane-petroleum ether (60-90 °C), m.p. 155.0– 159.0 °C. **^{31}P NMR (202MHz, $CDCl_3$):** δ 32.6 (s). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.75 – 7.68 (m, 2H), 7.51 – 7.41 (m, 3H), 6.47 (ddd, *J* = 27.2, 18.5, 12.5 Hz, 1H), 6.36 – 6.12 (m, 2H), 2.22 – 2.13 (m, 1H), 2.06 – 1.95 (m, 1H), 1.82 – 1.68 (m, 3H), 1.68 – 1.57 (m, 1H), 1.58 – 1.48 (m, 0H), 1.20 – 1.00 (m, 2H), 0.97 (d, *J* = 6.7 Hz, 0H), 0.91 – 0.86 (m, 5H), 0.83 (d, *J* = 6.8 Hz, 3H), 0.46 (d, *J* = 6.8 Hz, 3H). **HRMS (ESI+)** Calcd. for $C_{18}H_{27}OP$ [M+H^+]: 291.1878, Found: 291.1873.

The preparation of 12d

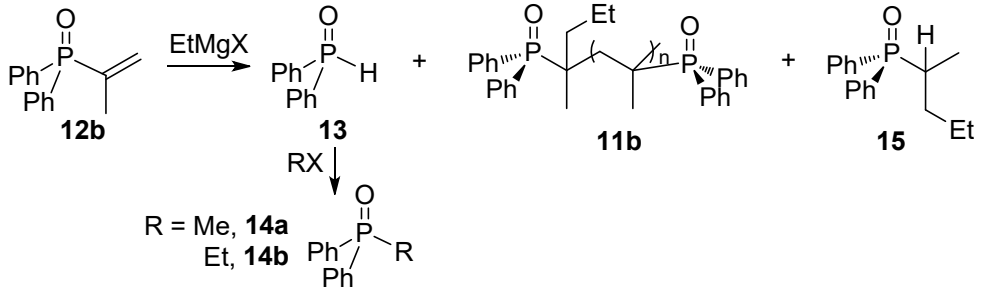
Similar to above procedure, except for vinyl magnesium bromide was replaced with isopropenyl magnesium bromide (22.2 mL, 11.1 mmol, 0.50 M solution in THF). The residue was purified by preparative TLC (silica gel, petroleum ether/ethyl acetate = 1:1 as eluent) to afford **12d**.

Menthyl (phenyl)(prop-1-en-2-yl)phosphine oxide (12d)



The crude **12d** was formed in a ratio of 49:51 (estimated by ^{31}P-NMR spectrum), the pure **12b** was obtained as a white solid (0.23 g, 10%, 4:96 dr) from preparative TLC (silica gel, dichloromethane as eluent) and then recrystallization with dichloromethane-petroleum ether (60-90 °C), m.p. 148.5-152.5 °C. **^{31}P NMR (202 MHz, $CDCl_3$):** δ 36.9 (s, 4%), 33.9 (s, 96%).**^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.91 – 7.75 (m, 2H), 7.58 – 7.40 (m, 3H), 6.04 (d, *J* = 17.5 Hz, 1H), 5.75 (dt, *J* = 35.2, 1.6 Hz, 1H), 2.19 – 2.10 (m, 1H), 2.00 (d, *J* = 11.3 Hz, 0H), 1.87 (d, *J* = 11.6 Hz, 3H), 1.82 – 1.74 (m, 3H), 1.45 – 1.35 (m, 1H), 1.37 – 1.23 (m, 1H), 1.13 – 1.01 (m, 2H), 1.00 – 0.90 (m, 4H), 0.86 – 0.81 (m, 1H), 0.78 (d, *J* = 6.7 Hz, 3H), 0.38 (d, *J* = 6.7 Hz, 3H). **HRMS (ESI+)** Calcd. for $C_{19}H_{29}OP$ [M+H$^+$]: 305.2034, Found: 305.2032.

Part 6. The reaction of 12 with Grignard reagents/alkyl halides.



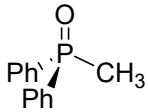
The reaction of diphenyl vinylphosphine oxide with Grignard reagents/alkyl halides

Typical procedure:

To the solution of **12b** (80.0 mg, 0.33 mmol) in THF (1 mL), was added *p*-tolyl Grignard reagent (0.66 ml, 0.66 mmol, 1 M solution in THF), and the mixture was stirred at room temperature for 30 min. Analysis of the reaction mixture with ^{31}P NMR spectrum exhibited a signal at 20.4 ppm was observed, which was assigned as diphenylphosphine oxide **13**. Alkyl halide (2.0 eq. to **12b**) was added. After the reaction was completed, as monitored with TLC, excessive copper ammonia solution was added. The resulting yellow solid was collected by filtration, and analyzed with IR spectrum (KBr). An absorption peak at 2254.48 cm^{-1} was observed, which assigned as the alkynyl bond of **22** (Figure S2).

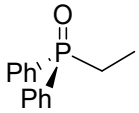
The filtrate was extracted with dichloromethane (3 × 5 mL), washed with water (3 × 5 mL), and dried over anhydrous magnesium sulfate. After removing solvent, the residue was purified by preparative TLC (silica gel, ethyl acetate as eluent) to afford **14** (rf = 0.4), **11b** (rf = 0) and trace amounts of **15b** (rf = 0.6). **15b** was analyzed by GC-MS, the peak at 334.2 as assigned as molecular ion peak (Figure S3).

Methyldiphenylphosphine oxide (14a)



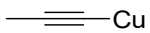
The yield of the crude **14a** is 47% (estimated by ^{31}P-NMR spectrum), the pure **14a** was obtained as a white solid (26.8 mg, 37.6%) from preparative TLC (silica gel, ethyl acetate as eluent) (60-90 °C). **^{31}P NMR (202 MHz, CDCl$_3$):** δ 29.9 (s). **^{1}H NMR (500 MHz, CDCl$_3$):** δ 7.66 (dd, *J* = 11.8, 7.4 Hz, 4H), 7.45 (d, *J* = 6.8 Hz, 2H), 7.43 – 7.35 (m, 4H), 1.95 (d, *J* = 13.2 Hz, 3H). **HRMS (ESI+)** Calcd. for $C_{13}H_{13}OP$ [M+K$^+$]: 255.0341, Found: 255.0346.

Ethyldiphenylphosphine oxide (14b)



The yield of the crude **14b** is 79% (estimated by ^{31}P-NMR spectrum), the pure **14b** was obtained as a white solid (48.1 mg, 63.2%) from preparative TLC (silica gel, ethyl acetate as eluent). **^{31}P NMR (202 MHz, $CDCl_3$):** δ 34.2 (s).**^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.77 – 7.69 (m, 4H), 7.51 (d, *J* = 6.4 Hz, 2H), 7.49 – 7.43 (m, 4H), 2.34 – 2.21 (m, 2H), 1.20 (dt, *J* = 17.1, 7.6 Hz, 3H). **HRMS (ESI+)** Calcd. for $C_{14}H_{15}OP$ [M+Na^+]: 253.0759, Found: 253.0749.

Propynylcopper (the cuprous salt of 22)



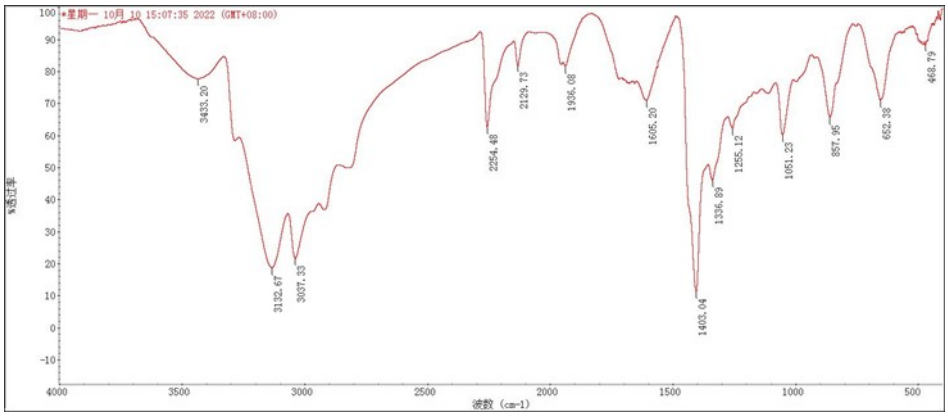
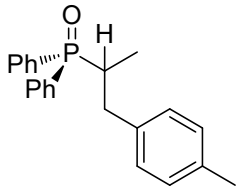


Figure S2. The IR spectrum of cuprous salt of propyne.

Diphenyl(1-(p-tolyl)propan-2-yl)phosphine oxide (15b)



^{31}P NMR (202 MHz, $CDCl_3$): δ 36.3 (s).

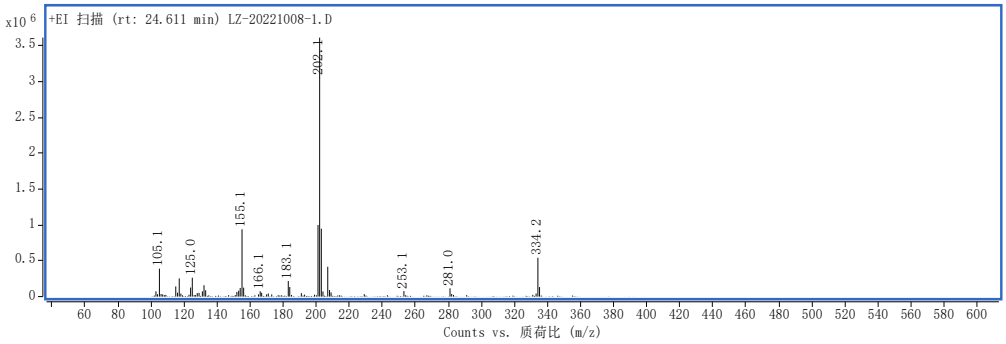
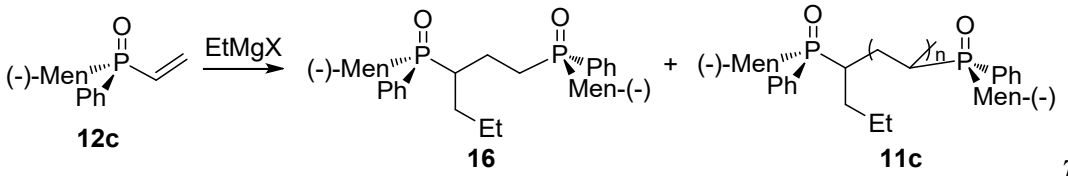


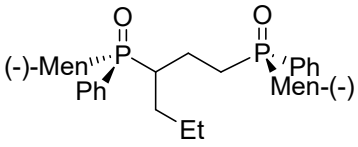
Figure S3. The GC-MS spectrum of 15b.



Typical procedure:

To the solution of **12c** (80.0 mg, 0.28 mmol) in THF (1mL), was added ethylmagnesium bromide (0.56 ml, 0.56 mmol, 1 M solution in THF), and the mixture was stirred at room temperature for 30 min. The reaction was quenched with aq. ammonium chloride, and the solvent was removed in vacuo. The mixture was extracted with dichloromethane (3 × 5 mL), washed with water (3 × 5 mL), and dried over anhydrous magnesium sulfate. After removing the solvents, the residue was analyzed with NMR spectrum. Then the residue was purified by preparative TLC (silica gel, petroleum ether/ethyl acetate = 1:2 as eluent) to afford **16** (rf = 0.1) and **11c** (rf = 0.5).

(R_P,R_P)-Menthyl menthylphenylphosphorylhexan-3-yl phenylphosphine oxide (16)

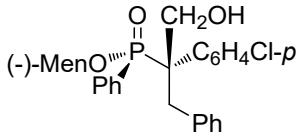


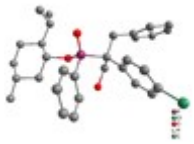
16 was obtained as a colorless oil (40.0 mg, 48.1% 29:30:6:35) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 1:2 as eluent). **^{31}P NMR (202 MHz, $CDCl_3$):** δ 48.7 (s, 29%), 47.8 (s, 30%), 47.0 (s, 6%), 43.4 (s, 35%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.11 (d, *J* = 7.4 Hz, 0H), 7.81 – 7.70 (m, 1H), 7.49 (dq, *J* = 17.1, 10.0, 8.9 Hz, 4H), 7.30 (d, *J* = 6.1 Hz, 1H), 7.21 (d, *J* = 26.6 Hz, 2H), 7.08 – 7.01 (m, 1H), 6.97 – 6.89 (m, 1H), 2.83 – 2.70 (m, 1H), 2.40 – 2.14 (m, 3H), 2.12 – 1.80 (m, 8H), 1.77 – 1.57 (m, 7H), 1.53 (s, 1H), 1.47 – 1.38 (m, 2H), 1.18 – 1.07 (m, 2H), 0.97 (d, *J* = 10.8 Hz, 4H), 0.95 – 0.87 (m, 6H), 0.83 (t, *J* = 6.0 Hz, 6H), 0.67 (d, *J* = 6.7 Hz, 3H), 0.40 (d, *J* = 6.6 Hz, 2H), 0.31 (d, *J* = 6.6 Hz, 2H), 0.24 (dd, *J* = 15.4, 8.4 Hz, 1H), 0.14 (d, *J* = 6.6 Hz, 2H).**HRMS (ESI+)** Calcd. for $C_{38}H_{60}O_2P_2$[M+Na^+]: 633.3967, Found: 633.3948.

Part 7. Crystallographic information.

Crystallography data of S_P,S_C-6db

The single crystal suited for the X-ray diffraction was obtained from the evaporation of the solution of **S_P,S_C-6db** in dichloromethane and petroleum ether (60-90 °C).

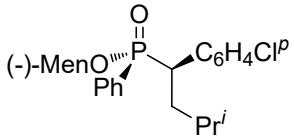


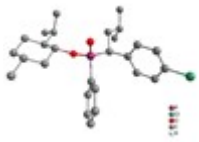


Empirical formula	C31 H38 Cl O3 P
Crystal system	Monoclinic
space group	P212121
Formula weight	525.03
a, Å	6.5468(7)
b, Å	16.2047(16)
c, Å	27.749(3)
α, deg	90
β, deg	90
γ, deg	90
V, Å3	2943.8(5)
Z	4
F(000)	1120.0
T, K	298.15
ρ, Mg m-3	1.185
Rint	0.0963
R1 [I N 2σ(I)]	0.0740
R1 (all data)	0.1602
wR2 [I N 2σ(I)]	0.1692
wR2 (all data)	0.2052
GOOF	0.874
CCDC	2216572

Crystallography data of S_P,S_C-6ca

The single crystal suited for the X-ray diffraction was obtained from the evaporation of the solution of **S_P,S_C-6ca** in dichloromethane and petroleum ether (60-90 ºC).

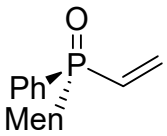


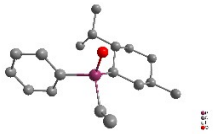


Empirical formula	C27H38ClO2P
Crystal system	monoclinic
space group	P21
Formula weight	460.99
a, Å	12.7102(11)
b, Å	5.9519(5)
c, Å	18.9788(18)
α, deg	90
β, deg	99.214(2)
γ, deg	90
V, Å3	1417.2(2)
Z	2
F(000)	496.0
T, K	298.15
ρ, Mg m-3	1.080
Rint	0.1000
R1 [I N 2σ(I)]	0.1149
R1 (all data)	0.1743
wR2 [I N 2σ(I)]	0.2925
wR2 (all data)	0.3311
GOOF	0.989
CCDC	2216573

Crystallography data of R_P-12c

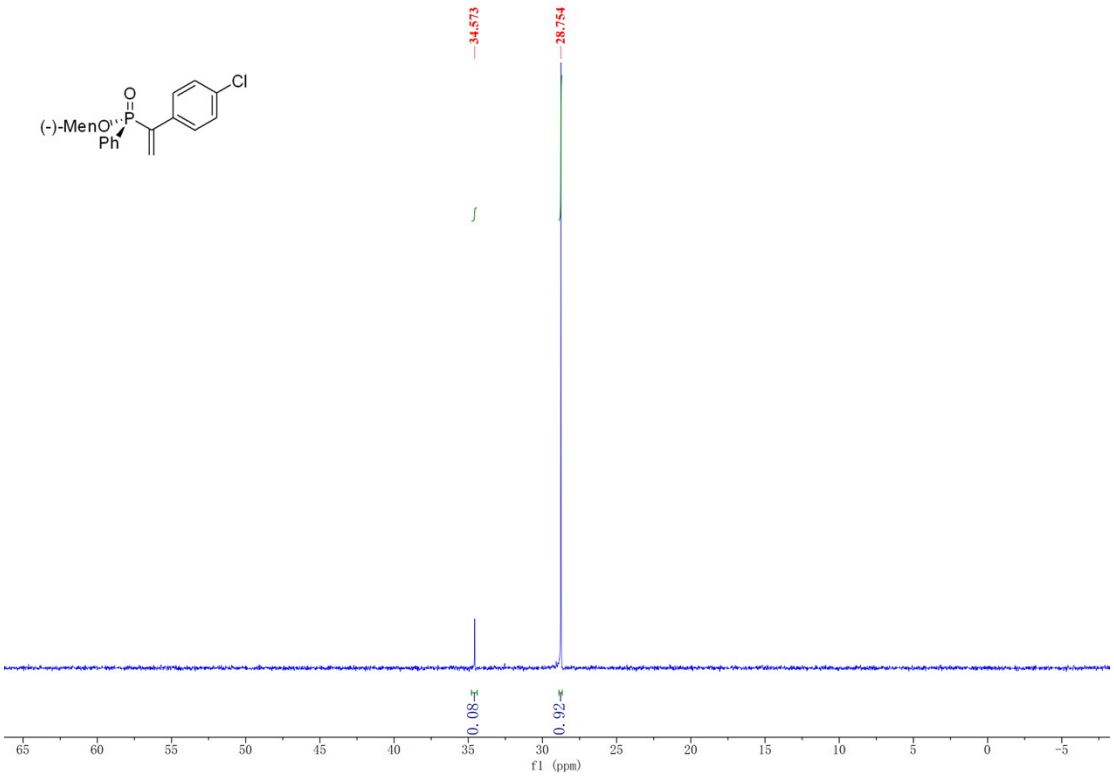
The single crystal suited for the X-ray diffraction was obtained from the evaporation of the solution of ***R*P-12c** in dichloromethane and petroleum ether (60-90 °C).

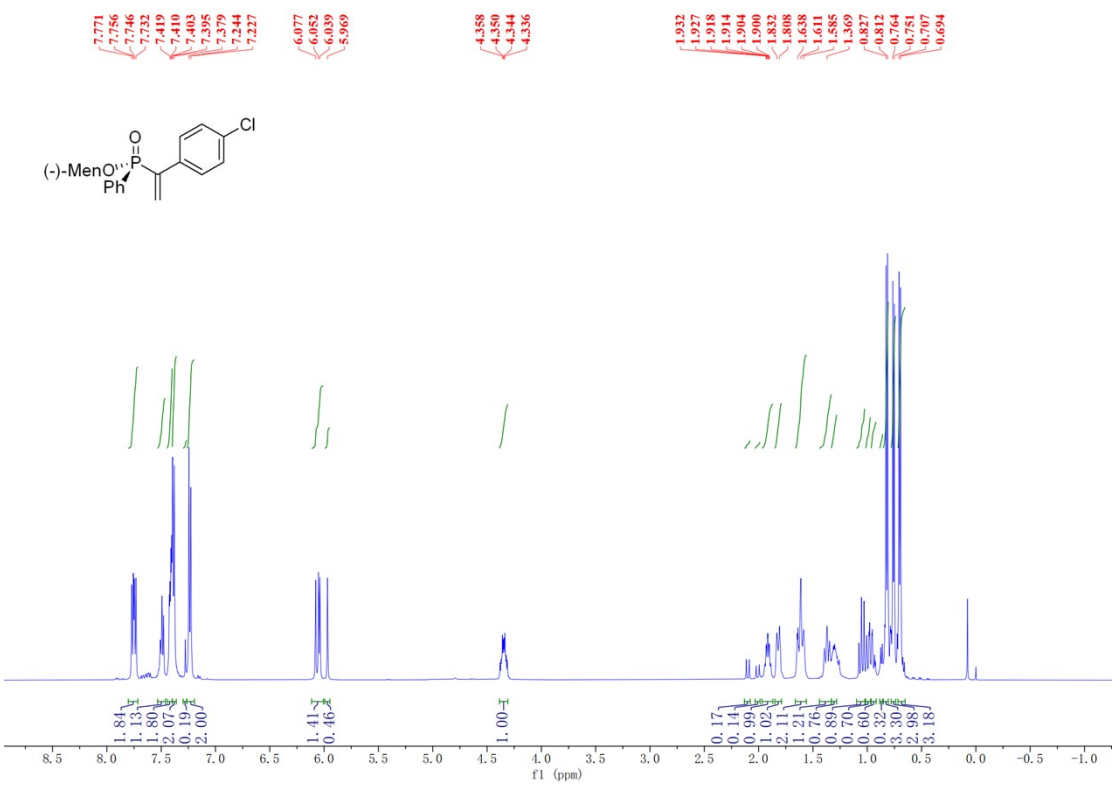


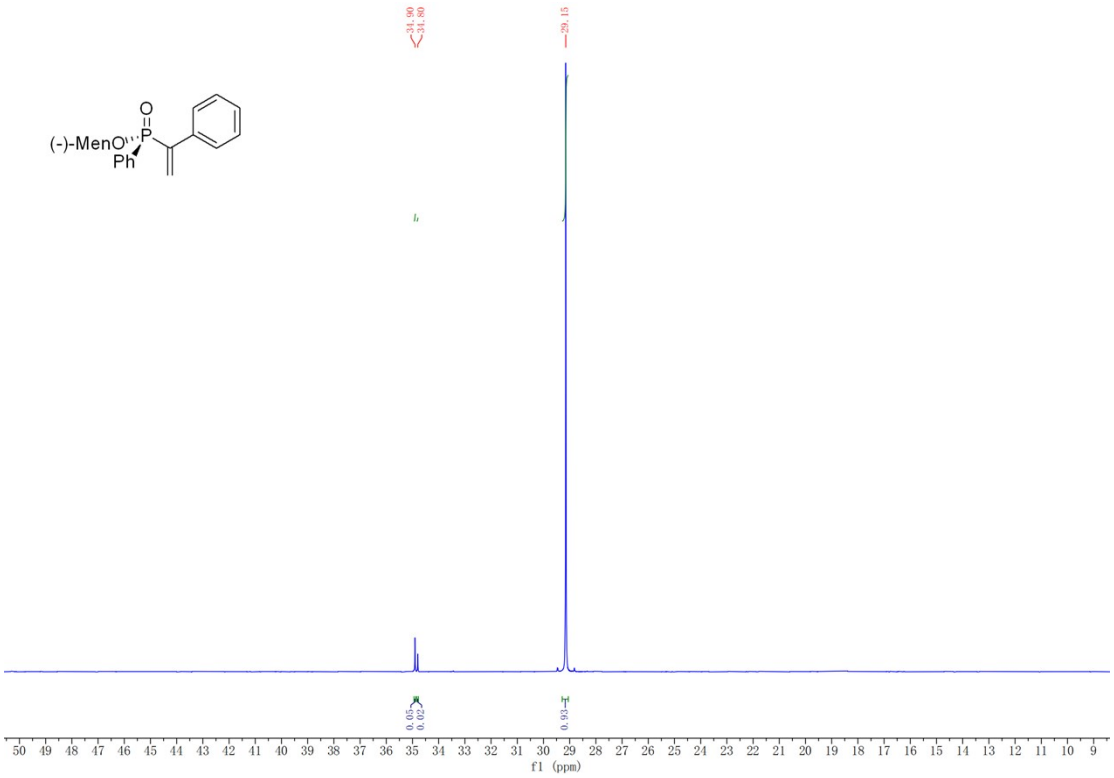


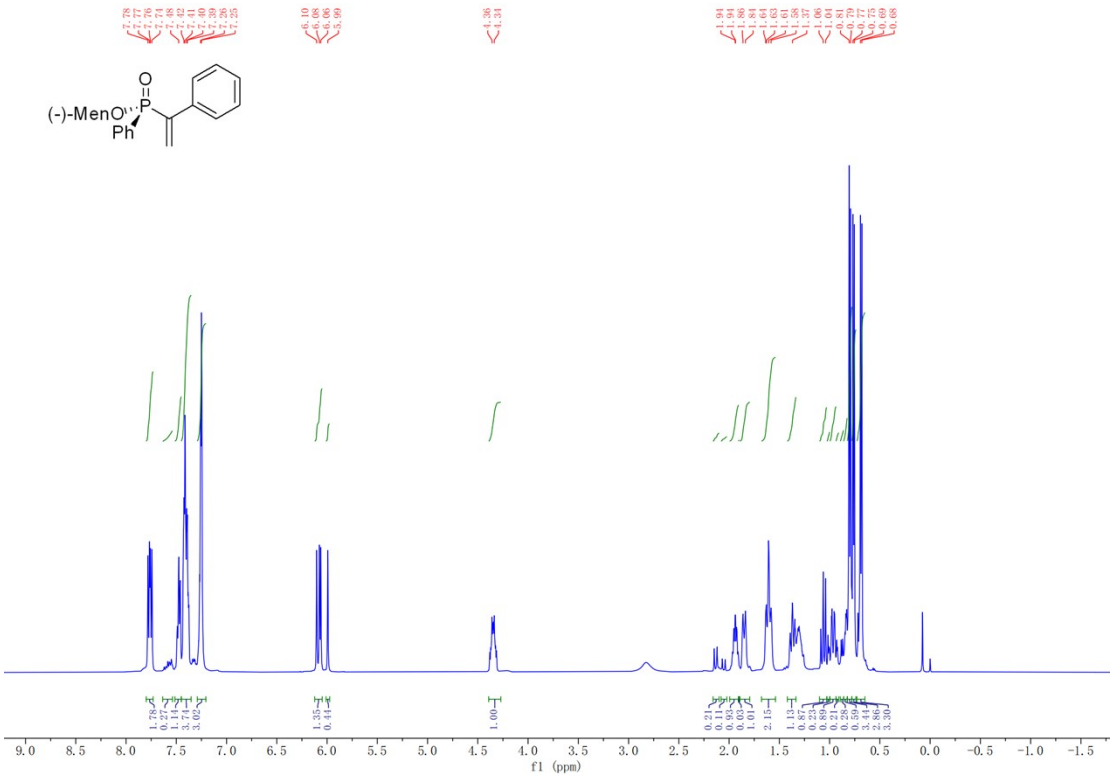
Empirical formula	C18 H27 O P
Crystal system	monoclinic
space group	P21
Formula weight	290.36
a, Å	9.3136(8)
b, Å	10.1805(9)
c, Å	9.9531(8)
α, deg	90
β, deg	111.262(4)
γ, deg	90
V, Å3	879.49(13)
Z	2
F(000)	316.0
T, K	298.15
ρ, Mg m-3	1.096
Rint	0.0527
R1 [I N 2σ(I)]	0.0961
R1 (all data)	0.1432
wR2 [I N 2σ(I)]	0.2053
wR2 (all data)	0.2228
GOOF	1.100
CCDC	2217203

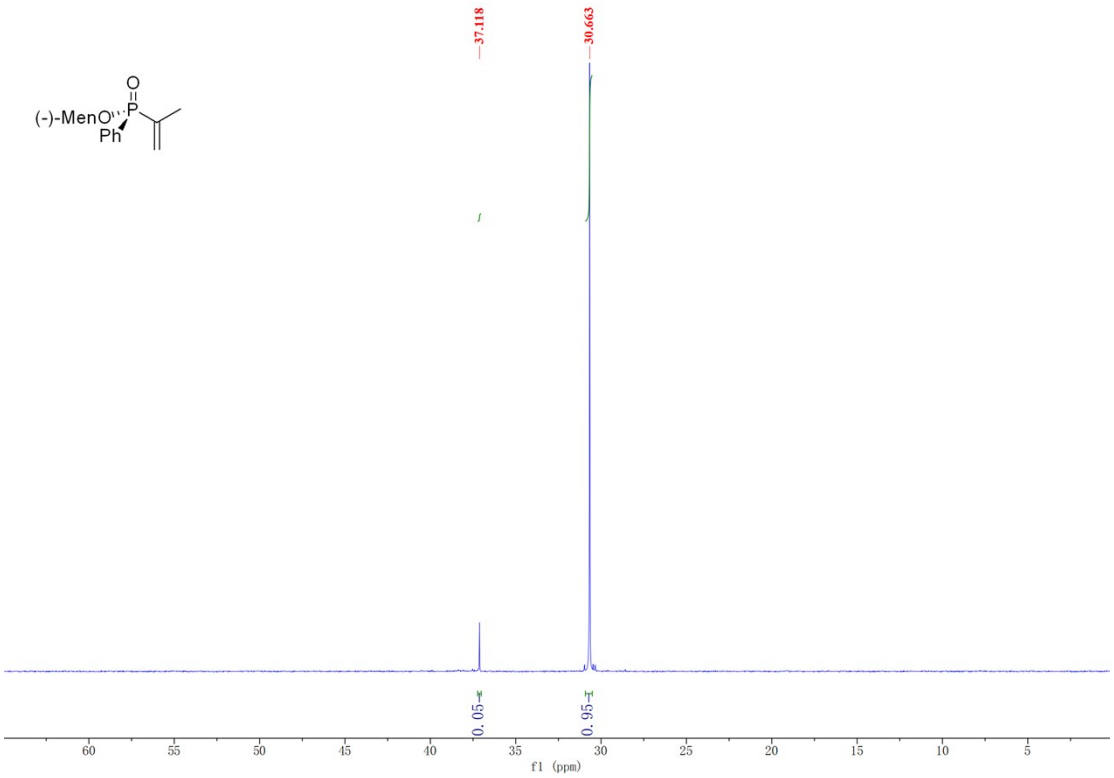
Part 8. Selected photocopies of ^{1}H, ^{31}P and ^{13}C NMR spectrum.






(-)-MenO
Ph
f1 (ppm)


(-)-MenO
Ph
f1 (ppm)


(-)-MenO
Ph
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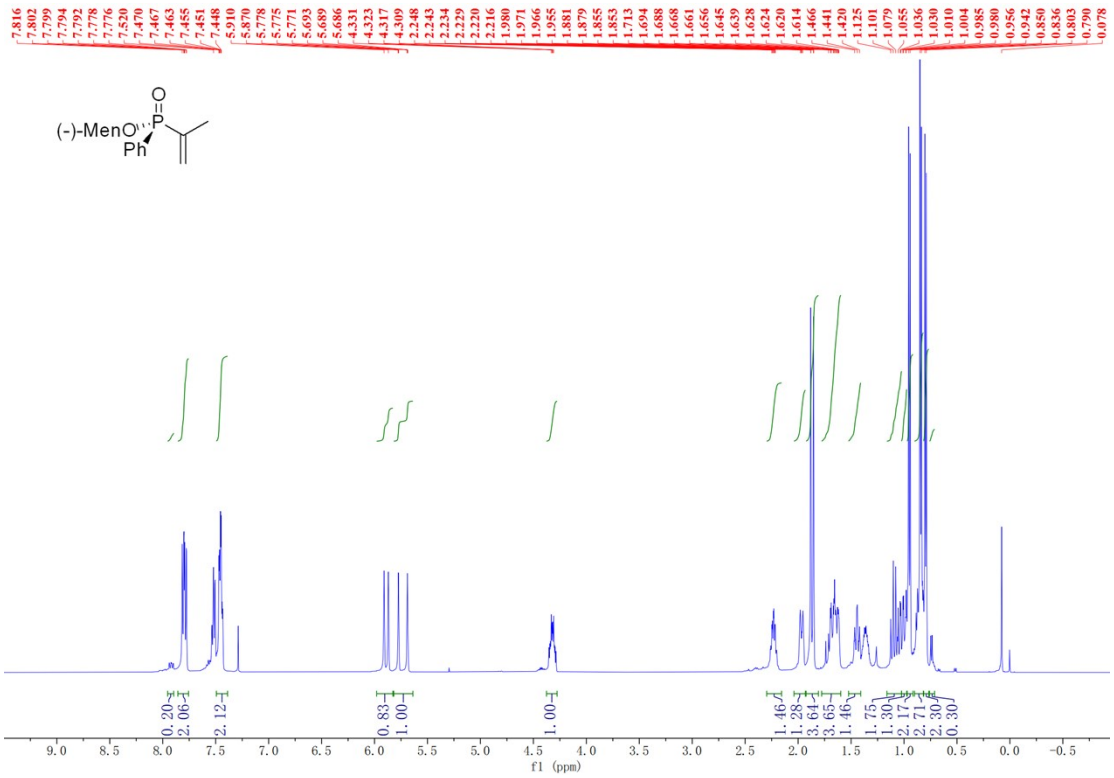
30.663
0.05
0.95
f1 (ppm)


(-)-MenO
Ph
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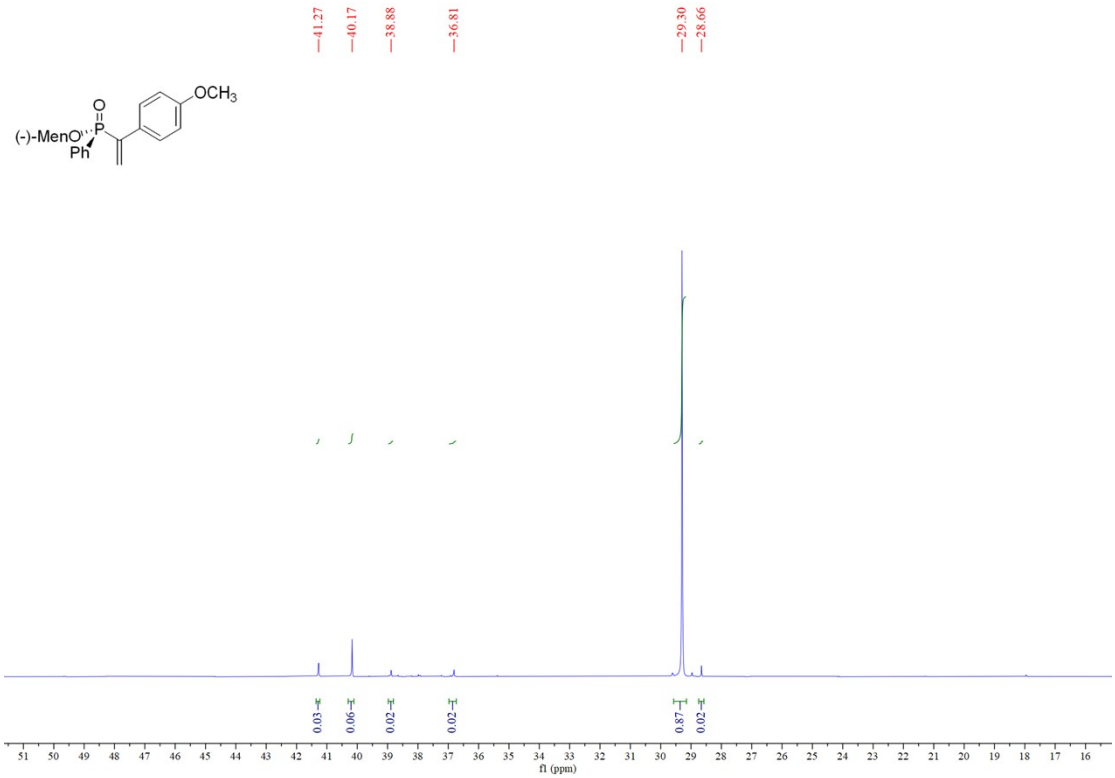
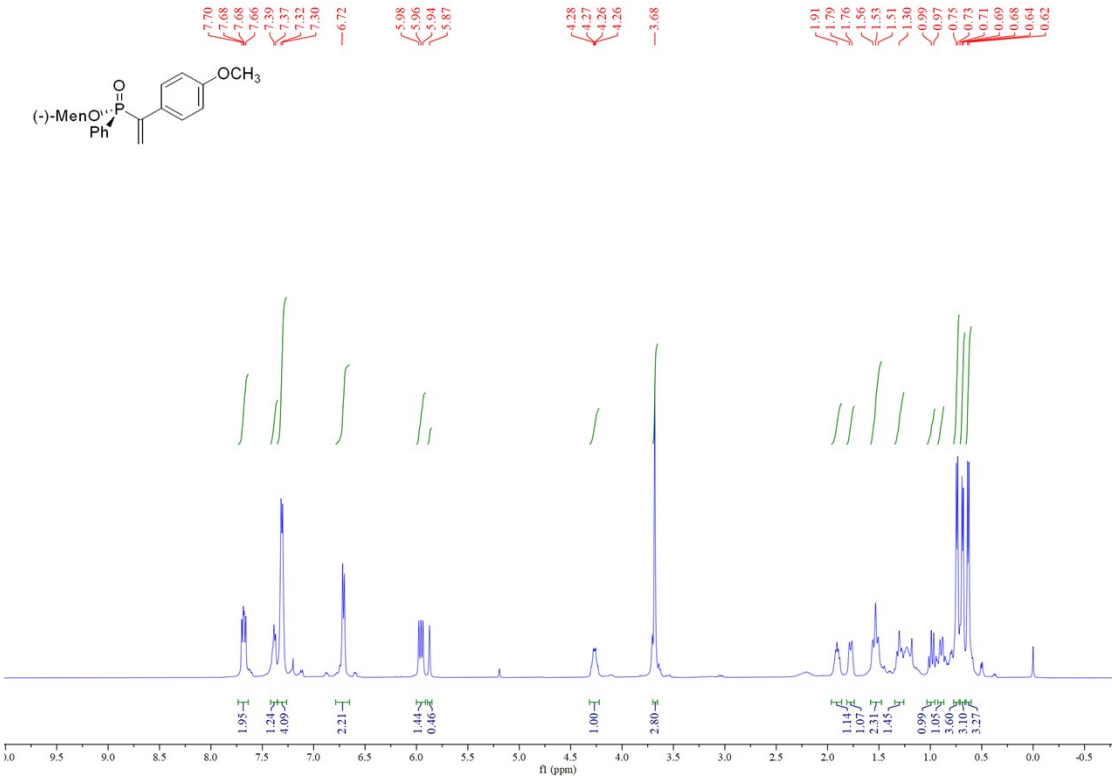
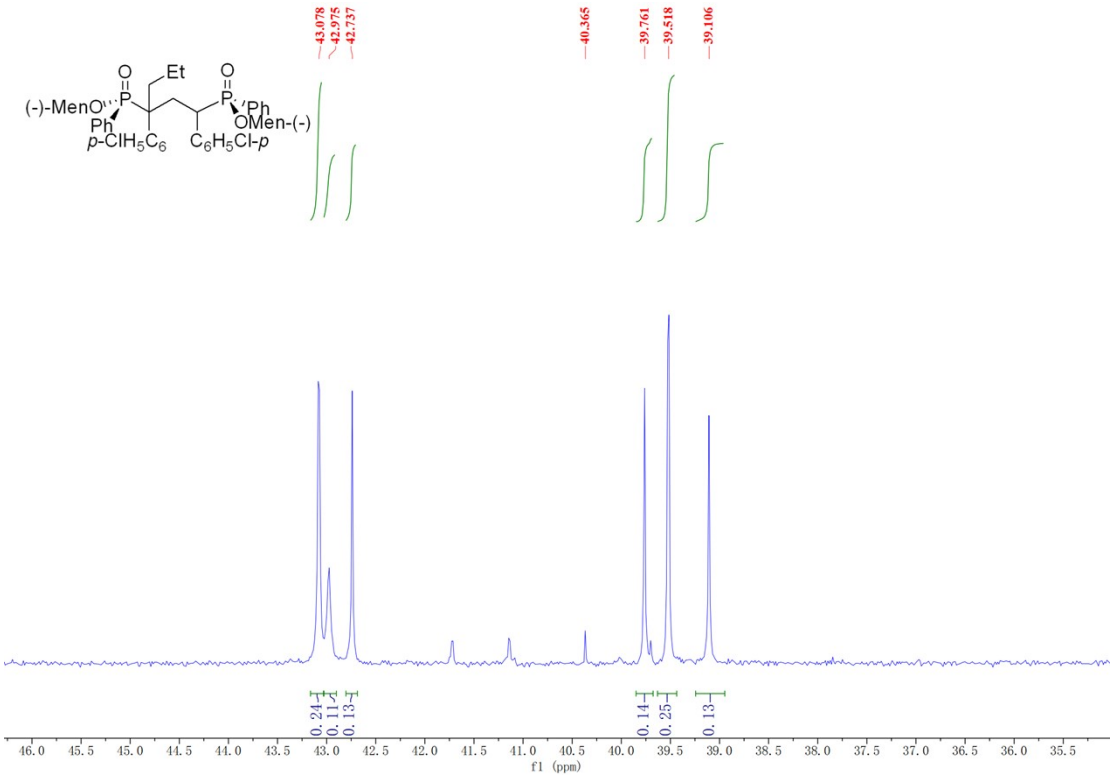
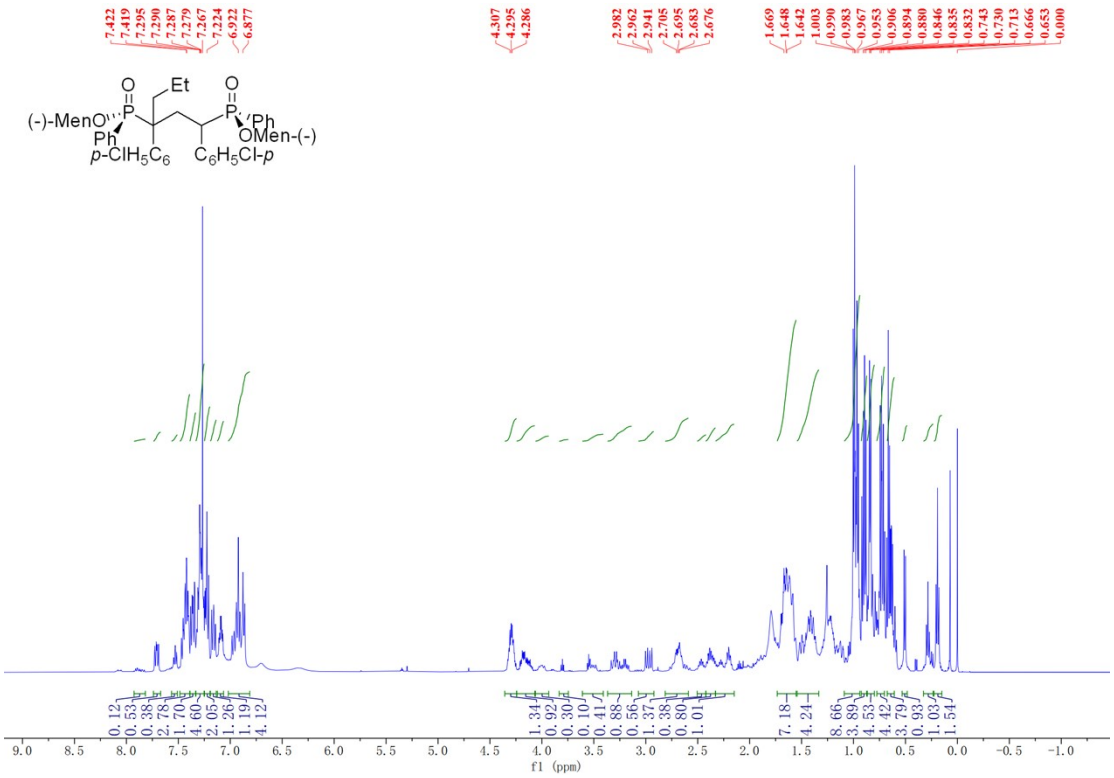
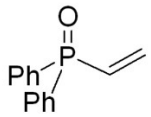
2.06
2.12
0.83
1.00
1.00
1.46
1.28
3.64
3.65
1.46
1.75
1.30
2.17
2.71
2.30
0.30
f1 (ppm)


41.27
40.17
38.88
36.81
29.30
28.66
OCH3
(-)-MenO
Ph
0.03
0.06
0.02
0.02
0.87
0.02
fl (ppm)


7.70
7.68
7.68
7.66
7.39
7.37
7.32
7.30
6.72
5.98
5.96
5.94
5.87
4.28
4.27
4.26
4.26
3.68
1.91
1.79
1.76
1.56
1.53
1.51
1.30
0.99
0.97
0.75
0.73
0.71
0.69
0.68
0.64
0.62
OCH3
(-)-MenO
Ph
1.95
1.24
4.09
2.21
1.44
0.46
1.00
2.80
1.14
1.07
2.31
1.45
0.99
1.05
3.60
3.10
3.27
fl (ppm)


(-)-MenO
Et
Ph
p-ClH5C6
C6H5Cl-p
OMen-(-)
43.078
42.975
42.737
40.365
39.761
39.518
39.106
0.24
0.11
0.13
0.14
0.25
0.13
f1 (ppm)


(-)-MenO
Et
Ph
p-ClH5C6
C6H5Cl-p
OMen-(-)
7.422
7.419
7.295
7.290
7.287
7.279
7.267
7.224
6.922
6.877
4.307
4.295
4.286
2.982
2.962
2.941
2.705
2.695
2.683
2.676
1.669
1.648
1.642
1.003
0.990
0.983
0.967
0.953
0.906
0.894
0.880
0.846
0.835
0.832
0.743
0.730
0.713
0.666
0.653
0.000
0.12
0.53
0.38
2.78
1.70
4.60
2.05
1.26
1.19
4.12
1.34
0.92
0.30
0.10
0.41
0.88
0.56
1.37
0.38
0.80
1.01
7.18
4.24
8.66
3.89
4.53
4.42
3.79
0.93
1.03
1.54
f1 (ppm)

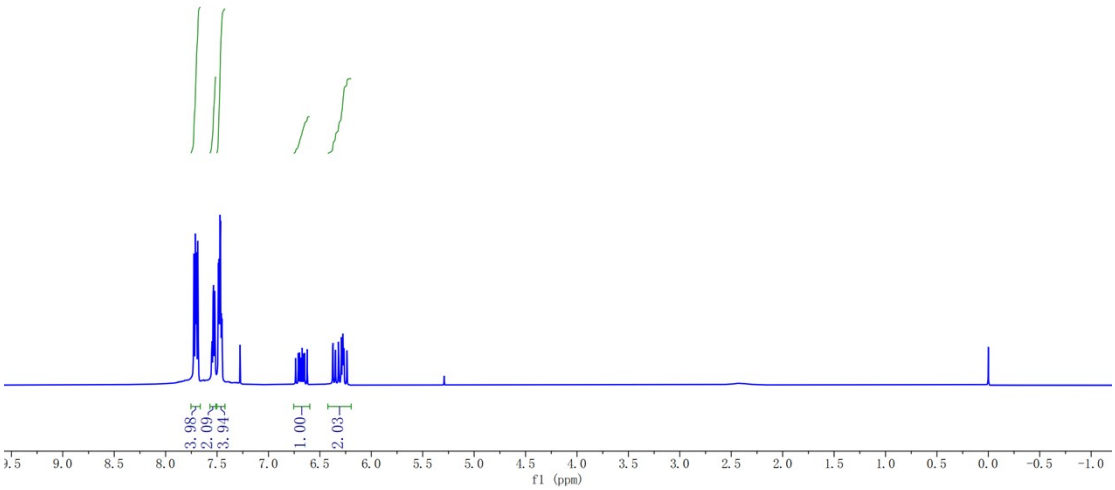

O
Ph
P
Ph

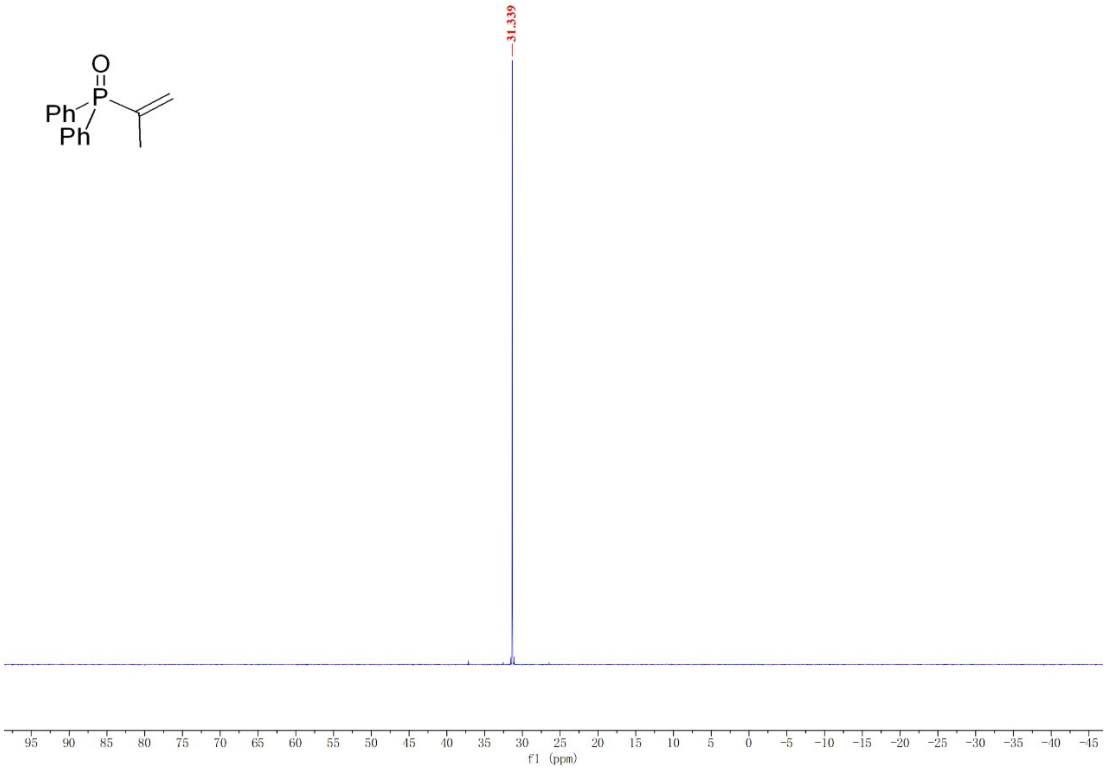
24.11
48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2
f1 (ppm)

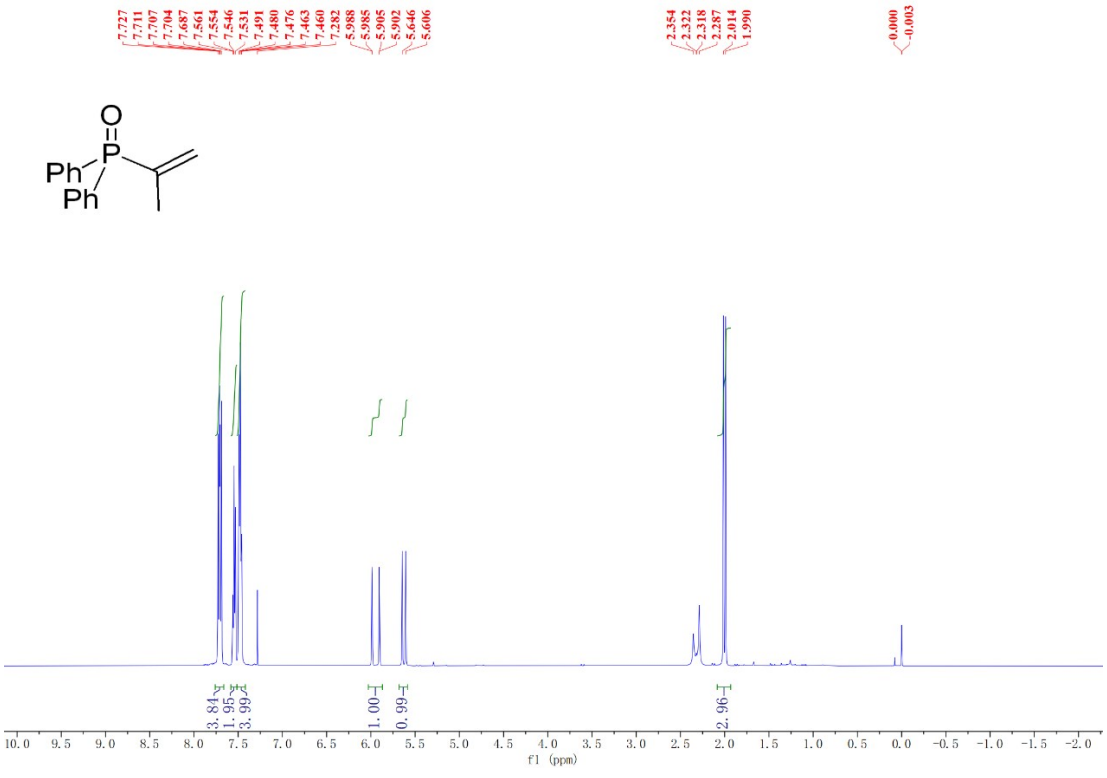

7.725
7.711
7.708
7.700
7.686
7.684
7.537
7.534
7.522
7.520
7.487
7.482
7.472
7.469
7.466
7.458
7.455
6.710
6.698
6.686
6.673
6.661
6.649
6.624
6.376
6.372
6.350
6.347
6.320
6.316
5.292

O
Ph
P
Ph

-0.000


3.98
2.09
3.94
1.00
2.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


31.339
f1 (ppm)


7.727
7.711
7.707
7.704
7.687
7.661
7.554
7.546
7.531
7.491
7.480
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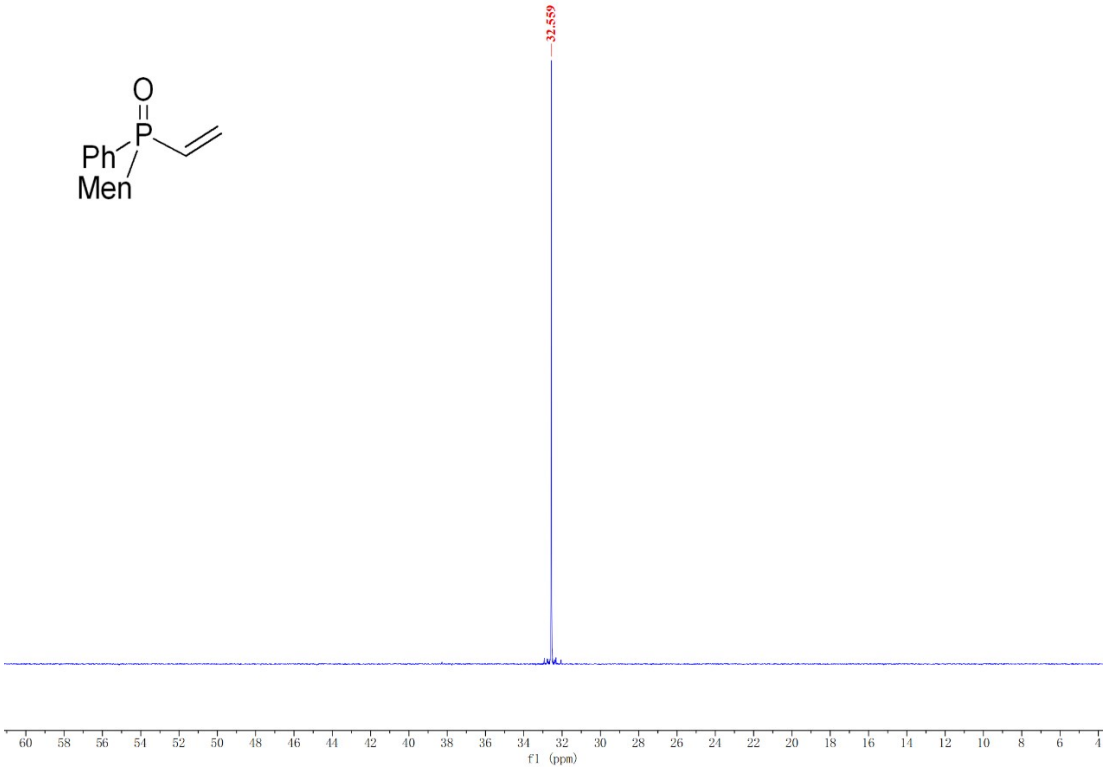
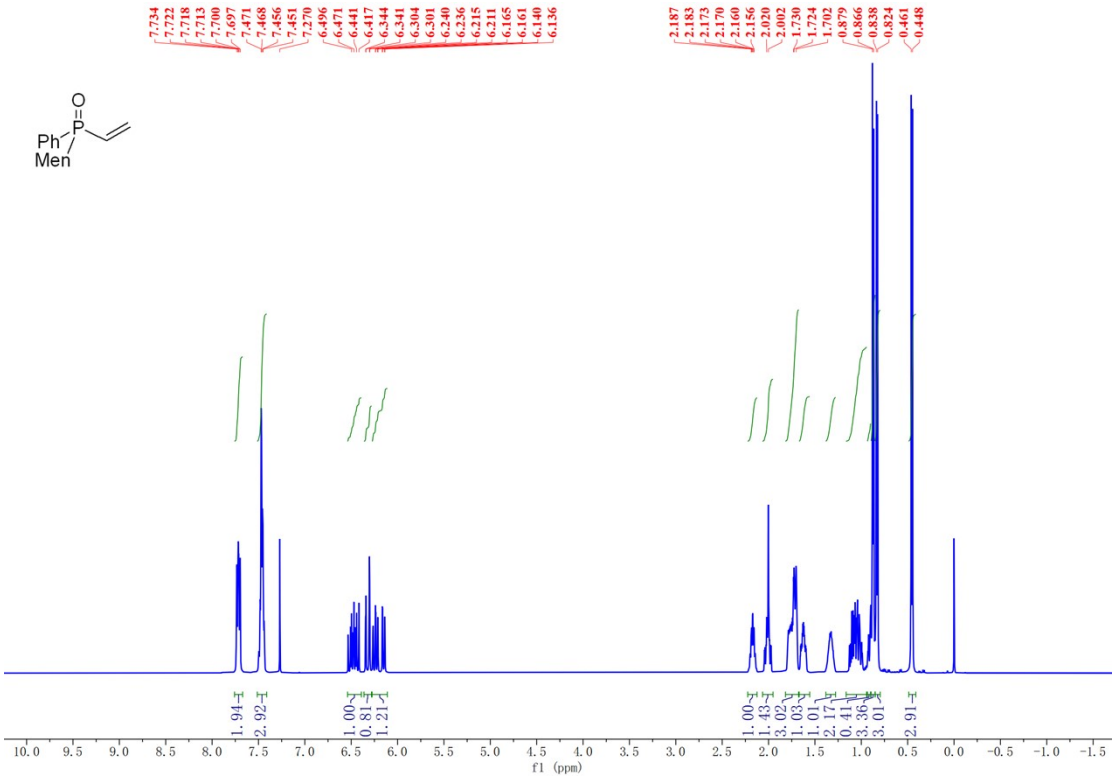
7.463
7.460
7.282
5.988
5.985
5.905
5.902
5.646
5.606
2.354
2.322
2.318
2.287
2.014
1.990
0.000
-0.003
3.84
1.95
3.99
1.00
0.99
2.96
f1 (ppm)


O
P
Ph
Men
32.559
f1 (ppm)


7.734
7.722
7.718
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7.700
7.697
7.471
7.468
7.456
7.451
7.270
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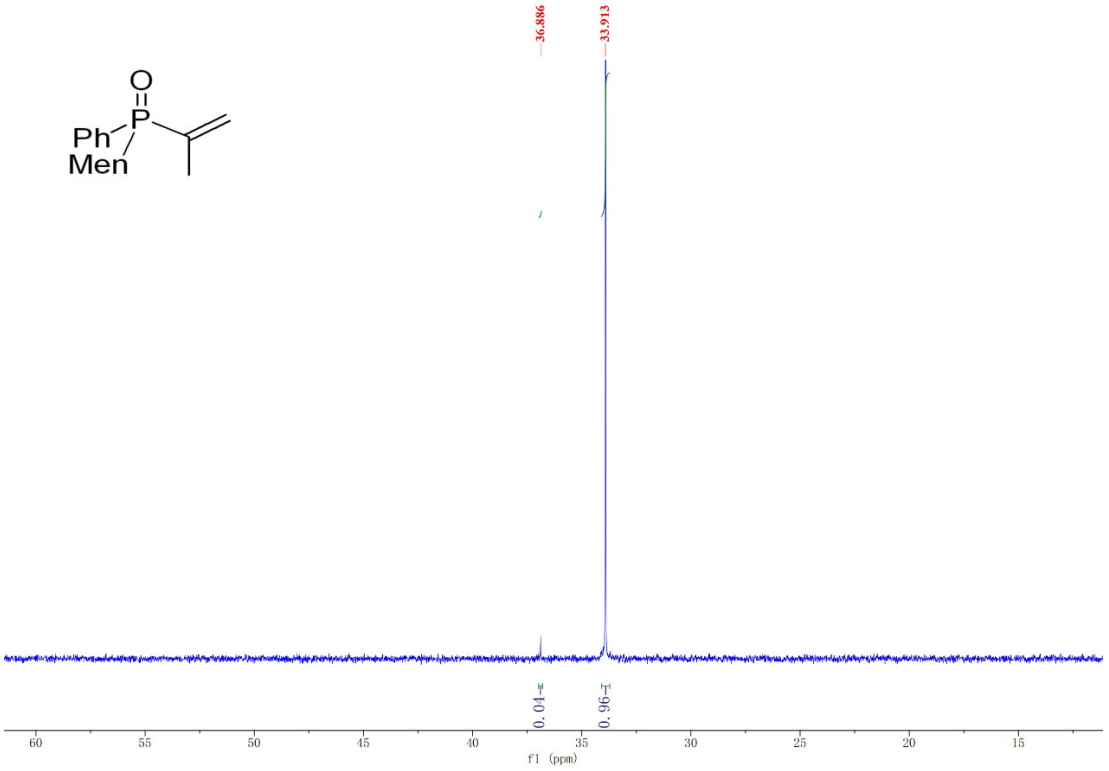
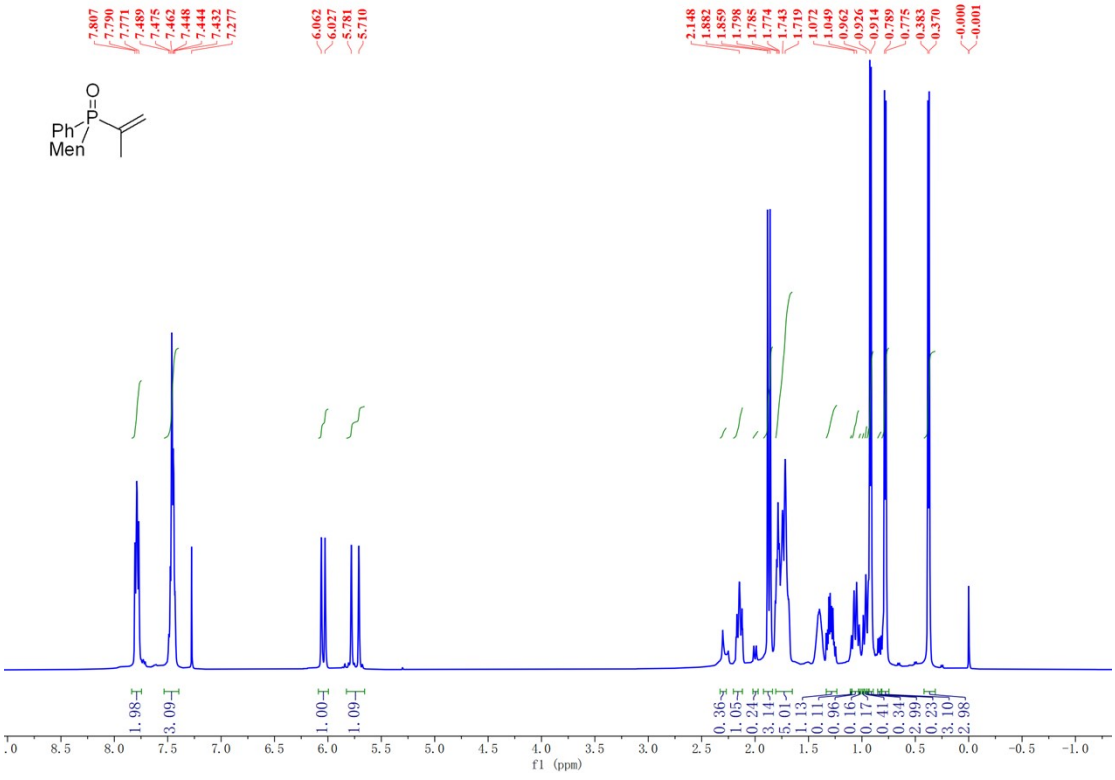
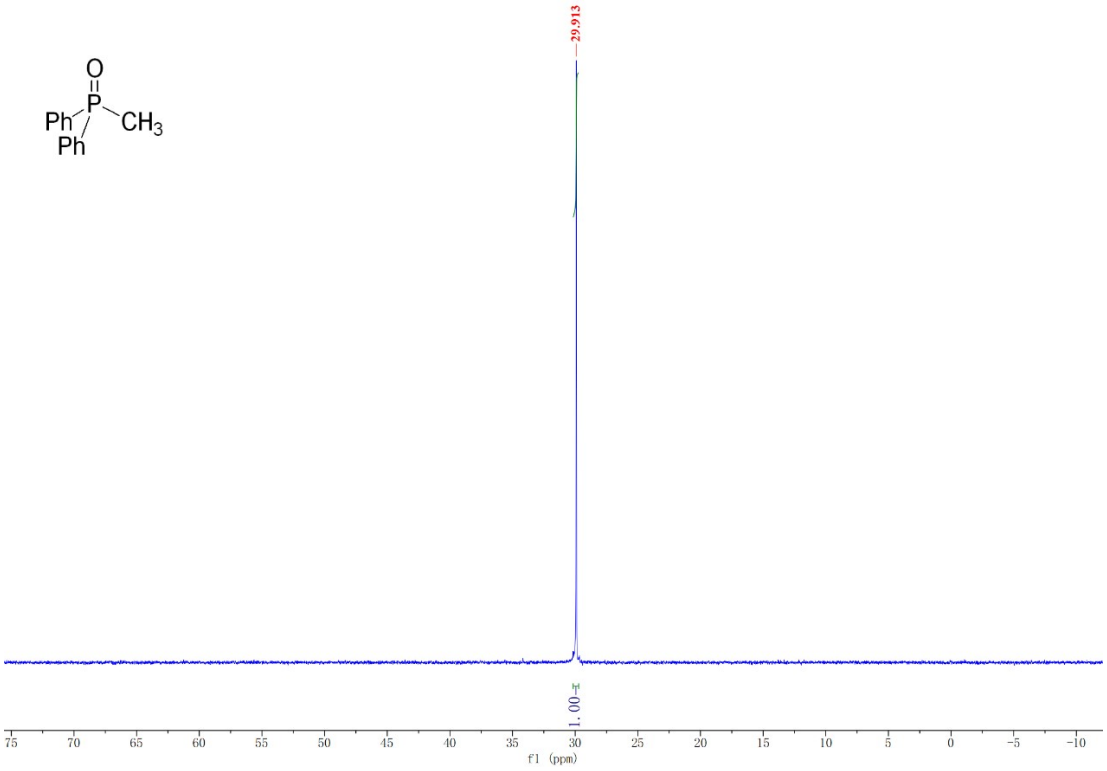
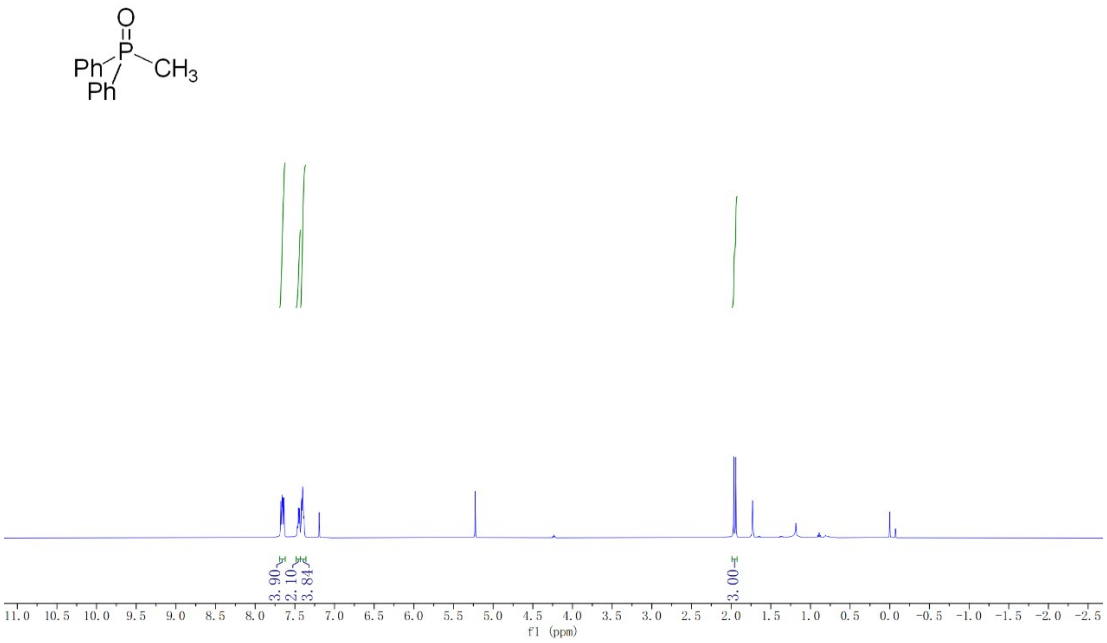
6.471
6.441
6.417
6.344
6.341
6.304
6.301
6.240
6.236
6.215
6.211
6.165
6.161
6.140
6.136
2.187
2.183
2.173
2.170
2.160
2.156
2.020
2.002
1.730
1.724
1.702
0.879
0.866
0.838
0.824
0.461
0.448
O
P
Ph
Men
1.94
2.92
1.00
0.81
1.21
1.00
1.43
3.02
1.03
1.01
2.17
0.41
3.36
3.01
2.91
f1 (ppm)

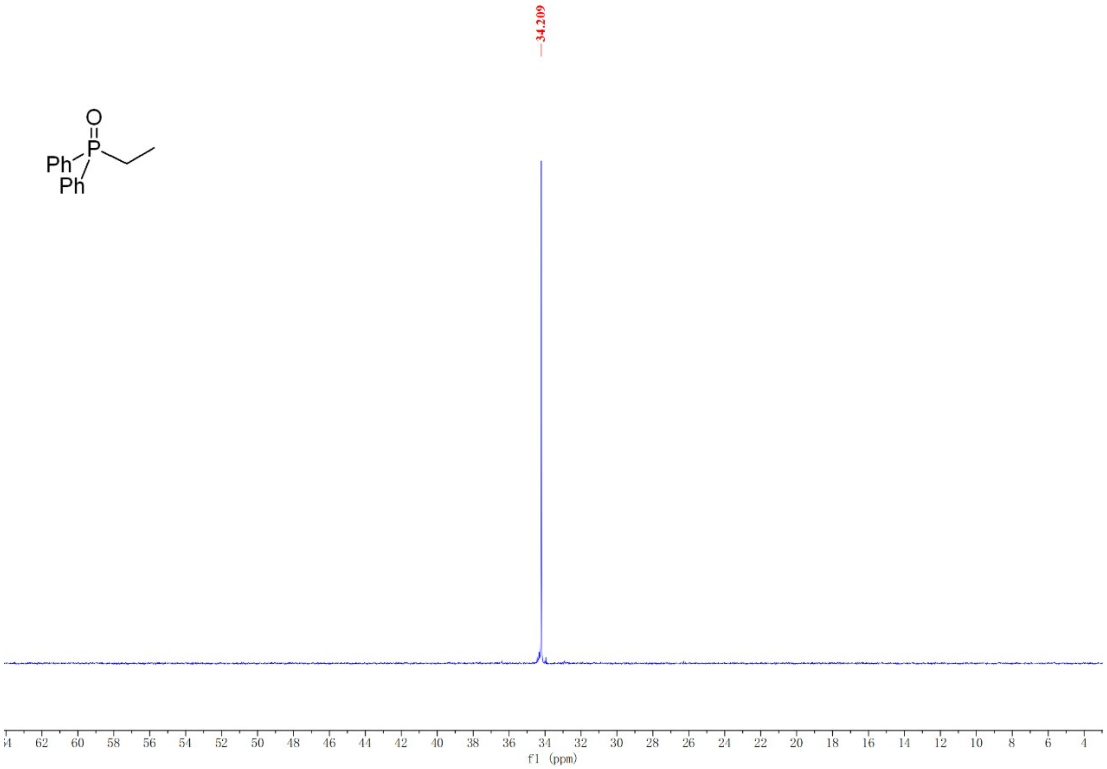

O
P
Ph
Men
36.886
33.913
0.04
0.96
f1 (ppm)

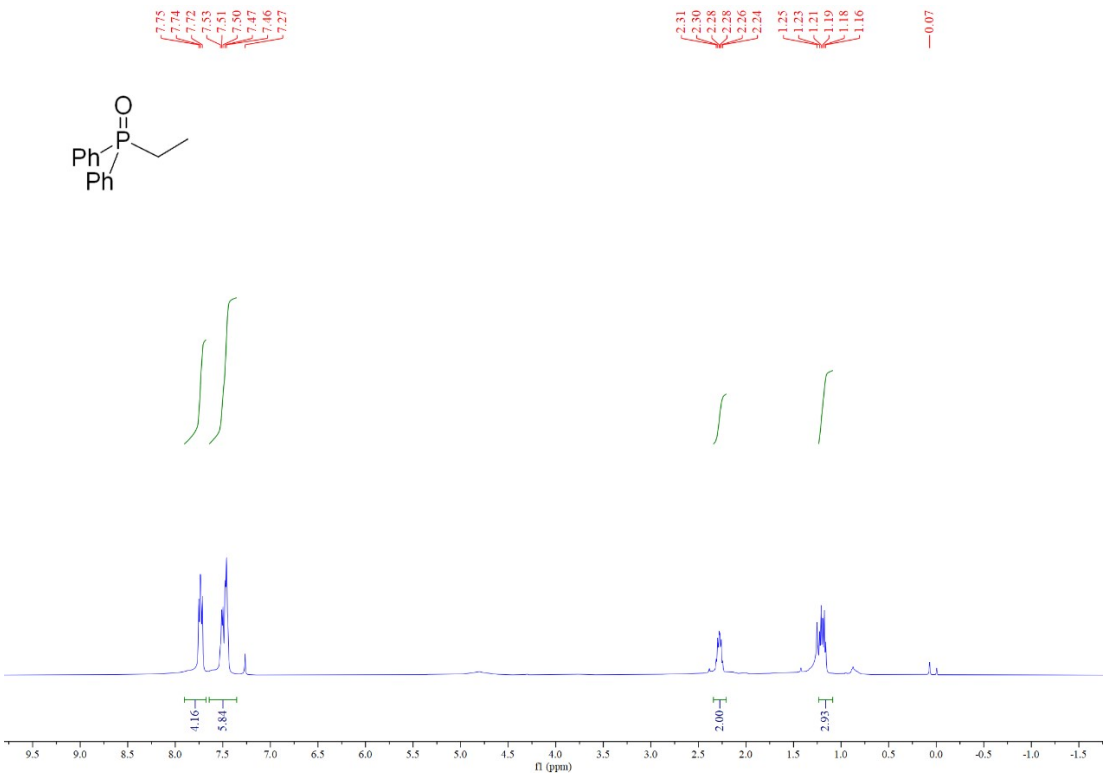

7.807
7.790
7.771
7.489
7.475
7.462
7.448
7.444
7.432
7.277
6.062
6.027
5.781
5.710
2.148
1.882
1.859
1.798
1.785
1.774
1.743
1.719
1.072
1.049
0.962
0.926
0.914
0.789
0.775
0.383
0.370
-0.000
-0.001
O
P
Ph
Men
1.98
3.09
1.00
1.09
0.36
1.05
0.24
3.14
5.01
1.13
0.11
0.96
0.16
0.17
0.41
0.34
2.99
0.23
3.10
2.98
f1 (ppm)

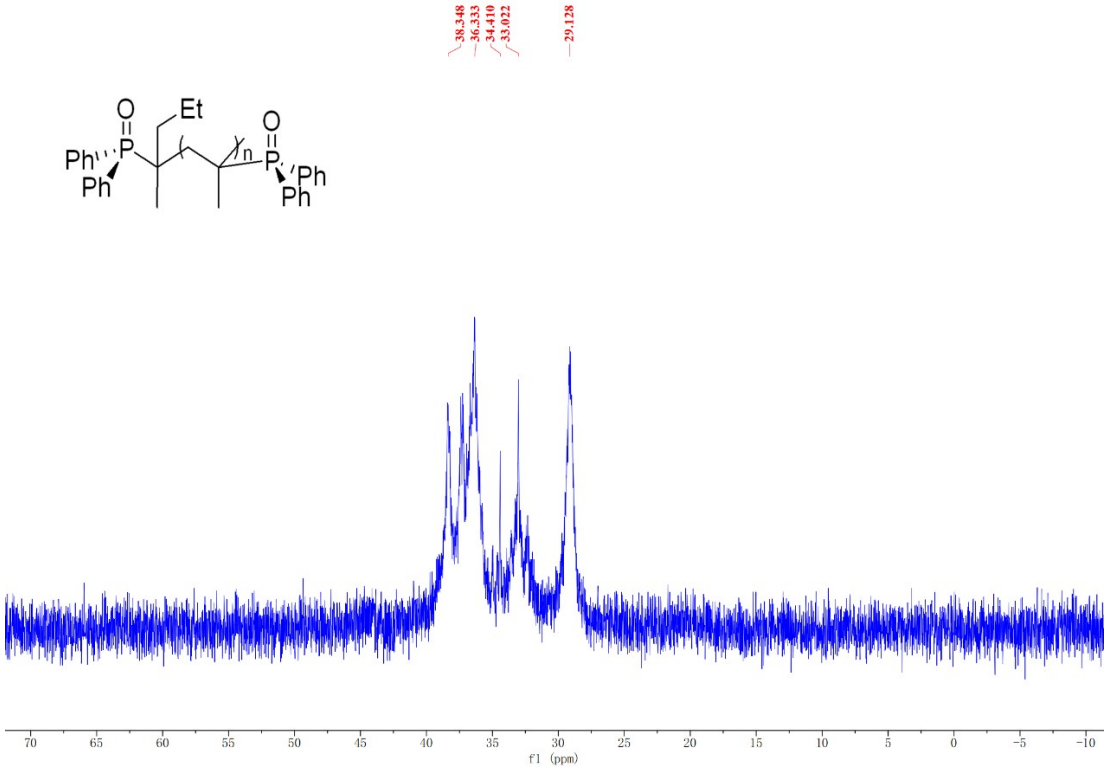

O
P
Ph
Ph
CH3
29.913
1.00
f1 (ppm)

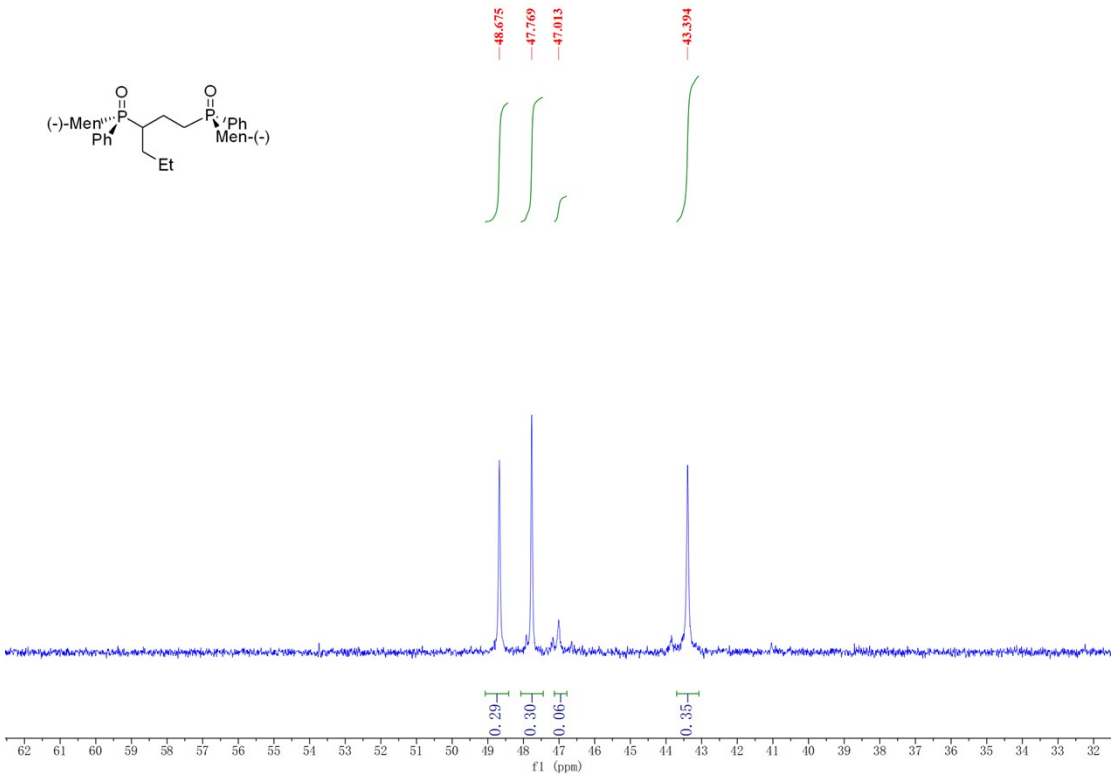

9.114
9.106
7.676
7.661
7.652
7.638
7.471
7.470
7.467
7.455
7.442
7.417
7.413
7.402
7.388
7.194
5.226
1.967
1.940
1.729
1.184
0.890
0.000

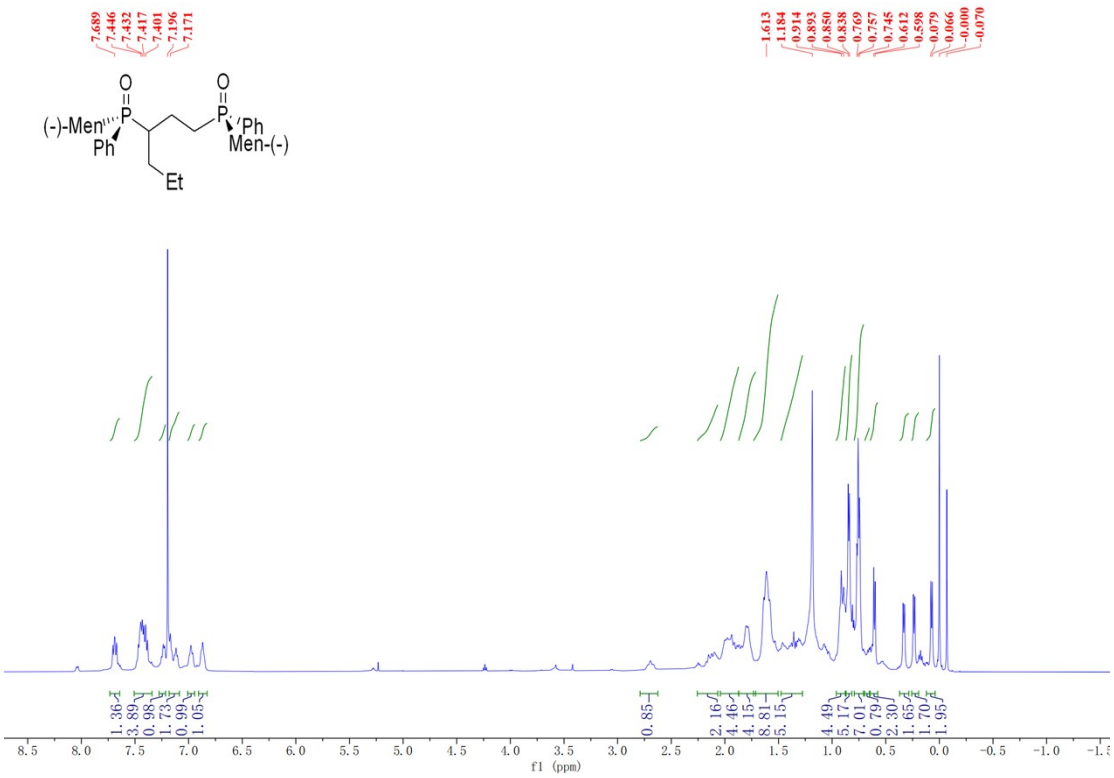

O
P
Ph
Ph
CH3
3.90
2.10
3.84
3.00
f1 (ppm)

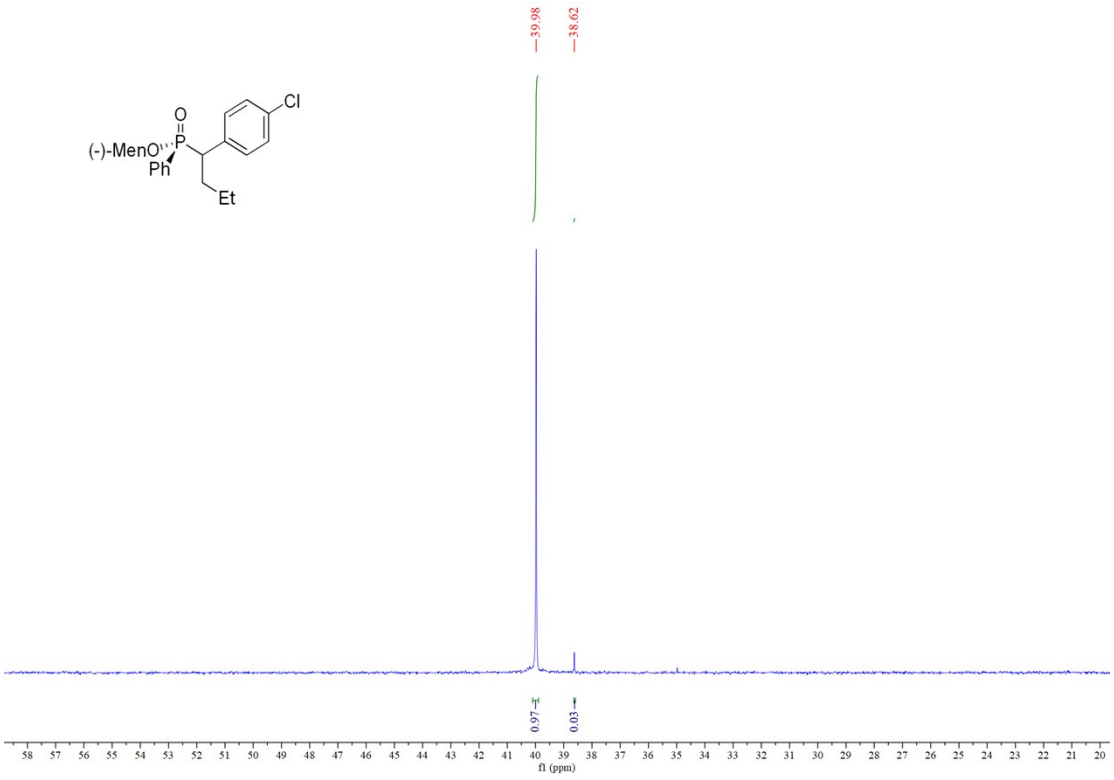

34.209
O
P
Ph
Ph
f1 (ppm)

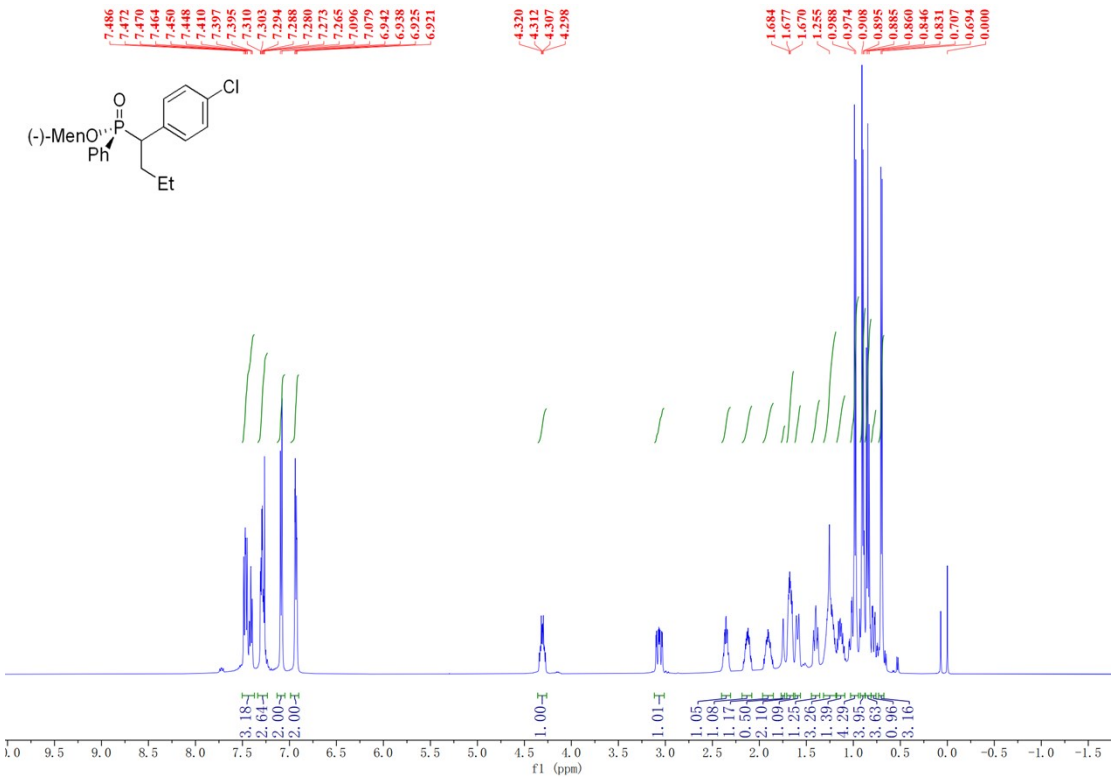

7.75
7.74
7.72
7.53
7.51
7.50
7.47
7.46
7.27
2.31
2.30
2.28
2.28
2.26
2.24
1.25
1.23
1.21
1.19
1.18
1.16
0.07
O
P
Ph
Ph
4.16
5.84
2.00
2.93
f1 (ppm)

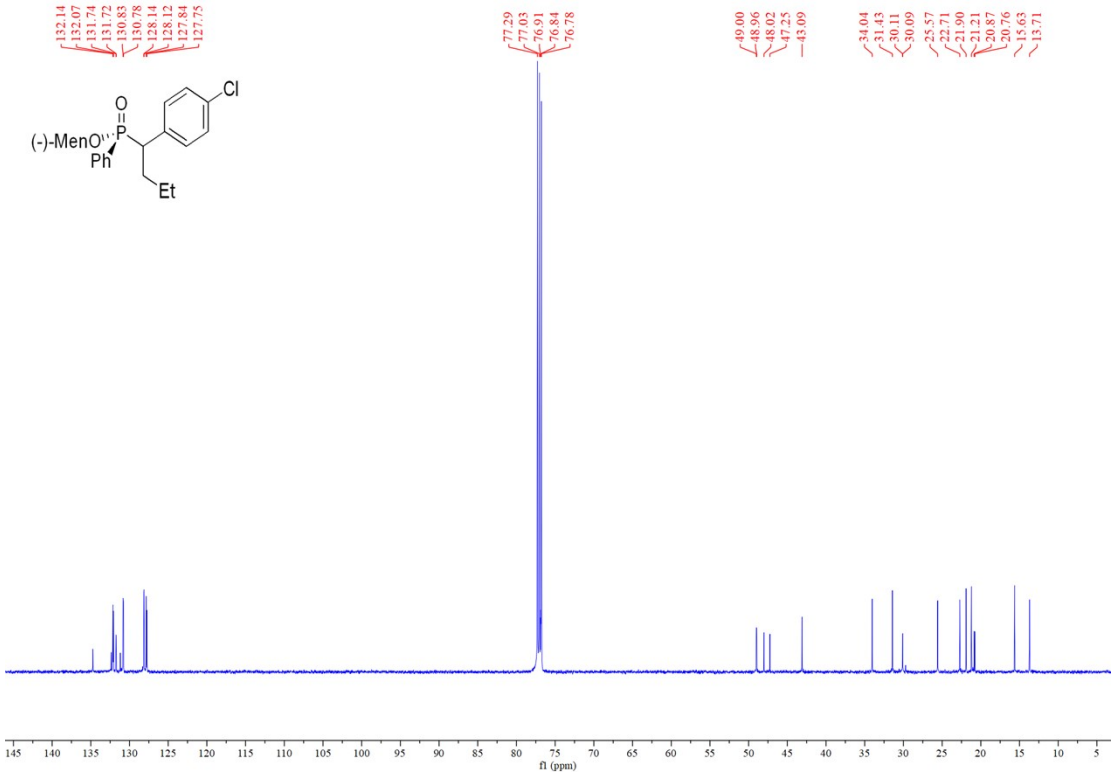

38.348
36.333
34.410
33.022
29.128
Et
O
P
Ph
Ph
n
O
P
Ph
Ph
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10
f1 (ppm)

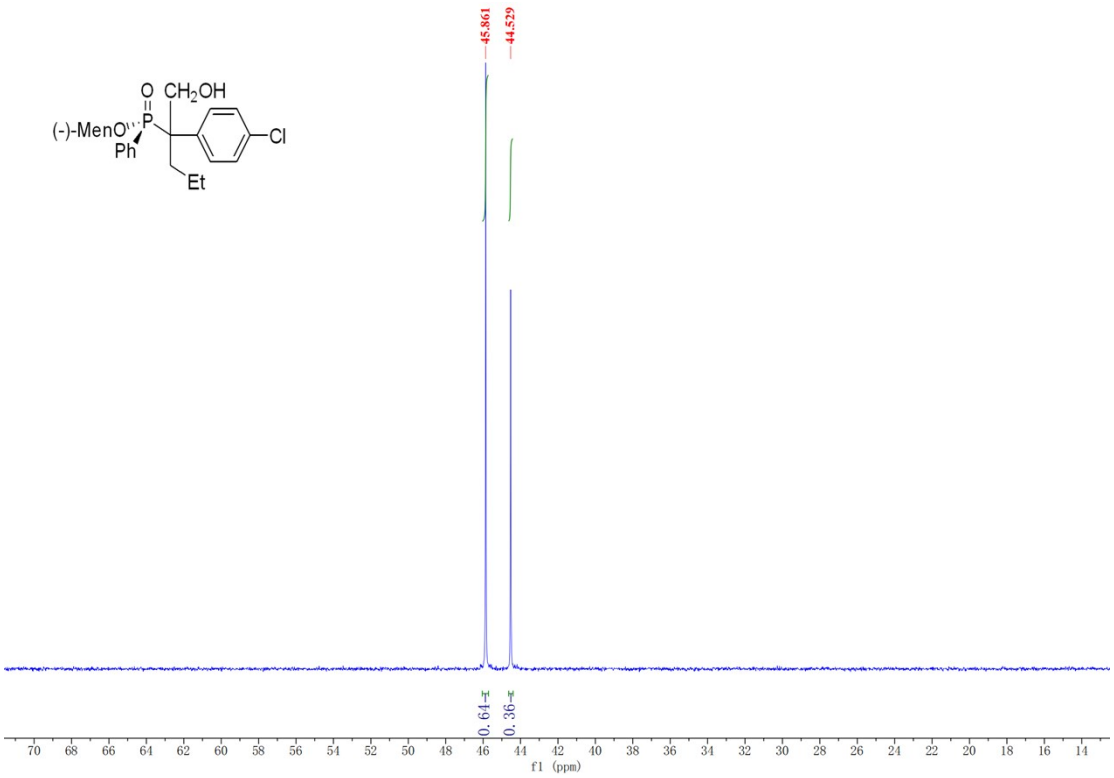

48.675
47.769
47.013
43.394
(-)-Men
O
P
Ph
Et
O
P
Ph
Men-(-)
0.29
0.30
0.06
0.35
62 61 60 59 58 57 56 55 54 53 52 51 50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32
f1 (ppm)

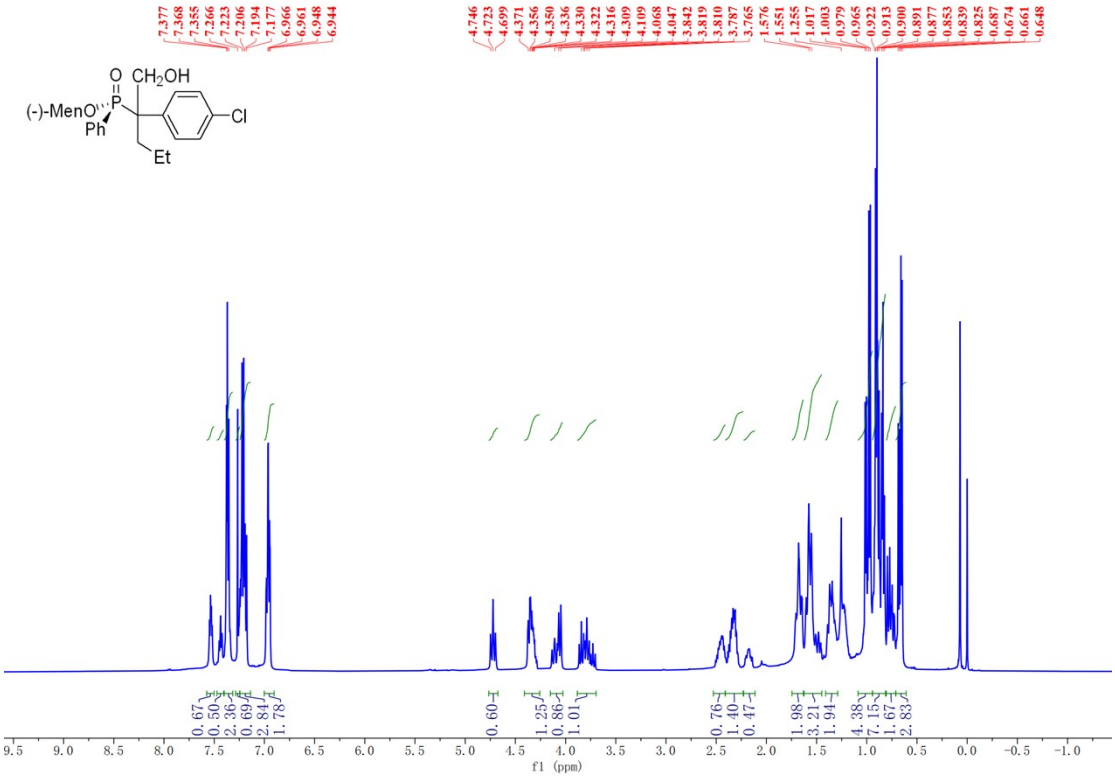

7.689
7.446
7.432
7.417
7.401
7.196
7.171
1.613
1.184
0.914
0.893
0.850
0.838
0.769
0.757
0.745
0.612
0.598
0.079
0.066
0.000
-0.070
(-)-Men
Ph
Ph
Men-(-)
Et
f1 (ppm)

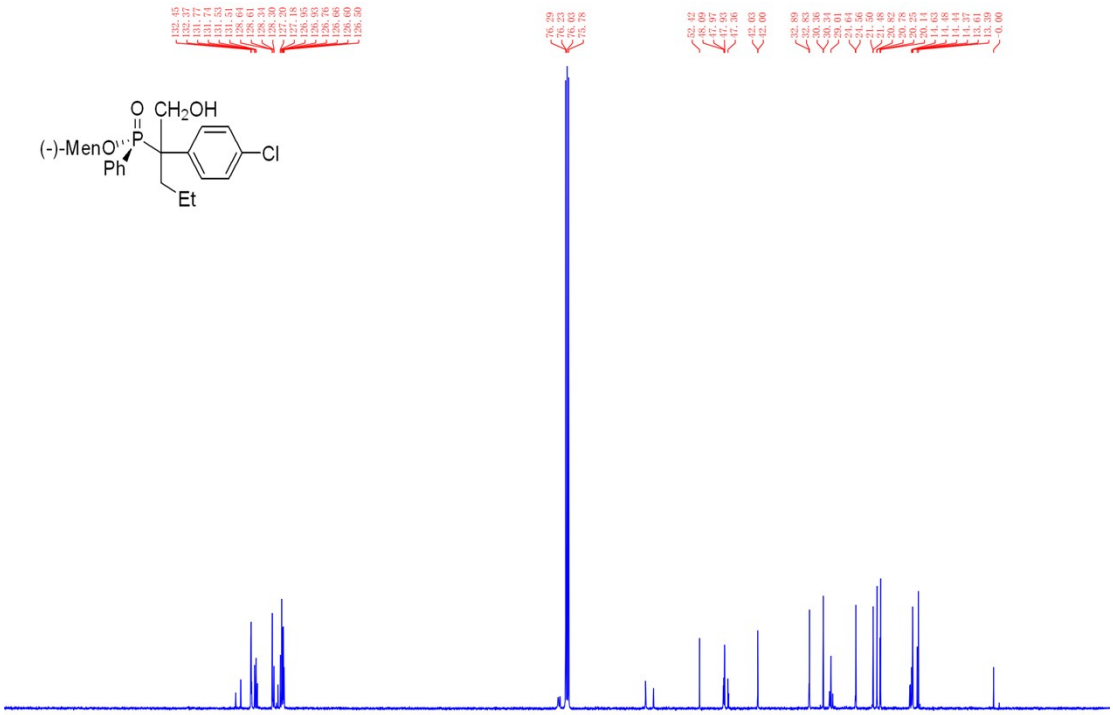

39.98
38.62
(-)-MenO
Ph
Cl
Et
f1 (ppm)

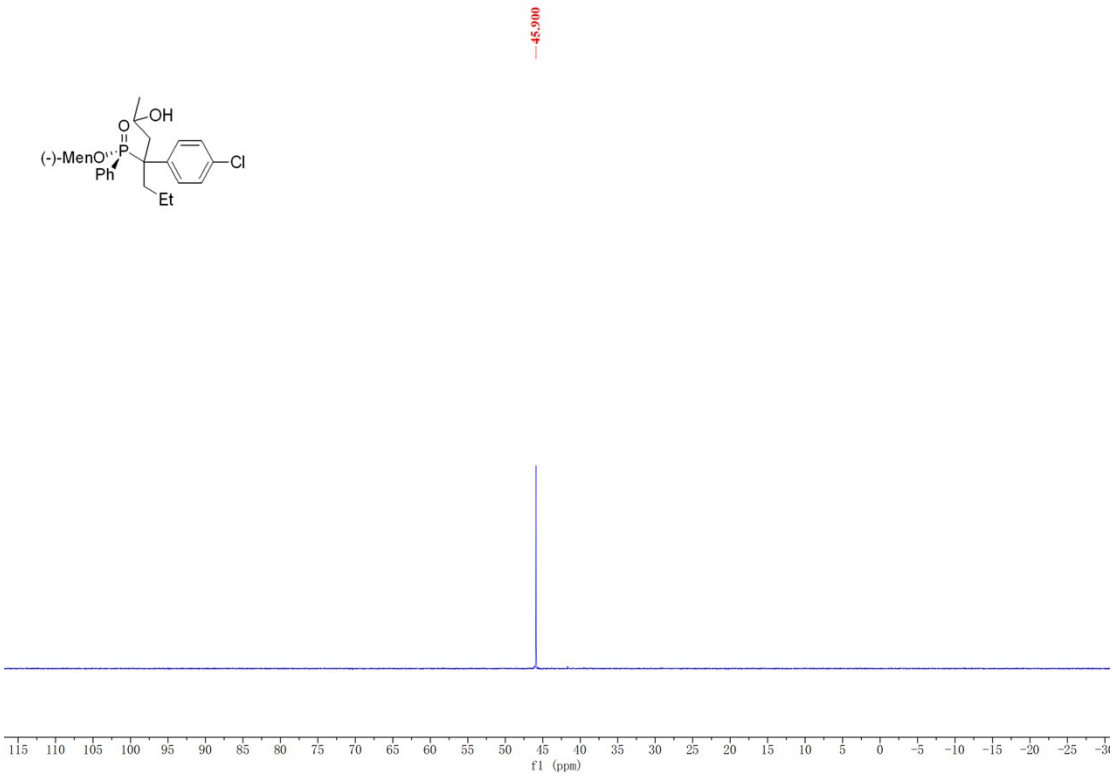

7.486
7.472
7.470
7.464
7.450
7.448
7.410
7.397
7.395
7.310
7.303
7.294
7.288
7.280
7.273
7.265
7.096
7.079
6.942
6.938
6.925
6.921
4.320
4.312
4.307
4.298
1.684
1.677
1.670
1.255
0.988
0.974
0.908
0.895
0.885
0.860
0.846
0.831
0.707
0.694
0.000
O
P
(-)-MenO
Ph
Et
Cl
3.18
2.64
2.00
2.00
2.00
1.00
1.01
1.05
1.08
1.17
0.50
2.10
1.09
1.25
3.26
1.39
4.29
3.95
3.63
0.96
3.16
f1 (ppm)

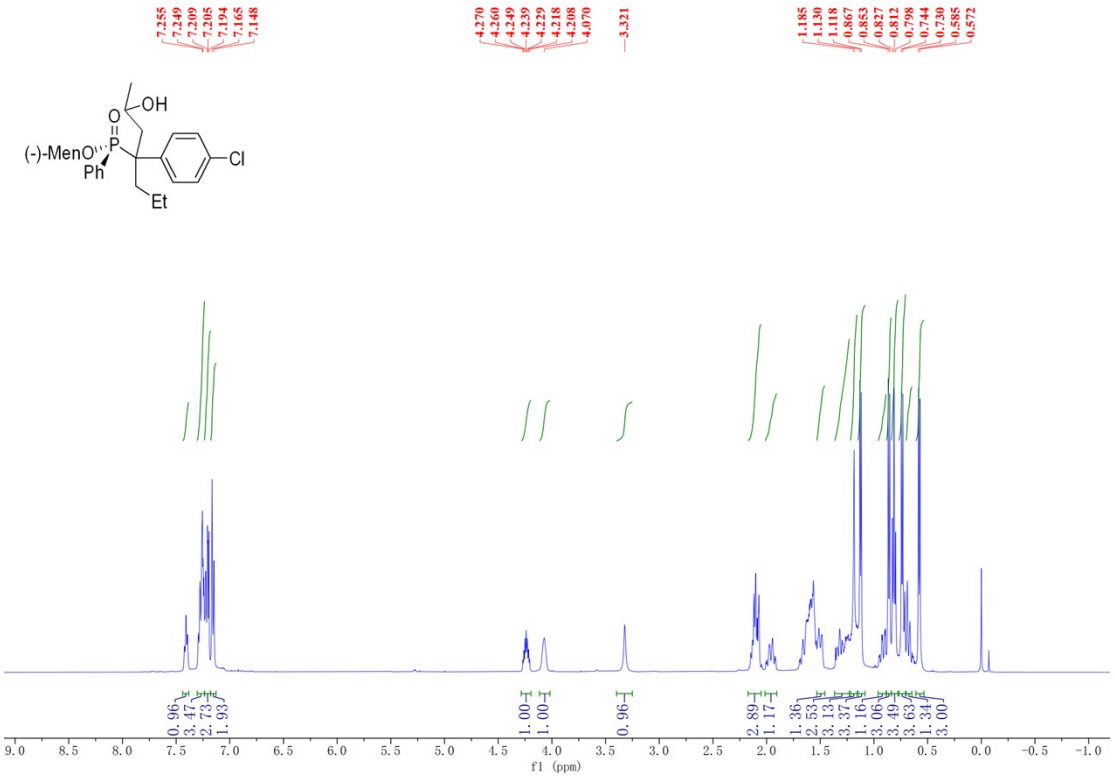

132.14
132.07
131.74
131.72
130.83
130.78
128.14
128.12
127.84
127.75
77.29
77.03
76.91
76.84
76.78
49.00
48.96
48.02
47.25
43.09
34.04
31.43
30.11
30.09
25.57
22.71
21.90
21.21
20.87
20.76
15.63
13.71
O
P
(-)-MenO
Ph
Et
Cl
f1 (ppm)

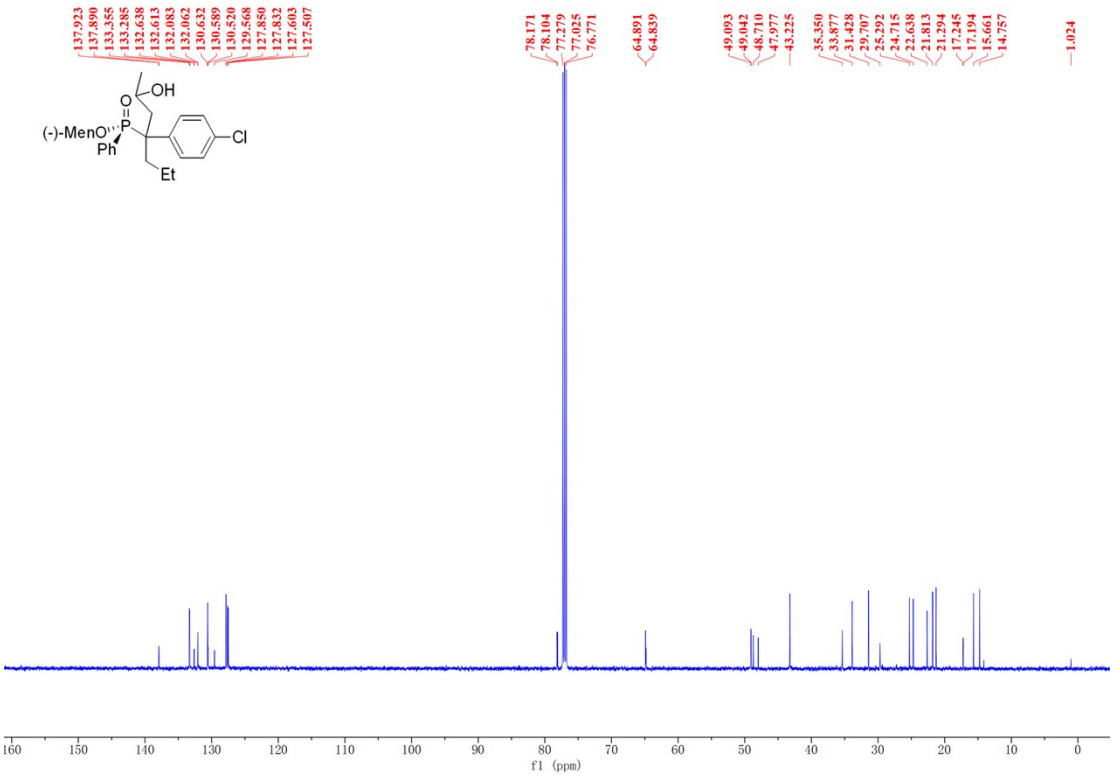

45.861
44.529
O
CH2OH
(-)-MenO
P
Ph
Et
Cl
0.64
0.36
f1 (ppm)

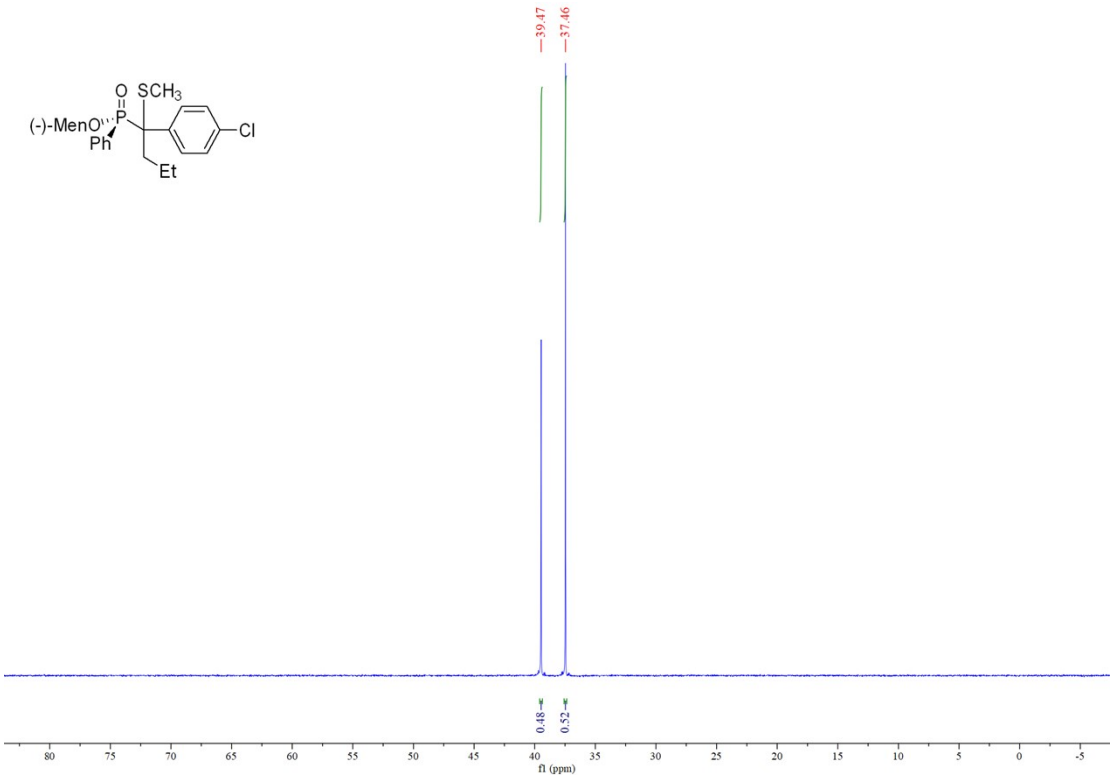

7.377
7.368
7.355
7.266
7.223
7.206
7.194
7.177
6.966
6.948
6.944
4.746
4.723
4.699
4.371
4.356
4.350
4.336
4.330
4.322
4.316
4.309
4.109
4.068
4.047
3.842
3.819
3.810
3.787
3.765
1.576
1.551
1.255
1.017
1.003
0.979
0.965
0.922
0.913
0.900
0.891
0.877
0.853
0.839
0.825
0.687
0.674
0.661
0.648
O
CH2OH
(-)-MenO
P
Ph
Et
Cl
0.67
0.50
2.36
0.69
2.84
1.78
0.60
1.25
0.86
1.01
0.76
1.40
0.47
1.98
3.21
1.94
4.38
7.15
1.67
2.83
f1 (ppm)


O
CH2OH
(-)-MenO
P
Ph
Et
Cl

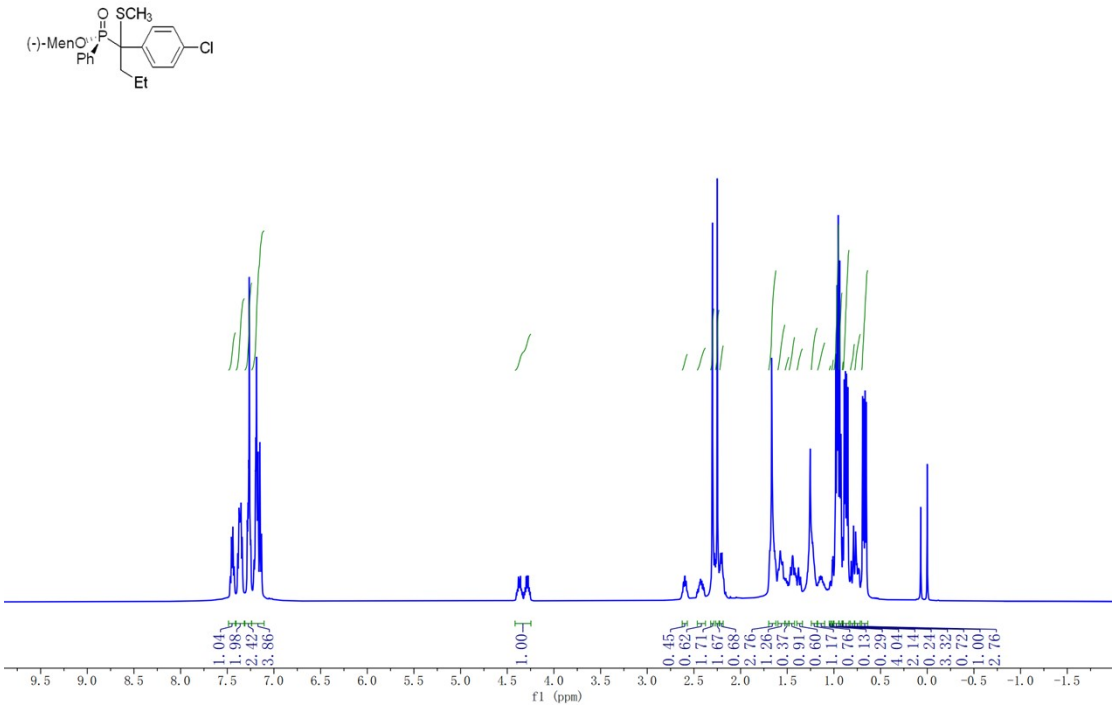

45.900
OH
O
(-)-MenO
P
Ph
Et
Cl
f1 (ppm)

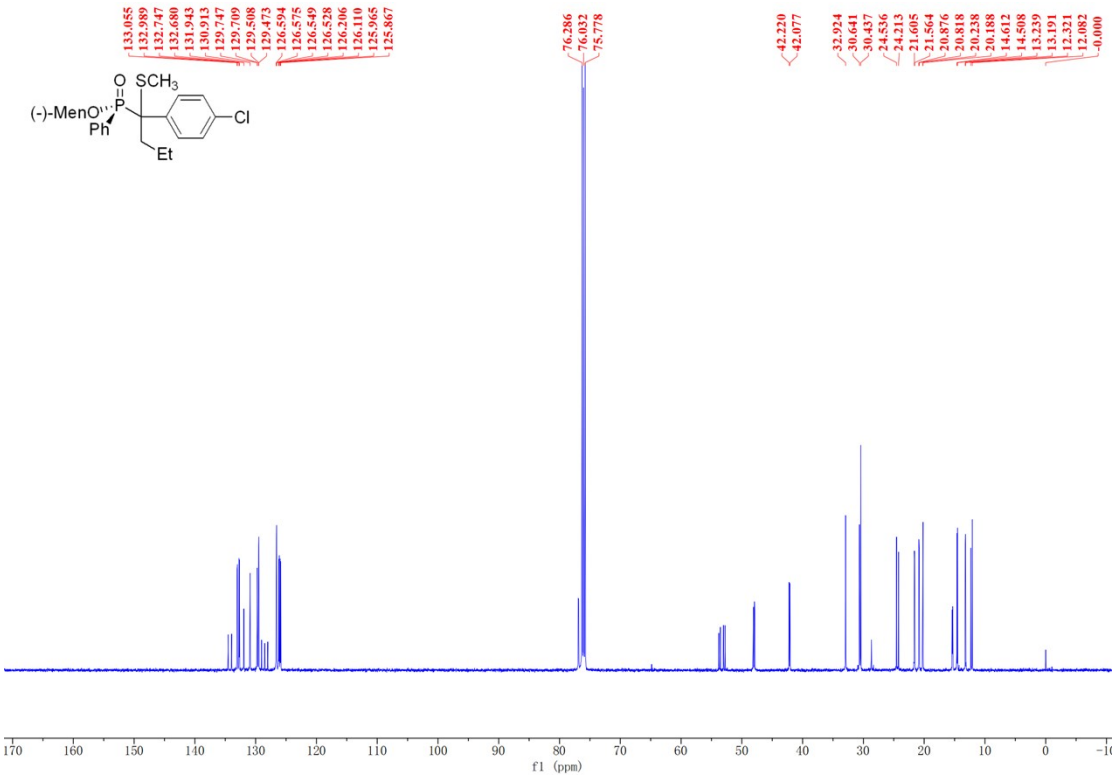

7.255
7.249
7.209
7.205
7.194
7.165
7.148
4.270
4.260
4.249
4.239
4.229
4.218
4.208
4.070
3.321
1.185
1.130
1.118
0.867
0.853
0.827
0.812
0.798
0.744
0.730
0.585
0.572
OH
O
P
(-)-MenO
Ph
Cl
Et
0.96
3.47
2.73
1.93
1.00
1.00
0.96
2.89
1.17
1.36
2.53
3.13
3.37
1.16
3.06
3.49
3.63
1.34
3.00
f1 (ppm)

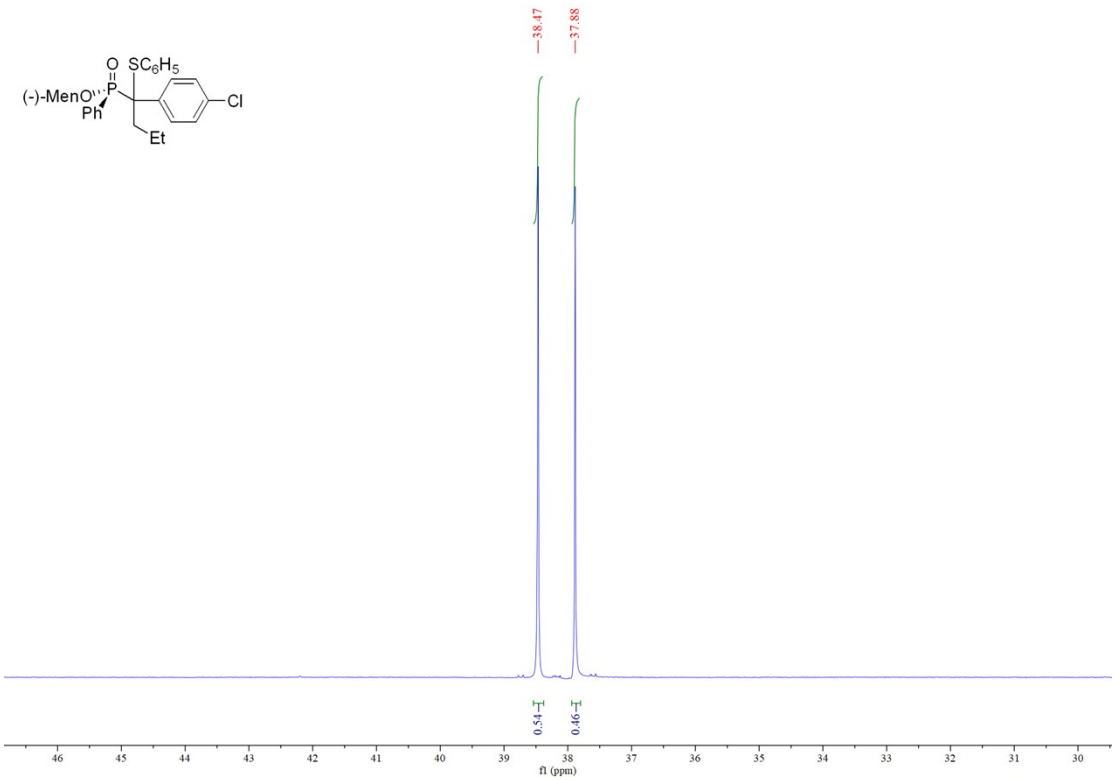

137.923
137.890
133.355
133.285
132.638
132.613
132.083
132.062
130.632
130.589
130.520
129.568
127.850
127.832
127.603
127.507
78.171
78.104
77.279
77.025
76.771
64.891
64.839
49.093
49.042
48.710
47.977
43.225
35.350
33.877
31.428
29.707
25.292
24.715
22.638
21.813
21.294
17.245
17.194
15.661
14.757
1.024
OH
O
P
(-)-MenO
Ph
Cl
Et
f1 (ppm)

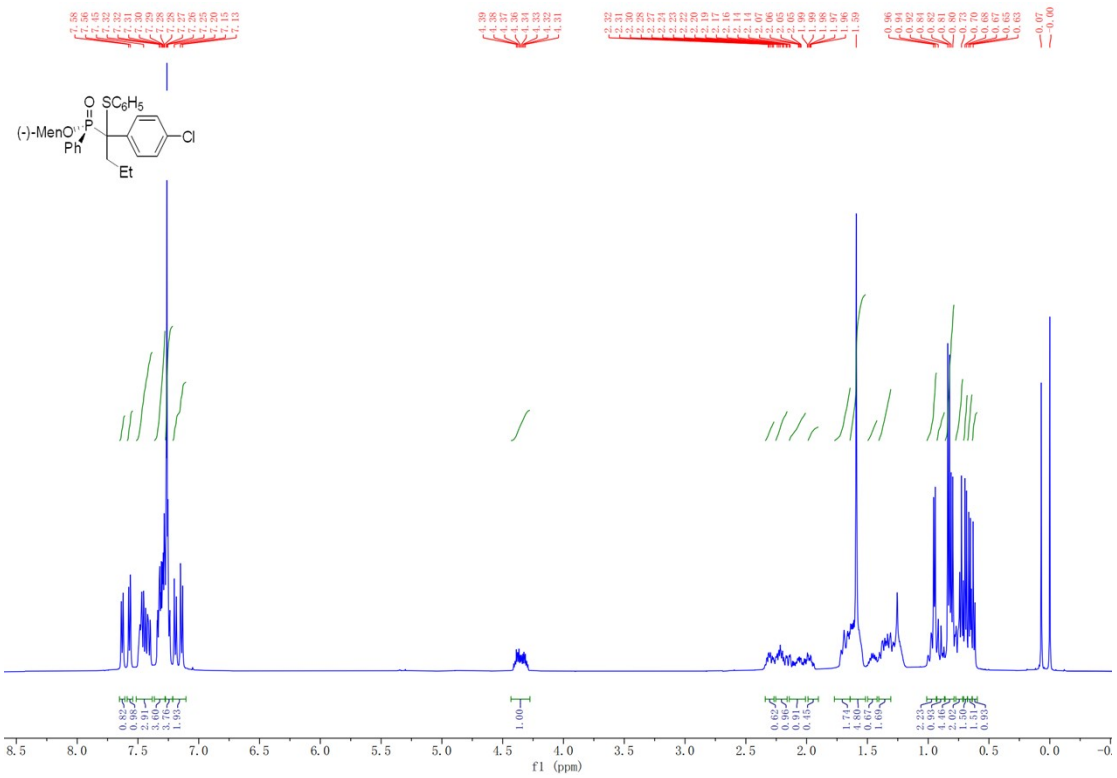


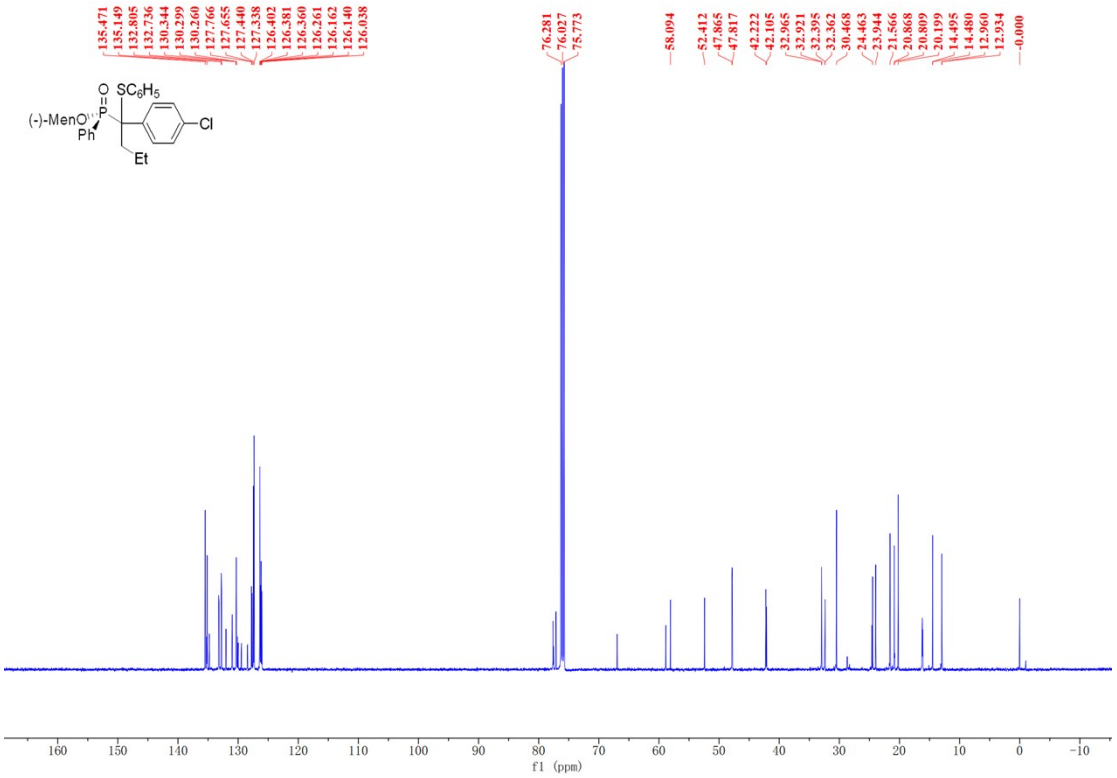
7.455 7.440 7.374 7.362 7.353 7.341 7.264 7.194 7.186 7.150
4.381 4.372 4.368 4.359 4.297 4.286 4.276
2.302 2.250
1.666 1.254 0.980 0.969 0.966 0.955 0.939 0.924 0.890 0.876 0.864 0.851 0.693 0.680 0.666 0.653

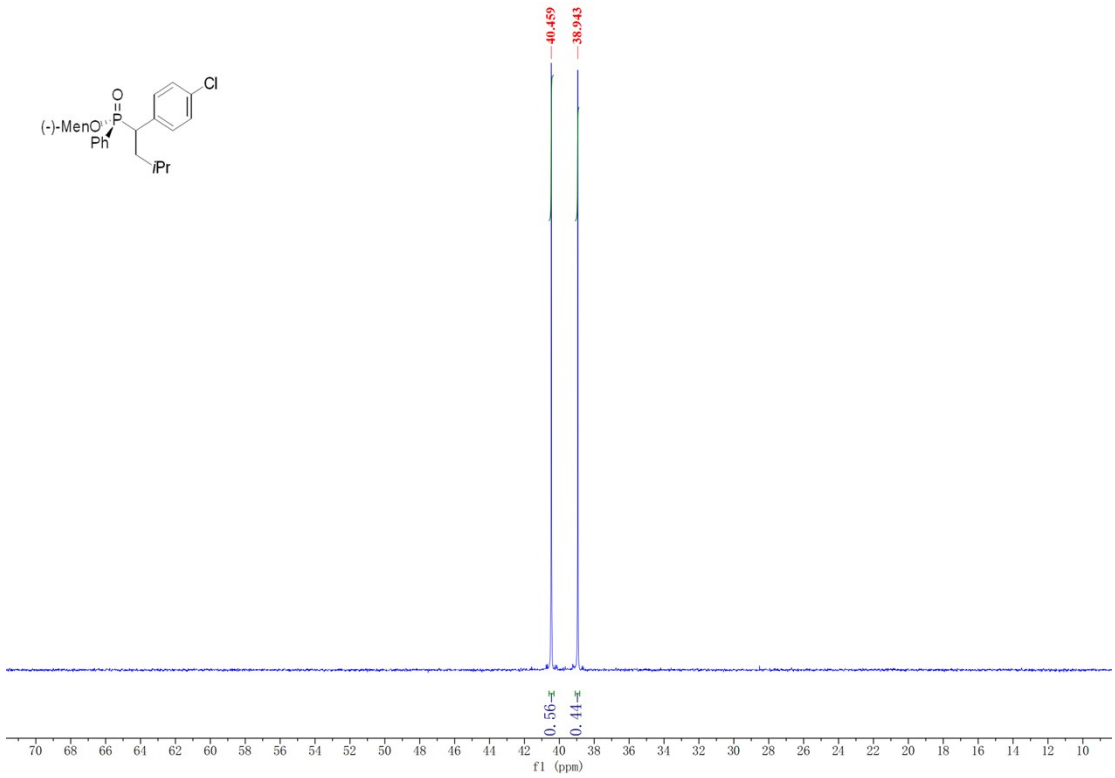


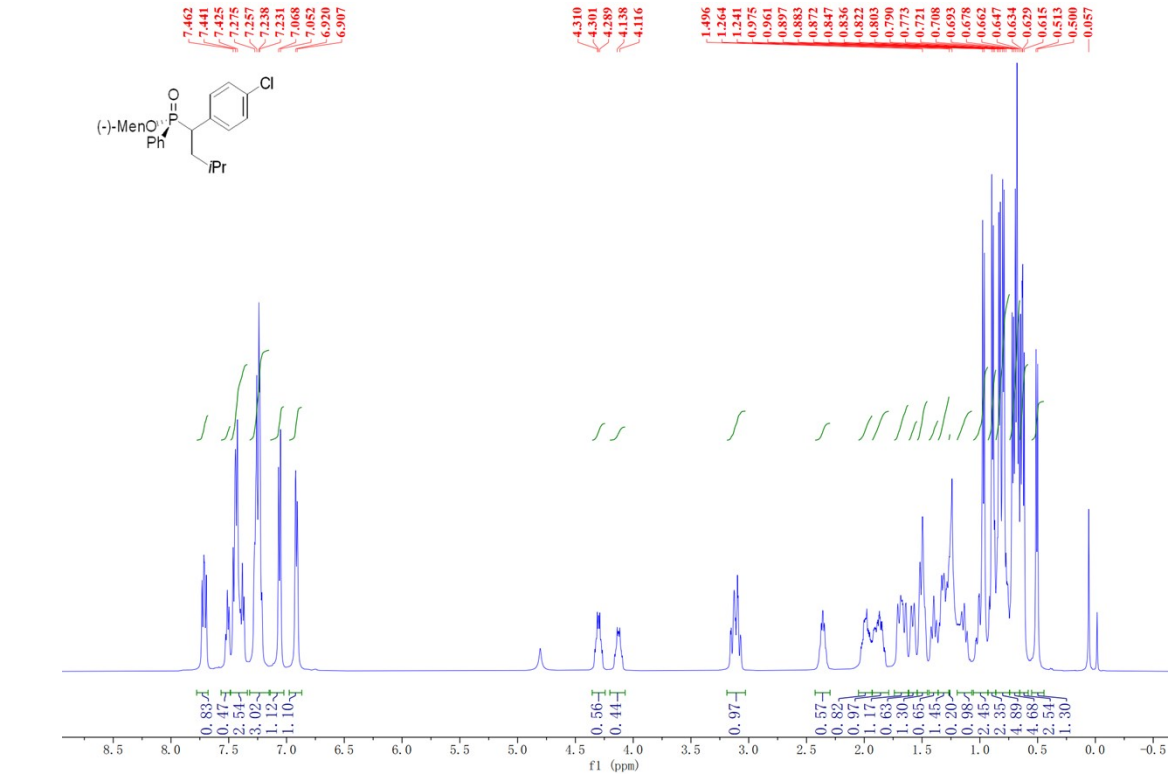

133.055
132.989
132.747
132.680
131.943
130.913
129.747
129.709
129.508
129.473
126.594
126.575
126.549
126.528
126.206
126.110
125.965
125.867
76.286
76.032
75.778
42.220
42.077
32.924
30.641
30.437
24.536
24.213
21.695
21.564
20.876
20.818
20.238
20.188
14.612
14.508
13.239
13.191
12.321
12.082
-0.000
O
SCH3
(-)-MenO
P
Ph
Et
Cl
f1 (ppm)

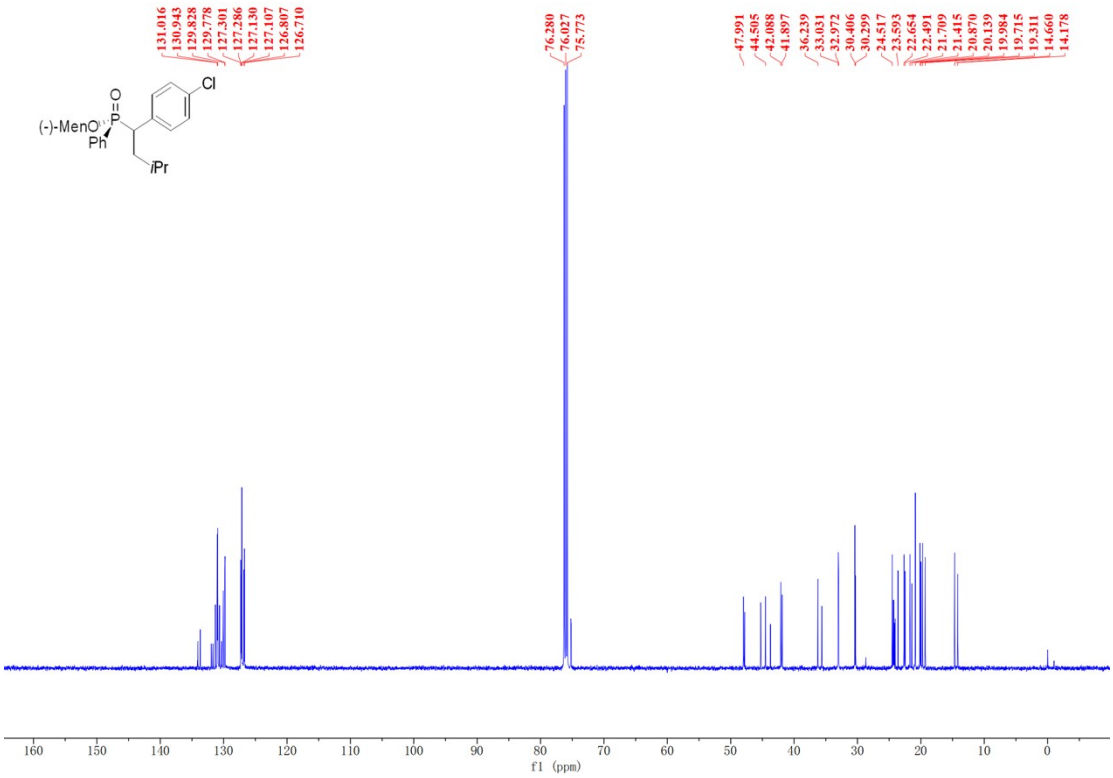

38.47
37.88
O
SC6H5
(-)-MenO
P
Ph
Et
Cl
0.54
0.46
f1 (ppm)


O
SC6H5
(-)-MenO
P
Ph
Et
Cl
f1 (ppm)


O
SC6H5
(-)-MenO
P
Ph
Et
Cl
f1 (ppm)


(-)-MenO
Ph
O
P
Cl
iPr
40.459
38.943
0.56
0.44
f1 (ppm)


7.462
7.441
7.425
7.275
7.257
7.238
7.231
7.068
7.052
6.920
6.907
4.310
4.301
4.289
4.138
4.116
1.496
1.264
1.241
0.975
0.961
0.897
0.883
0.872
0.847
0.836
0.822
0.803
0.790
0.773
0.721
0.708
0.693
0.678
0.662
0.647
0.634
0.629
0.615
0.513
0.500
0.057
(-)-MenO
Ph
O
P
Cl
iPr
0.83
0.47
2.54
3.02
1.12
1.10
0.56
0.44
0.97
0.57
0.82
0.97
1.17
0.63
1.30
0.65
1.45
0.20
0.98
2.45
2.35
4.89
4.68
2.54
1.30
f1 (ppm)


131.016
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129.828
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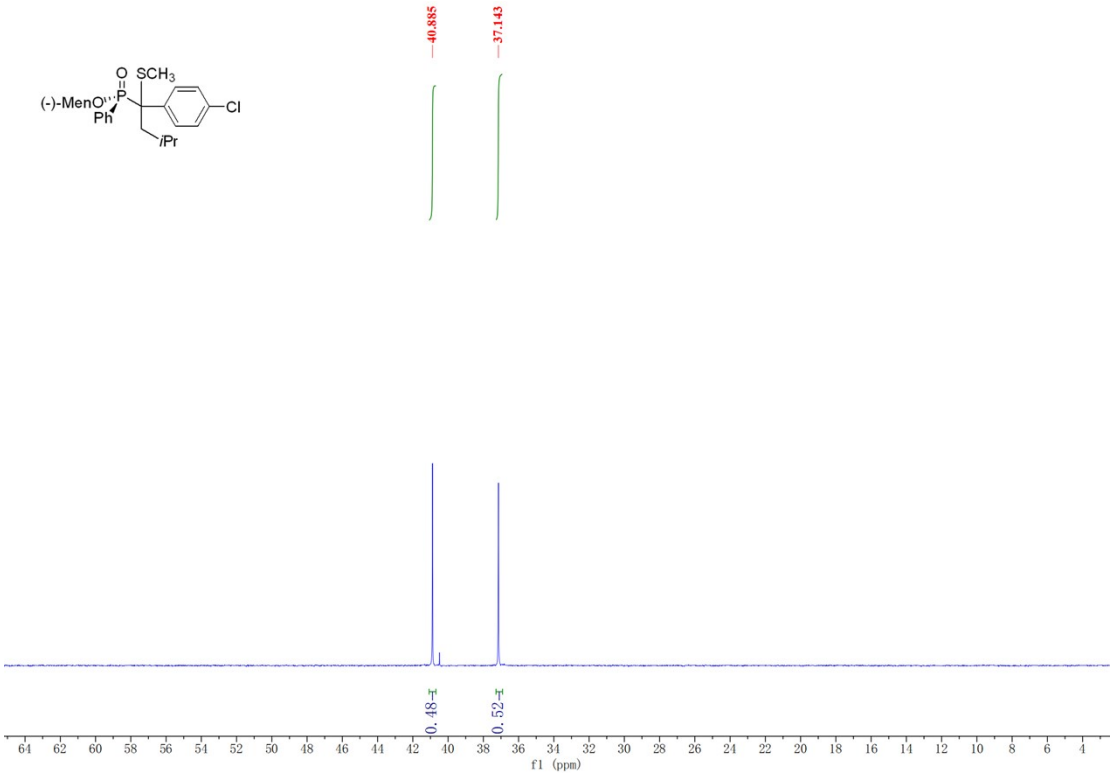
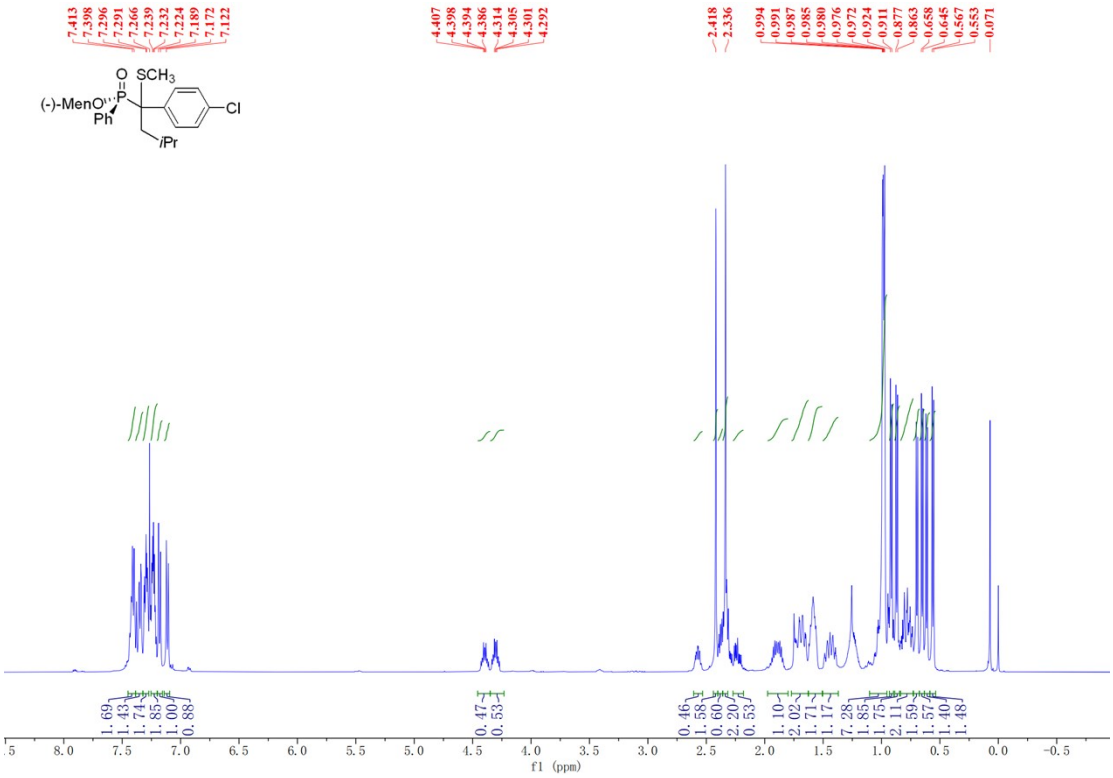
127.286
127.130
127.107
126.807
126.710
76.280
76.027
75.773
47.991
44.505
42.088
41.897
36.239
33.031
32.972
30.406
30.299
24.517
23.593
22.654
22.491
21.709
21.415
20.870
20.139
19.984
19.715
19.311
14.660
14.178
(-)-MenO
Ph
O
P
Cl
iPr
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


40.885
37.143
(-)-MenO
Ph
O
P
SCH3
Cl
iPr
0.48
0.52
64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4
f1 (ppm)


7.413
7.398
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7.291
7.266
7.239
7.232
7.224
7.189
7.172
7.122
4.407
4.398
4.394
4.386
4.314
4.305
4.301
4.292
2.418
2.336
0.994
0.991
0.987
0.985
0.980
0.976
0.972
0.924
0.911
0.877
0.863
0.658
0.645
0.567
0.553
0.071
O
SCH3
(-)-MenO
P
Ph
Cl
iPr
1.69
1.43
1.74
1.85
1.00
0.88
0.47
0.53
0.46
1.58
0.60
2.20
0.53
1.10
2.02
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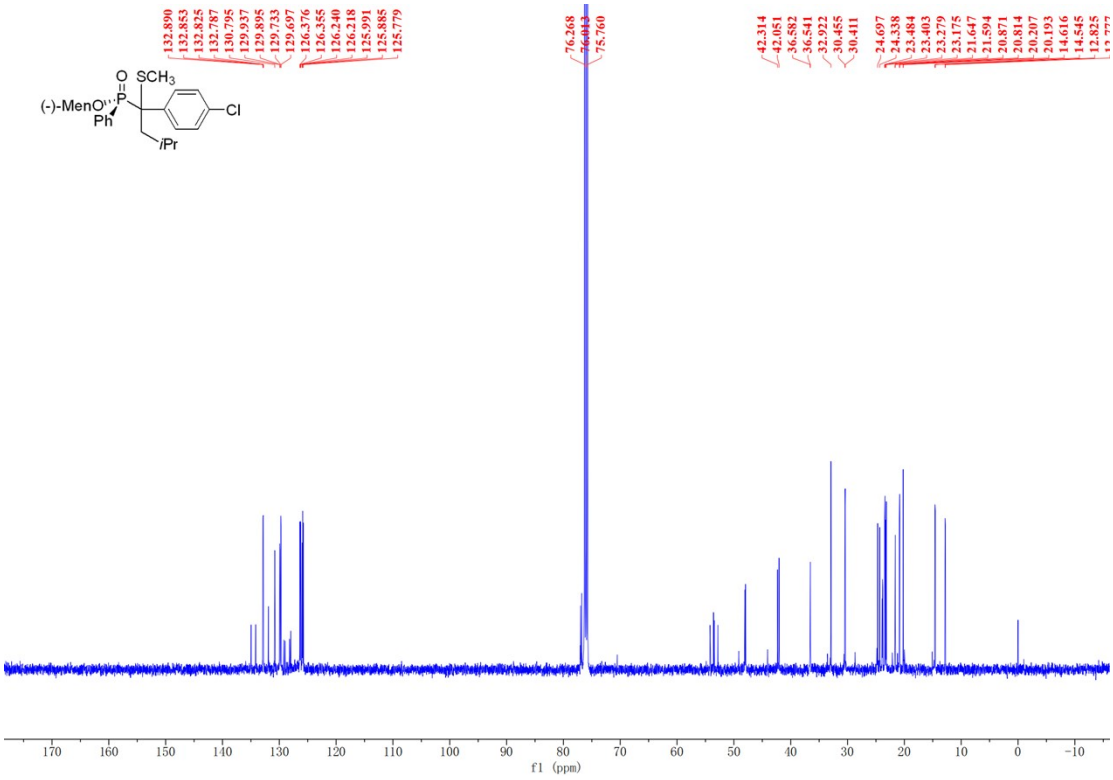
1.57
1.40
1.48
f1 (ppm)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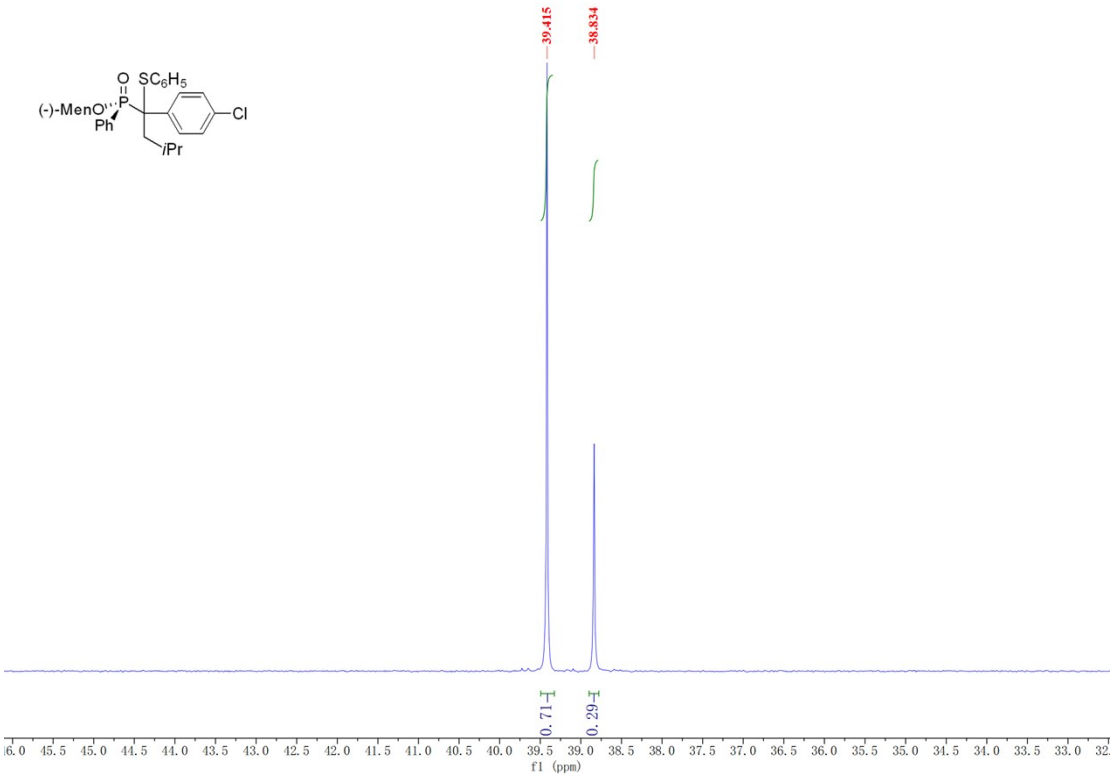
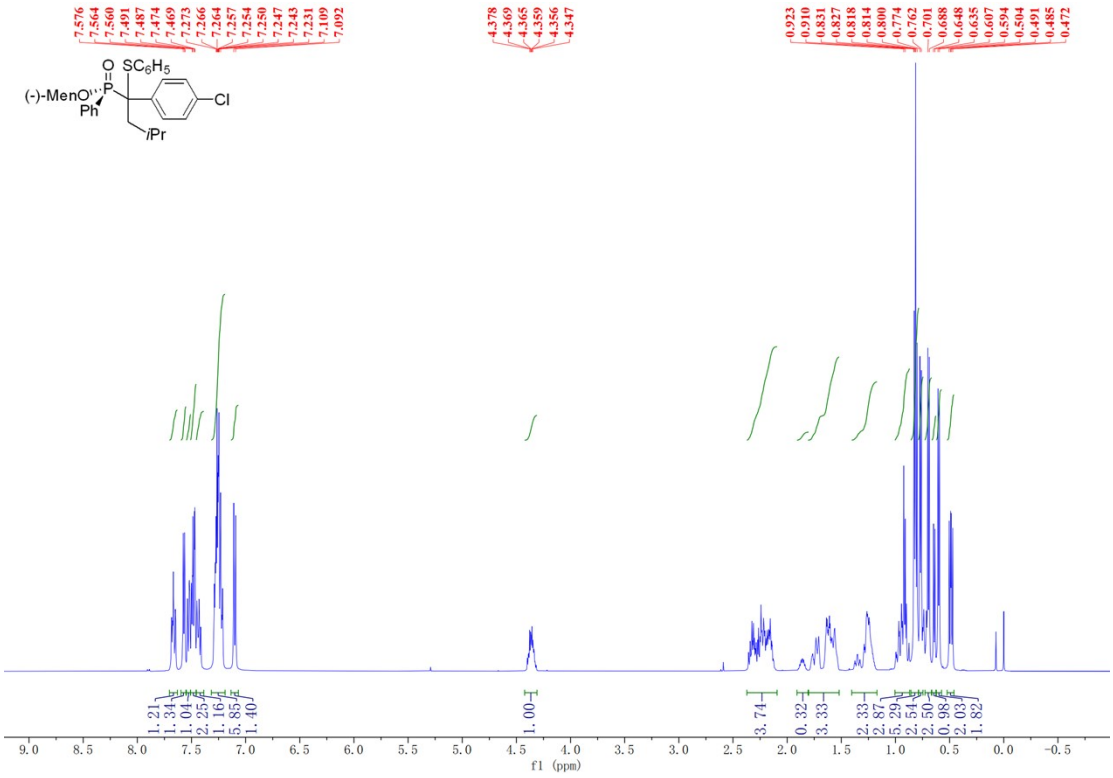
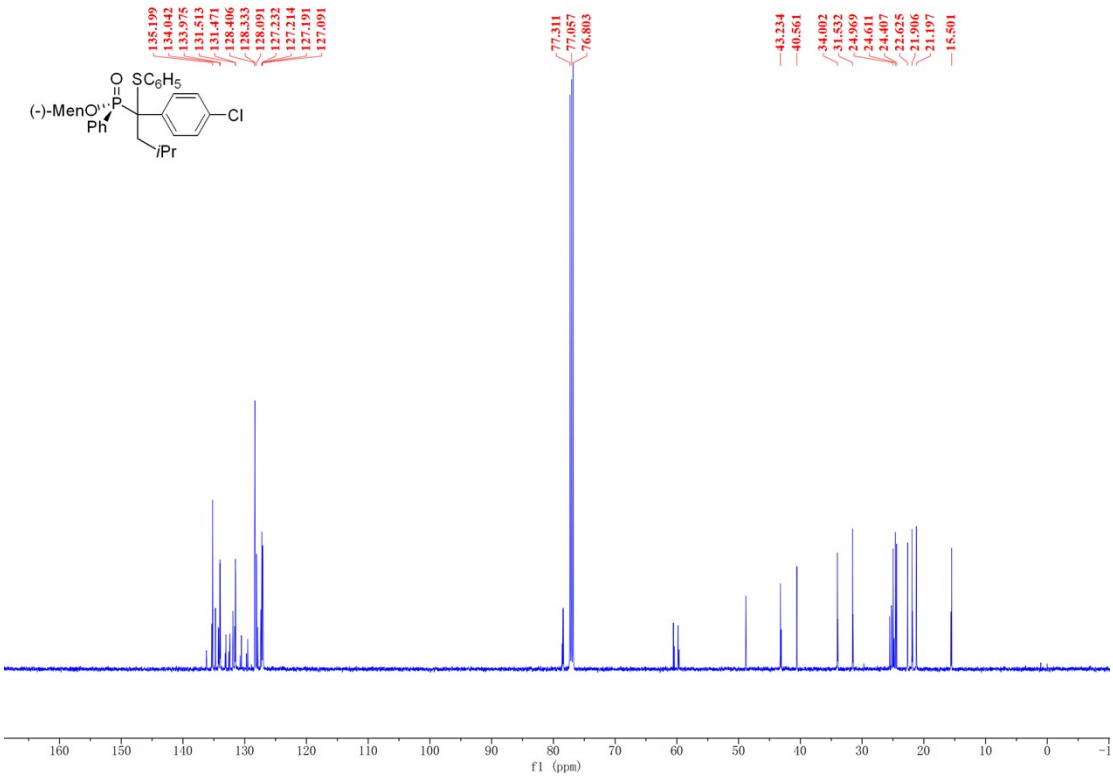
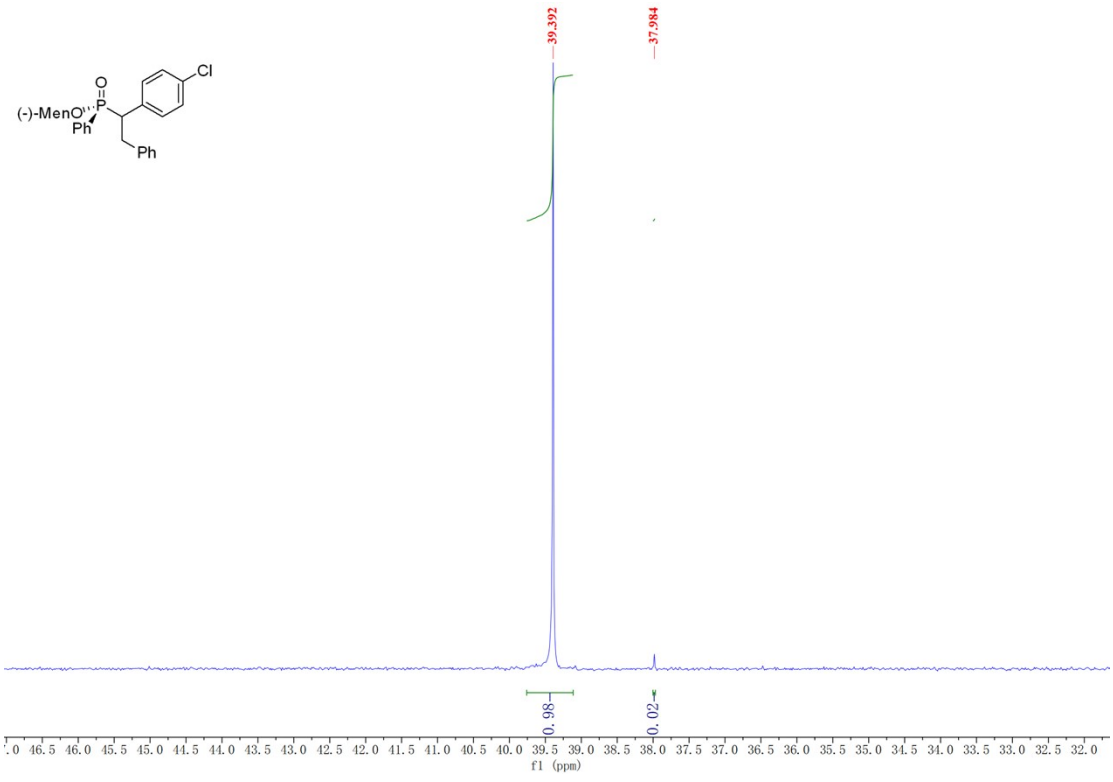
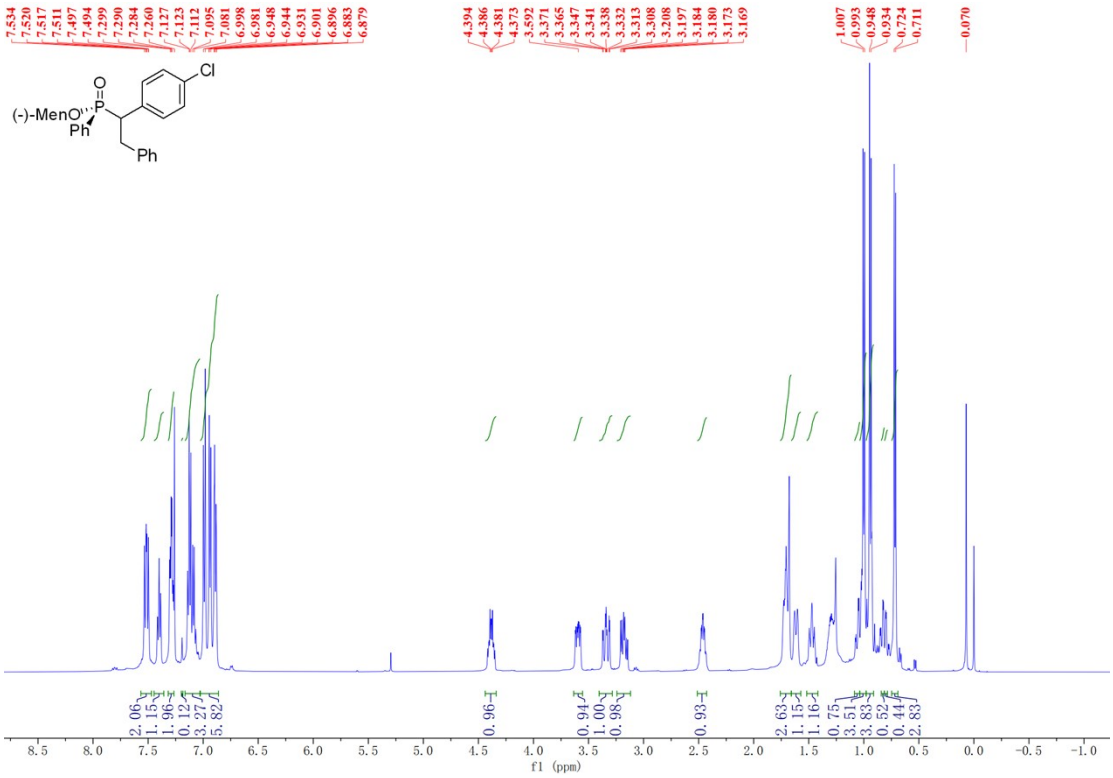
132.853
132.825
132.787
130.795
129.937
129.895
129.733
129.697
126.376
126.355
126.240
126.218
125.991
125.885
125.779
76.268
76.013
75.760
42.314
42.051
36.582
36.541
32.922
30.455
30.411
24.697
24.338
23.484
23.403
23.279
23.175
21.647
21.594
20.871
20.814
20.207
20.193
14.616
14.545
12.825
O
SCH3
(-)-MenO
P
Ph
Cl
iPr
f1 (ppm)

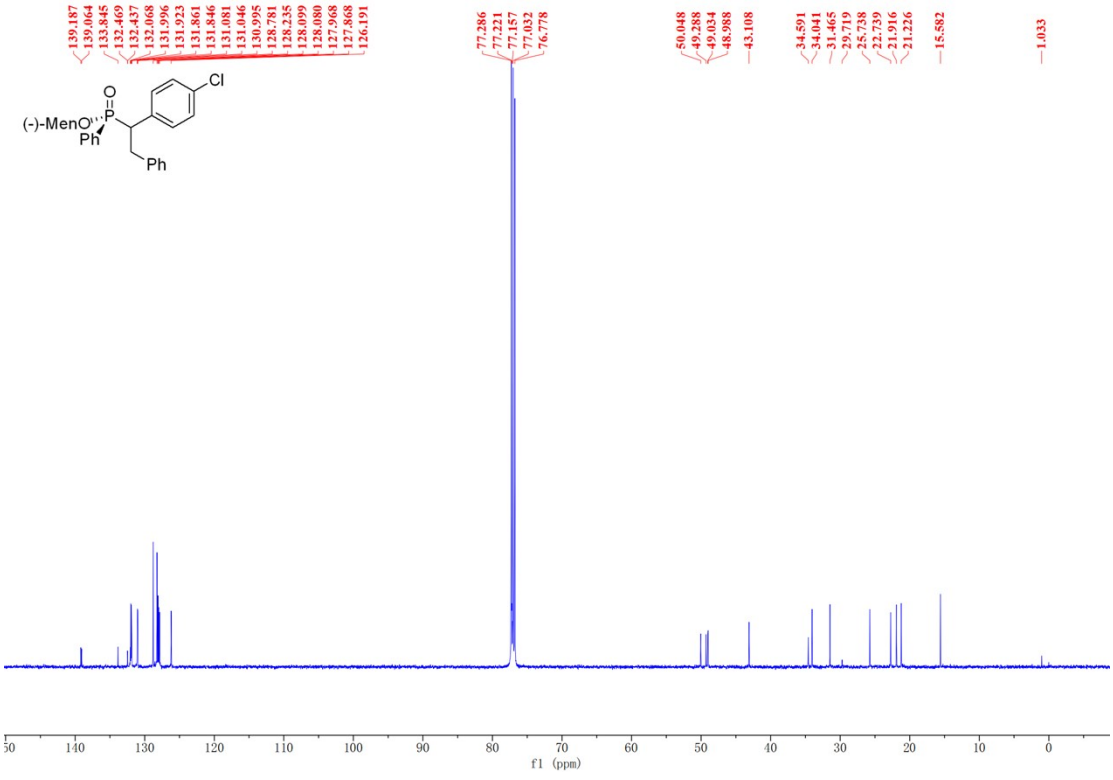

39.415
38.834
0.71
0.29
f1 (ppm)

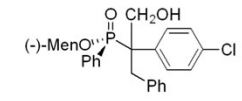

1.21
1.34
1.04
2.25
1.16
5.85
1.40
1.00
3.74
0.32
3.33
2.33
2.87
5.29
2.54
2.50
0.98
2.03
1.82
f1 (ppm)


135.199
134.042
133.975
131.513
131.471
128.406
128.333
128.091
127.232
127.214
127.191
127.091
77.311
77.057
76.803
43.234
40.561
34.002
31.532
24.969
24.611
24.407
22.625
21.906
21.197
15.501
(-)-MenO
Ph
O
P
SC6H5
Cl
iPr
f1 (ppm)

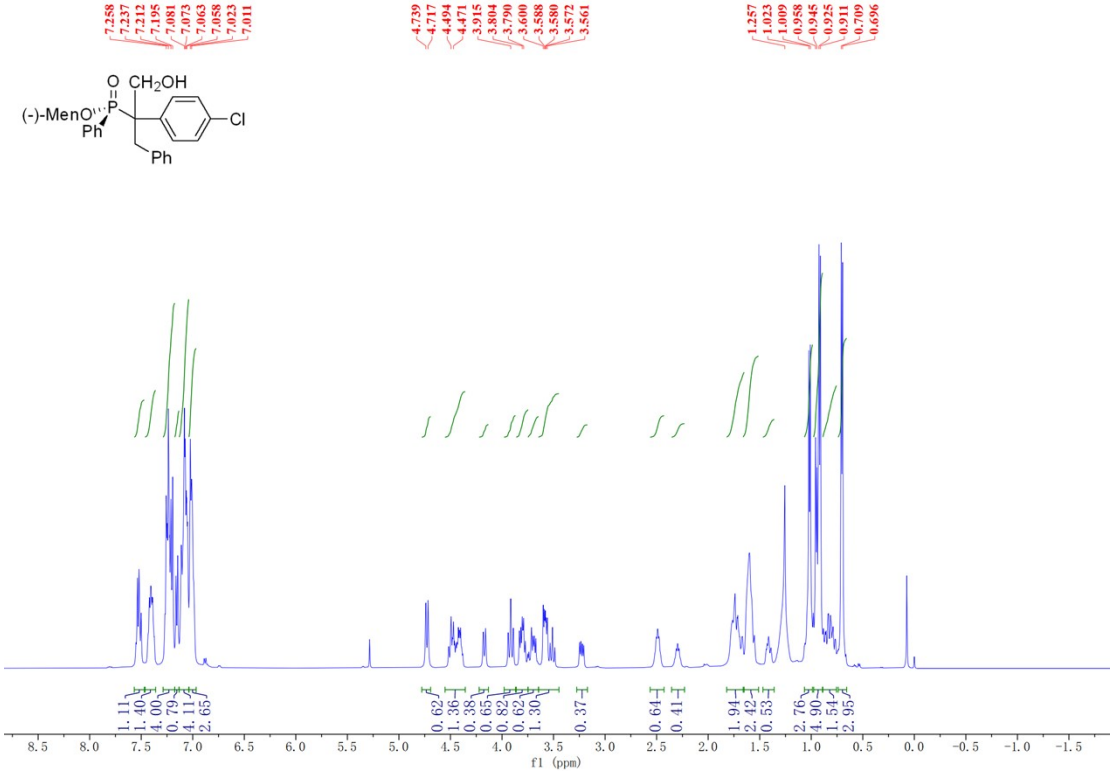

39.392
37.984
(-)-MenO
Ph
O
P
Cl
Ph
0.98
0.02
f1 (ppm)

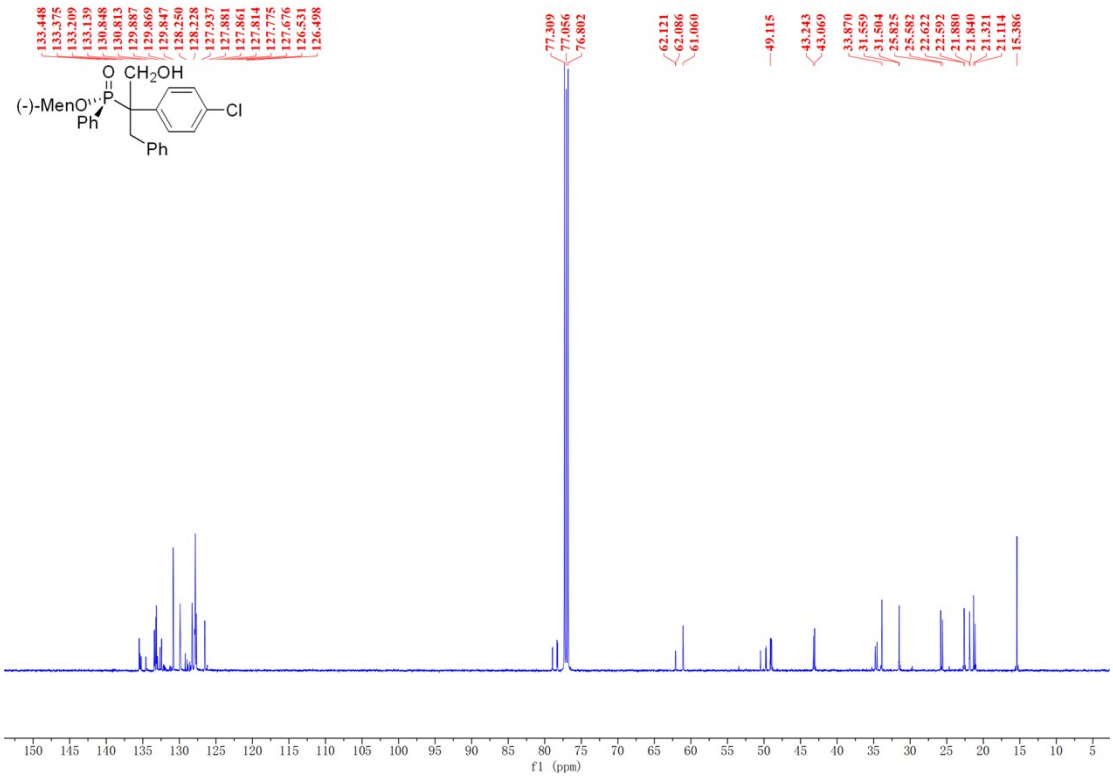

7.534
7.520
7.517
7.511
7.497
7.494
7.299
7.290
7.284
7.260
7.127
7.123
7.112
7.095
7.081
6.998
6.981
6.948
6.944
6.931
6.901
6.896
6.883
6.879
4.394
4.386
4.381
4.373
3.592
3.371
3.365
3.347
3.341
3.338
3.332
3.313
3.308
3.208
3.197
3.184
3.180
3.173
3.169
1.007
0.993
0.948
0.934
0.724
0.711
0.070
(-)-MenO
P
O
Ph
Cl
Ph
2.06
1.15
1.96
0.12
3.27
5.82
0.96
0.94
1.00
0.98
0.93
2.63
1.15
1.16
0.75
3.51
3.83
0.52
0.44
2.83
f1 (ppm)

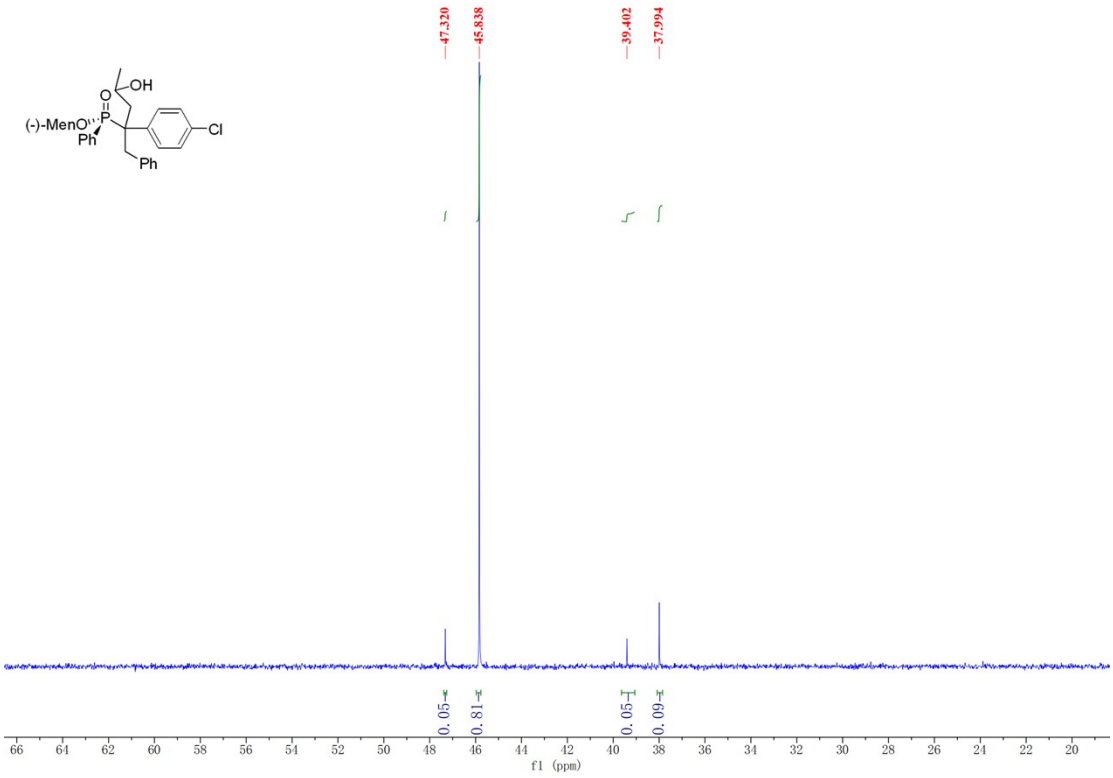

139.187
139.064
133.845
132.469
132.437
132.068
131.996
131.923
131.861
131.846
131.081
131.046
130.995
128.781
128.235
128.099
128.080
127.968
127.868
126.191
77.286
77.221
77.157
77.032
76.778
50.048
49.288
49.034
48.988
43.108
34.591
34.041
31.465
29.719
25.738
22.739
21.916
21.226
15.582
1.033
(-)-MenO
P
O
Ph
Cl
Ph
f1 (ppm)

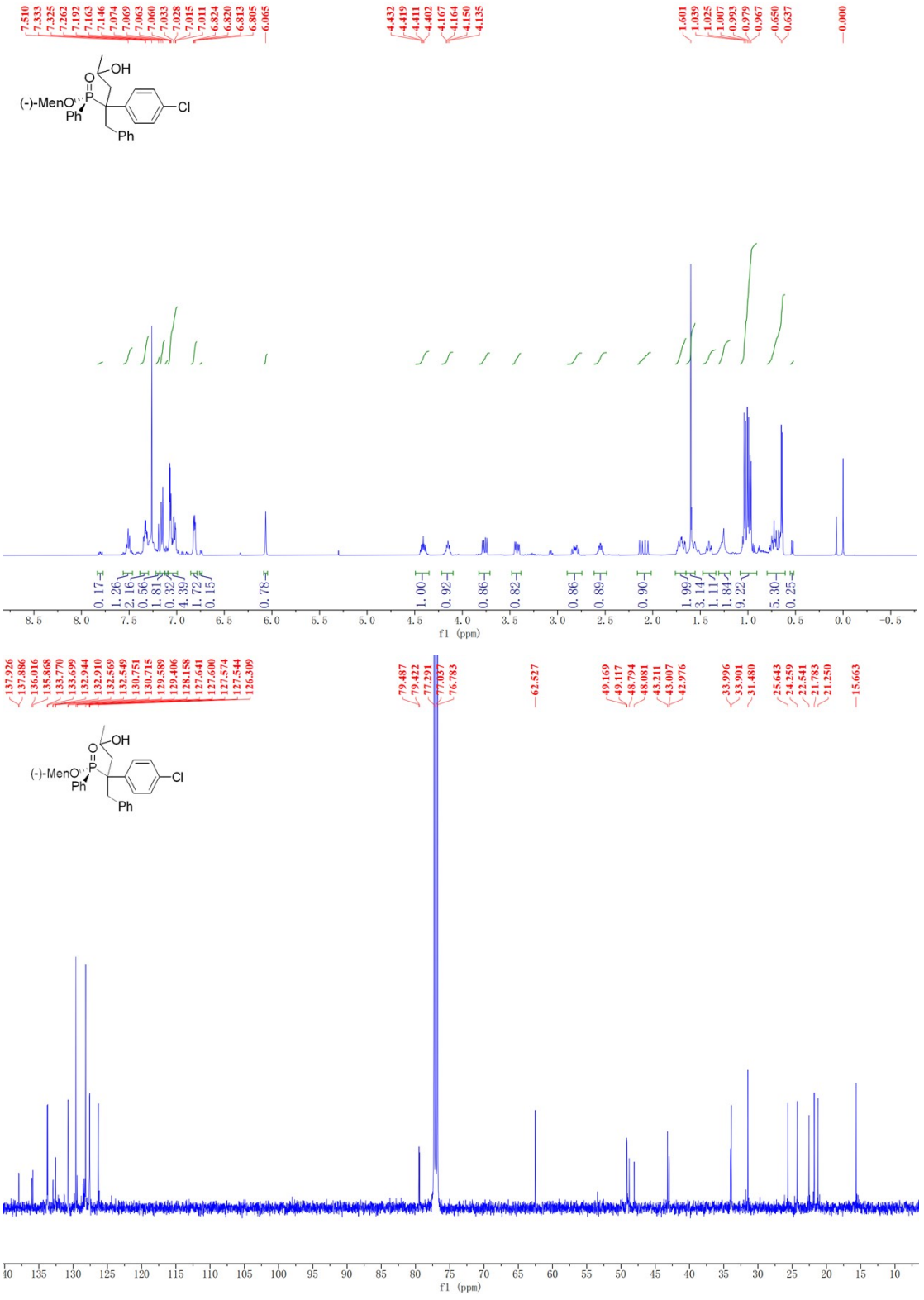

O
CH2OH
(-)-MenO
P
Ph
Cl
Ph

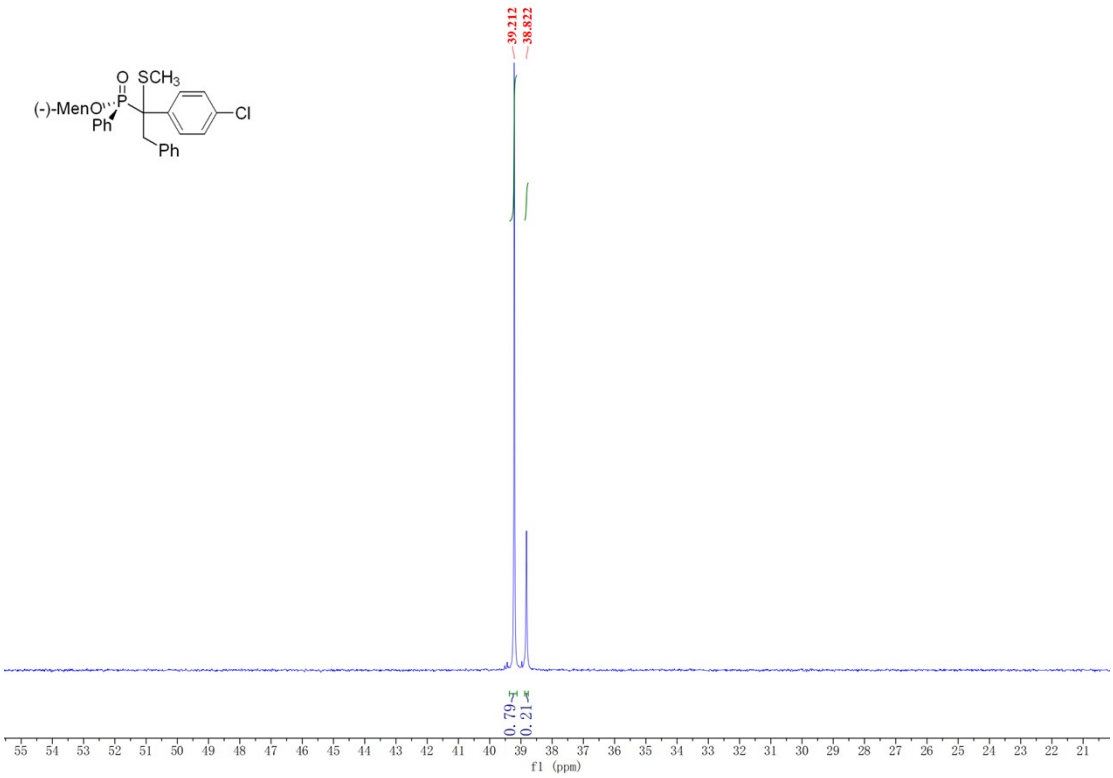
46.403
44.437
0.36
0.64
f1 (ppm)

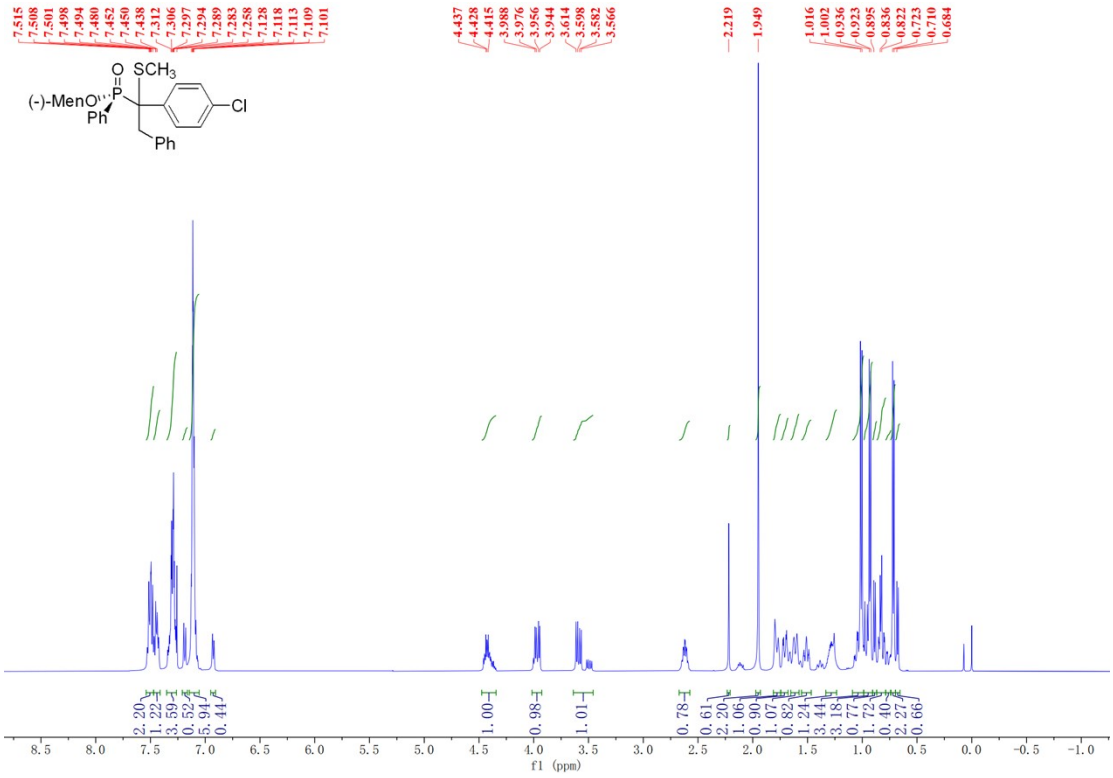

7.258
7.237
7.212
7.195
7.081
7.073
7.063
7.058
7.023
7.011
4.739
4.717
4.494
4.471
3.915
3.804
3.790
3.600
3.588
3.580
3.572
3.561
1.257
1.023
1.009
0.958
0.945
0.925
0.911
0.709
0.696
1.11
1.40
4.00
0.79
4.11
2.65
0.62
1.36
0.38
0.65
0.82
0.62
1.30
0.37
0.64
0.41
1.94
2.42
0.53
2.76
4.90
1.54
2.95
f1 (ppm)

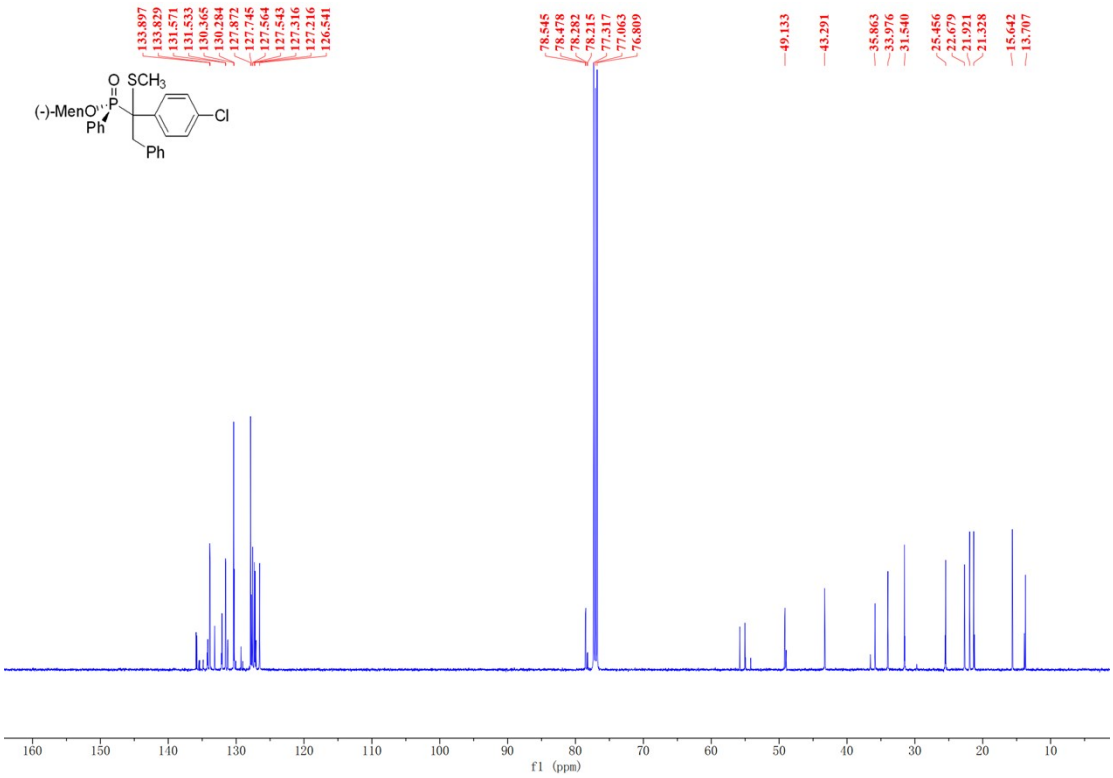

133.448
133.375
133.209
133.139
130.848
130.813
129.887
129.869
129.847
128.250
128.228
127.937
127.881
127.861
127.814
127.775
127.676
126.531
126.498
77.309
77.056
76.802
62.121
62.086
61.060
49.115
43.243
43.069
33.870
31.559
31.504
25.825
25.582
23.622
22.592
21.880
21.840
21.321
21.114
15.386
O
CH2OH
(-)-MenO
P
Ph
Cl
Ph
f1 (ppm)


47.320
45.838
39.402
37.994
OH
O
(-)-MenO
P
Ph
Cl
Ph
0.05
0.81
0.05
0.09
f1 (ppm)


7.510
7.333
7.325
7.262
7.192
7.163
7.146
7.074
7.069
7.063
7.060
7.033
7.028
7.015
7.011
6.824
6.820
6.813
6.805
6.065
4.432
4.419
4.411
4.402
4.167
4.164
4.150
4.135
1.601
1.039
1.025
1.007
0.993
0.979
0.967
0.650
0.637
0.000
OH
O
P
(-)-MenO
Ph
Cl
Ph
0.17
1.26
2.16
0.56
1.81
0.32
4.39
1.72
0.15
0.78
1.00
0.92
0.86
0.82
0.86
0.89
0.90
1.99
3.14
1.11
1.84
9.22
5.30
0.25
f1 (ppm)
137.926
137.886
136.016
135.868
133.770
133.699
132.944
132.910
132.569
132.549
130.751
130.715
129.589
129.406
128.158
127.641
127.600
127.574
127.544
126.309
79.487
79.422
77.291
77.037
76.783
62.527
49.169
49.117
48.794
48.081
43.211
43.007
42.976
33.996
33.901
31.480
25.643
24.259
22.541
21.783
21.250
15.663
f1 (ppm)


O
SCH3
(-)-MenO
P
Ph
Cl
Ph
39.212
38.822
0.79
0.21
f1 (ppm)


7.515
7.508
7.501
7.498
7.494
7.480
7.452
7.450
7.438
7.312
7.306
7.297
7.294
7.289
7.283
7.258
7.128
7.118
7.113
7.109
7.101
4.437
4.428
4.415
3.988
3.976
3.956
3.944
3.614
3.598
3.582
3.566
2.219
1.949
1.016
1.002
0.936
0.923
0.895
0.836
0.822
0.723
0.710
0.684
O
SCH3
(-)-MenO
P
Ph
Cl
Ph
2.20
1.22
3.59
0.52
5.94
0.44
1.00
0.98
1.01
0.78
0.61
2.20
1.06
0.90
1.07
0.82
1.24
3.44
3.18
0.77
1.72
0.40
2.27
0.66
f1 (ppm)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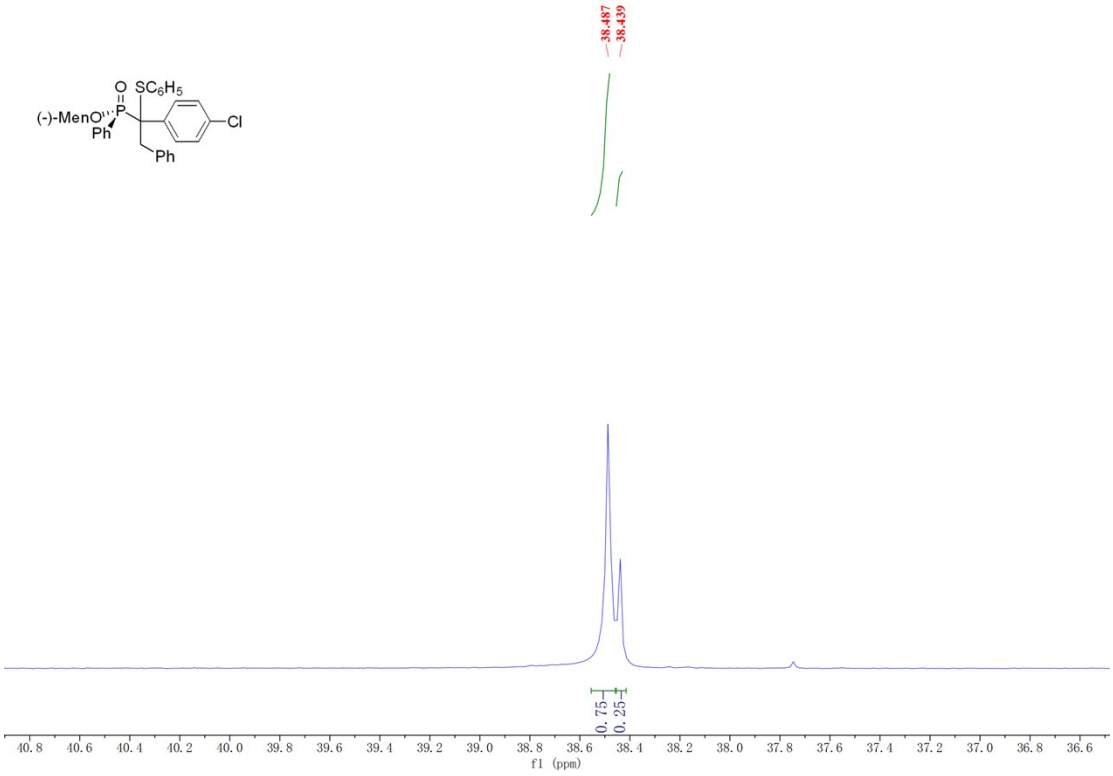
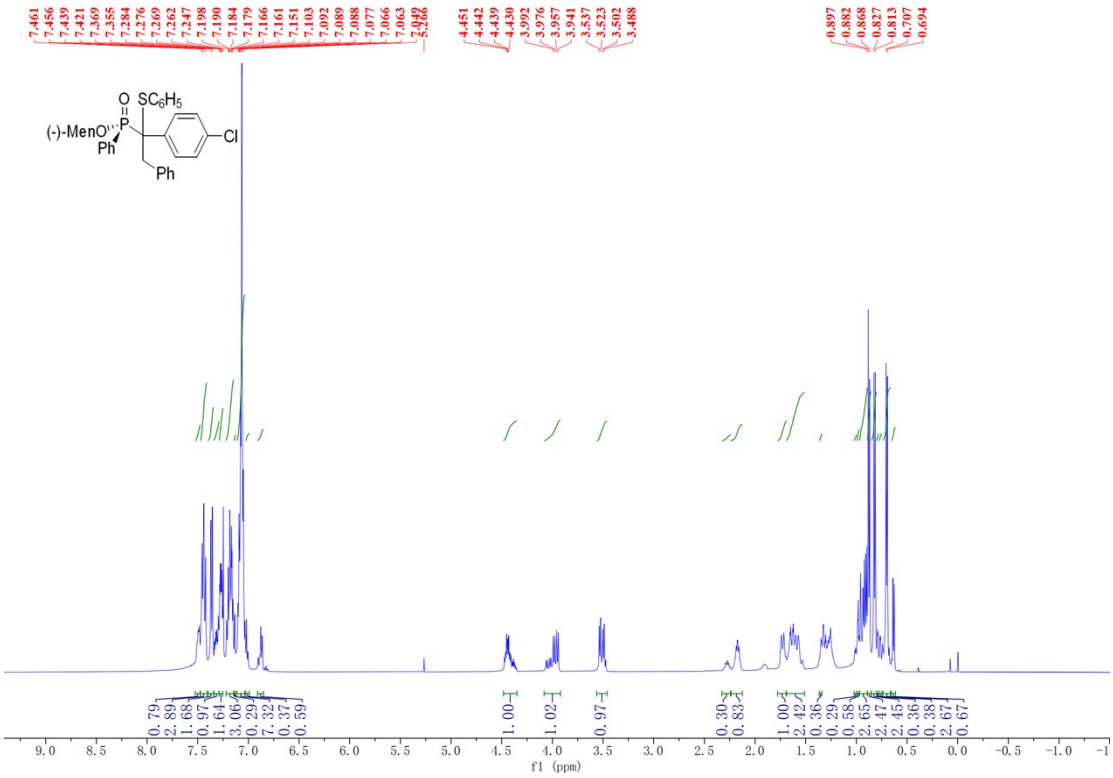
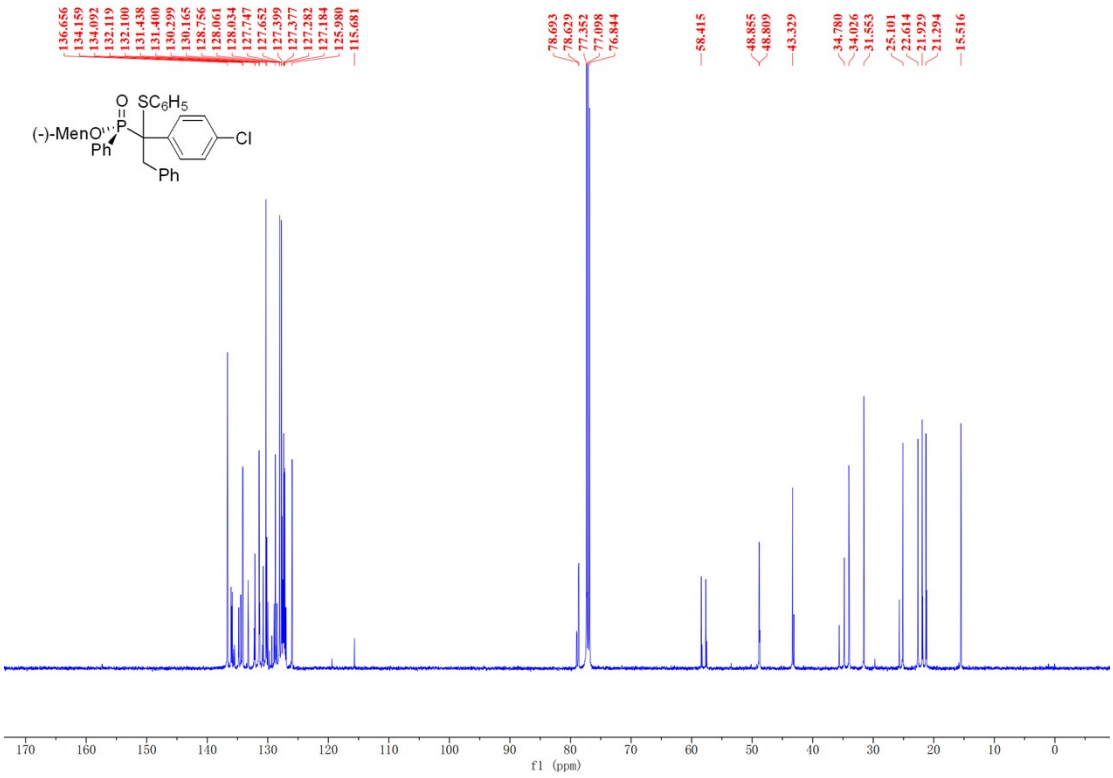
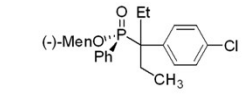
133.829
131.571
131.533
130.365
130.284
127.872
127.745
127.564
127.543
127.316
127.216
126.541
78.545
78.478
78.282
78.215
77.317
77.063
76.809
49.133
43.291
35.863
33.976
31.540
25.456
22.679
21.921
21.328
15.642
13.707
O
SCH3
(-)-MenO
P
Ph
Cl
Ph
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

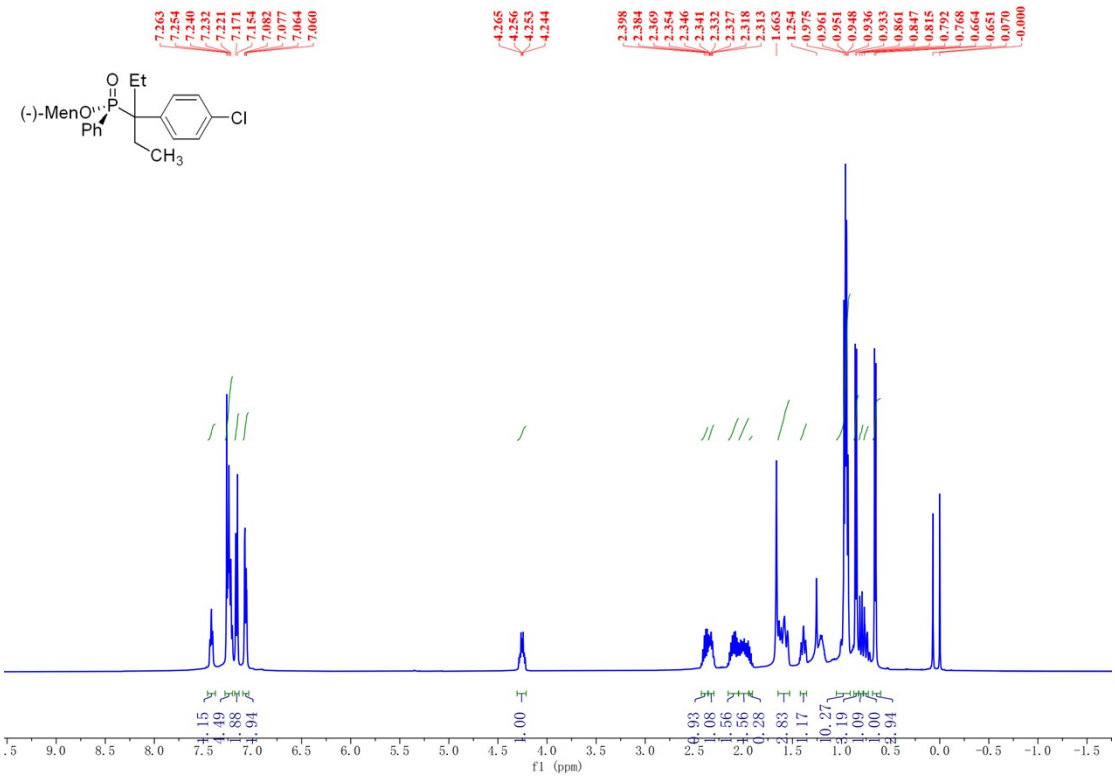

38.487
38.439
O
SC6H5
(-)-MenO
P
Ph
Cl
Ph
0.75
0.25
40.8
40.6
40.4
40.2
40.0
39.8
39.6
39.4
39.2
39.0
38.8
38.6
38.4
38.2
38.0
37.8
37.6
37.4
37.2
37.0
36.8
36.6
f1 (ppm)

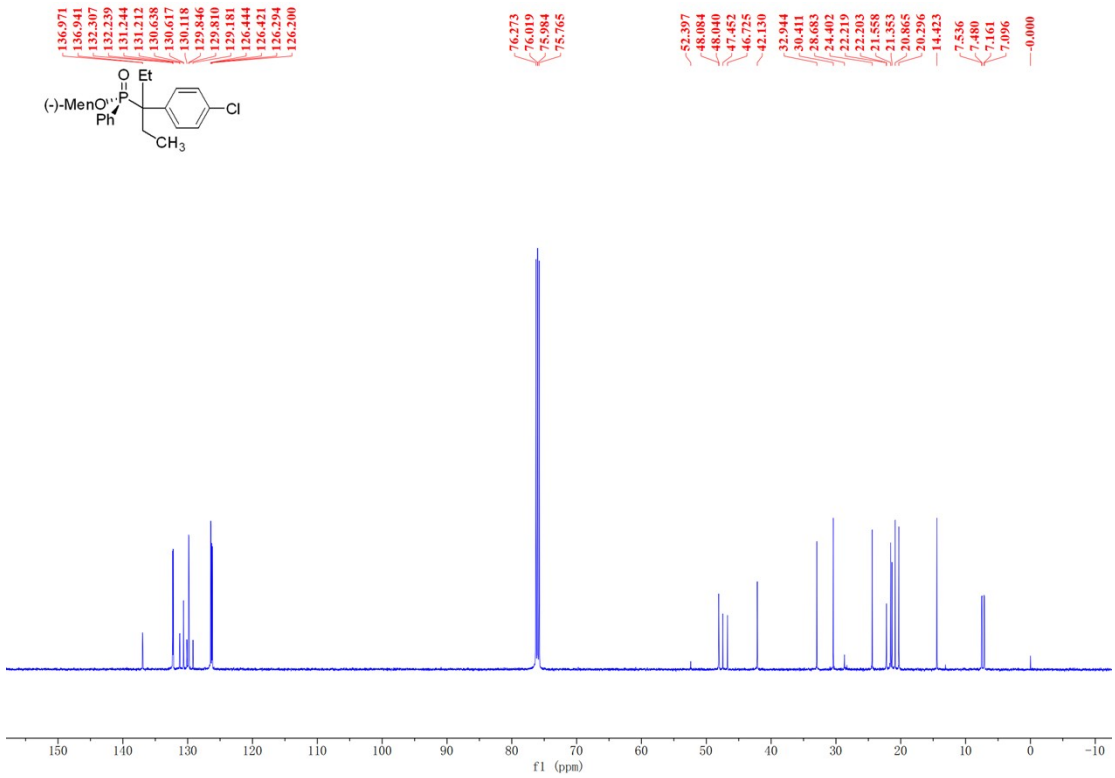

7.461
7.456
7.439
7.421
7.369
7.355
7.284
7.276
7.269
7.262
7.247
7.198
7.190
7.184
7.179
7.166
7.161
7.151
7.103
7.092
7.089
7.088
7.077
7.066
7.063
5.266
4.451
4.442
4.439
4.430
3.992
3.976
3.957
3.941
3.537
3.523
3.502
3.488
0.897
0.882
0.868
0.827
0.813
0.707
0.694
O
SC6H5
(-)-MenO
P
Ph
Cl
Ph
0.79
2.89
1.68
0.97
1.64
3.06
0.29
7.32
0.37
0.59
1.00
1.02
0.97
0.30
0.83
1.00
2.42
0.36
0.29
0.58
2.65
2.47
2.45
0.36
0.38
2.67
0.67
f1 (ppm)

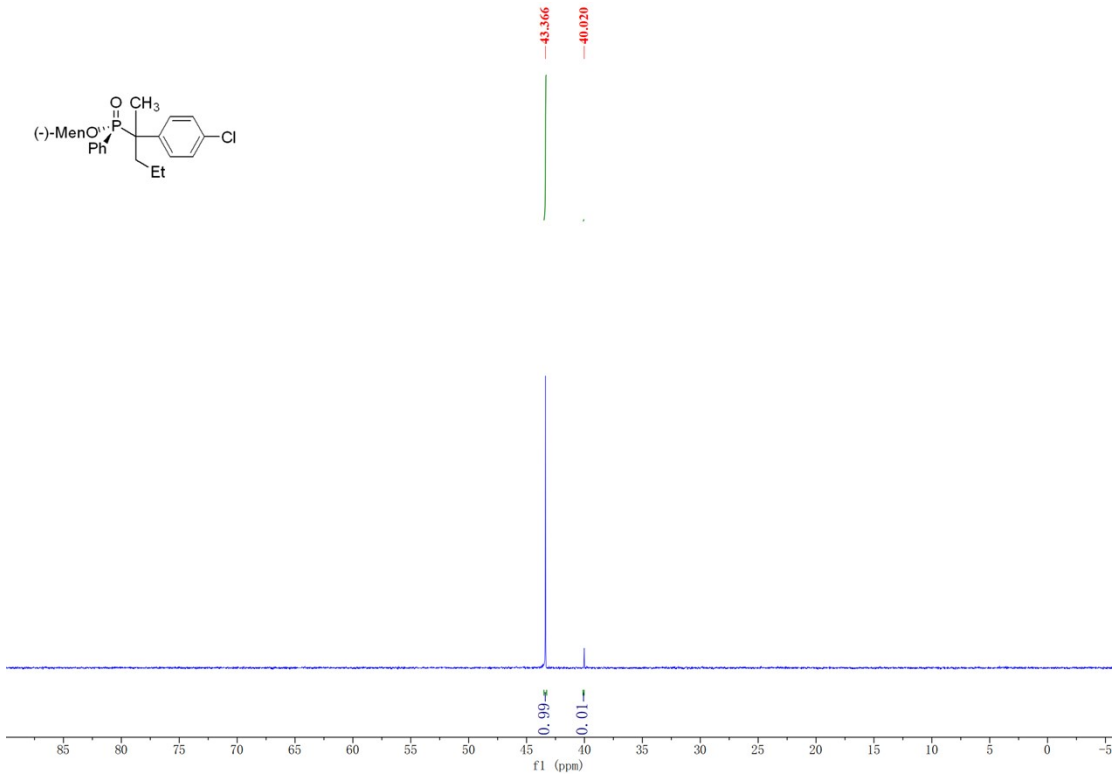

136.656
134.159
134.092
132.119
132.100
131.438
131.400
130.299
130.165
128.756
128.061
128.034
127.747
127.652
127.399
127.377
127.282
127.184
125.980
115.681
78.693
78.629
77.352
77.098
76.844
58.415
48.855
48.809
43.329
34.780
34.026
31.553
25.101
22.614
21.929
21.294
15.516
O
SC6H5
(-)-MenO
P
Ph
Cl
Ph
f1 (ppm)

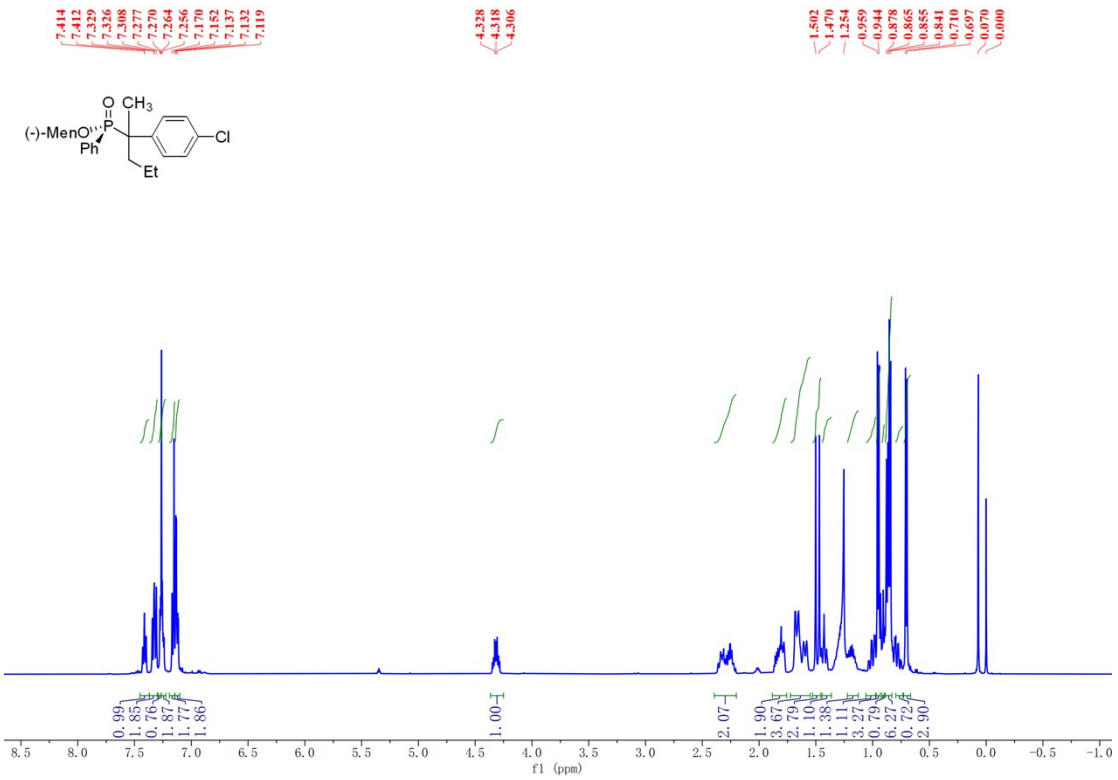

O
Et
(-)-MenO
P
Ph
Cl
CH3

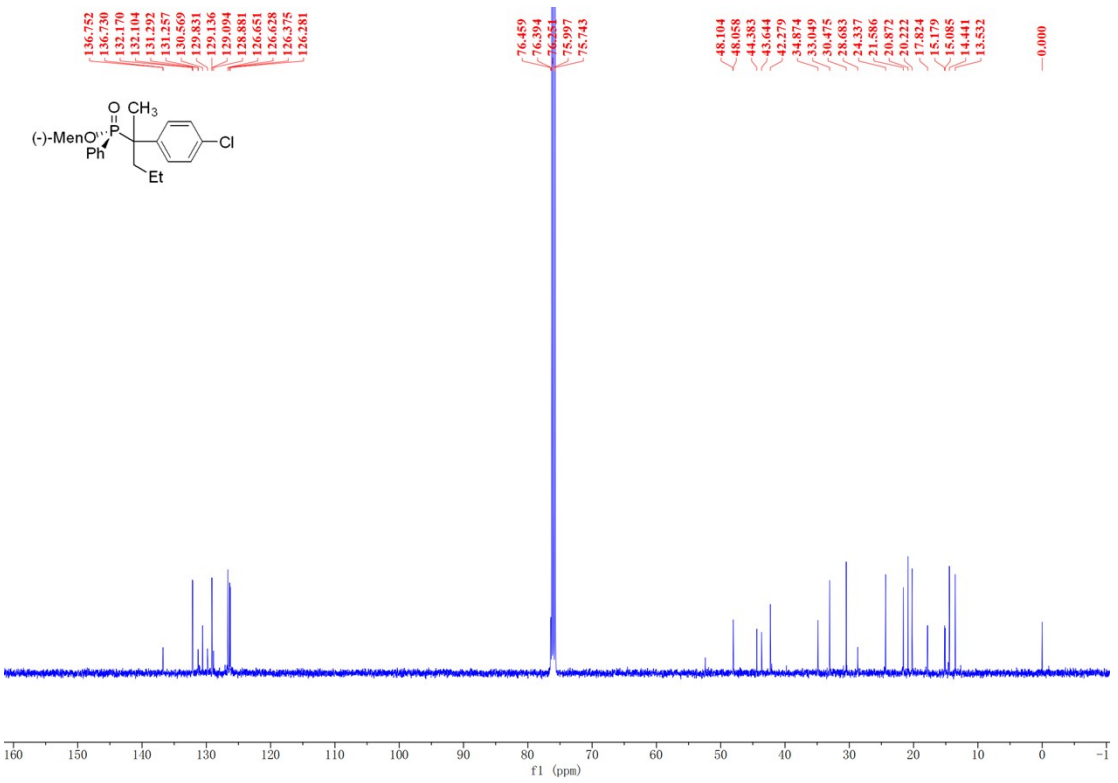
43.248
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
f1 (ppm)


7.263
7.254
7.240
7.232
7.221
7.171
7.154
7.082
7.077
7.064
7.060
4.265
4.256
4.253
4.244
2.398
2.384
2.369
2.354
2.346
2.341
2.332
2.327
2.318
2.313
1.663
1.254
0.975
0.961
0.951
0.948
0.936
0.933
0.861
0.847
0.815
0.792
0.768
0.664
0.651
0.070
-0.000
4.15
4.49
1.88
1.94
1.00
6.93
1.08
1.56
4.56
0.28
2.83
1.17
10.27
3.19
1.09
1.00
2.94
f1 (ppm)


136.971
136.941
132.307
132.239
131.244
131.212
130.638
130.617
130.118
129.846
129.810
129.181
126.444
126.421
126.294
126.200
76.273
76.019
75.984
75.765
52.397
48.084
48.040
47.452
46.725
42.130
32.944
30.411
28.683
24.402
22.219
22.203
21.558
21.353
20.865
20.296
14.423
7.536
7.480
7.161
7.096
0.000
O
Et
P
(-)-MenO
Ph
Cl
CH3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


43.366
40.020
O
CH3
P
(-)-MenO
Ph
Cl
Et
0.99
0.01
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
−5
f1 (ppm)


7.414
7.412
7.329
7.326
7.308
7.277
7.270
7.264
7.256
7.170
7.152
7.137
7.132
7.119
4.328
4.318
4.306
1.502
1.470
1.254
0.959
0.944
0.878
0.865
0.855
0.841
0.710
0.697
0.070
0.000
O
CH3
(-)-MenO
P
Ph
Et
Cl
0.99
1.85
0.76
1.87
1.77
1.86
1.00
2.07
1.90
3.67
2.79
1.10
1.38
1.11
3.27
0.79
6.27
0.72
2.90
f1 (ppm)


136.752
136.730
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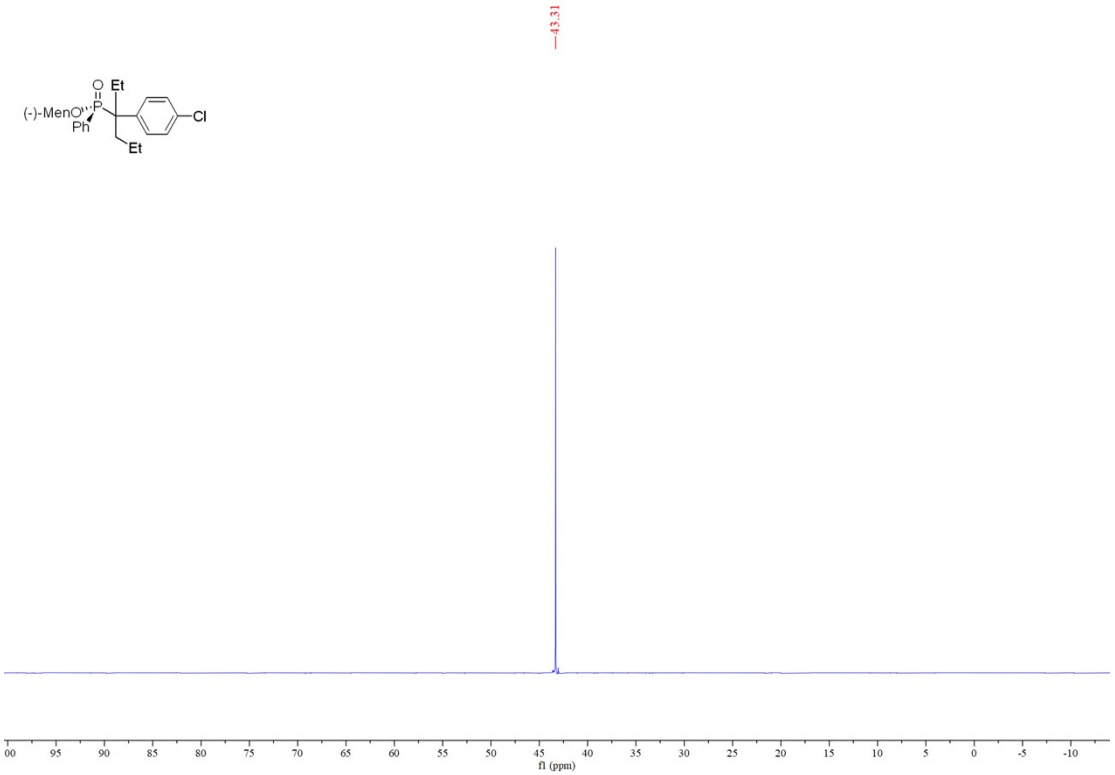
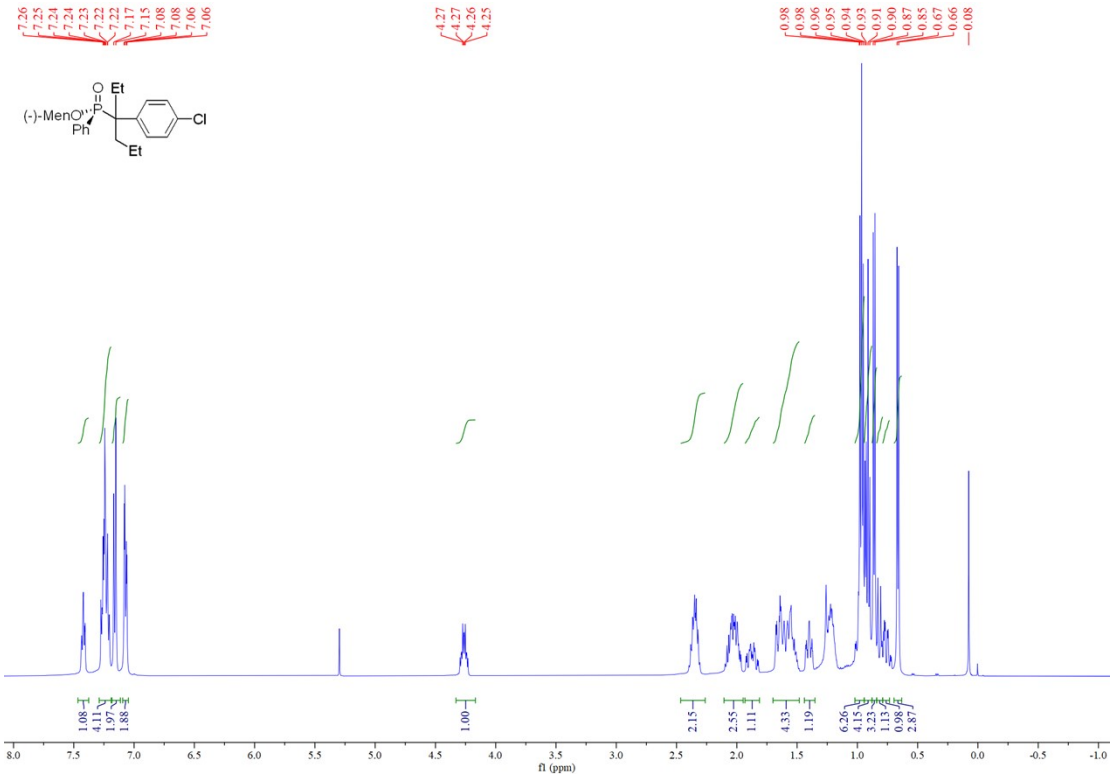
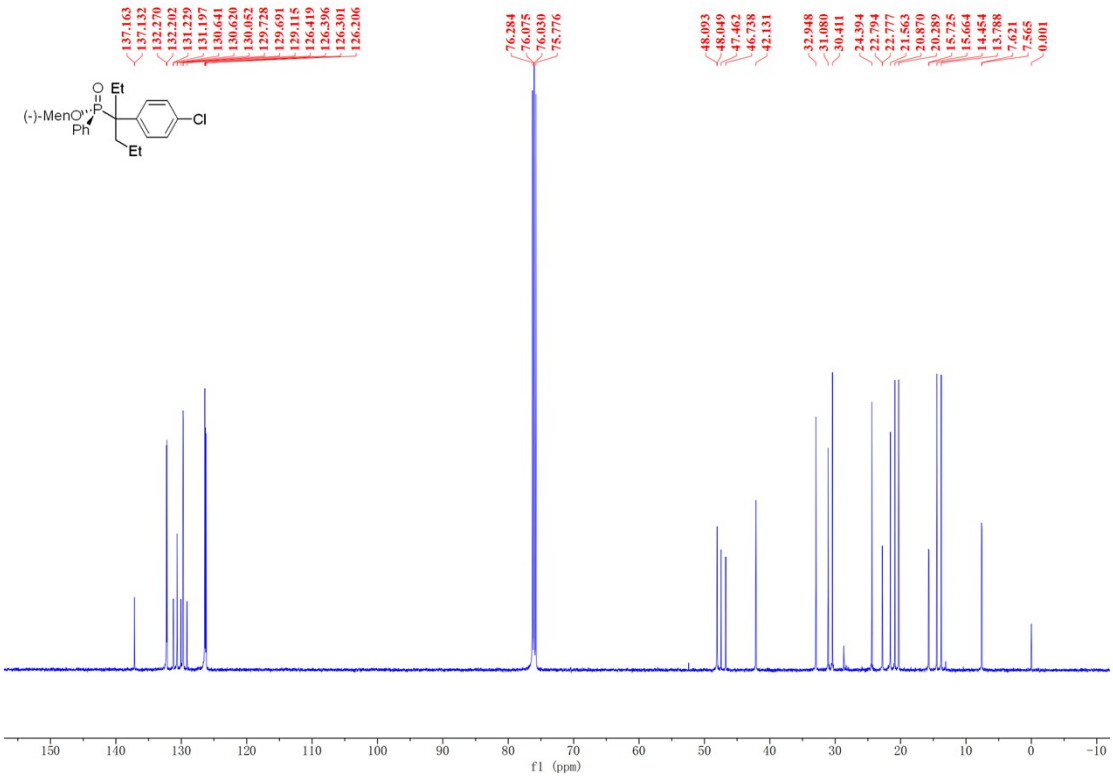
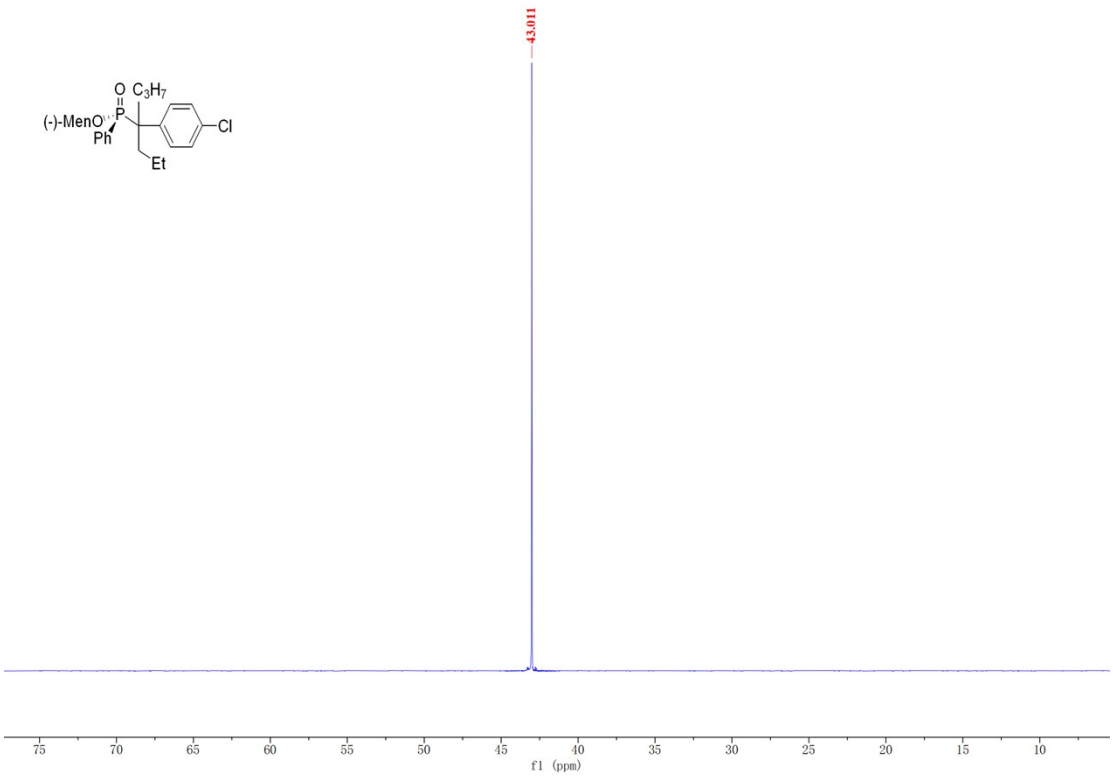
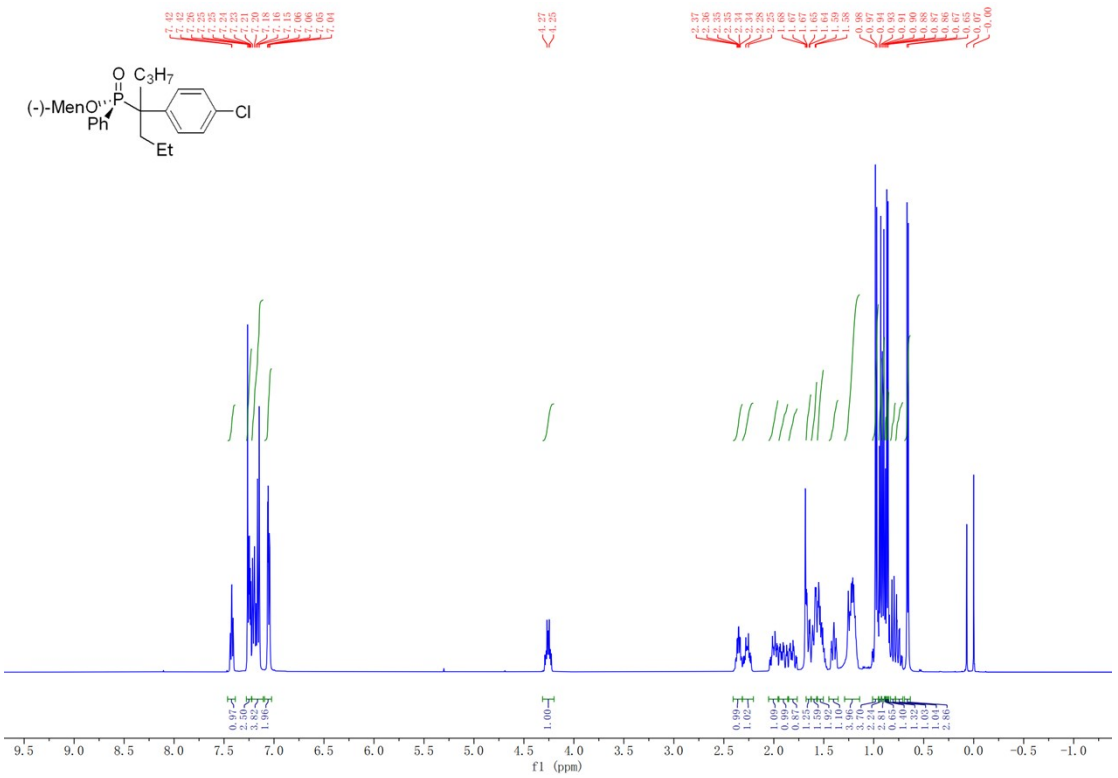
132.104
131.292
131.257
130.569
129.831
129.136
129.094
128.881
126.651
126.628
126.375
126.281
76.459
76.394
76.263
75.997
75.743
48.104
48.058
44.383
43.644
42.279
34.874
33.049
30.475
28.683
24.337
21.586
20.872
20.222
17.824
15.179
15.085
14.441
13.532
0.000
O
CH3
(-)-MenO
P
Ph
Et
Cl
f1 (ppm)

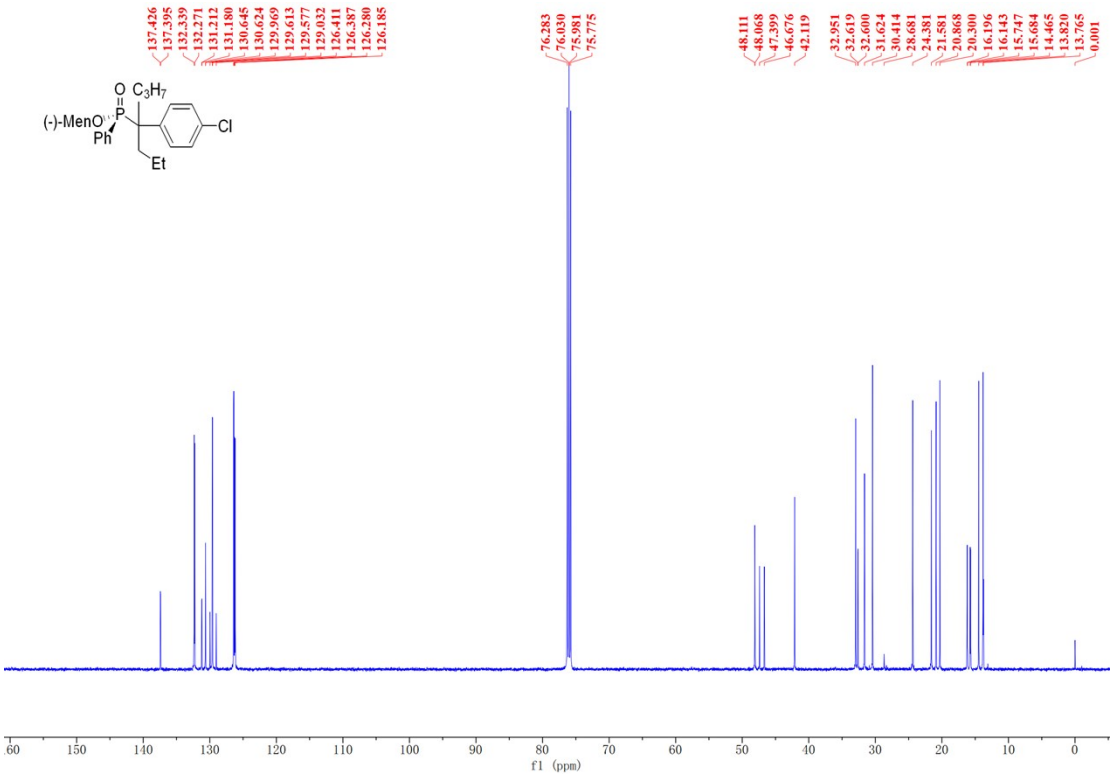

43.31
(-)-MenO
Ph
Et
Et
Cl
f1 (ppm)

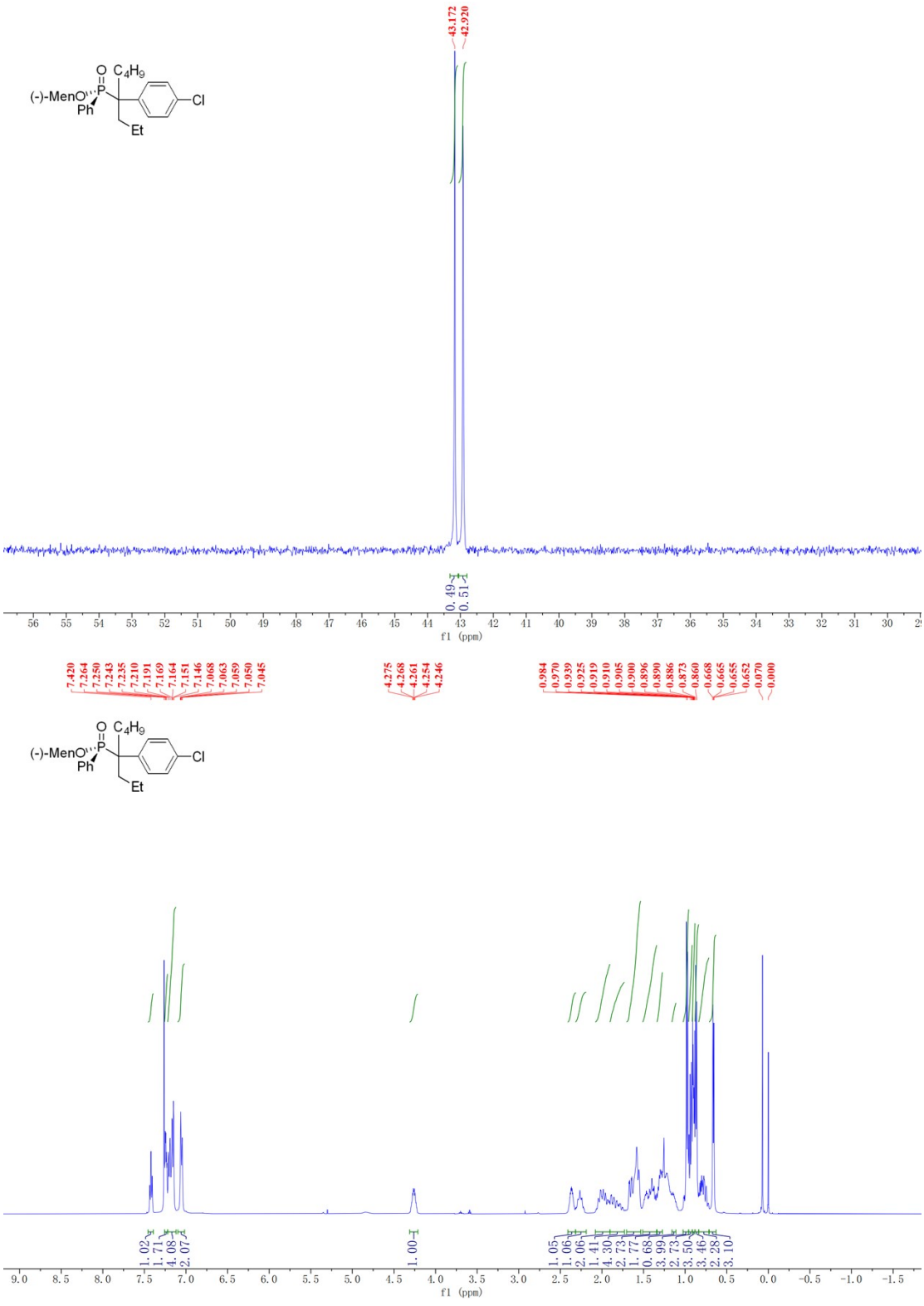

7.26
7.25
7.24
7.24
7.23
7.22
7.22
7.17
7.15
7.08
7.08
7.06
7.06
4.27
4.27
4.26
4.25
0.98
0.98
0.96
0.95
0.94
0.93
0.91
0.90
0.87
0.85
0.67
0.66
0.08
(-)-MenO
Ph
Et
Et
Cl
1.08
4.11
1.97
1.88
1.00
2.15
2.55
1.11
4.33
1.19
6.26
4.15
3.23
1.13
0.98
2.87
f1 (ppm)

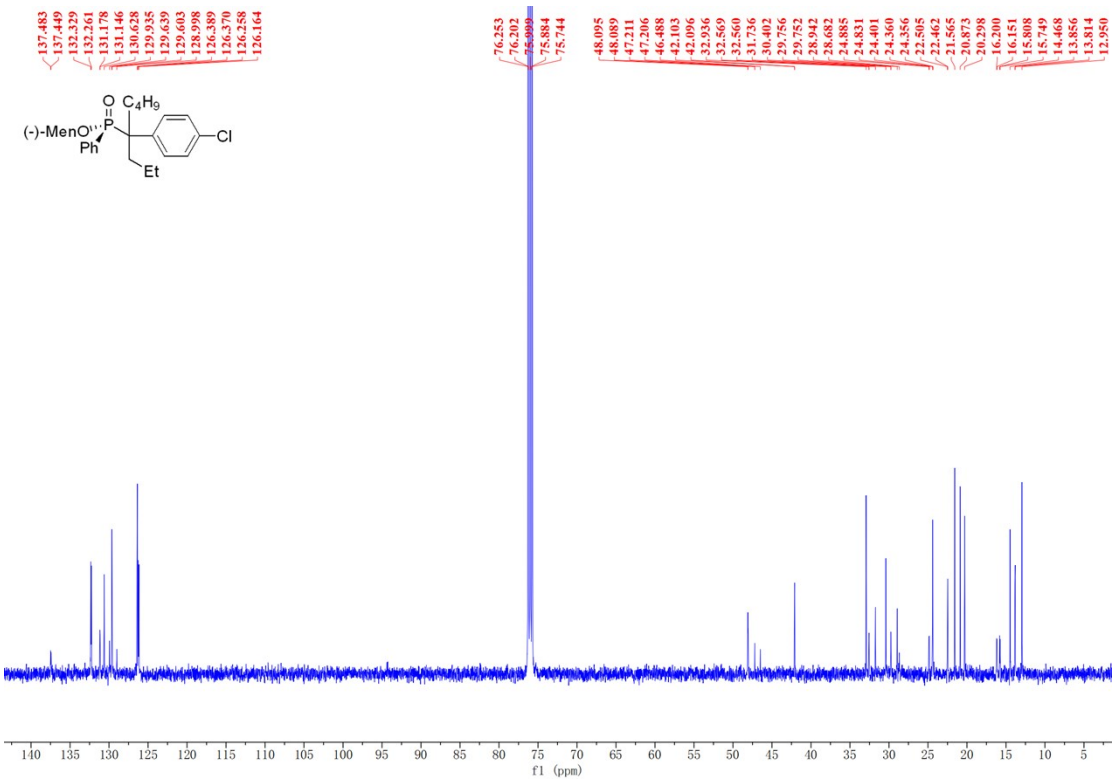

137.163
137.132
132.270
132.202
131.229
131.197
130.641
130.620
130.052
129.728
129.691
129.115
126.419
126.396
126.301
126.206
76.284
76.075
76.030
75.776
48.093
48.049
47.462
46.738
42.131
32.948
31.080
30.411
24.394
22.794
22.777
21.563
20.870
20.289
15.725
15.664
14.454
13.788
7.621
7.565
0.001
(-)-MenO
Ph
O
P
Et
Et
Cl
f1 (ppm)


43.011
(-)-MenO
Ph
O
P
C3H7
Et
Cl
f1 (ppm)


O
C3H7
(-)-MenO
P
Ph
Cl
Et
f1 (ppm)


O
C3H7
(-)-MenO
P
Ph
Cl
Et
f1 (ppm)


(-)-MenO
Ph
O
P
C4H9
Et
Cl
43.172
42.920
0.49
0.51
f1 (ppm)
7.420
7.264
7.250
7.243
7.235
7.210
7.191
7.169
7.164
7.151
7.146
7.068
7.063
7.059
7.050
7.045
4.275
4.268
4.261
4.254
4.246
0.984
0.970
0.939
0.925
0.919
0.910
0.905
0.900
0.896
0.890
0.886
0.873
0.860
0.668
0.665
0.655
0.652
0.070
0.000
1.02
1.71
4.08
2.07
1.00
1.05
1.06
2.06
1.41
4.30
2.73
1.77
0.68
3.99
2.73
3.50
3.46
2.28
3.10
f1 (ppm)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137.449
132.329
132.261
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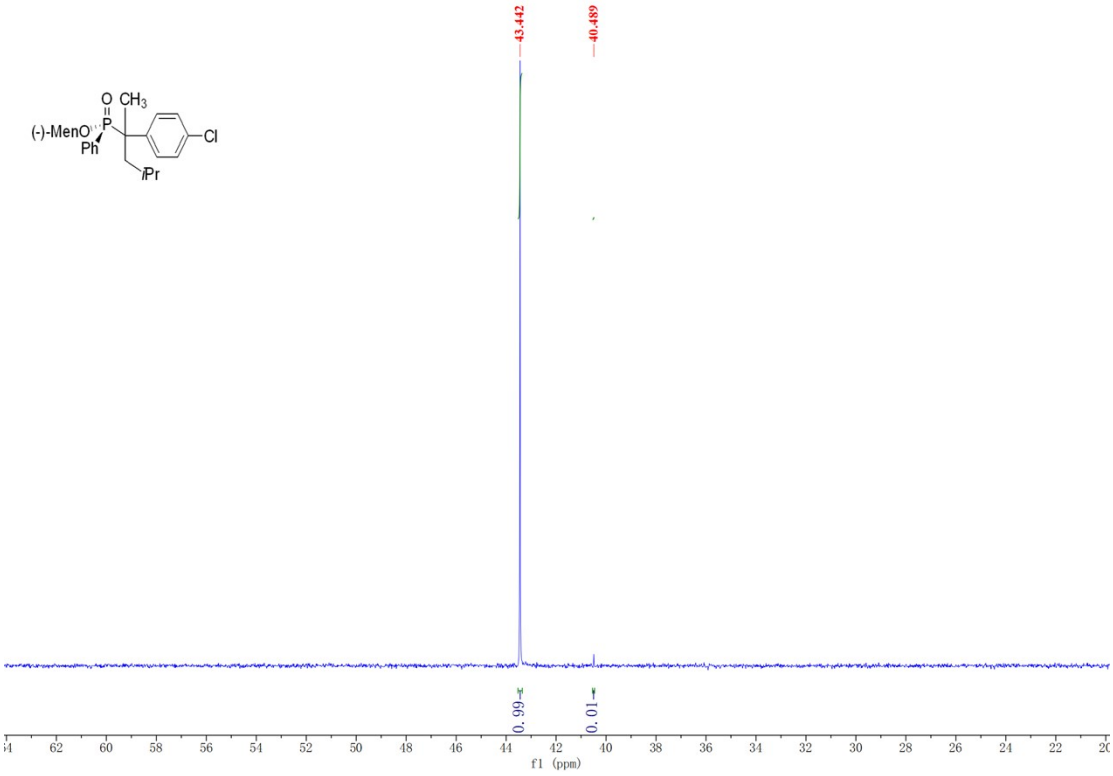
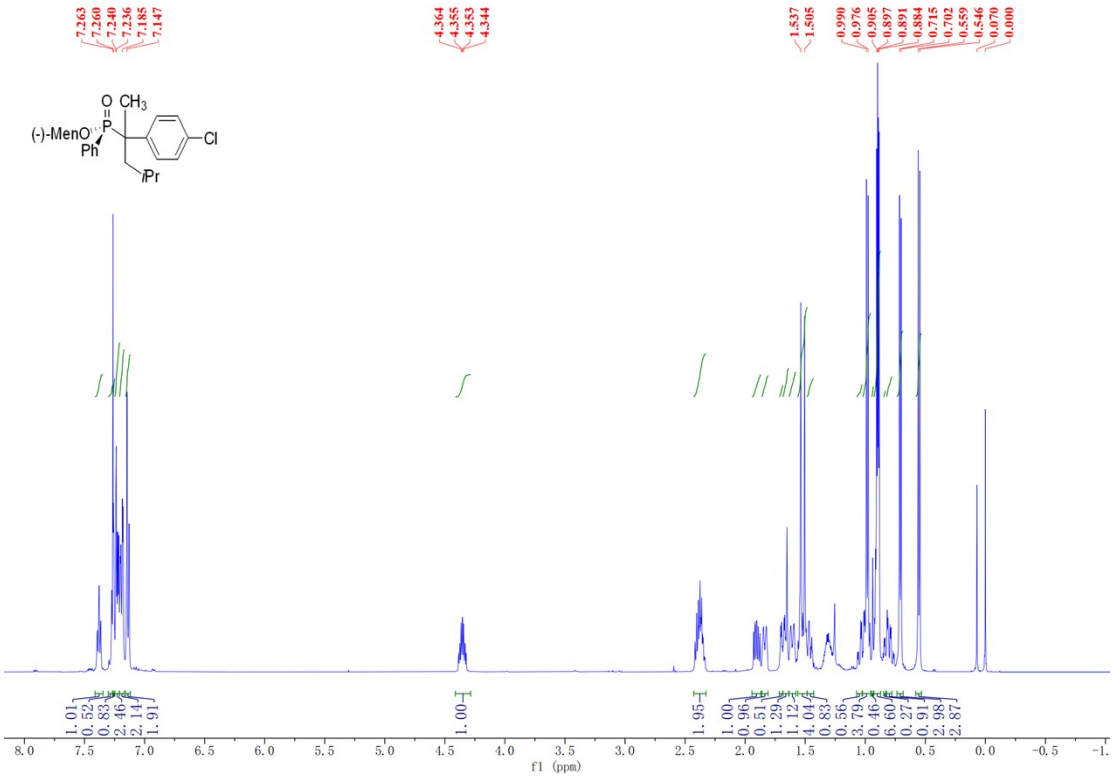
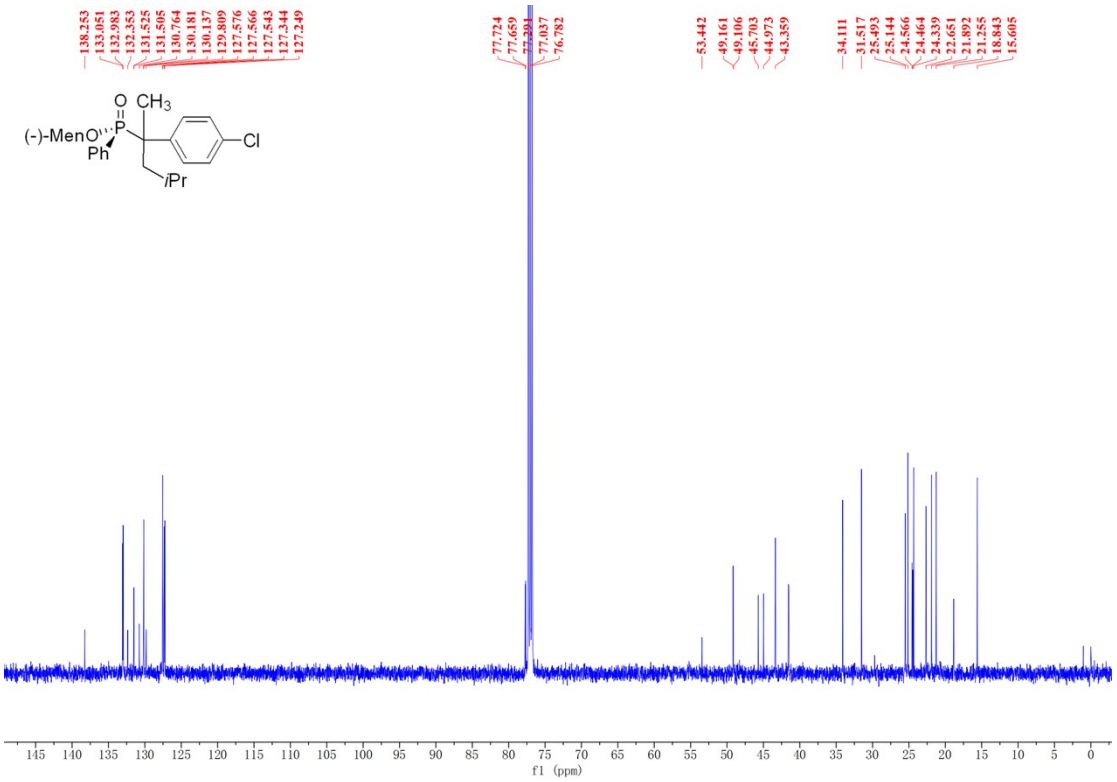
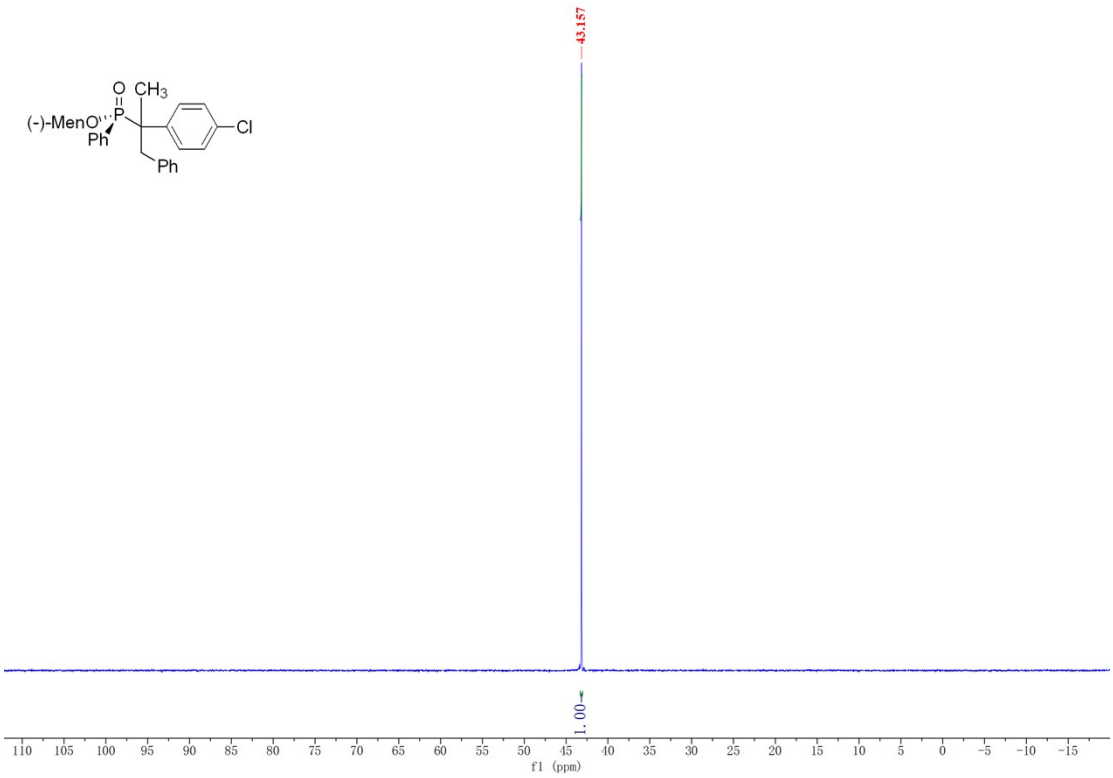
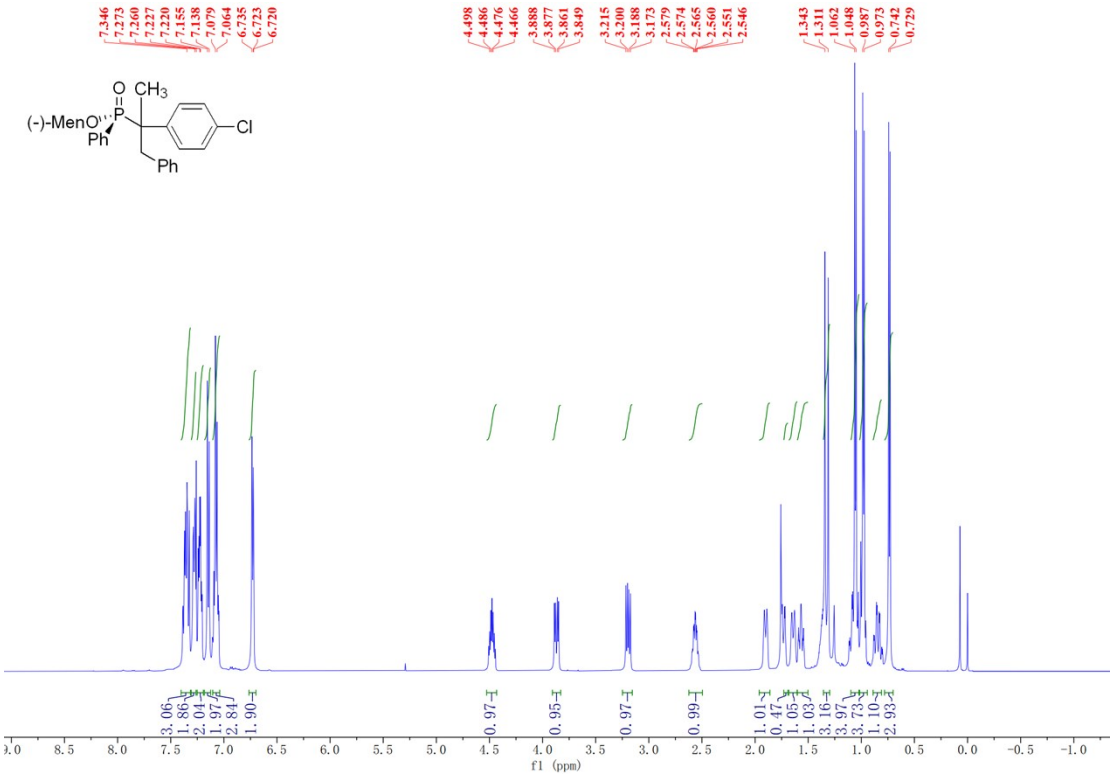
131.146
130.628
129.935
129.639
129.603
128.998
126.389
126.370
126.258
126.164
76.253
76.202
75.999
75.884
75.744
48.095
48.089
47.211
47.206
46.488
42.103
42.096
32.936
32.569
32.560
31.736
30.402
29.756
29.752
28.942
28.682
24.885
24.831
24.401
24.360
24.356
22.505
22.462
21.565
20.873
20.298
16.200
16.151
15.808
15.749
14.468
13.856
13.814
12.950
O
C4H9
(-)-MenO
P
Ph
Et
Cl
f1 (ppm)

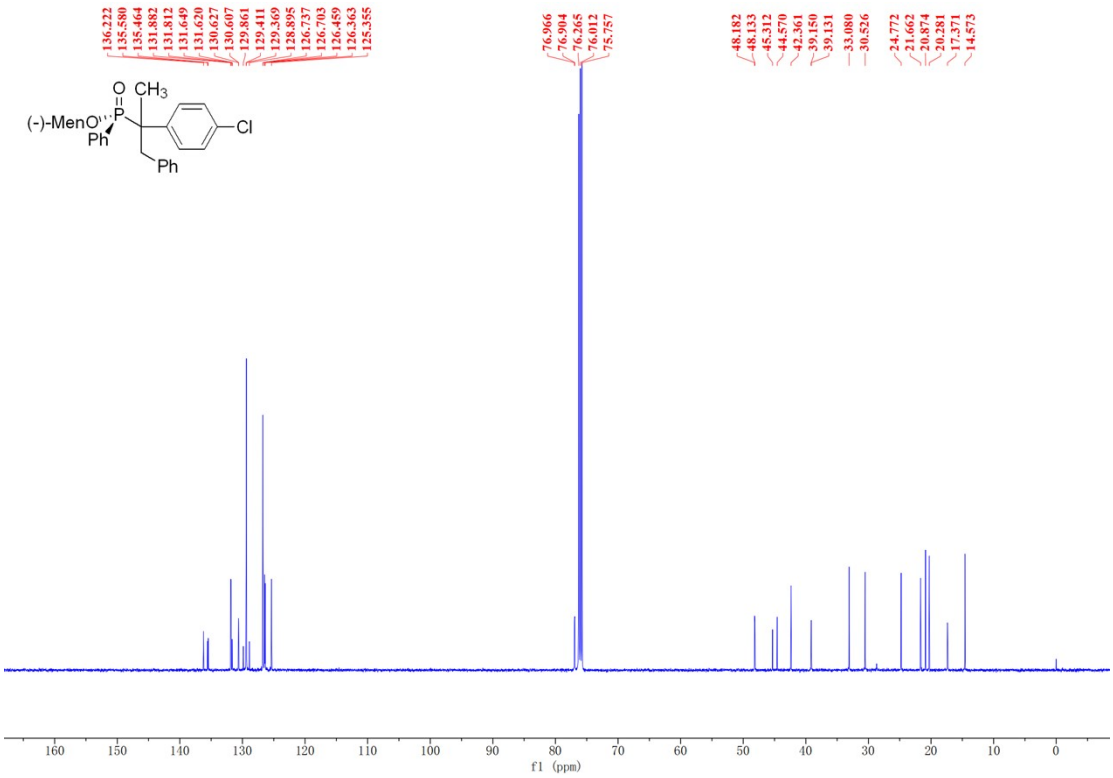

43.442
40.489
O
CH3
(-)-MenO
P
Ph
iPr
Cl
0.99
0.01
f1 (ppm)

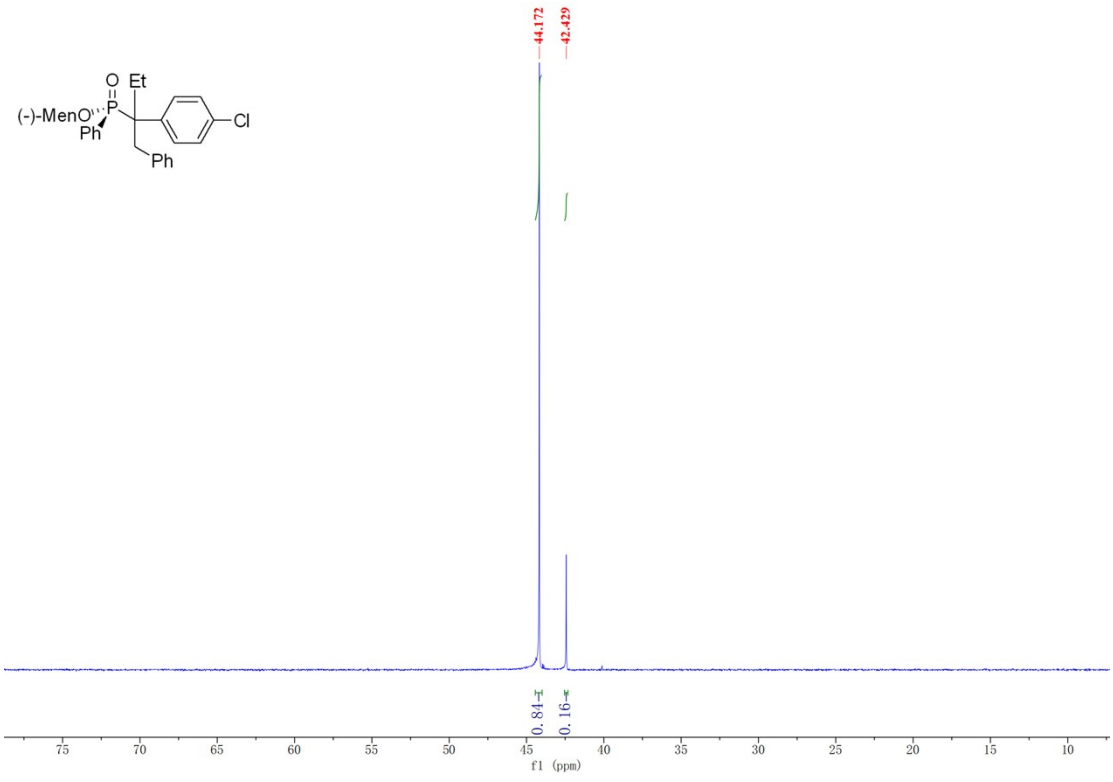

7.263
7.260
7.240
7.236
7.185
7.147
4.364
4.355
4.353
4.344
1.537
1.505
0.990
0.976
0.905
0.897
0.891
0.884
0.715
0.702
0.559
0.546
0.070
0.000
(-)-MenO
Ph
O
CH3
P
Cl
iPr
f1 (ppm)

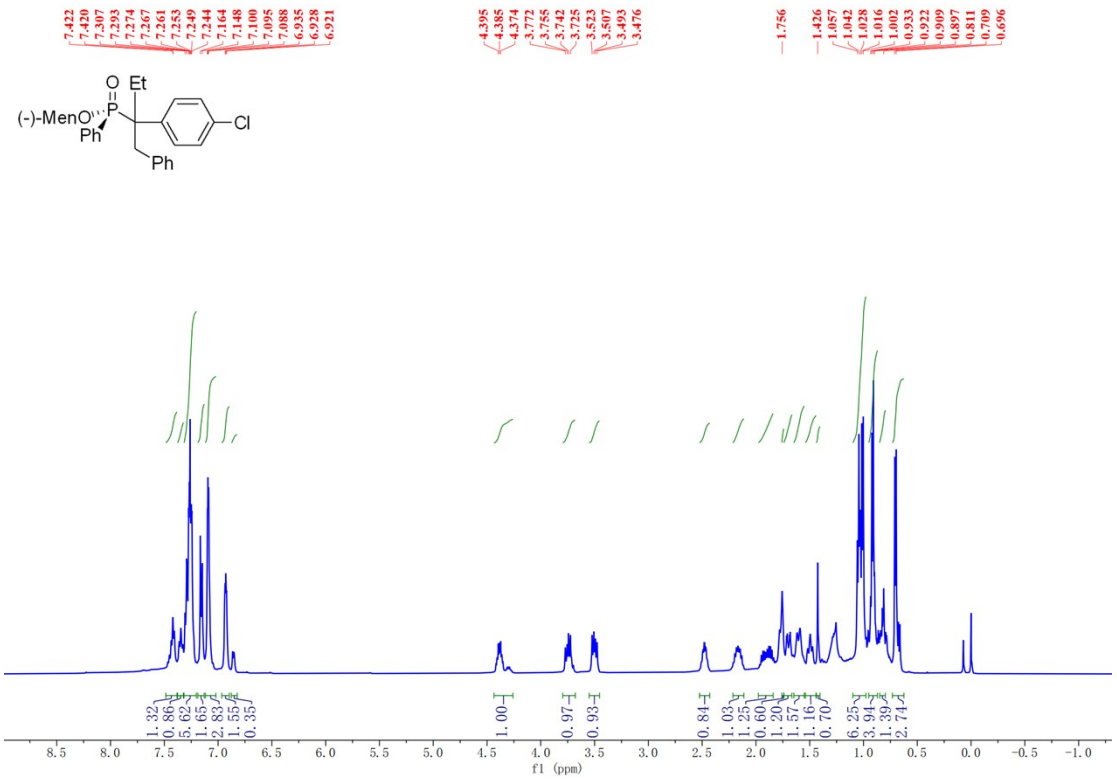

138.253
133.051
132.983
132.353
131.525
131.505
130.764
130.181
130.137
129.809
127.576
127.566
127.543
127.344
127.249
77.724
77.659
77.394
77.037
76.782
53.442
49.161
49.106
45.703
44.973
43.359
34.111
31.517
25.493
25.144
24.566
24.464
24.339
22.651
21.892
21.255
18.843
15.605
(-)-MenO
Ph
O
CH3
P
Cl
iPr
f1 (ppm)

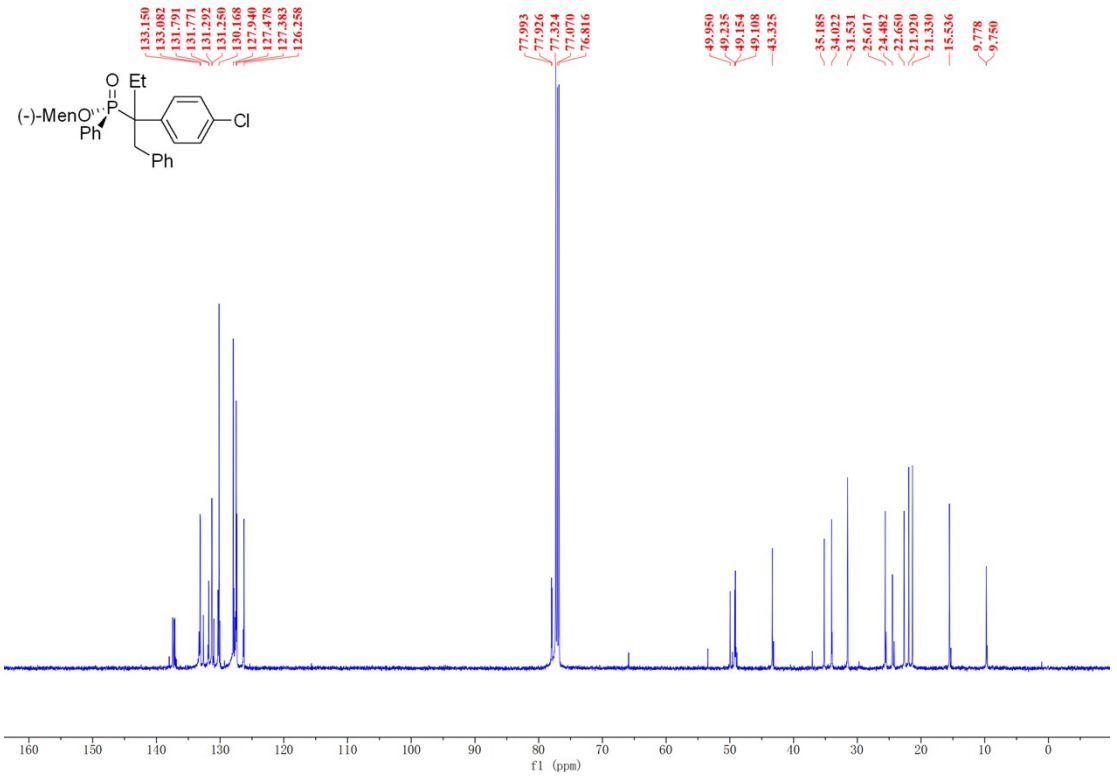

(-)-MenO
Ph
O
CH3
P
Cl
Ph
43.157
1.00
f1 (ppm)


(-)-MenO
Ph
O
CH3
P
Cl
Ph
7.346
7.273
7.260
7.227
7.220
7.155
7.138
7.079
7.064
6.735
6.723
6.720
4.498
4.486
4.476
4.466
3.888
3.877
3.861
3.849
3.215
3.200
3.188
3.173
2.579
2.574
2.565
2.560
2.551
2.546
1.343
1.311
1.062
1.048
0.987
0.973
0.742
0.729
3.06
1.86
2.04
1.97
2.84
1.90
0.97
0.95
0.97
0.99
1.01
0.47
1.05
3.16
3.97
3.73
1.10
2.93
f1 (ppm)


136.222
135.580
135.464
131.882
131.812
131.649
131.620
130.627
130.607
129.861
129.411
129.369
128.895
126.737
126.703
126.459
126.363
125.355
76.966
76.904
76.265
76.012
75.757
48.182
48.133
45.312
44.570
42.361
39.150
39.131
33.080
30.526
24.772
21.662
20.874
20.281
17.371
14.573
O
CH3
(-)-MenO
P
Ph
Cl
Ph
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


44.172
42.429
O
Et
(-)-MenO
P
Ph
Cl
Ph
0.84
0.16
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)


7.422
7.420
7.307
7.293
7.274
7.267
7.261
7.253
7.249
7.244
7.164
7.148
7.100
7.095
7.088
6.935
6.928
6.921
4.395
4.385
4.374
3.772
3.755
3.742
3.725
3.523
3.507
3.493
3.476
1.756
1.426
1.057
1.042
1.028
1.016
1.002
0.933
0.922
0.909
0.897
0.811
0.709
0.696
O
Et
(-)-MenO
P
Ph
Cl
Ph
1.32
0.86
5.62
1.65
2.83
1.55
0.35
1.00
0.97
0.93
0.84
1.03
1.25
0.60
1.20
1.57
1.16
0.70
6.25
3.94
1.39
2.74
f1 (ppm)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133.082
131.791
131.771
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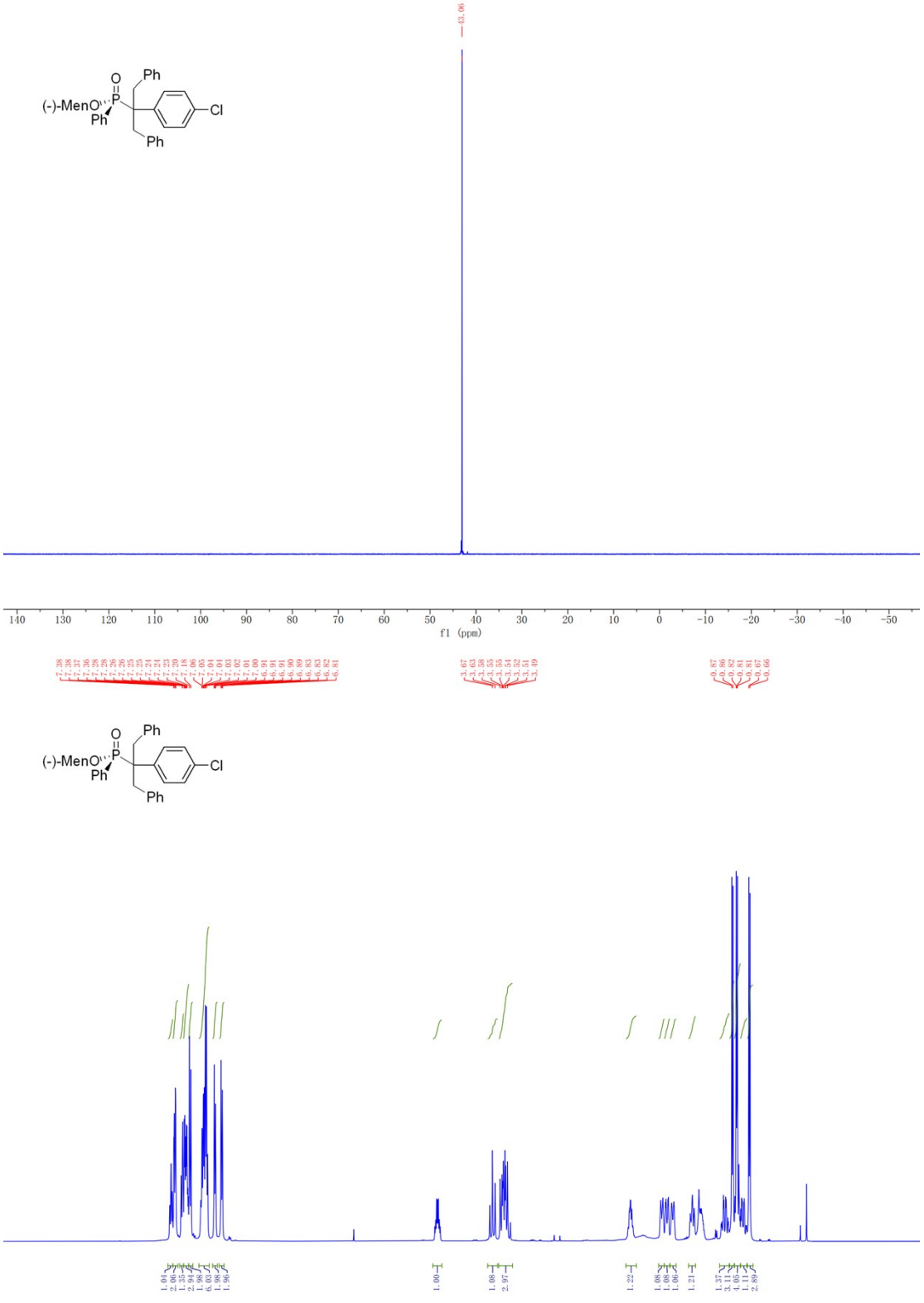
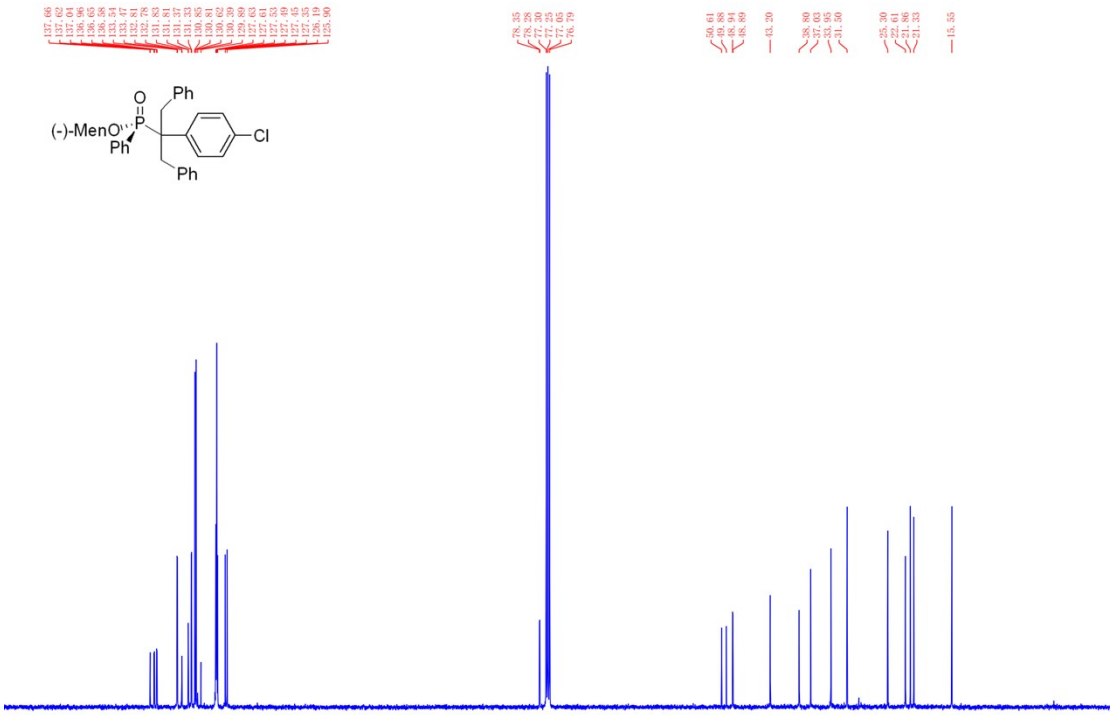
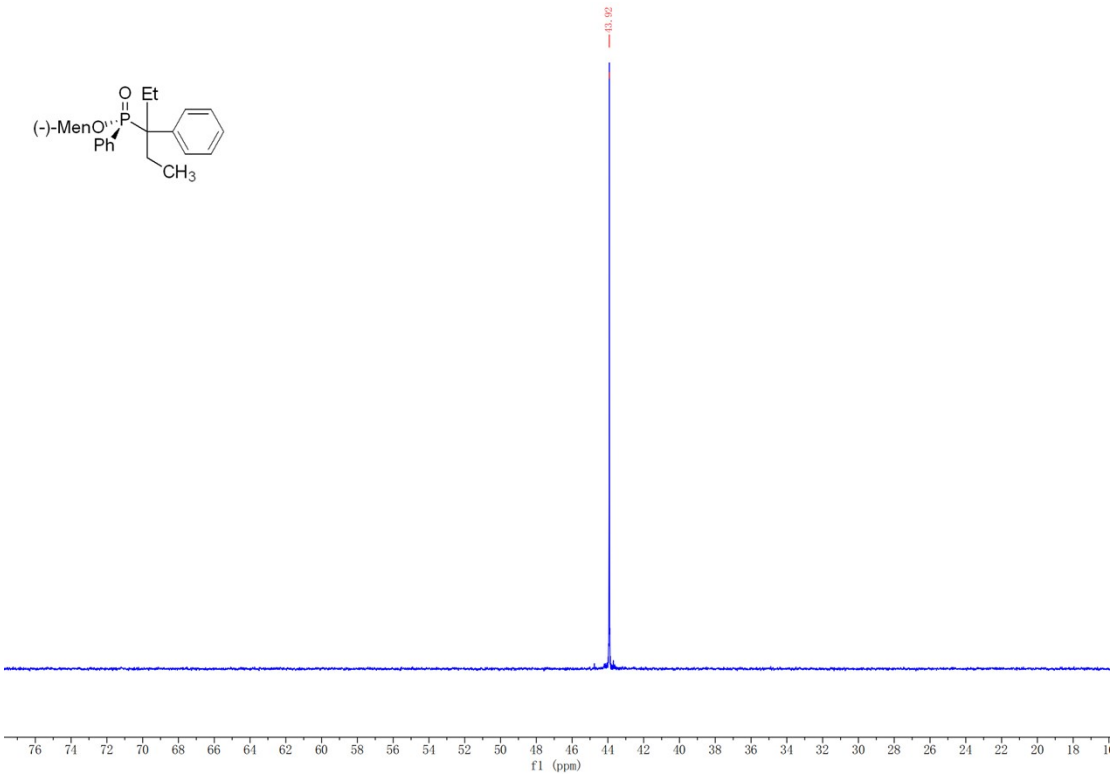
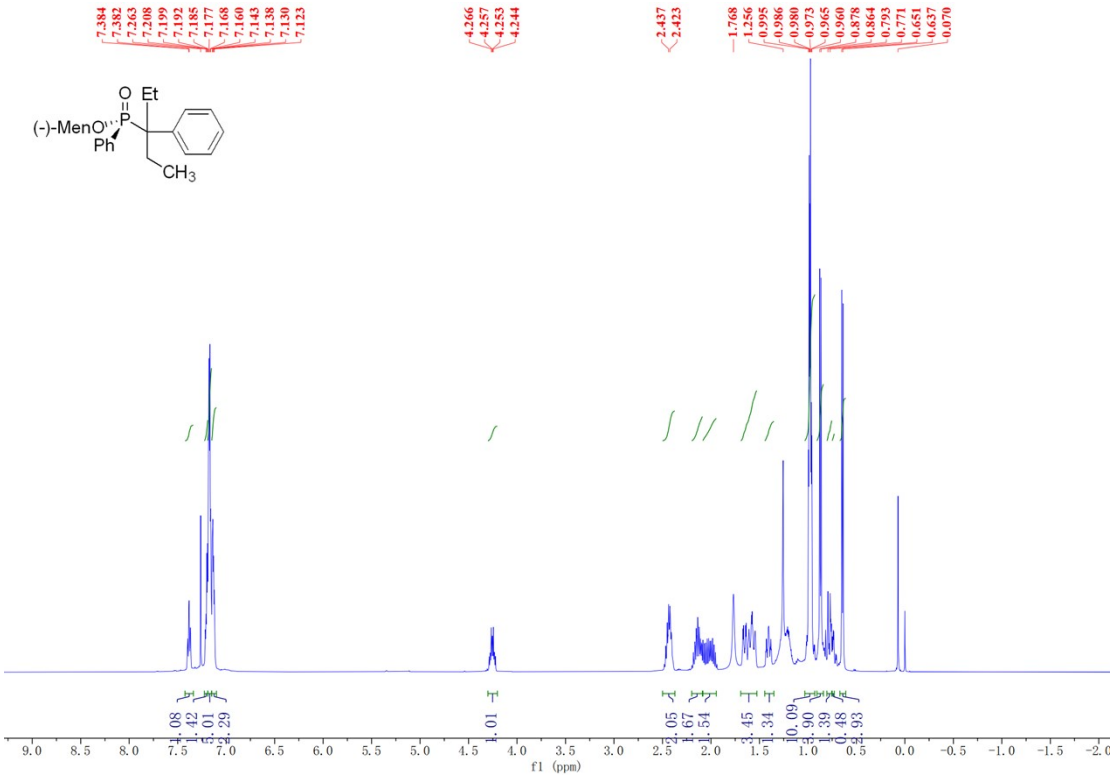
131.250
130.168
127.940
127.478
127.383
126.258
77.993
77.926
77.324
77.070
76.816
49.950
49.235
49.154
49.108
43.325
35.185
34.022
31.531
25.617
24.482
22.650
21.920
21.330
15.536
9.778
9.750
O
Et
(-)-MenO
P
Ph
Cl
Ph
f1 (ppm)


(-)-MenO
P
O
Ph
Ph
Ph
Cl
13.06
f1 (ppm)


137.66
137.62
131.64
136.96
136.65
136.58
133.54
133.47
132.78
131.83
131.81
131.37
131.33
130.85
130.81
130.62
130.39
129.89
127.61
127.61
127.53
127.49
127.45
127.35
126.19
125.90
78.35
78.28
77.30
77.25
77.05
76.79
50.61
49.88
48.94
48.69
43.39
38.80
37.03
34.95
31.50
25.30
22.61
21.86
21.33
15.55
O
P
(-)-MenO
Ph
Ph
Ph
Cl


43.92
O
P
Et
(-)-MenO
Ph
CH3
76
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
f1 (ppm)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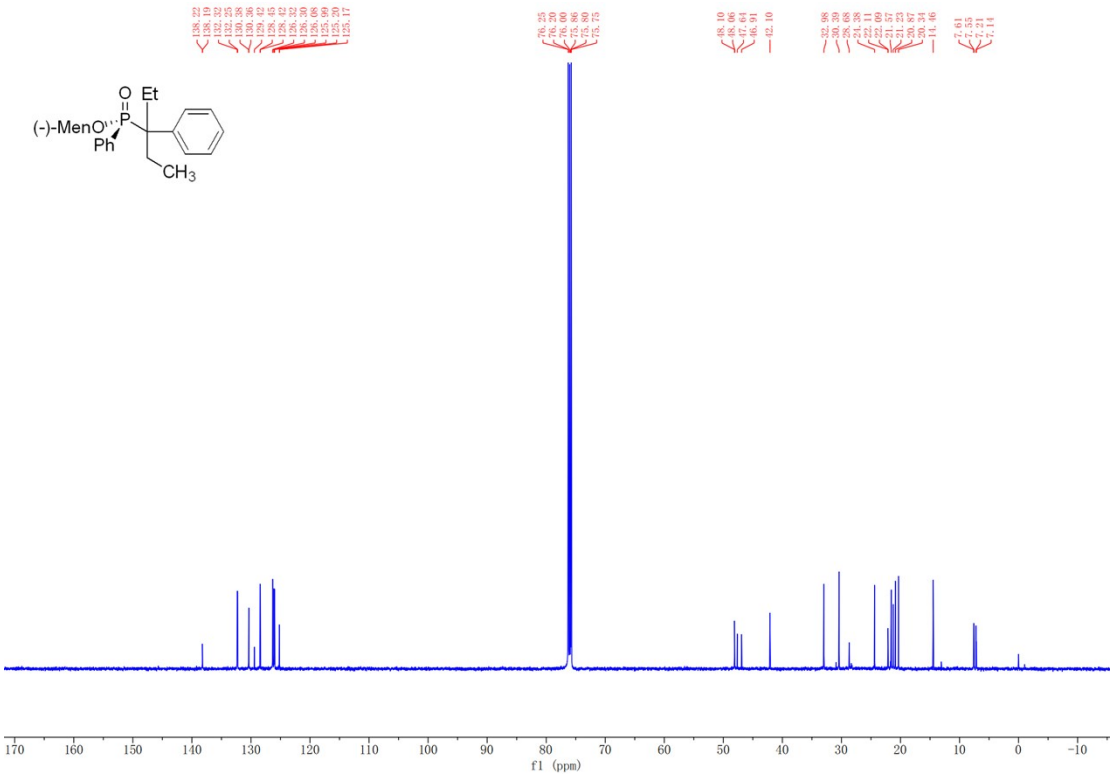
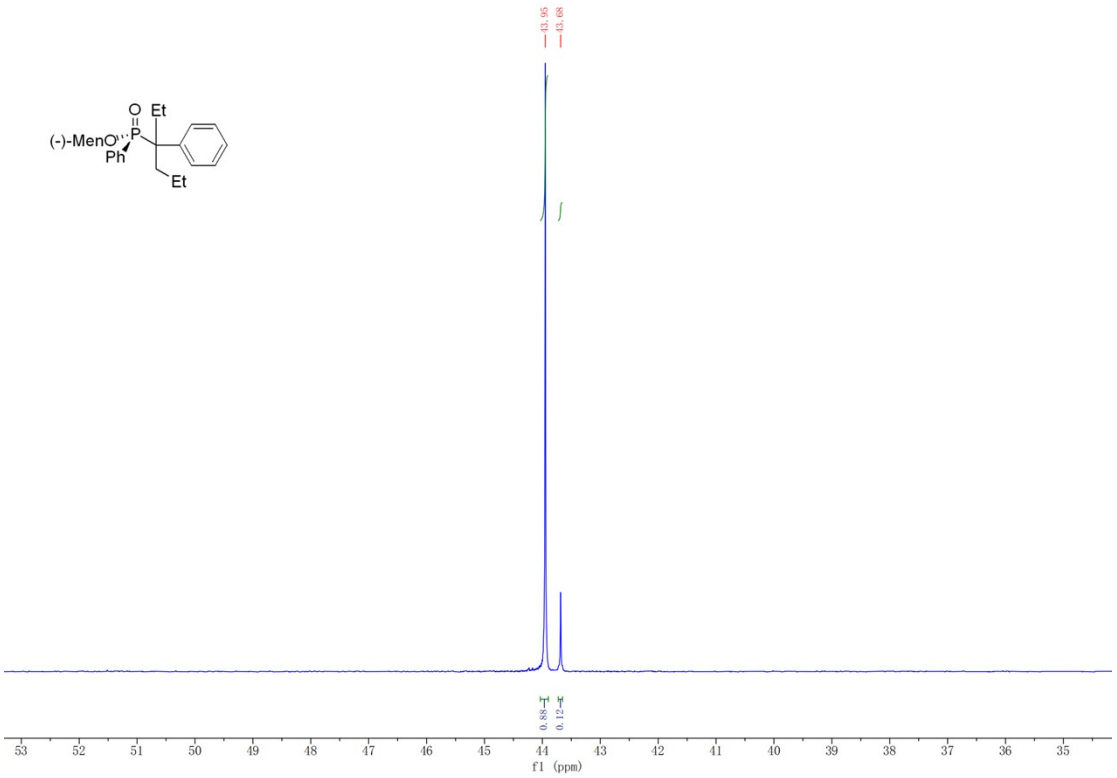
7.192
7.185
7.177
7.168
7.160
7.143
7.138
7.130
7.123
4.266
4.257
4.253
4.244
2.437
2.423
1.768
1.256
0.995
0.986
0.980
0.973
0.965
0.960
0.878
0.864
0.793
0.771
0.651
0.637
0.070
O
Et
(-)-MenO
P
Ph
CH3
f1 (ppm)


O
Et
(-)-MenO
P
Ph
CH3
f1 (ppm)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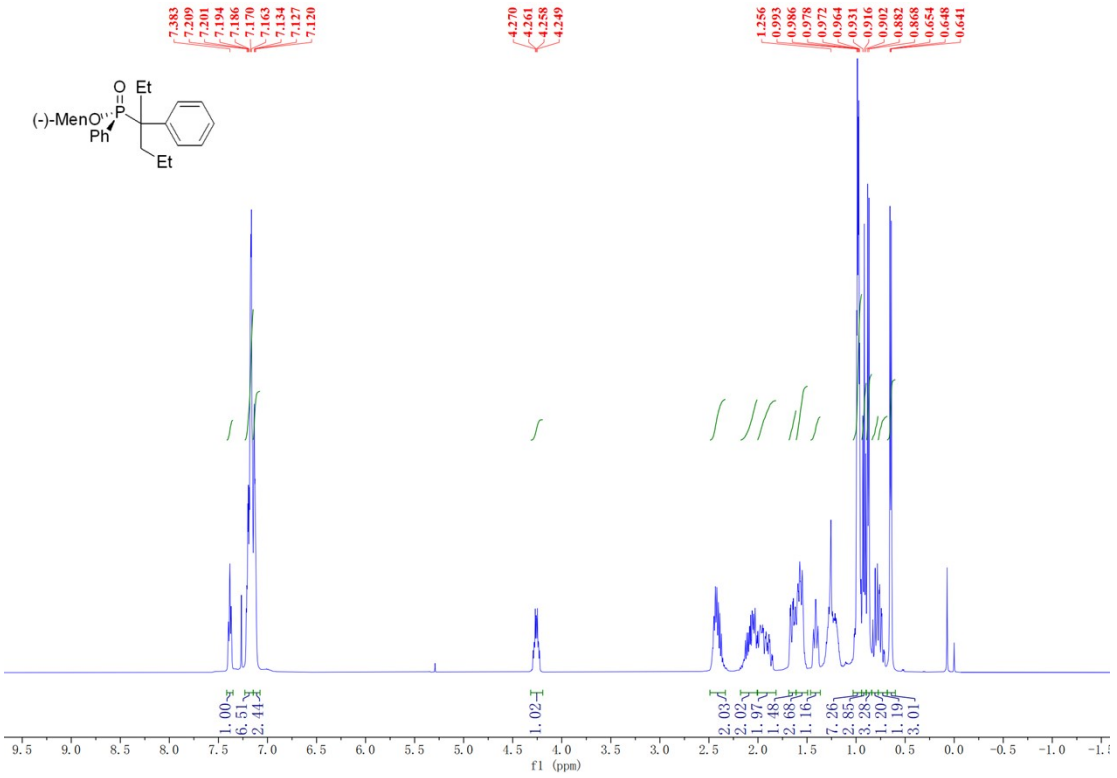
P
O
Et
Ph
Et
13.95
13.68
0.88
0.12
f1 (ppm)


(-)-MenO
P
O
Et
Ph
Et
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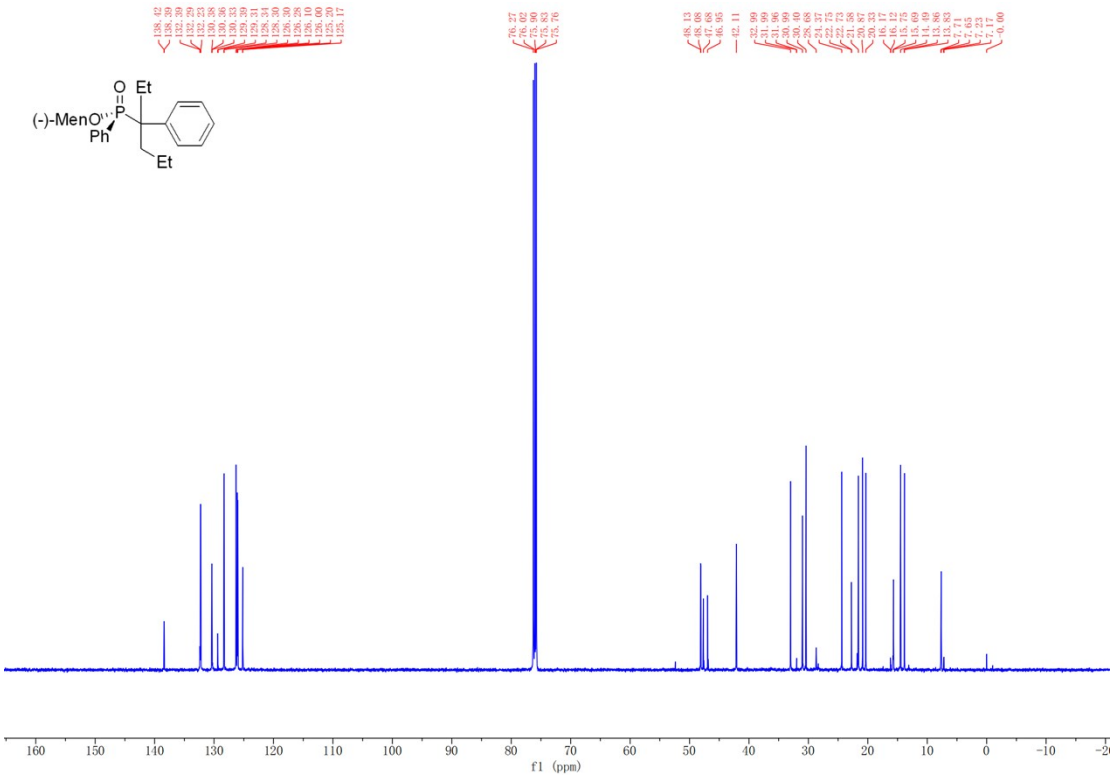
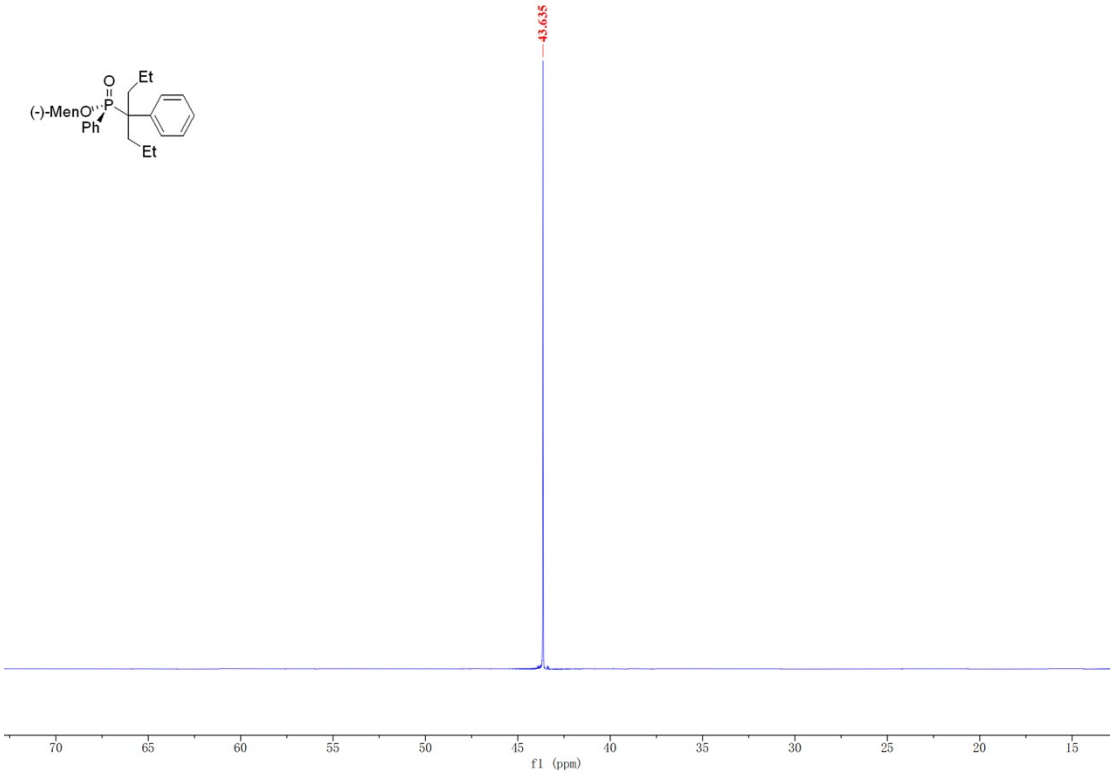
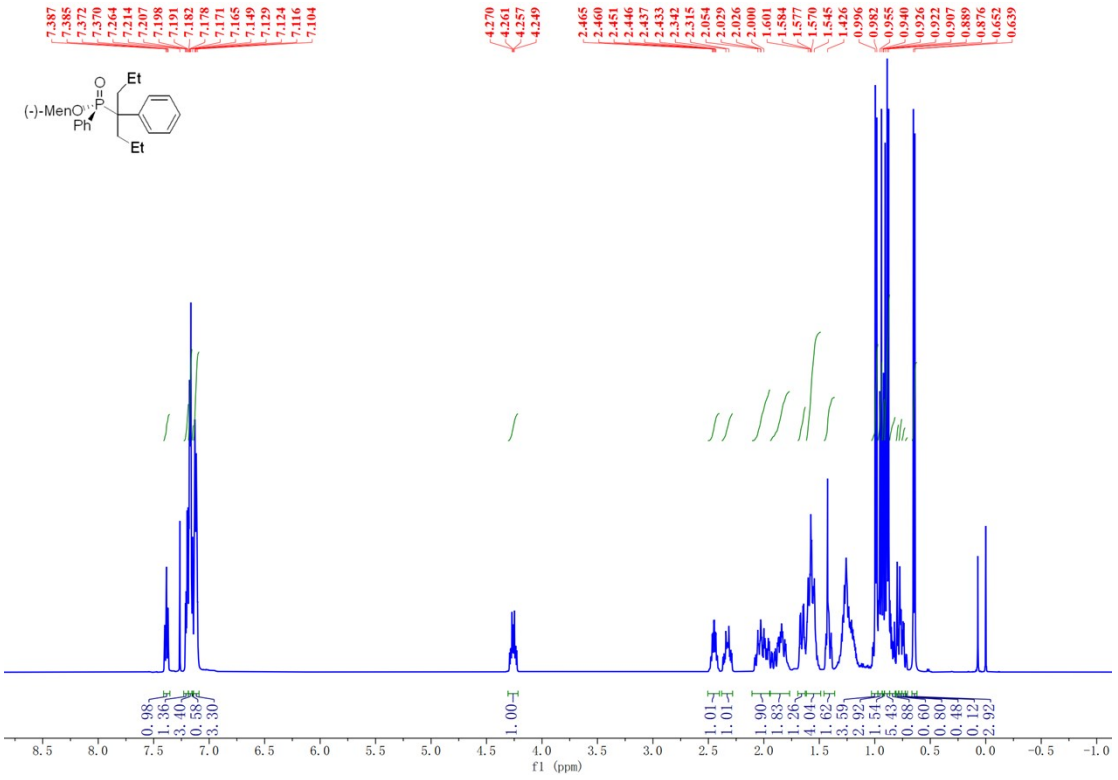
7.201
7.194
7.186
7.170
7.163
7.134
7.127
7.120
4.270
4.261
4.258
4.249
1.256
0.993
0.986
0.978
0.972
0.964
0.931
0.916
0.902
0.882
0.868
0.654
0.648
0.641
1.00
6.51
2.44
1.02
2.03
2.02
1.97
1.48
2.68
1.16
7.26
2.85
3.28
1.20
1.19
3.01
f1 (ppm)


(-)-MenO
Ph
O
P
Et
Et
f1 (ppm)


43.635
(-)-MenO
Ph
O
P
Et
Et
f1 (ppm)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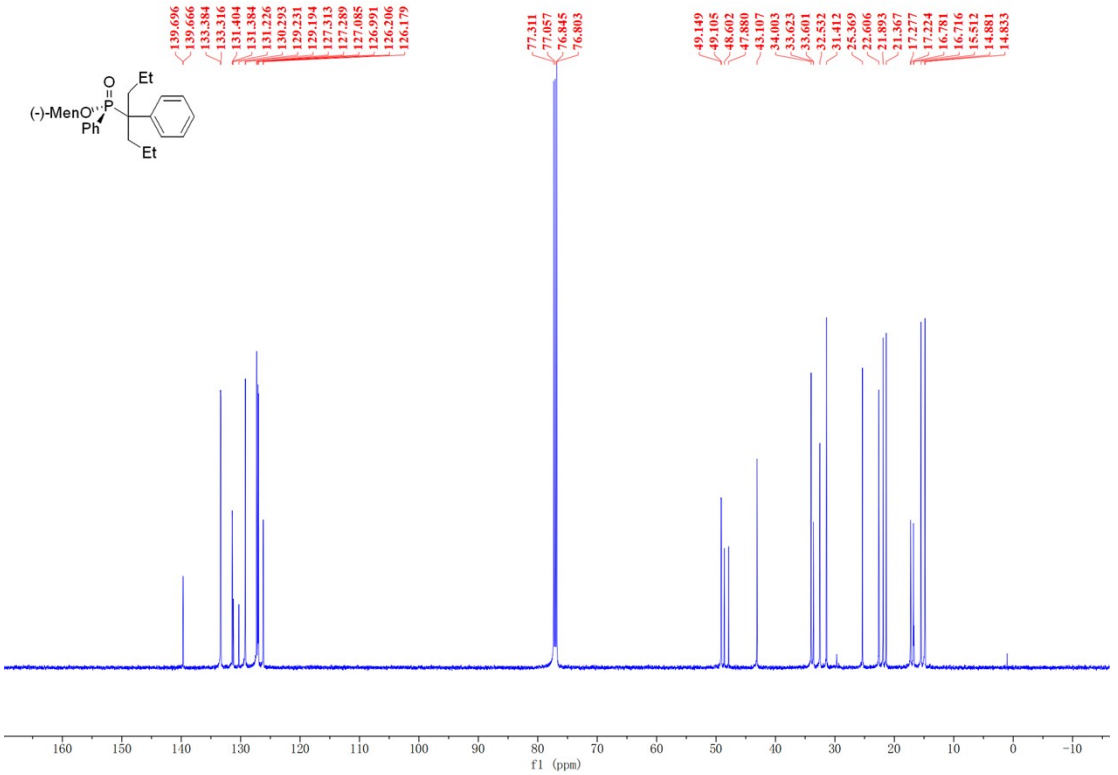
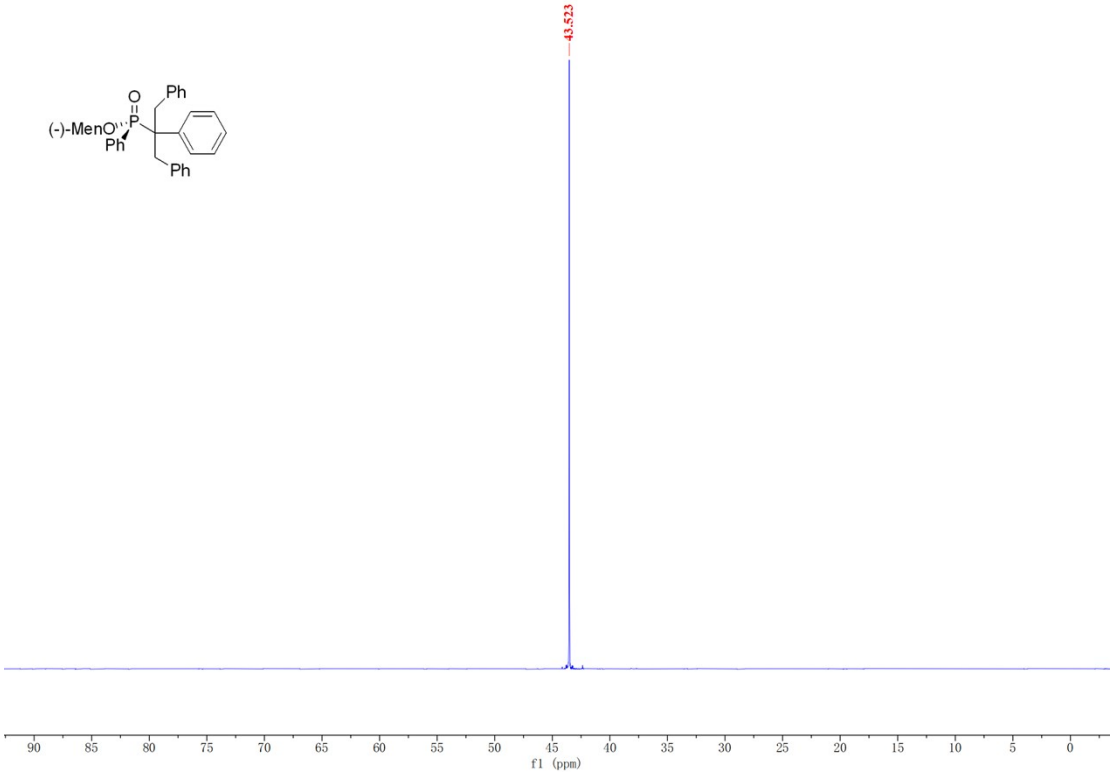
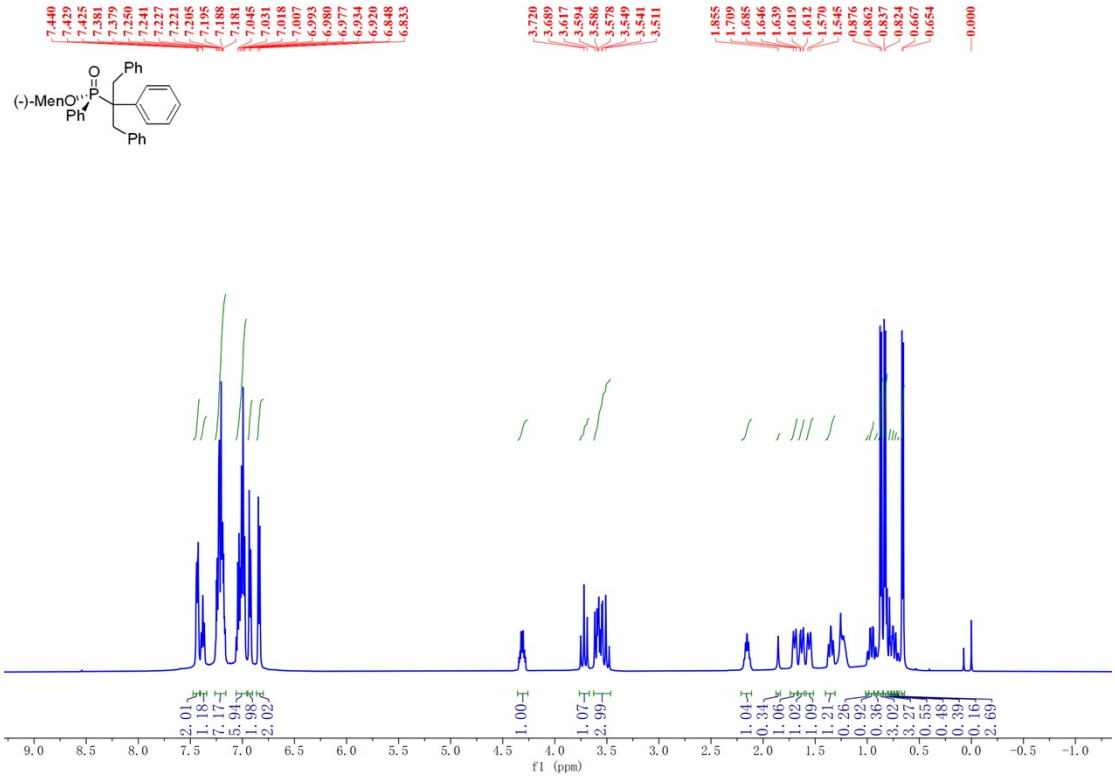
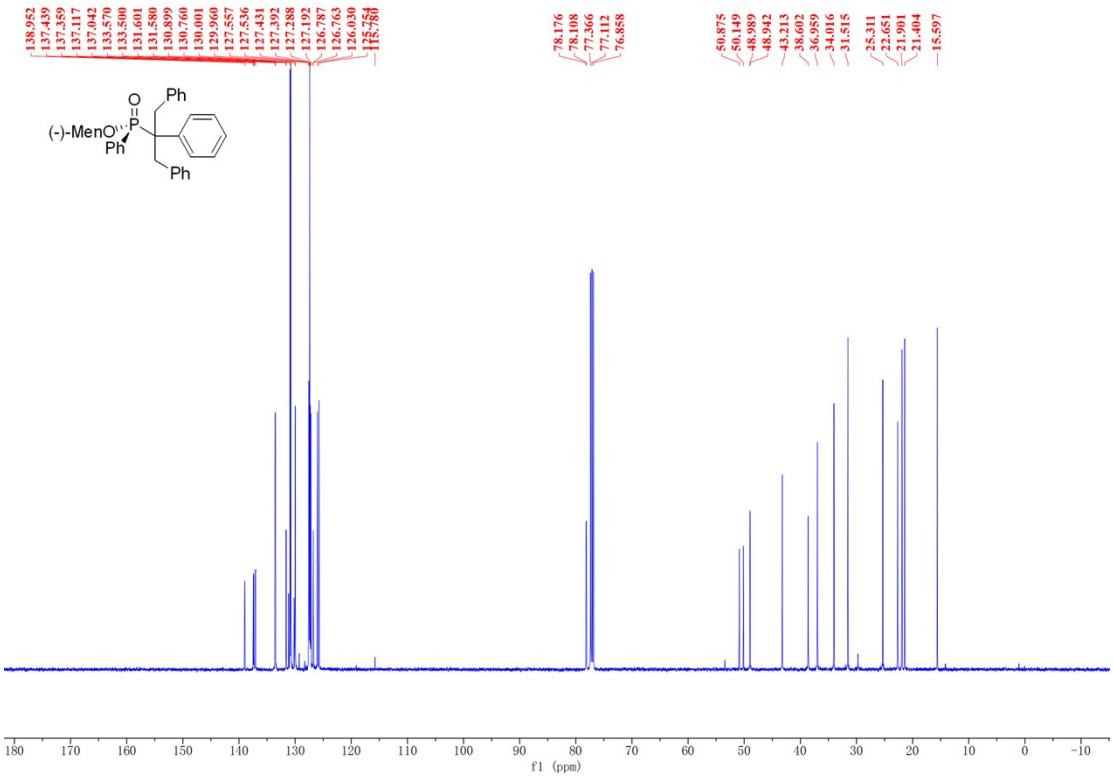
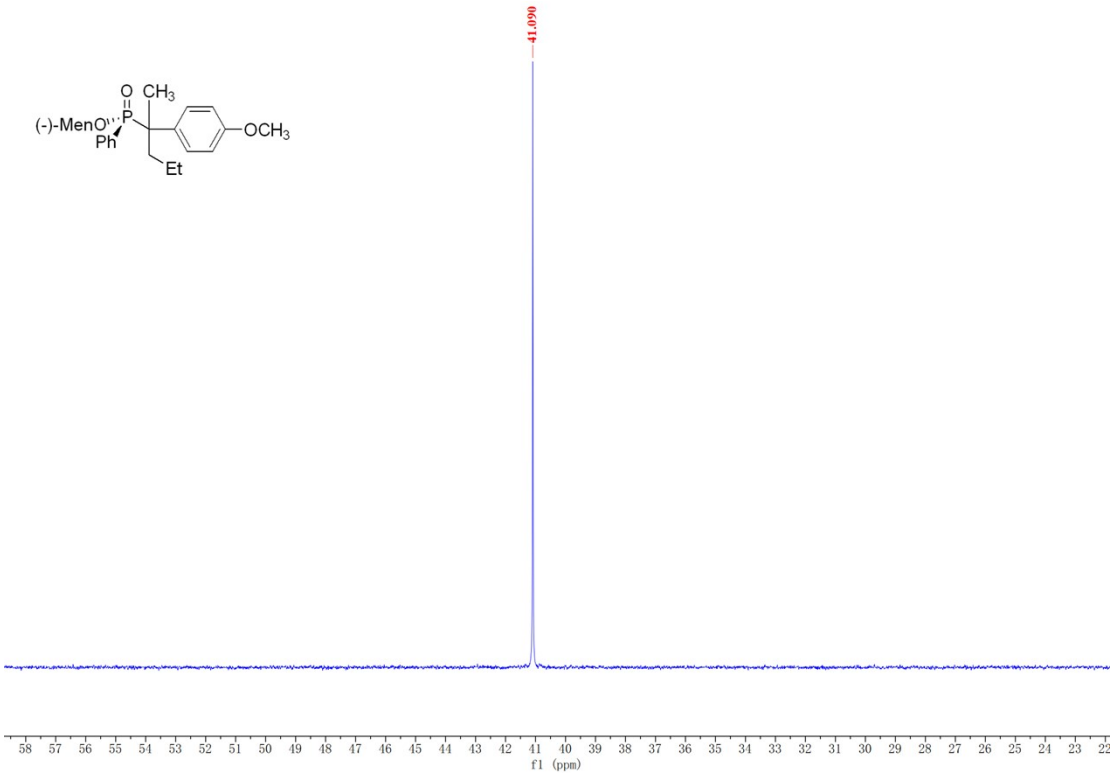
7.372
7.370
7.264
7.214
7.207
7.198
7.191
7.182
7.178
7.171
7.165
7.149
7.129
7.124
7.116
7.104
4.270
4.261
4.257
4.249
2.465
2.460
2.451
2.446
2.437
2.433
2.342
2.315
2.054
2.029
2.026
2.000
1.601
1.584
1.577
1.570
1.545
1.426
0.996
0.982
0.955
0.940
0.926
0.922
0.907
0.889
0.876
0.652
0.639
(-)-MenO
Ph
Et
Et
0.98
1.36
3.40
0.58
3.30
1.00
1.01
1.01
1.90
1.83
1.26
4.04
1.62
3.59
2.92
5.43
0.88
0.60
0.80
0.48
0.12
2.92
f1 (ppm)

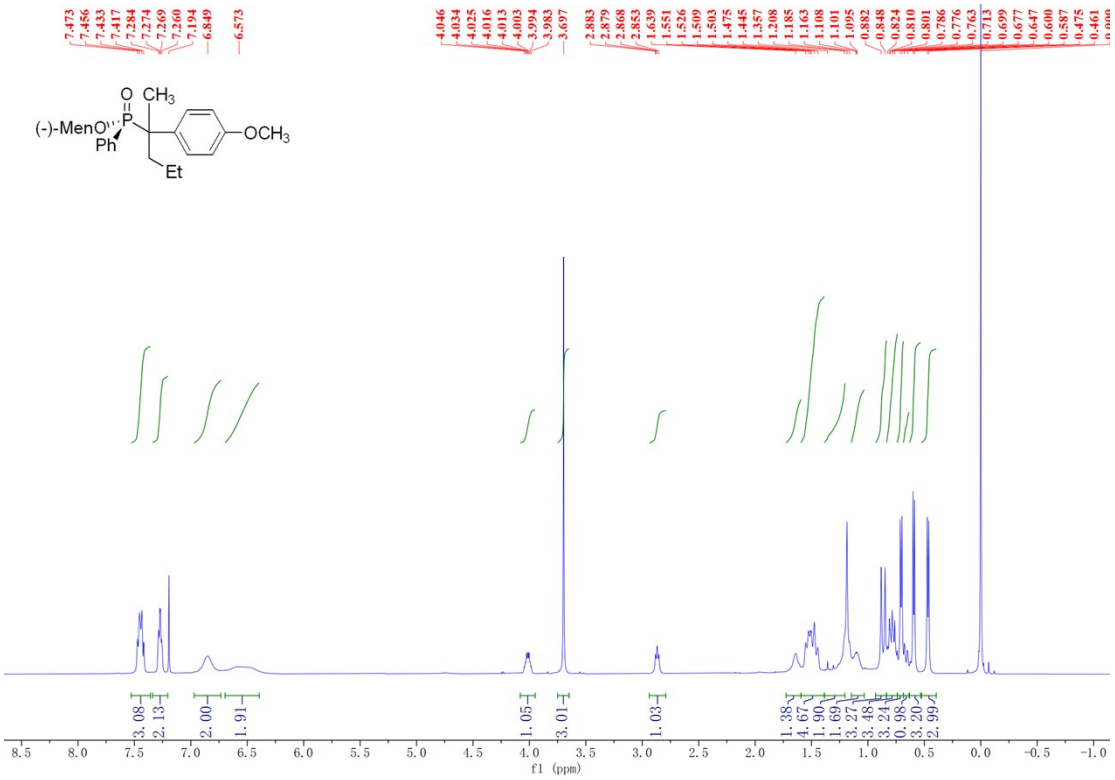

139.696
139.666
133.384
133.316
131.404
131.384
131.226
130.293
129.231
129.194
127.313
127.289
127.085
126.991
126.206
126.179
77.311
77.057
76.845
76.803
49.149
49.105
48.602
47.880
43.107
34.003
33.623
33.601
32.532
31.412
25.369
22.606
21.893
21.367
17.277
17.224
16.781
16.716
15.512
14.881
14.833
(-)-MenO
Ph
Et
Et
f1 (ppm)

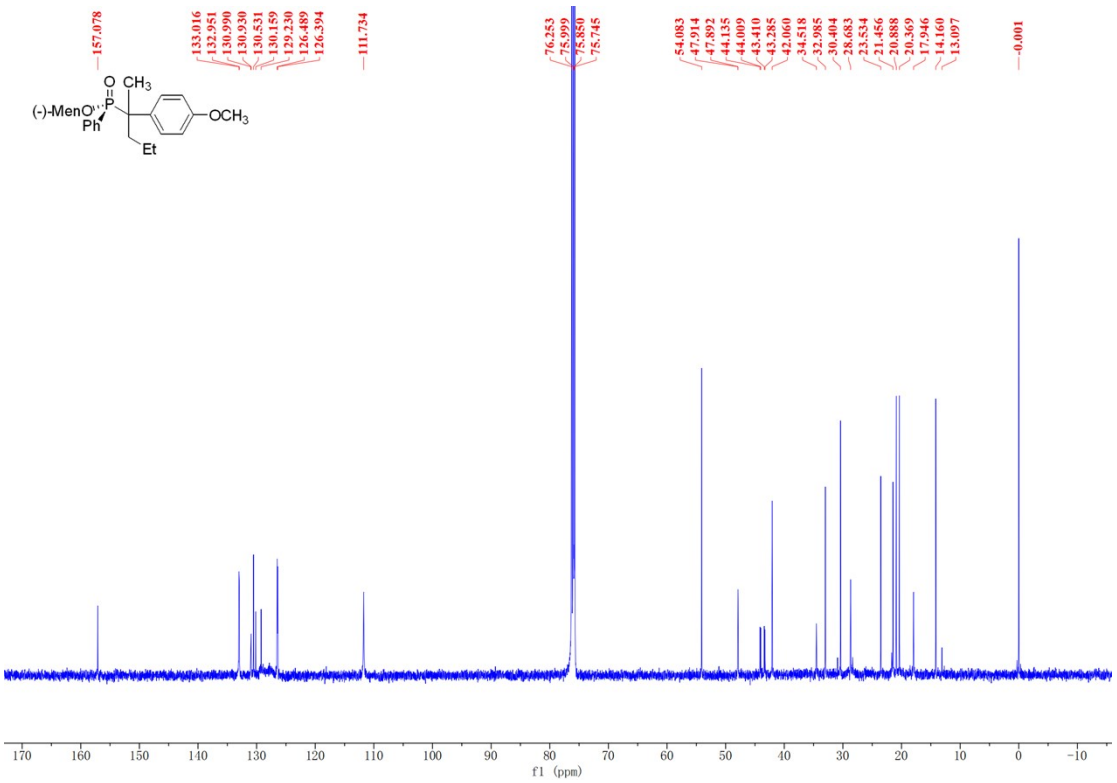

43.523
(-)-MenO
Ph
Ph
Ph
f1 (ppm)

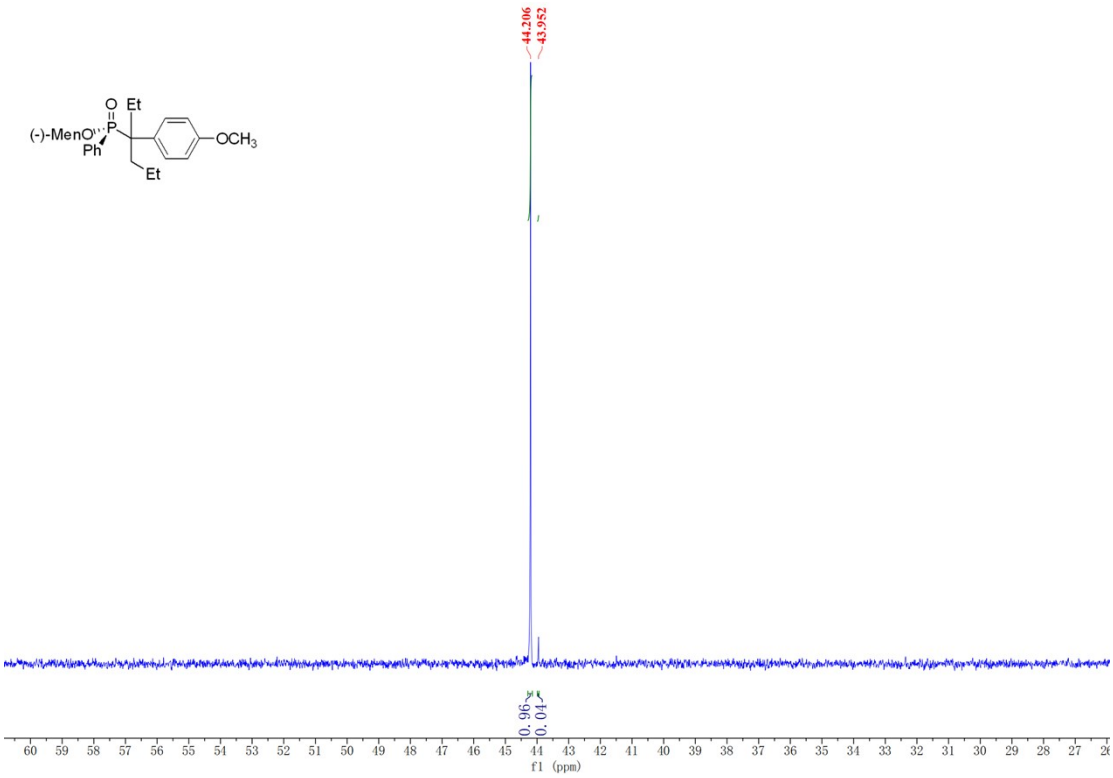

7.440
7.429
7.425
7.381
7.379
7.250
7.241
7.227
7.221
7.205
7.195
7.188
7.181
7.045
7.031
7.018
7.007
6.993
6.980
6.977
6.934
6.920
6.848
6.833
3.720
3.689
3.617
3.594
3.586
3.578
3.549
3.541
3.511
1.855
1.709
1.685
1.646
1.639
1.619
1.612
1.570
1.545
0.876
0.862
0.837
0.824
0.667
0.654
0.000
(-)-MenO
Ph
Ph
Ph
2.01
1.18
7.17
5.94
1.98
2.02
1.00
1.07
2.99
1.04
0.34
1.06
1.02
1.09
1.21
0.26
0.92
0.36
3.02
3.27
0.55
0.48
0.39
0.16
2.69
f1 (ppm)

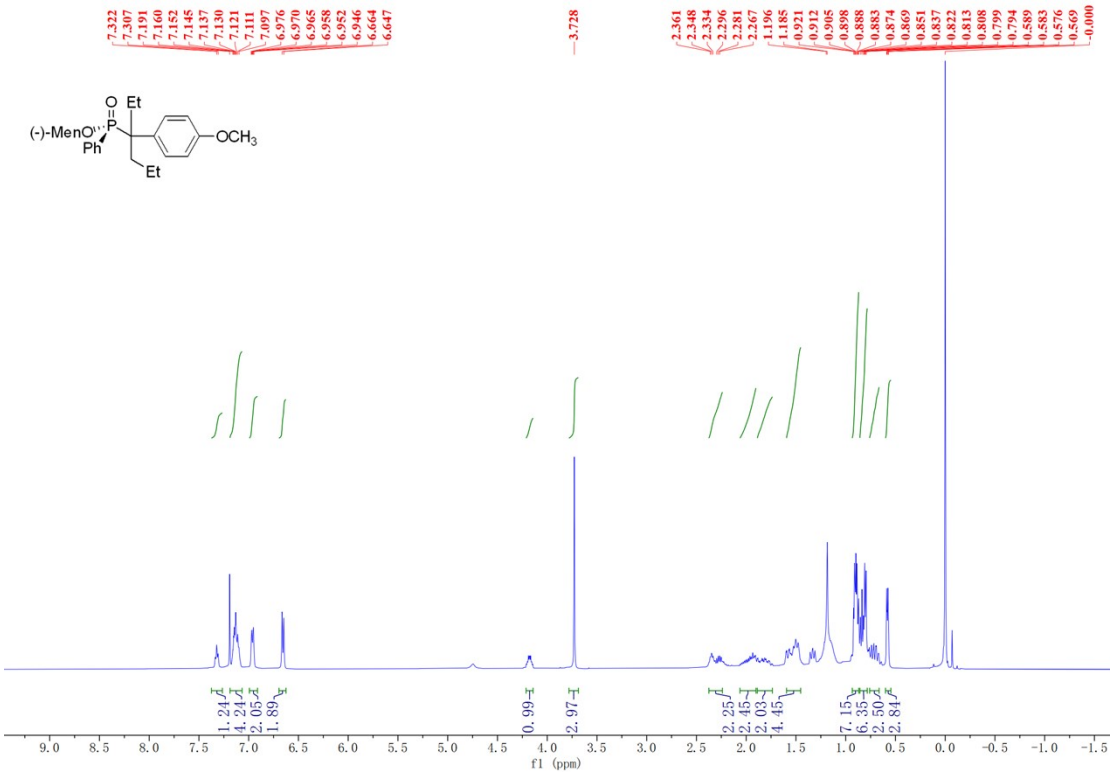

138.952
137.439
137.359
137.117
137.042
133.570
133.500
131.601
131.580
130.899
130.760
130.001
129.960
127.557
127.536
127.431
127.392
127.288
127.192
126.787
126.763
126.030
78.176
78.108
77.366
77.112
76.858
50.875
50.149
48.989
48.942
43.213
38.602
36.959
34.016
31.515
25.311
22.651
21.901
21.404
15.597
O
Ph
(-)-MenO
P
Ph
Ph
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

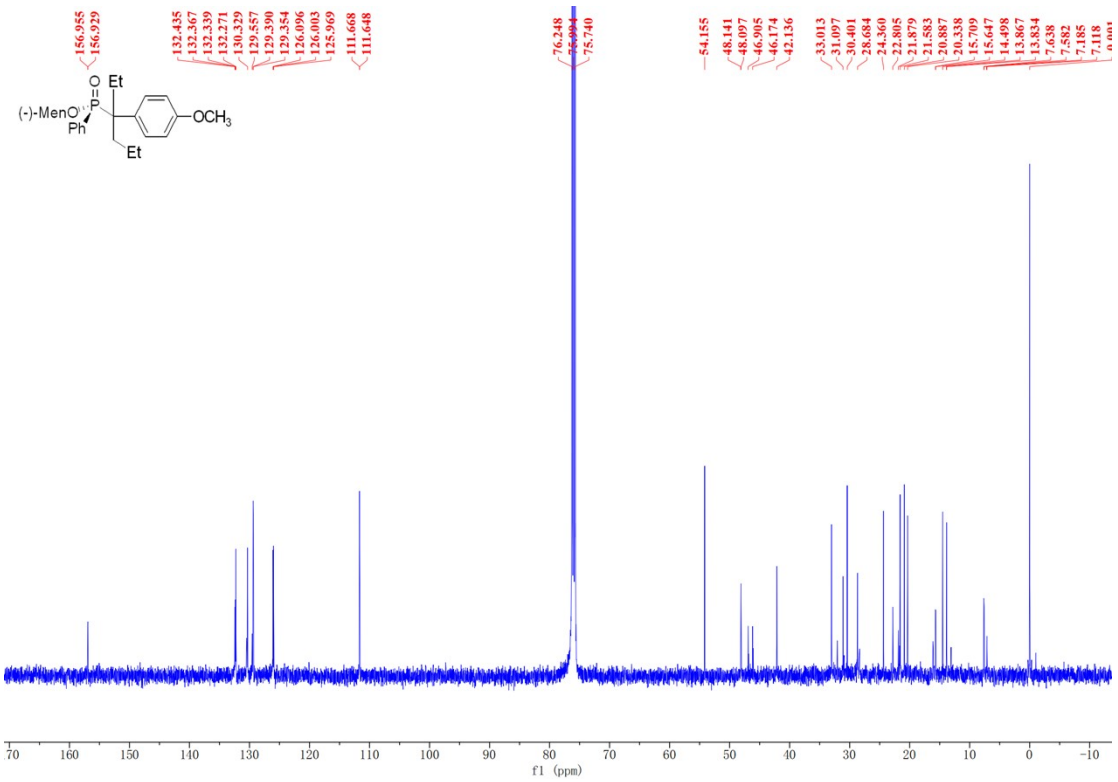

41.090
O
CH3
(-)-MenO
P
Ph
OCH3
Et
58 57 56 55 54 53 52 51 50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22
f1 (ppm)

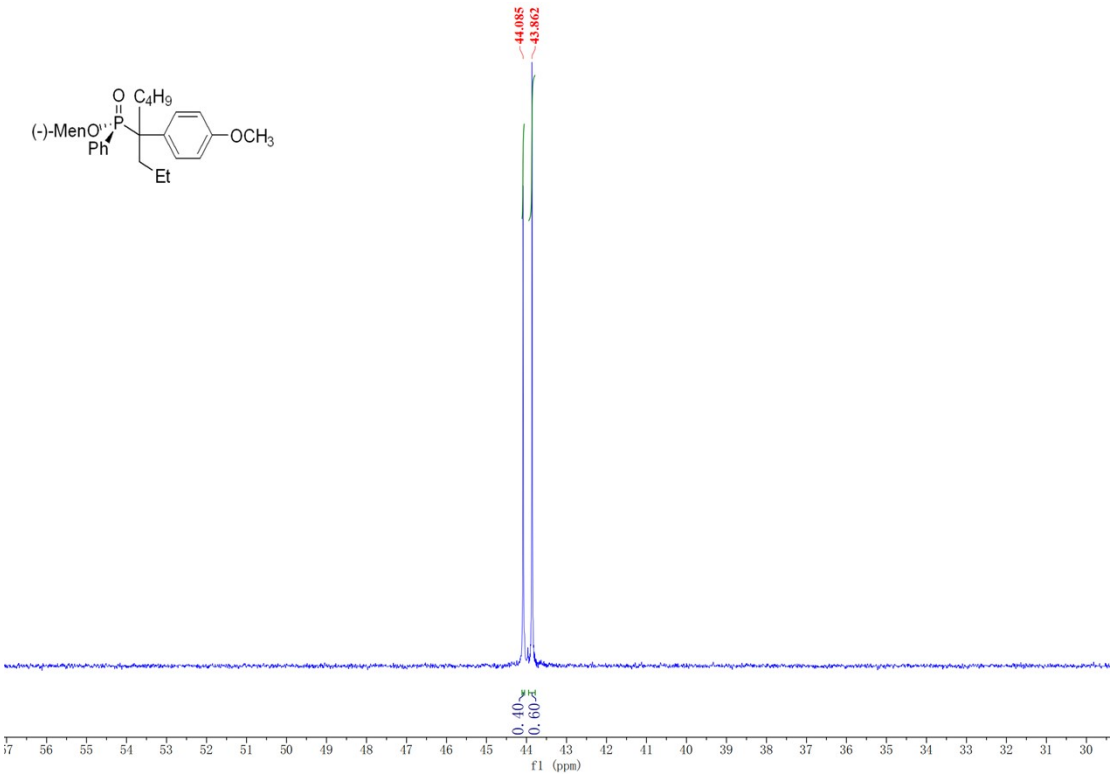

(-)-MenO
P
O
CH3
Ph
Et
OCH3
f1 (ppm)

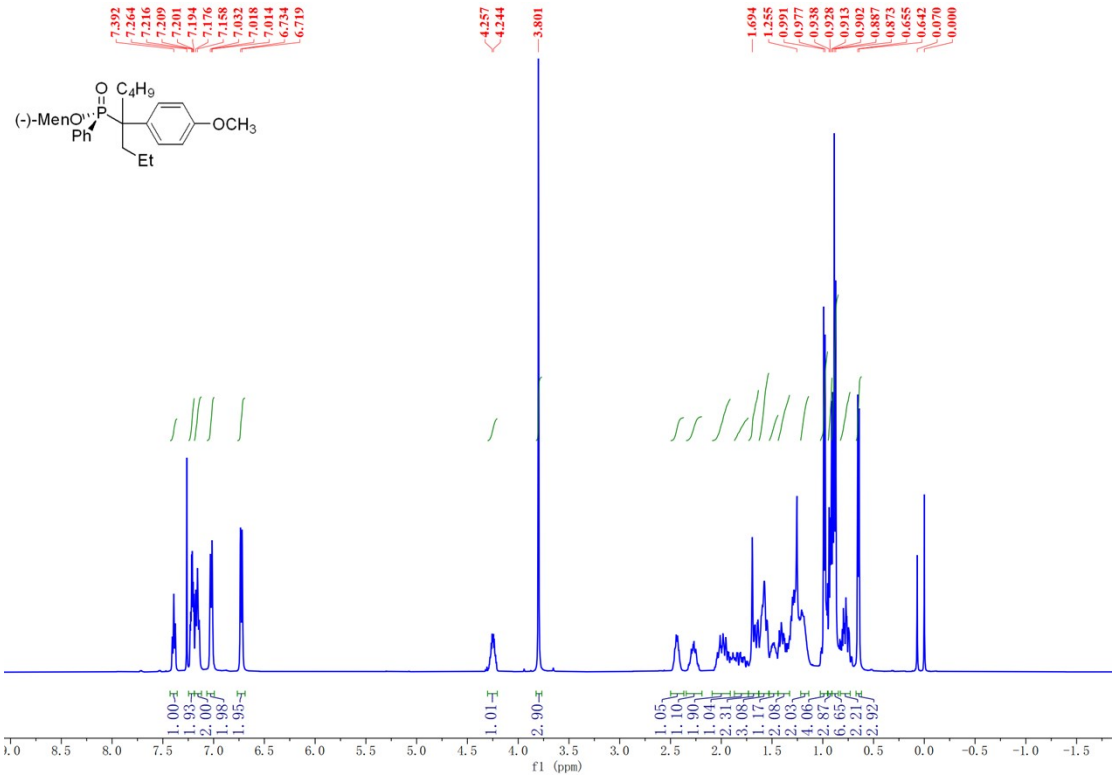

(-)-MenO
P
O
CH3
Ph
Et
OCH3
f1 (ppm)

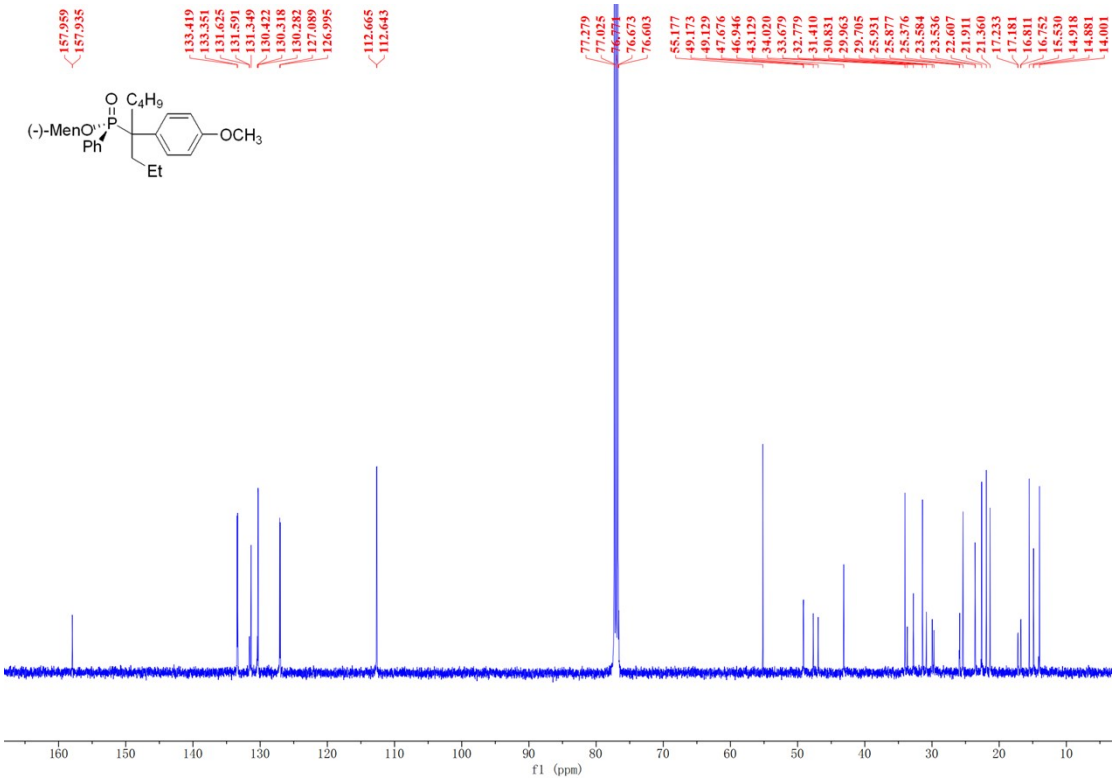

44.206
43.952
O Et
(-)-MenO
P
Ph
OCH3
Et
0.96
0.04
f1 (ppm)

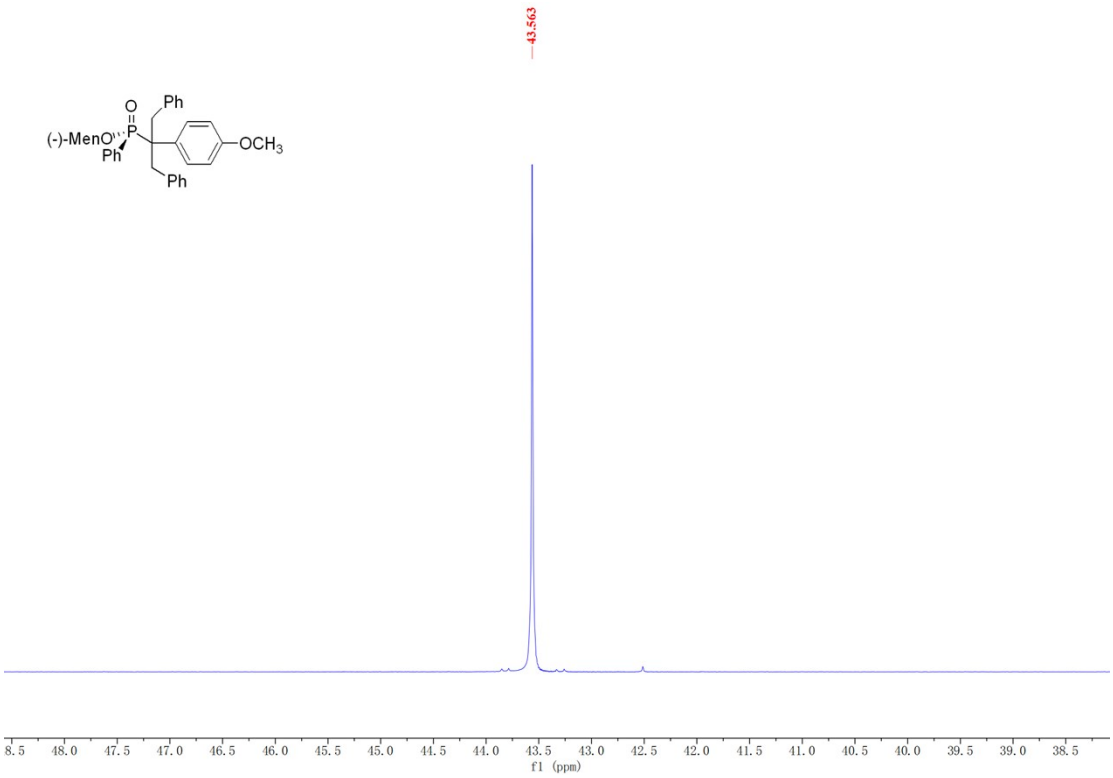

7.322
7.307
7.191
7.160
7.152
7.145
7.137
7.130
7.121
7.111
7.097
6.976
6.970
6.965
6.958
6.952
6.946
6.664
6.647
3.728
2.361
2.348
2.334
2.296
2.281
2.267
1.196
1.185
0.921
0.912
0.905
0.898
0.888
0.883
0.874
0.869
0.851
0.837
0.822
0.813
0.808
0.799
0.794
0.589
0.583
0.576
0.569
-0.000
O Et
(-)-MenO
P
Ph
OCH3
Et
1.24
4.24
2.05
1.89
0.99
2.97
2.25
2.45
2.03
4.45
7.15
6.35
2.50
2.84
f1 (ppm)

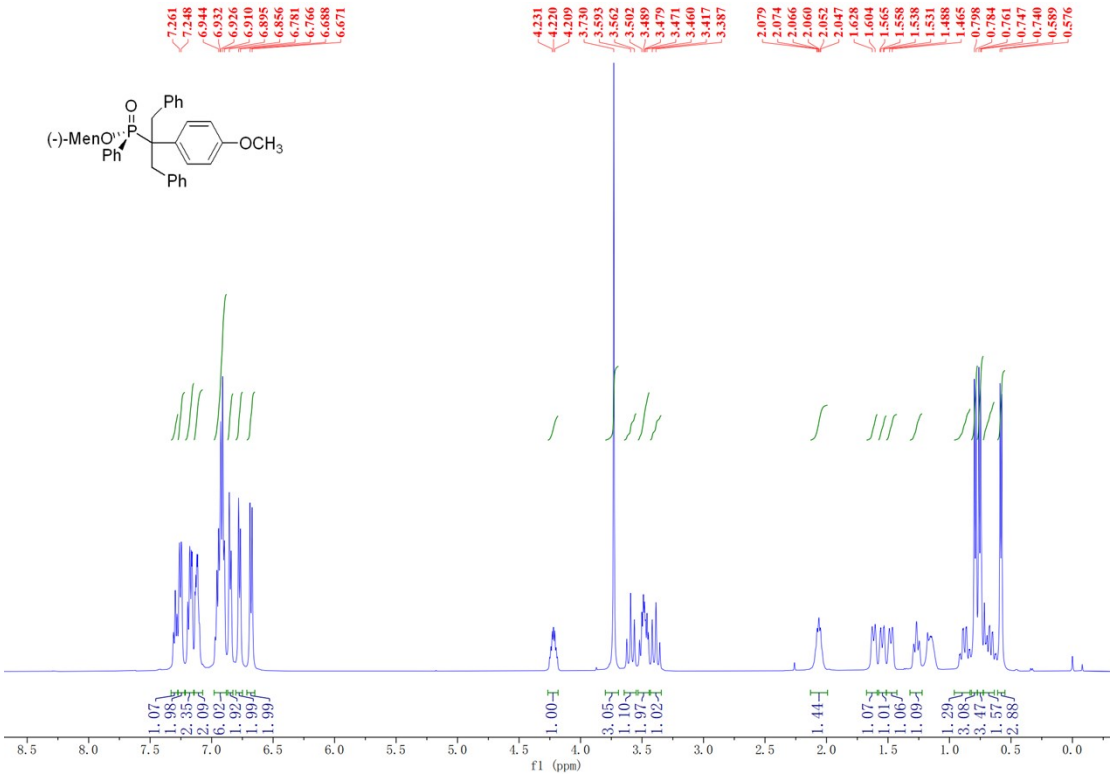

156.955
156.929
132.435
132.367
132.339
132.271
130.329
129.557
129.390
129.354
126.096
126.003
125.969
111.668
111.648
76.248
75.904
75.740
54.155
48.141
48.097
46.905
46.174
42.136
33.013
31.097
30.401
28.684
24.360
22.805
21.879
21.583
20.887
20.338
15.709
15.647
14.498
13.867
13.834
7.638
7.582
7.185
7.118
O
Et
P
(-)-MenO
Ph
OCH3
Et
f1 (ppm)

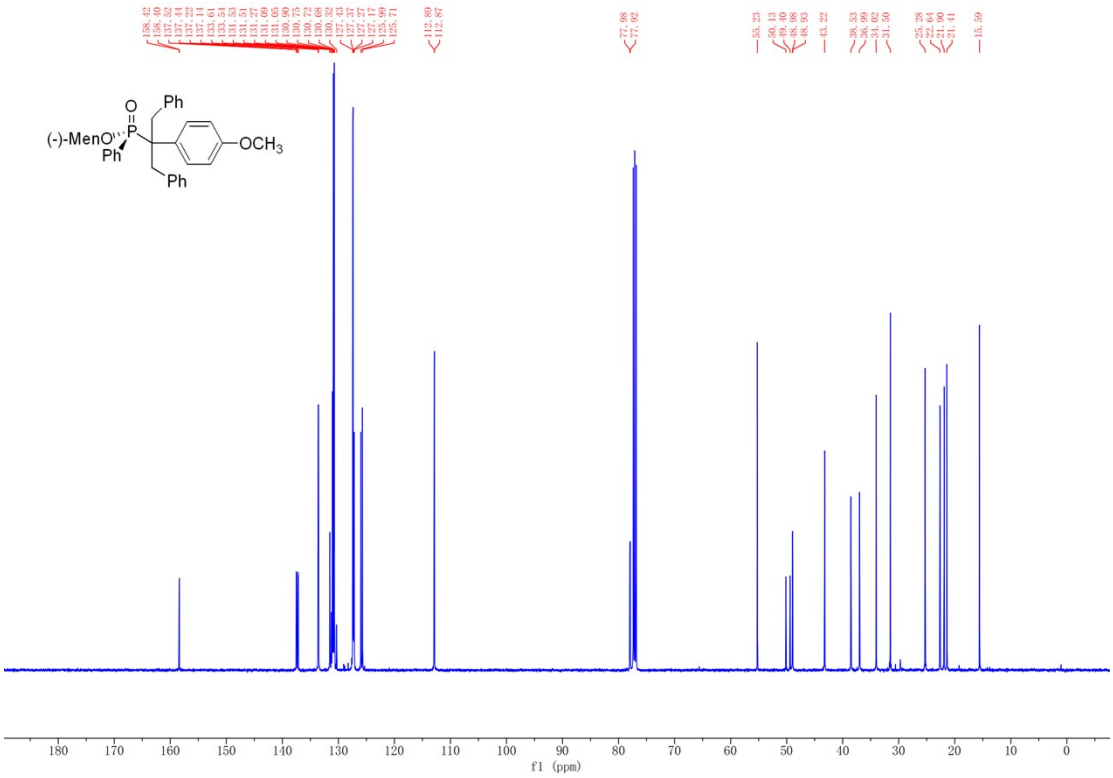

44.085
43.862
O
C4H9
P
(-)-MenO
Ph
OCH3
Et
0.40
0.60
f1 (ppm)


7.392
7.264
7.216
7.209
7.201
7.194
7.176
7.158
7.032
7.018
7.014
6.734
6.719
4.257
4.244
3.801
1.694
1.255
0.991
0.977
0.938
0.928
0.913
0.902
0.887
0.873
0.655
0.642
0.070
0.000
O
C4H9
P
(-)-MenO
Ph
OCH3
Et
1.00
1.93
2.00
1.98
1.95
1.01
2.90
1.05
1.10
1.90
1.04
2.31
3.08
1.17
2.08
2.03
4.06
2.87
6.65
2.21
2.92
f1 (ppm)


157.959
157.935
133.419
133.351
131.625
131.591
131.349
130.422
130.318
130.282
127.089
126.995
112.665
112.643
77.279
77.025
76.771
76.673
76.603
55.177
49.173
49.129
47.676
46.946
43.129
34.020
33.679
32.779
31.410
30.831
29.963
29.705
25.931
25.877
25.376
23.584
23.536
22.607
21.911
21.360
17.233
17.181
16.811
16.752
15.530
14.918
14.881
14.001
O
C4H9
P
(-)-MenO
Ph
OCH3
Et
f1 (ppm)


43.563
(-)-MenO
Ph
Ph
Ph
OCH3
f1 (ppm)


7.261
7.248
6.944
6.932
6.926
6.910
6.895
6.856
6.781
6.766
6.688
6.671
4.231
4.220
4.209
3.730
3.593
3.562
3.502
3.489
3.479
3.471
3.460
3.417
3.387
2.079
2.074
2.066
2.060
2.052
2.047
1.628
1.604
1.565
1.558
1.538
1.531
1.488
1.465
0.798
0.784
0.761
0.747
0.740
0.589
0.576
(-)-MenO
Ph
Ph
Ph
OCH3
1.07
1.98
2.35
2.09
6.02
1.92
1.99
1.99
1.00
3.05
1.10
1.97
1.02
1.44
1.07
1.01
1.06
1.09
1.29
3.08
3.47
1.57
2.88
f1 (ppm)


158.42
138.49
137.59
137.44
137.22
137.14
135.61
133.54
131.53
131.51
131.27
131.09
131.05
130.90
130.75
130.72
130.68
130.32
127.43
127.37
127.27
127.17
125.99
125.71
112.89
112.87
77.98
77.92
55.23
50.13
49.40
48.98
48.93
43.22
38.53
36.99
34.02
31.50
25.28
22.64
21.90
21.41
15.59
O
P
Ph
(-)-MenO
Ph
Ph
OCH3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)