

# A One-pot Process That Efficiently Generates Single Stereoisomers of 1,3-Bisphosphinylpropanes Having Five Chiral Centers

He Zhang<sup>†‡</sup>, Yong-Ming Sun<sup>†‡</sup>, Yalei Zhao<sup>§</sup>, Zhong-Yang Zhou<sup>†</sup>, Ji-Ping Wang<sup>†</sup>, Nana Xin<sup>†</sup>, Shao-Zhen Nie<sup>†</sup>, Chang-Qiu Zhao<sup>†\*</sup> and Li-Biao Han<sup>§\*</sup>

<sup>†</sup> College of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng, Shandong 252059, China

<sup>§</sup> National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan

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**General Chemistry:**

$^1\text{H}$  NMR spectra were recorded on a 400-MHz spectrometer. Chemical shift for  $^1\text{H}$  NMR spectra (in parts per million) relative to internal tetramethylsilane ( $\text{Me}_4\text{Si}$ ,  $\delta = 0.00$  ppm) with  $\text{CDCl}_3$  or DMSO.  $^{13}\text{C}$  NMR spectra were recorded at 101 MHz. Chemical shifts for  $^{13}\text{C}$  NMR spectra are reported (in parts per million) relative to  $\text{CDCl}_3$  ( $\delta = 77.0$  ppm) or  $\text{DMSO}-d^6$  ( $\delta = 39.6$  ppm).  $^{31}\text{P}$  NMR spectra were recorded at 162 MHz, and chemical shifts reported (in parts per million) relative to external 85% phosphoric acid ( $\delta = 0.0$  ppm). TLC plates were visualized by UV. Elemental analyses were performed with a PE-2400II apparatus. HRMS was recorded by JEOL JMS-T100GCv or JEOL JMS-T100LP.

**Reagent and solvents:**

All starting material were purchased from commercial sources and used as received. The solvents were distilled under  $\text{N}_2$  and dried according to standard procedures.

 **$^{31}\text{P}$  NMR Yield measurements:**

$^{31}\text{P}$  NMR spectra were referenced to phosphoric acid. The NMR yields of article are determined by integration of all the resonances in the  $^{31}\text{P}$  spectra. The yields obtained by the approach are generally accurate and reproducible

## Part S1. Investigation of reaction condition of **1** with cinnimic aldehyde **2a**

**Typical procedure:** To the solution of *R<sub>P</sub>*-(*-*)menthylphenylphosphine oxide **1** (0.1 g, 0.38 mmol) in DMSO or DMF (0.5 ml), cinnimic aldehyde **2a** (57 mg, 55  $\mu$ l, 0.41 mmol, 1.1 equiv) and base (0.25 equiv) were added in turn. The mixture was stirred at room temperature (25 °C), and the reaction was monitored with <sup>31</sup>P NMR spectroscopy (ca. 0.1 ml reaction mixture dissolved in 0.4 ml chloroform, followed by addition of drops acetic acid). After the reaction finished, aqueous saturated ammonium chloride solution (2 ml, in the case KOH was used), or acetic acid (0.1 ml, in the cases of other bases were used) was added to the mixture, followed by addition of methanol (3 ml). The mixture was filtered through silica gel, concentrated under vacuum, and analyzed with NMR spectroscopy.

When the ratio of **1/2a** was 1:1, as the above, and the two starting materials were stirred for 3 h, four peaks located at 50.21 (7 %), 49.46 (43 %), 43.29 (7 %) and 42.11 (43 %) ppm on <sup>31</sup>P-NMR spectroscopy, which were assigned as two stereomers *S<sub>γ-C</sub>-3a/S<sub>γ-C</sub>-3a'*, in the ratio of 86:14. The two smaller peaks nearly disappeared after 9 h.

When **2a** (114 mg, 110  $\mu$ l, 0.82 mmol, 2.2 equiv) was used, complicated <sup>31</sup>P-NMR spectra was observed. Beside the configuration of two phosphorus atoms kept retention, the two asymmetric carbon atoms was thought being formed in different configuration. The complicated peaks between 40-50 ppm might be ascribed to various stereomers of 1,2 or 1,4-adduct, bis-adduct and by-products. Excluding the peaks of *S<sub>γ-C</sub>-3a/S<sub>γ-C</sub>-3a'*, the peaks from 44 to 46 ppm on <sup>31</sup>P-NMR spectroscopy were speculated to belong to another pair of stereomers *R<sub>γ-C</sub>-3a/R<sub>γ-C</sub>-3a'* that have *R* configuration on  $\gamma$ -carbon. The ratio of *S<sub>γ-C</sub>-3a/S<sub>γ-C</sub>-3a'* or *R<sub>γ-C</sub>-3a/R<sub>γ-C</sub>-3a'* was also improved with time. After 24 h, four major peaks were observed at 44.00, 45.09, 45.96 and 46.12 ppm, together with some smaller ones, in near equal integrations to the peaks of *S<sub>γ-C</sub>-3a/S<sub>γ-C</sub>-3a'*.

When two molar of **1** (0.2 g, 0.76 mmol) was used, the peaks from 44 to 46 ppm disappeared, *S<sub>γ-C</sub>-3a/S<sub>γ-C</sub>-3a'* were formed in the ratio of 86:14, accompanied with 30% yield of by-products having two multi peaks around 42.14 and 49.90 ppm.

We supposed that in the presence of excess **2a**, the mixture of *S<sub>C</sub>-5a/R<sub>C</sub>-5a* was generated via 1,4-addition of route B, which were converted to two pairs of stereomers *S<sub>γ-C</sub>-3a/S<sub>γ-C</sub>-3a'* and *R<sub>γ-C</sub>-3a/R<sub>γ-C</sub>-3a'*, respectively, by addition with **1**. The complicated multi peaks on <sup>31</sup>P-NMR spectroscopy exhibited formation of various stereomers. However, equal molar of **1** and **2a**, in perfect ratio for formation of **4a** that underwent rearrangement and intermolecular *P*-migration. The reaction was scarcely influenced by unconsumed **1** or **2a**, therefore excellent stereoselectivity was achieved via route A. In the present of excess **1**, kinetic 1,2-adduct *S<sub>C</sub>-4a/R<sub>C</sub>-4a* was dominantly afforded and 1,4-addition was not significant. In this case, **3a** was generated from *S<sub>C</sub>-4a/R<sub>C</sub>-4a* via route A, accompanied with unconfirmed by-products.

The trace amount of water in DMSO, or in KOH due to its high hygroscopic feature, has almost any influence to the yield and selectivity. When the reaction was carried out in water-containing DMSO, the selectivity did not decreased obviously. It looked like **1a** was more solvable in water-containing DMSO.

## Part S2. Preparation of 1,3-Bisphosphinylpropanes **3**

### S2-1. Preparation of $\alpha$ -hydroxyphosphinates **4a**

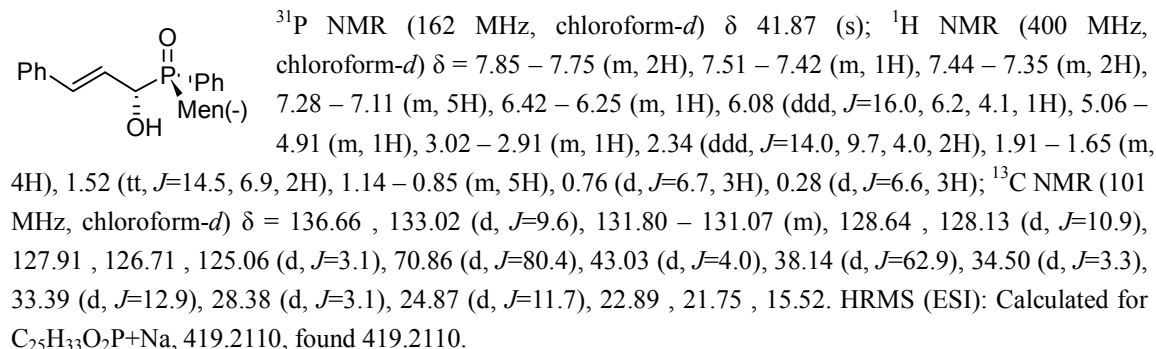
#### (*R<sub>P</sub>*)-(–)-Menthyl[(*E*)-1-hydroxy-3-phenylallyl]phenylphosphine oxide, *S<sub>C</sub>-4a/R<sub>C</sub>-4a*:

To the solution of *R<sub>P</sub>*-(*-*)menthylphenylphosphine oxide **1** (300 mg, 1.14 mmol) in DMF (1.5 ml), cinnamic aldehyde **2a** (153 mg, 146  $\mu$ l, 1.14 mmol) and calcium hydroxide (22.8 mg 0.28 mmol) were added in turn. The mixture was stirred at room temperature for 0.7 hours, then was quenched with acetic acid (0.3 ml), following by addition of methanol (6 ml). The mixture was filtered through silica gel and concentrated under vacuum. The residue was purified by recrystallization with MeOH/Et<sub>2</sub>O to afford *S<sub>C</sub>-4a/R<sub>C</sub>-4a* as

white solid, weighted 130 mg, yield 28%.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  41.87 (**S<sub>C</sub>-4a**, s, 70 %), 40.36 (**R<sub>C</sub>-4a**, s, 30 %).

**(R<sub>p</sub>)-(-)-Menthyl[(S,E)-1-hydroxy-3-phenylallyl]phenylphosphine oxide, S<sub>C</sub>-4a:**

The compound was prepared according similar procedure as above, except the reaction time prolonged to 24 hours. The optically pure **S<sub>C</sub>-4a** was obtained as white solid, weighted 371 mg (yield 82%), m. p. 196-198 °C.



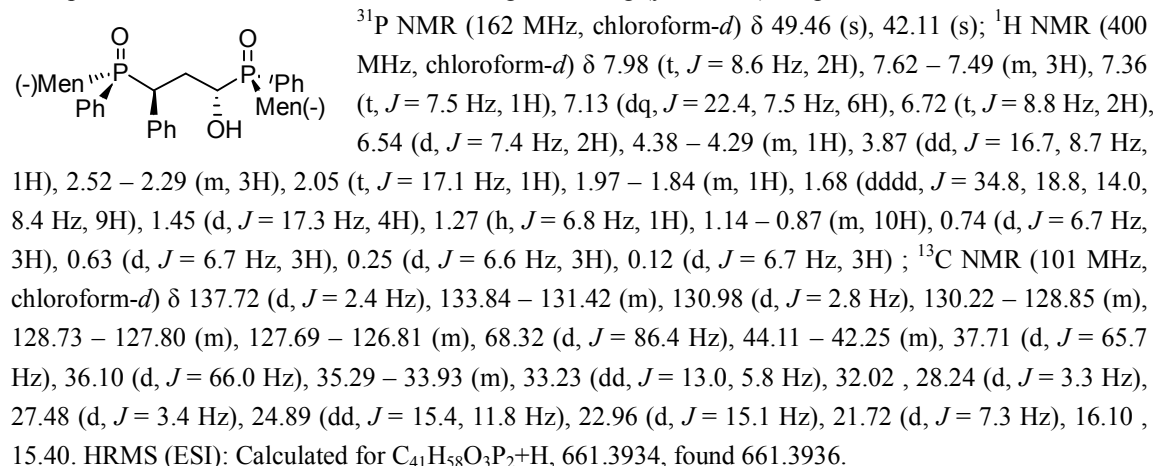
**S-2-2. Treatment of 4a with KOH in DMSO (Path 1):**

To the solution of **S<sub>C</sub>-4a** (130 mg, 0.33 mmol) in DMSO (0.5 ml), KOH (7 mg, 0.12 mmol) was added. The mixture was stirred at room temperature, and was monitored with  $^{31}\text{P}$  NMR spectra (ca. 0.1 ml mixture was dissolved in 0.5 ml chloroform, followed by addition of drops of aqueous HCl or HOAc. When aqueous HCl was used, the solution was dried with anhydrous sodium sulfate). At 0.5 h, four peaks on  $^{31}\text{P}$  NMR spectra were observed as similar as the above monitored reaction when the ratio of **1/2a** was 1:1 (Part S1). After 9 h, only two peaks at 49.46 (50%) and 42.11 (50%) were observed. Beside of the two peaks that were confirmed as **S<sub>γ-C</sub>-3a**, no other peaks were observed on  $^{31}\text{P}$  NMR spectra. The mixture of **S<sub>C</sub>-4a/R<sub>C</sub>-4a** gave the same result to the single stereomer of **S<sub>C</sub>-4a**.

Aqueous saturated ammonium chloride solution (2 ml) was added. The resulted solid was collected by filtration, dried under air and purified by recrystallization with  $\text{Et}_2\text{O}/\text{PE}$  (petroleum ether, b.p 30-60 °C) to afford **S<sub>γ-C</sub>-3a**.

**(1S,3S,R<sub>α-P</sub>,S<sub>γ-P</sub>)-1-Phenyl-3-hydroxypropane-1,3-diylbismenthylphenylphosphine oxide, 3a:**

The specimen was obtained as white solid, weighted 84 mg (yield 78%), m. p. 206-208 °C.



**S2-3. One pot reaction of 1 with 2 catalyzed by KOH (Path 2):**

**General procedure:** To the solution of *R<sub>p</sub>*-(-)-menthylphenylphosphine oxide **1** (0.1 g, 0.38 mmol) in

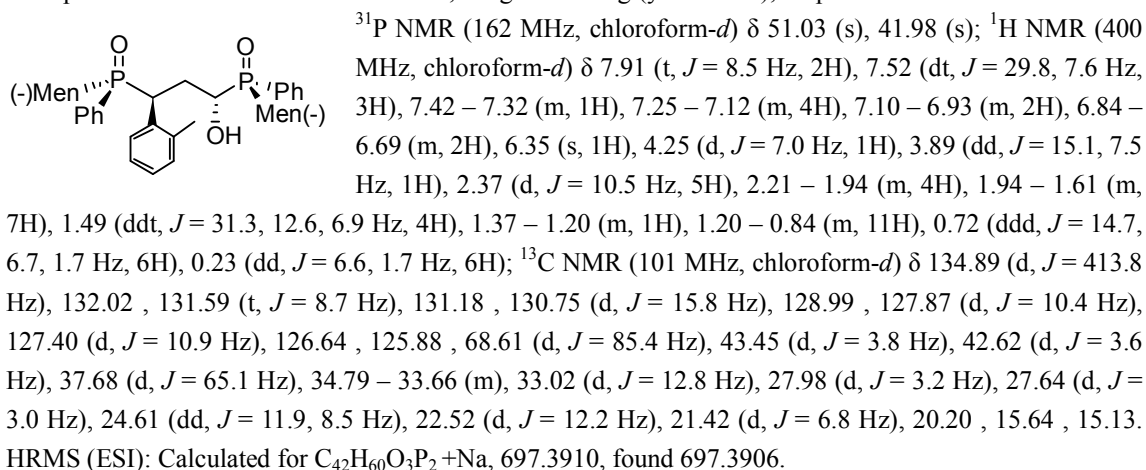
DMSO (0.5 ml), vinyl aldehyde **2** (0.38 mmol) and potassium hydroxide (6 mg, 0.10 mmol) were added in turn. The mixture was stirred at room temperature for 9 hours or so, and the reaction was monitored with  $^{31}\text{P}$  NMR spectroscopy (ca. 0.1 ml reaction mixture dissolved in 0.4 ml chloroform). After the reaction finished, aqueous saturated ammonium chloride solution (2 ml) was added. The resulted solid was collected by filtration, dried under air and purified by recrystallization with Et<sub>2</sub>O/PE (petroleum ether, b.p 30-60 °C) to afford pure **3**.

**(1*S*,3*S*,*R*<sub>α-P</sub>,*S*<sub>γ-P</sub>)-1-Phenyl-3-hydroxypropane-1,3-diylbismenthylphenylphosphine oxide, 3a:**

The specimen weighted 95 mg (yield 76 %), which have the same spectra data to **S-2-2**.

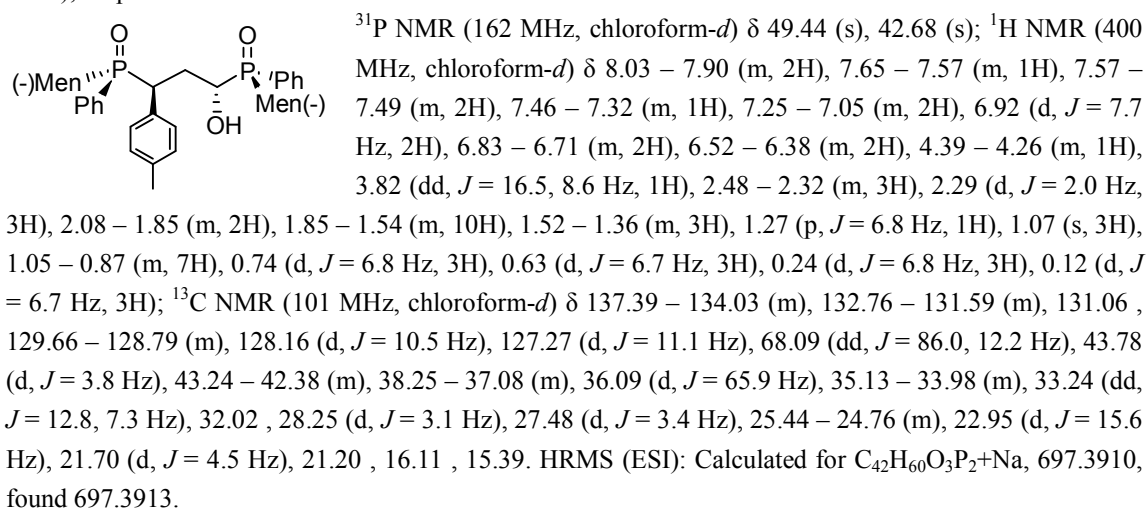
**(1*S*,3*S*,*R*<sub>α-P</sub>,*S*<sub>γ-P</sub>)-1-*o*-Tolyl-3-hydroxypropane-1,3-diylbismenthylphenylphosphine oxide, 3b:**

The specimen was obtained as white solid, weighted 96 mg (yield 75 %), m. p. 185-187 °C.



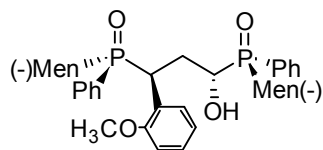
**(1*S*,3*S*,*R*<sub>α-P</sub>,*S*<sub>γ-P</sub>)-1-*p*-Tolyl-3-hydroxypropane-1,3-diylbismenthylphenylphosphine oxide, 3c:**

The specimen was obtained in the similar procedure to **3a** with 12h as white solid, weighted 101 mg (yield 79 %), m. p. 218-220 °C.



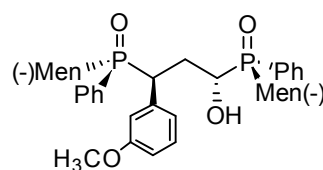
**(1*S*,3*S*,*R*<sub>α-P</sub>,*S*<sub>γ-P</sub>)-1-*o*-Methoxyphenyl-3-hydroxypropane-1,3-diylbismenthylphenylphosphine oxide, 3d:**

The specimen was obtained as white solid, weighted 106 mg (yield 81 %), m. p. 196-198 °C.



$^{31}\text{P}$  NMR (162 MHz, chloroform-*d*)  $\delta$  51.28 (s), 42.58 (s);  $^1\text{H}$  NMR (400 MHz, chloroform-*d*)  $\delta$  8.12 – 7.89 (m, 2H), 7.54 (dq,  $J$  = 14.0, 7.4, 6.9 Hz, 3H), 7.32 (t,  $J$  = 7.7 Hz, 1H), 7.09 (d,  $J$  = 8.4 Hz, 4H), 6.91 (d,  $J$  = 9.3 Hz, 2H), 6.74 (d,  $J$  = 8.2 Hz, 1H), 6.53 (t,  $J$  = 7.7 Hz, 1H), 5.99 (d,  $J$  = 7.6 Hz, 1H), 4.41 – 4.24 (m, 2H), 3.79 (s, 3H), 2.68 – 2.46 (m, 1H), 2.46 – 2.28 (m, 2H), 2.25 – 1.56 (m, 7H), 1.57 – 1.31 (m, 5H), 1.26 (s, 1H), 1.00 (dd,  $J$  = 18.8, 5.9 Hz, 11H), 0.69 (dd,  $J$  = 41.4, 6.6 Hz, 6H), 0.21 (dd,  $J$  = 25.3, 6.5 Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz, chloroform-*d*)  $\delta$  155.89 (d,  $J$  = 5.5 Hz), 132.80 (d,  $J$  = 80.7 Hz), 131.92 (dd,  $J$  = 7.8, 2.5 Hz), 131.41 (d,  $J$  = 3.0 Hz), 131.24 (d,  $J$  = 4.4 Hz), 131.06, 130.41, 128.15 (d,  $J$  = 10.7 Hz), 127.26 (d,  $J$  = 10.9 Hz), 126.61, 120.62 (d,  $J$  = 2.8 Hz), 109.98, 68.51 (d,  $J$  = 86.6 Hz), 55.29, 43.82 (d,  $J$  = 4.0 Hz), 42.79 (d,  $J$  = 3.5 Hz), 41.19, 38.09 (d,  $J$  = 23.3 Hz), 37.45 (d,  $J$  = 24.7 Hz), 34.86 – 33.96 (m), 33.38 (dd,  $J$  = 28.4, 13.1 Hz), 32.92, 28.22 (d,  $J$  = 3.2 Hz), 27.54 (d,  $J$  = 3.1 Hz), 24.97 (dd,  $J$  = 32.4, 11.8 Hz), 22.93 (d,  $J$  = 6.0 Hz), 21.71 (d,  $J$  = 5.5 Hz), 16.15, 15.39. HRMS (ESI): Calculated for  $\text{C}_{42}\text{H}_{60}\text{O}_4\text{P}_2+\text{Na}$ , 713.3859, found 713.3861.

**(1*S*,3*S*,*R*<sub>α-P</sub>,*S*<sub>γ-P</sub>)-1-*m*-Methoxyphenyl-3-hydroxypropane-1,3-diylbismenthylphenylphosphine oxide, 3e:**

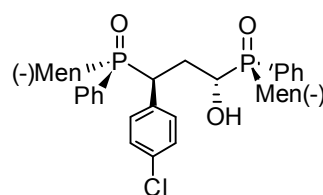


The specimen was obtained from the similar procedure to **3a** as white solid, weighted 108 mg (yield 82 %), m. p. 198-200 °C.  $^{31}\text{P}$  NMR (162 MHz, chloroform-*d*)  $\delta$  49.46 (s), 42.27 (s);  $^1\text{H}$  NMR (400 MHz, chloroform-*d*)  $\delta$  7.97 (t,  $J$  = 8.5 Hz, 2H), 7.66 – 7.48 (m, 3H), 7.37 (t,  $J$  = 7.6 Hz, 1H), 7.13 (dt,  $J$  = 16.0, 9.8 Hz, 3H), 7.04 (t,  $J$  = 7.9 Hz, 1H), 6.84 – 6.65 (m, 3H), 6.23 (d,  $J$  = 7.6 Hz, 1H), 5.98 (d,  $J$  = 2.7 Hz, 1H), 4.32 (d,  $J$  = 9.7 Hz, 1H), 3.84 (dd,  $J$  = 16.7, 8.6 Hz, 1H), 3.58 (s, 3H), 2.53 – 2.28 (m, 3H), 2.14 – 1.82 (m, 4H), 1.81 – 1.53 (m, 7H), 1.46 (q,  $J$  = 8.0, 7.2 Hz, 3H), 1.35 – 1.20 (m, 1H), 1.01 (dt,  $J$  = 39.0, 8.4 Hz, 11H), 0.74 (d,  $J$  = 6.6 Hz, 3H), 0.63 (d,  $J$  = 6.7 Hz, 3H), 0.24 (d,  $J$  = 6.6 Hz, 3H), 0.13 (d,  $J$  = 6.6 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz, chloroform-*d*)  $\delta$  159.90 – 138.17 (m), 132.98 (d,  $J$  = 80.5 Hz), 132.20 (d,  $J$  = 8.0 Hz), 131.99 (d,  $J$  = 7.5 Hz), 131.73 (d,  $J$  = 2.9 Hz), 131.00 (d,  $J$  = 2.9 Hz), 129.95, 129.26 (d,  $J$  = 2.6 Hz), 129.10, 128.10 (d,  $J$  = 10.3 Hz), 127.26 (d,  $J$  = 11.1 Hz), 121.77 (d,  $J$  = 5.0 Hz), 114.94 (d,  $J$  = 4.7 Hz), 113.18 (d,  $J$  = 3.0 Hz), 68.27 (d,  $J$  = 86.5 Hz), 55.13, 43.81 (d,  $J$  = 4.0 Hz), 43.22 (dd,  $J$  = 55.7, 14.9 Hz), 42.76 (d,  $J$  = 3.5 Hz), 37.66 (d,  $J$  = 65.8 Hz), 36.14 (d,  $J$  = 66.0 Hz), 35.23 – 33.98 (m), 33.26 (d,  $J$  = 13.0 Hz), 31.99, 28.24 (d,  $J$  = 3.2 Hz), 27.51 (d,  $J$  = 3.3 Hz), 24.90 (dd,  $J$  = 17.4, 11.7 Hz), 22.96 (d,  $J$  = 15.2 Hz), 21.72 (d,  $J$  = 5.2 Hz), 16.12, 15.40. HRMS (ESI): Calculated for  $\text{C}_{42}\text{H}_{60}\text{O}_4\text{P}_2+\text{Na}$ , 713.3859, found 713.3853.

**(1*S*,3*S*,*R*<sub>α-P</sub>,*S*<sub>γ-P</sub>)-1-*p*-Chlorophenyl-3-hydroxypropane-1,3-diylbismenthylphenylphosphine oxide, 3f:**

To the solution of *R*<sub>P</sub>(-)-menthylphenylphosphine oxide **1** (0.1 g, 0.38 mmol) in DMF (0.5 ml), *p*-chlorocinnamaldehyde **2** (65 mg, 0.38 mmol) and calcium hydroxide (7.6 mg, 0.10 mmol) were added in turn. After the mixture was stirred at room temperature for 24 hours, potassium hydroxide (3 mg, 0.04 mmol) was added, and the mixture was further stirred at room temperature for 9 hours. The reaction was monitored with  $^{31}\text{P}$  NMR spectroscopy (ca. 0.1 ml reaction mixture was dissolved in 0.4 ml chloroform). After the reaction finished, acetic acid (0.1 ml) was added to the mixture, followed by addition of methanol (3 ml). The mixture was filtered through silica gel and concentrated under vacuum. The residue was purified by recrystallization with Et<sub>2</sub>O/PE (petroleum ether, b.p 30-60 °C) to afford pure **3f**.

The specimen was obtained as white solid, weighted 92 mg (yield 70 %), m. p. 201-203 °C.

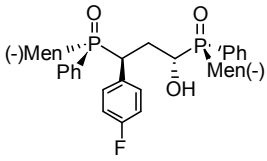


$^{31}\text{P}$  NMR (162 MHz, chloroform-*d*)  $\delta$  49.01 (s), 42.23 (s);  $^1\text{H}$  NMR (400 MHz, chloroform-*d*)  $\delta$  7.96 (t,  $J$  = 8.5 Hz, 2H), 7.64 – 7.48 (m, 3H), 7.39

(t,  $J = 7.7$  Hz, 1H), 7.22 – 6.98 (m, 5H), 6.76 (t,  $J = 8.8$  Hz, 2H), 6.52 – 6.42 (m, 2H), 4.30 (d,  $J = 11.5$  Hz, 1H), 3.83 (dd,  $J = 16.4, 8.5$  Hz, 1H), 2.36 (d,  $J = 11.9$  Hz, 3H), 2.10 – 1.84 (m, 2H), 1.83 – 1.54 (m, 9H), 1.53 – 1.36 (m, 4H), 1.30 (dt,  $J = 13.2, 6.6$  Hz, 1H), 1.13 – 0.82 (m, 10H), 0.74 (d,  $J = 6.7$  Hz, 3H), 0.64 (d,  $J = 6.7$  Hz, 3H), 0.24 (d,  $J = 6.6$  Hz, 3H), 0.14 (d,  $J = 6.6$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz, chloroform- $d$ )  $\delta$  136.28 – 132.84 (m), 131.95 – 131.53 (m), 130.75 (d,  $J = 2.7$  Hz), 130.44 (d,  $J = 4.8$  Hz), 129.11 (d,  $J = 85.4$  Hz), 128.22 (d,  $J = 2.4$  Hz), 127.83 (d,  $J = 10.3$  Hz), 127.17 (d,  $J = 11.1$  Hz), 68.04 (d,  $J = 86.0$  Hz), 43.54 (d,  $J = 4.0$  Hz), 42.51 (d,  $J = 3.5$  Hz), 37.56 (d,  $J = 65.8$  Hz), 36.07 (d,  $J = 66.1$  Hz), 34.71 (d,  $J = 3.5$  Hz), 34.37, 34.14 (d,  $J = 2.8$  Hz), 34.00, 32.97 (dd,  $J = 13.0, 5.2$  Hz), 31.98, 27.97 (d,  $J = 3.2$  Hz), 27.28 (d,  $J = 3.5$  Hz), 24.62 (t,  $J = 12.8$  Hz), 22.62 (d,  $J = 13.7$  Hz), 21.39 (d,  $J = 5.4$  Hz), 15.78, 15.08. HRMS (ESI): Calculated for  $\text{C}_{41}\text{H}_{57}\text{ClO}_3\text{P}_2 + \text{Na}$ , 717.3364, found 717.3361.

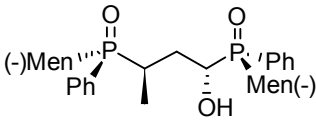
**(1*S*,3*S*,*R* <sub>$\alpha$ -P</sub>,*S* <sub>$\gamma$ -P</sub>)-1-*p*-Fluorophenyl-3-hydroxypropane-1,3-diylbismenthylphenylphosphine oxide, 3g:**

The specimen was obtained in the similar procedure to **3a** as white solid, weighted 103 mg (yield 80 %), m. p. 193-195 °C.

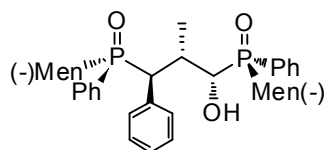
  $^{31}\text{P}$  NMR (162 MHz, chloroform- $d$ )  $\delta$  49.49 (d,  $J = 5.4$  Hz), 44.39 (s);  $^1\text{H}$  NMR (400 MHz, chloroform- $d$ )  $\delta$  7.87 (t,  $J = 8.6$  Hz, 2H), 7.70 – 7.50 (m, 3H), 7.42 (t,  $J = 7.5$  Hz, 1H), 7.18 (dd,  $J = 8.0, 5.2$  Hz, 2H), 6.82 (dt,  $J = 21.2, 8.5$  Hz, 4H), 6.65 – 6.52 (m, 2H), 4.23 – 4.11 (m, 1H), 3.95 – 3.81 (m, 1H), 2.52 – 2.24 (m, 3H), 1.91 (t,  $J = 12.7$  Hz, 3H), 1.68 (dtd,  $J = 27.2, 14.8, 14.3, 6.2$  Hz, 8H), 1.56 – 1.39 (m, 3H), 1.37 – 1.24 (m, 2H), 1.01 (dd,  $J = 41.7, 6.3$  Hz, 10H), 0.69 (dd,  $J = 37.7, 6.7$  Hz, 6H), 0.19 (dd,  $J = 29.7, 6.7$  Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz, chloroform- $d$ )  $\delta$  161.98 (dd,  $J = 247.4, 3.2$  Hz), 132.81 – 132.55 (m), 132.18 – 131.96 (m), 131.76 (d,  $J = 8.0$  Hz), 131.66 – 131.39 (m), 131.29, 131.01 (dd,  $J = 8.0, 4.9$  Hz), 129.22 (d,  $J = 85.9$  Hz), 128.39 (d,  $J = 10.7$  Hz), 127.59 (d,  $J = 11.1$  Hz), 115.38 (dd,  $J = 21.5, 2.5$  Hz), 67.09 (dd,  $J = 85.8, 3.2$  Hz), 43.83 (d,  $J = 4.0$  Hz), 42.90 (d,  $J = 3.6$  Hz), 41.40 (dd,  $J = 57.6, 14.2$  Hz), 37.46 (d,  $J = 65.2$  Hz), 36.41 (d,  $J = 65.4$  Hz), 34.88 (d,  $J = 3.5$  Hz), 34.49, 34.24, 34.15 (d,  $J = 3.1$  Hz), 33.18 (dd,  $J = 13.0, 5.5$  Hz), 31.46 (d,  $J = 4.1$  Hz), 28.27 (d,  $J = 3.3$  Hz), 27.57 (d,  $J = 3.3$  Hz), 24.81 (dd,  $J = 18.4, 11.9$  Hz), 22.79 (d,  $J = 18.7$  Hz), 21.48, 15.99, 15.25. HRMS (EI+): Calculated for  $\text{C}_{41}\text{H}_{57}\text{FO}_3\text{P}_2$ , 678.3767, found 678.3760.

**(1*S*,3*S*,*R* <sub>$\alpha$ -P</sub>,*S* <sub>$\gamma$ -P</sub>)-1-Hydroxybutane-1,3-diylbismenthylphenylphosphine oxide, 3h:**

The specimen was obtained in the similar procedure to **3a** as white solid, weighted 86 mg (yield 76 %), m. p. 168-170 °C.

  $^{31}\text{P}$  NMR (162 MHz, chloroform- $d$ )  $\delta$  50.84 (s), 42.06 (s);  $^1\text{H}$  NMR (400 MHz, )  $\delta$  8.01 – 7.86 (m, 2H), 7.54 – 7.45 (m, 1H), 7.40 (ddd,  $J = 19.3, 8.0, 4.6$  Hz, 3H), 7.32 – 7.14 (m, 4H), 4.27 (dd,  $J = 11.0, 6.7$  Hz, 1H), 2.47 – 2.23 (m, 3H), 2.12 (t,  $J = 11.2$  Hz, 1H), 1.90 – 1.81 (m, 1H), 1.81 – 1.64 (m, 8H), 1.60 (dd,  $J = 21.0, 6.6$  Hz, 1H), 1.47 (tq,  $J = 15.9, 6.6, 5.8$  Hz, 5H), 1.11 – 0.81 (m, 14H), 0.73 (dd,  $J = 12.7, 6.7$  Hz, 6H), 0.22 (t,  $J = 6.4$  Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz, chloroform- $d$ )  $\delta$  133.02 (d,  $J = 80.9$  Hz), 132.00 (d,  $J = 7.6$  Hz), 131.58 – 130.75 (m), 129.99 (d,  $J = 83.7$  Hz), 127.95 (dd,  $J = 23.5, 10.6$  Hz), 68.32 (d,  $J = 88.4$  Hz), 43.26 (d,  $J = 4.1$  Hz), 42.81 (d,  $J = 3.5$  Hz), 37.83 (d,  $J = 65.8$  Hz), 35.74 (d,  $J = 66.3$  Hz), 35.12 – 33.94 (m), 33.40 (dd,  $J = 21.9, 12.9$  Hz), 32.72 – 31.50 (m), 28.08 (dd,  $J = 36.8, 3.4$  Hz), 24.83 (d,  $J = 11.6$  Hz), 22.86 (d,  $J = 3.2$  Hz), 21.76 (d,  $J = 5.0$  Hz), 16.54, 15.73, 15.31. HRMS (ESI): Calculated for  $\text{C}_{36}\text{H}_{56}\text{O}_3\text{P}_2 + \text{Na}$ , 621.3597, found 621.3595.

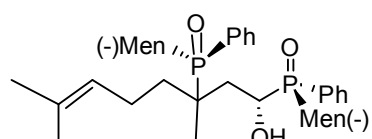
**(1*S*,3*S*,*R* <sub>$\alpha$ -P</sub>,*S* <sub>$\gamma$ -P</sub>)-1-Phenyl-2-methyl-3-hydroxypropane-1,3-diylbismenthylphenylphosphine oxide, 3i:**



The specimen was obtained in the similar procedure to **3f**, as white solid, weighted 64 mg (yield 50 %), m. p. 204-206 °C.  $^{31}\text{P}$  NMR (162 MHz, chloroform-*d*)  $\delta$  49.00 (s), 43.32 (s);  $^1\text{H}$  NMR (400 MHz, chloroform-*d*)  $\delta$  8.06 (t,  $J$  = 8.3 Hz, 2H), 7.74 – 7.56 (m, 3H), 7.49 – 7.40 (m, 1H), 7.18 (ddd,  $J$  = 17.5, 13.2, 7.2 Hz, 6H), 6.87 (dd,  $J$  = 10.1, 7.4 Hz, 2H), 6.77 (s, 1H), 3.94 (ddd,  $J$  = 18.0, 13.3, 5.5 Hz, 2H), 2.57 – 2.35 (m, 2H), 2.12 (d,  $J$  = 41.7 Hz, 2H), 1.90 – 1.56 (m, 8H), 1.51 (d,  $J$  = 5.9 Hz, 2H), 1.45 – 1.14 (m, 3H), 1.11 – 0.80 (m, 11H), 0.73 (d,  $J$  = 6.7 Hz, 3H), 0.66 (dd,  $J$  = 11.1, 6.7 Hz, 6H), 0.25 (dd,  $J$  = 12.8, 6.6 Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz, chloroform-*d*)  $\delta$  134.17 – 133.49 (m), 133.06 – 131.99 (m), 131.06 (d,  $J$  = 10.8 Hz), 128.80 – 128.20 (m), 127.90, 127.73 – 127.31 (m), 72.55 (dd,  $J$  = 324.9, 50.3 Hz), 47.35 (dd,  $J$  = 241.2, 11.7 Hz), 43.61 (d,  $J$  = 14.8 Hz), 42.85, 38.61 – 36.77 (m), 34.71, 34.55 – 33.86 (m), 33.27 (t,  $J$  = 56.7 Hz), 27.98, 27.53, 25.33 – 24.51 (m), 22.93, 22.01 – 21.44 (m), 16.34, 15.53. HRMS (ESI): Calculated for  $\text{C}_{42}\text{H}_{60}\text{O}_3\text{P}_2+\text{Na}$ , 697.3910, found 697.3907.

**(1*S*,*R*<sub>α</sub>,*S*<sub>γ</sub>,*P*)-1-Hydroxy-3,7-dimethyloct-6-ene-1,3-diylbismenthylphenylphosphine oxide, 3j-A:**

The crude product was obtained from (*Z/E*)-citral in the similar procedure to **3a**, as a mixture of two isomers. After purified with preparative TLC (silica gel, PE/EtOAc=3:1 as eluent. *R*<sub>f</sub> of **3j-A** was round 0.4, and that of a mixture of **3j-A** and **3j-A** was 0.3), one isomer was isolated as yellow liquid, weighted 39 mg (yield 30%).



$^{31}\text{P}$  NMR (162 MHz, chloroform-*d*)  $\delta$  54.56 (s), 42.59 (s);  $^1\text{H}$  NMR (400 MHz, chloroform-*d*)  $\delta$  7.95 – 7.86 (m, 2H), 7.56 (t,  $J$  = 8.5 Hz, 3H), 7.52 – 7.44 (m, 2H), 7.43 – 7.35 (m, 3H), 7.29 (dt,  $J$  = 7.3, 3.7 Hz, 1H), 5.11 (t,  $J$  = 6.8 Hz, 1H), 4.44 (t,  $J$  = 10.6 Hz, 1H), 2.55 (s, 1H), 2.49 – 2.33 (m, 2H), 2.23 (d,  $J$  = 11.3 Hz, 2H), 2.17 – 2.02 (m, 2H), 1.96 (d,  $J$  = 25.9 Hz, 3H), 1.89 – 1.35 (m, 18H), 1.21 – 0.93 (m, 10H), 0.90 – 0.70 (m, 6H), 0.26 (d,  $J$  = 6.7 Hz, 3H), 0.06 (d,  $J$  = 6.7 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz, chloroform-*d*)  $\delta$  133.49 – 132.34 (m), 131.92 (dd,  $J$  = 7.8, 2.7 Hz), 130.92 – 130.47 (m), 128.03, 127.93, 127.71, 127.61, 123.55, 64.36 (d,  $J$  = 90.1 Hz), 44.41 (d,  $J$  = 3.9 Hz), 43.15 (d,  $J$  = 3.6 Hz), 41.70 (dd,  $J$  = 60.3, 13.3 Hz), 40.55 (d,  $J$  = 60.9 Hz), 38.25 (d,  $J$  = 66.0 Hz), 37.29 (d,  $J$  = 3.3 Hz), 36.76 (d,  $J$  = 2.7 Hz), 34.71, 34.53 (d,  $J$  = 3.2 Hz), 34.27 (d,  $J$  = 3.0 Hz), 34.13, 33.52 (dd,  $J$  = 20.4, 12.8 Hz), 28.28 (d,  $J$  = 3.2 Hz), 27.88 (d,  $J$  = 3.2 Hz), 25.87 (d,  $J$  = 5.3 Hz), 24.94 (dd,  $J$  = 11.4, 9.2 Hz), 22.96 (d,  $J$  = 10.0 Hz), 21.75 (d,  $J$  = 8.0 Hz), 21.16 (d,  $J$  = 10.9 Hz), 17.72 (d,  $J$  = 22.7 Hz), 15.23 (d,  $J$  = 4.7 Hz). HRMS (ESI+): Calculated for  $\text{C}_{42}\text{H}_{66}\text{O}_3\text{P}_2+\text{H}$ , 681.4565, found 681.4566.

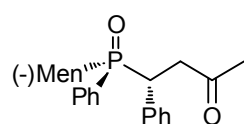
**Part S3. Addition to 4-phenylbutene-2-one **6** by various phosphorus species**

**S3-1. Addition to 4-phenylbutene-2-one **6** by **1****

To the solution of **1** (0.1 g, 0.38 mmol) in DMSO (0.5 ml), 4-phenylbutene-2-one **6** (56 mg, 0.38 mmol) and potassium hydroxide (6 mg 0.10 mmol) were added in turn. The mixture was stirred at 30 °C for 5 hours, and the reaction was monitored with  $^{31}\text{P}$  NMR spectroscopy (ca. 0.1 ml reaction mixture was dissolved in 0.4 ml chloroform). After the reaction finished, aqueous saturated ammonium chloride solution (2 ml) was added to the mixture. The resulting mixture was extracted with Et<sub>2</sub>O, washed with brine, dried over MgSO<sub>4</sub>, and concentrated under vacuum. The residue was analyzed with NMR spectroscopy.  $^{31}\text{P}$  NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  45.18 (*S*<sub>C</sub>-7, s, 24 %), 46.75 (*R*<sub>C</sub>-7, s, 76 %).

**(*S*<sub>P</sub>)-4-[(*R*)-(-)-Menthylphenylphosphoryl]-4-phenylbutan-2-one, *R*<sub>C</sub>-7:**

The above residue was purified with preparative TLC (silica gel, PE/EtOAc=3:1 as eluent), *R*<sub>C</sub>-7 was obtained as yellow oil, weighted 94 mg (yield 60%).



$^{31}\text{P}$  NMR (162 MHz, chloroform-*d*)  $\delta$  46.75 (s);  $^1\text{H}$  NMR (400 MHz,



chloroform-*d*)  $\delta$  7.82 – 7.74 (m, 2H), 7.63 – 7.56 (m, 2H), 7.56 – 7.46 (m, 3H), 7.36 – 7.22 (m, 3H), 4.12 (ddd,  $J$  = 10.4, 6.1, 2.3 Hz, 1H), 3.17 (ddd,  $J$  = 18.0, 10.4, 3.6 Hz, 1H), 2.71 (ddd,  $J$  = 18.1, 10.4, 2.3 Hz, 1H), 2.45 (pd,  $J$  = 6.8, 2.3 Hz, 1H), 1.89 (s, 3H), 1.87 – 1.75 (m, 2H), 1.54 (dd,  $J$  = 11.6, 3.5 Hz, 1H), 1.42 (ddd,  $J$  = 13.0, 6.3, 3.2 Hz, 1H), 1.02 (dtd,  $J$  = 29.6, 11.8, 11.0, 4.7 Hz, 2H), 0.79 (d,  $J$  = 6.3 Hz, 3H), 0.76 – 0.60 (m, 2H), 0.57 (dd,  $J$  = 13.4, 6.7 Hz, 7H);  $^{13}\text{C}$  NMR (101 MHz, chloroform-*d*)  $\delta$  206.01 (d,  $J$  = 12.3 Hz), 137.52 (d,  $J$  = 4.4 Hz), 133.38 (d,  $J$  = 85.0 Hz), 132.07 – 130.95 (m), 130.27 (d,  $J$  = 5.8 Hz), 129.26 – 128.35 (m), 127.54 (d,  $J$  = 2.0 Hz), 45.88, 43.30 (d,  $J$  = 3.2 Hz), 42.27 (d,  $J$  = 63.8 Hz), 38.46 (d,  $J$  = 62.1 Hz), 35.05 (d,  $J$  = 1.8 Hz), 34.57 (d,  $J$  = 1.8 Hz), 33.30 (d,  $J$  = 13.2 Hz), 30.95, 28.08 (d,  $J$  = 1.8 Hz), 25.14 (d,  $J$  = 12.9 Hz), 22.75, 21.40, 16.00. HRMS (EI<sup>+</sup>): Calculated for  $\text{C}_{26}\text{H}_{35}\text{O}_2\text{P}$ , 410.2375, found 410.2373.

### S3-2. Reaction of 4-phenylbutene-2-one **6** with $S_{\text{C}}\text{-4a}$

**General procedure:** To the solution of  $S_{\text{C}}\text{-4a}$  (0.2 g, 0.5 mmol) in DMSO (1 ml), 4-phenylbutene-2-one **6** (0.5 mmol or 1 mmol) and potassium hydroxide (9 mg, 0.13 mmol) were added in turn. The mixture was stirred at room temperature for 6 hours or so, and the reaction was monitored with  $^{31}\text{P}$  NMR spectroscopy (ca. 0.1 ml reaction mixture was dissolved in 0.4 ml chloroform). After the reaction finished, acetic acid (0.1 ml) was added to the mixture, followed by addition of methanol (3 ml). The mixture was filtered through silica gel, concentrated under vacuum, and analyzed with NMR spectroscopy.

The same stereomers  $S_{\text{C}}\text{-7}/R_{\text{C}}\text{-7}$ , only in different ratio, were obtained from route A and B, which confirmed the same *P*-retention mechanism for them. The structure of  $S_{\text{C}}\text{-7}$  was determined based on route A and the ratio in Scheme 3.

When **6** (1 mmol) was used, the peaks of crude product located at  $\delta$  49.46 ( $S_{\gamma\text{-C}}\text{-3a}$ , s, 4 %), 46.75 ( $R_{\text{C}}\text{-7}$ , s, 12 %), 45.18 ( $S_{\text{C}}\text{-7}$ , s, 72 %), 42.11 ( $S_{\gamma\text{-C}}\text{-3a}$ , s, 4 %), and other unconfirmed peaks (8 %).

When **6** (0.5 mmol) was used, the peaks of crude product located at  $\delta$  49.46 ( $S_{\gamma\text{-C}}\text{-3a}$ , s, 28 %), 46.75 ( $R_{\text{C}}\text{-7}$ , s, 3.5 %), 45.18 ( $S_{\text{C}}\text{-7}$ , s, 26.5 %), 42.11 ( $S_{\gamma\text{-C}}\text{-4a}$ , s, 28 %), and other unconfirmed peaks (14 %).

### Part S4. Reaction of $S_{\gamma\text{-C}}\text{-3a}$ with aldehydes in the presence of KOH

To the solution of  $S_{\gamma\text{-C}}\text{-3a}$  (0.33 g, 0.5 mmol) in DMSO (2 ml), *o*-chlorobenzaldehyde (70 mg, 56  $\mu\text{l}$ , 0.5 mmol) and potassium hydroxide (9 mg 0.13 mmol) were added in turn. The mixture was stirred at room temperature, and the reaction was monitored with  $^{31}\text{P}$  NMR spectroscopy (ca. 0.1 ml reaction mixture was dissolved in 0.4 ml chloroform). After 17 hours, aqueous saturated ammonium chloride solution (2 ml) was added to the mixture. The resulted solid was collected by filtration, dried under the air, and analyzed with NMR spectroscopy (162 MHz, chloroform-*d*), which showed that  $S_{\gamma\text{-C}}\text{-3a}$  was recovered.

The peaks of crude product located at  $\delta$  49.46 ( $S_{\gamma\text{-C}}\text{-3a}$ , s, >49%), 42.11 ( $S_{\gamma\text{-C}}\text{-3a}$ , s, >49 %).

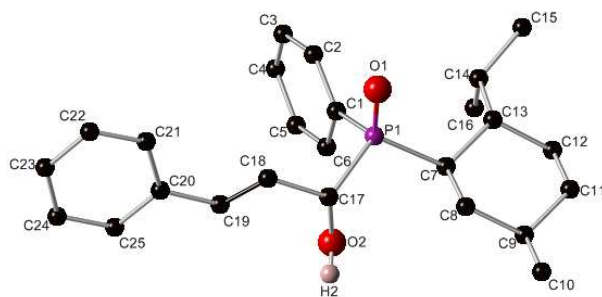
## Part S5. Crystallographic Information

### S5-1. Crystal Structure Report for S<sub>C</sub>-4a (ccdc 989825)

A clear colorless block-like specimen of C<sub>25</sub>H<sub>33</sub>O<sub>2</sub>P, approximate dimension 0.28 mm x 0.29 mm x 0.40 mm was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 0.5 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm, the integration of the data using an orthorhombic unit cell yielded a total of 11524 reflections to a maximum  $\theta$  angle of 25.01°, of which 4046 were independent (average redundancy 2.848,  $R_{\text{int}} = 4.84\%$ ,  $R_{\text{sig}} = 5.91\%$ ) and 2606 (64.41%) were greater than  $2\sigma(F^2)$ . The final cell constants of  $a = 8.1842(6)$  Å,  $b = 11.2368(11)$  Å,  $c = 24.851(2)$  Å, volume = 2285.4(3) Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of 2644 reflections above  $20\sigma(I)$  with  $5.24^\circ < 2\theta < 42.96^\circ$ .

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 21 21 21, with  $Z = 4$  for the formula unit, C<sub>25</sub>H<sub>33</sub>O<sub>2</sub>P. The final anisotropic full-matrix least-squares refinement on  $F^2$  with 257 variables converged at  $R1 = 4.53\%$ , for the observed data and  $wR2 = 10.94\%$  for all data. The goodness-of-fit was 1.039. The largest peak in the final difference electron density synthesis was 0.151 e<sup>-</sup>/Å<sup>3</sup> and the largest hole was -0.237 e<sup>-</sup>/Å<sup>3</sup> with an RMS deviation of 0.036 e<sup>-</sup>/Å<sup>3</sup>. On the basis of the final model the calculated density was 1.152 g/cm<sup>3</sup> and  $F(000)$ , 856 e<sup>-</sup>.

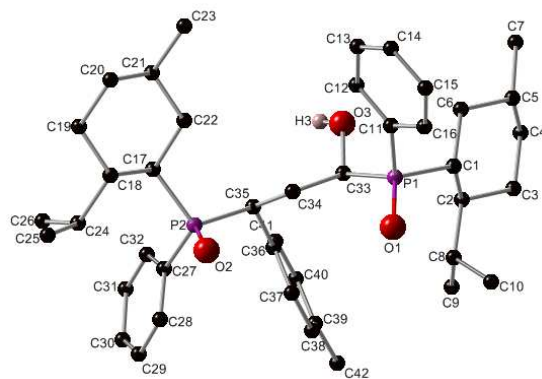
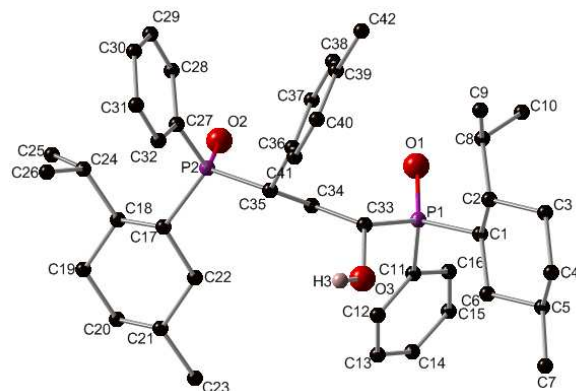


## S5-2. Crystal Structure Report for 3c (ccdc 989827)

A clear colorless block-like specimen of  $C_{42}H_{60}O_3P_2$ , approximate dimension 0.11 mm x 0.23 mm x 0.48 mm was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

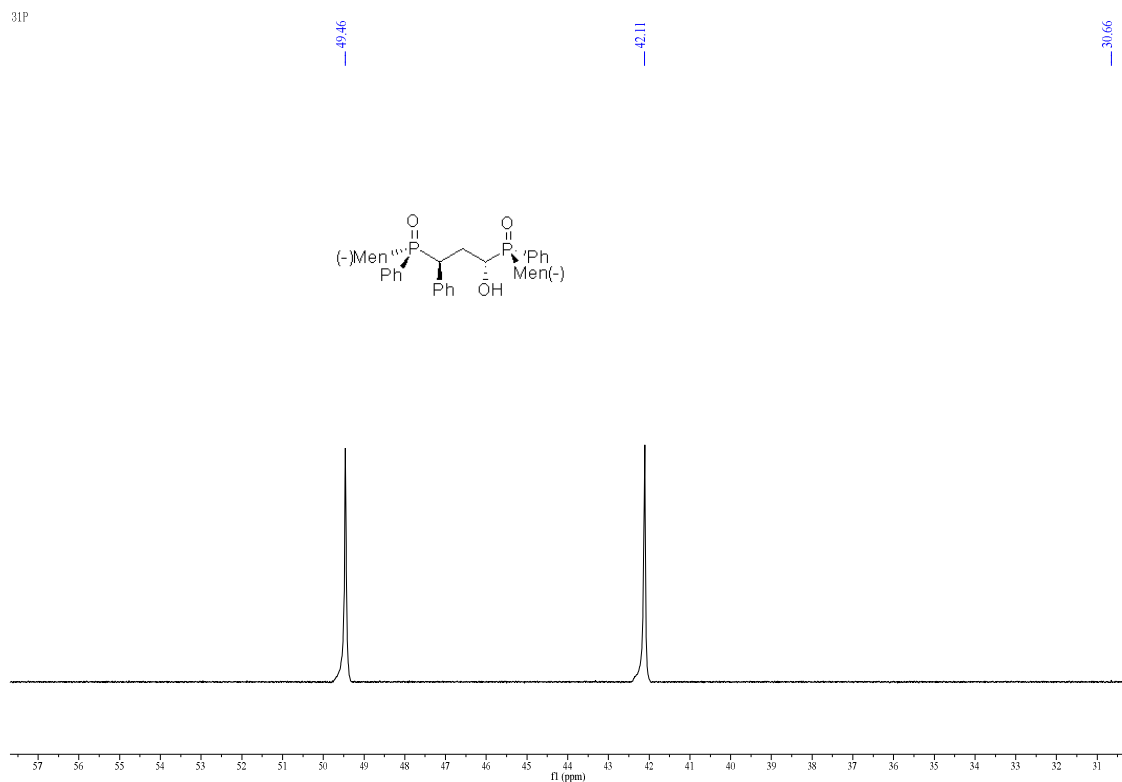
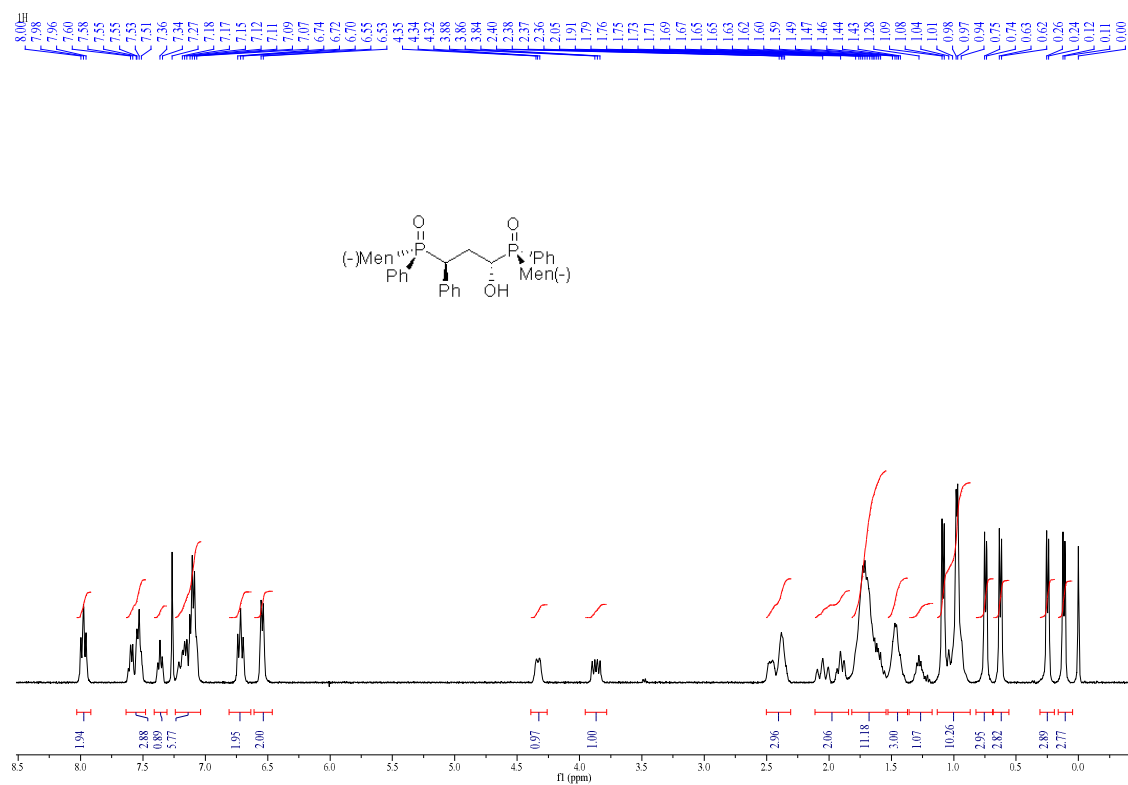
The total exposure time was 1.42 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm, the integration of the data using an Monoclinic unit cell yielded a total of 10226 reflections to a maximum  $\theta$  angle of  $25.02^\circ$ , of which 6679 were independent (average redundancy 1.531,  $R_{\text{int}} = 6.34\%$ ,  $R_{\text{sig}} = 15.13\%$ ) and 3373 (50.50%) were greater than  $2\sigma(F^2)$ . The final cell constants of  $a = 12.9832(11) \text{ \AA}$ ,  $b = 6.1872(6) \text{ \AA}$ ,  $c = 25.679(3) \text{ \AA}$ , volume =  $2021.7(3) \text{ \AA}^3$ , are based upon the refinement of the XYZ-centroids of 1372 reflections above  $20 \sigma(I)$  with  $6.28^\circ < 2\theta < 39.34^\circ$ .

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 21, with  $Z = 2$  for the formula unit,  $C_{42}H_{60}O_3P_2$ . The final anisotropic full-matrix least-squares refinement on  $F^2$  with 432 variables converged at  $R1 = 6.37\%$ , for the observed data and  $wR2 = 12.47\%$  for all data. The goodness-of-fit was 0.961. The largest peak in the final difference electron density synthesis was  $0.305 \text{ e}/\text{\AA}^3$  and the largest hole was  $-0.316 \text{ e}/\text{\AA}^3$  with an RMS deviation of  $0.045 \text{ e}/\text{\AA}^3$ . On the basis of the final model the calculated density was  $1.109 \text{ g}/\text{cm}^3$  and  $F(000)$ , 732  $e^-$ .

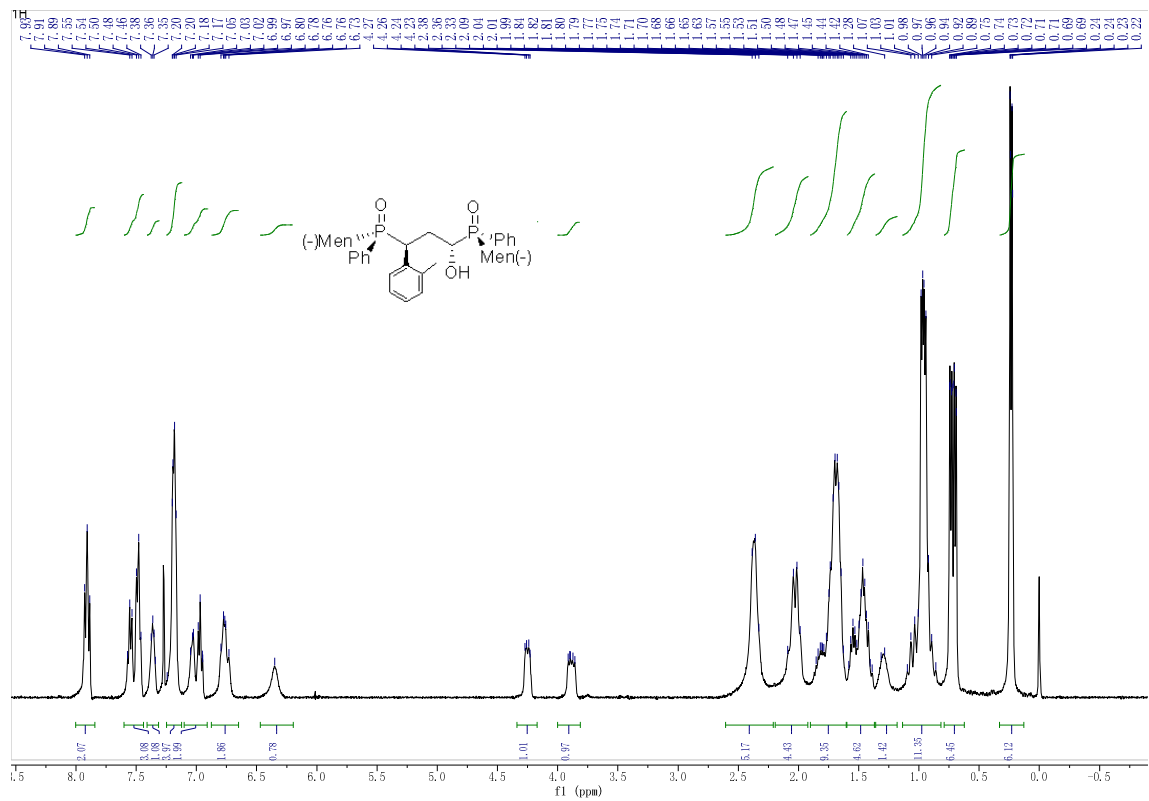


Part S6. Selected Spectra of compounds 3, 4 and 7.

(1*S*,3*S*,*R*<sub>α-P</sub>,*S*<sub>γ-P</sub>)-1-Phenyl-3-hydroxypropane-1,3-diylbismethylphenylphosphine oxide, 3a

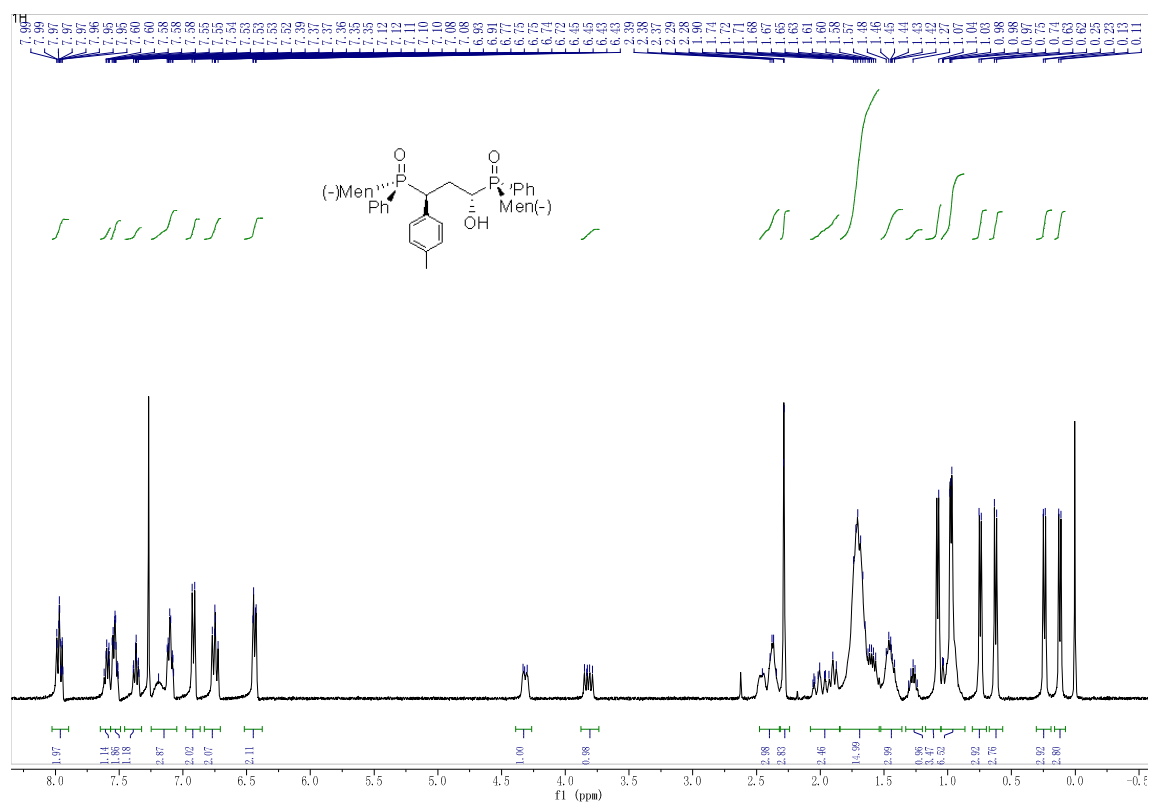


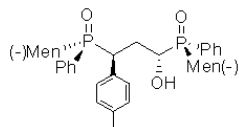
**(1*S*,3*S*,*R*<sub>α-P</sub>,*S*<sub>γ-P</sub>)-1-*o*-Tolyl-3-hydroxypropane-1,3-diylbismenthylphenylphosphine oxide, 3b**





**(1*S*,3*S*,*R*<sub>α-P</sub>,*S*<sub>γ-P</sub>)-1-*p*-Tolyl-3-hydroxypropane-1,3-diylbismenthylphenylphosphine oxide, 3c**





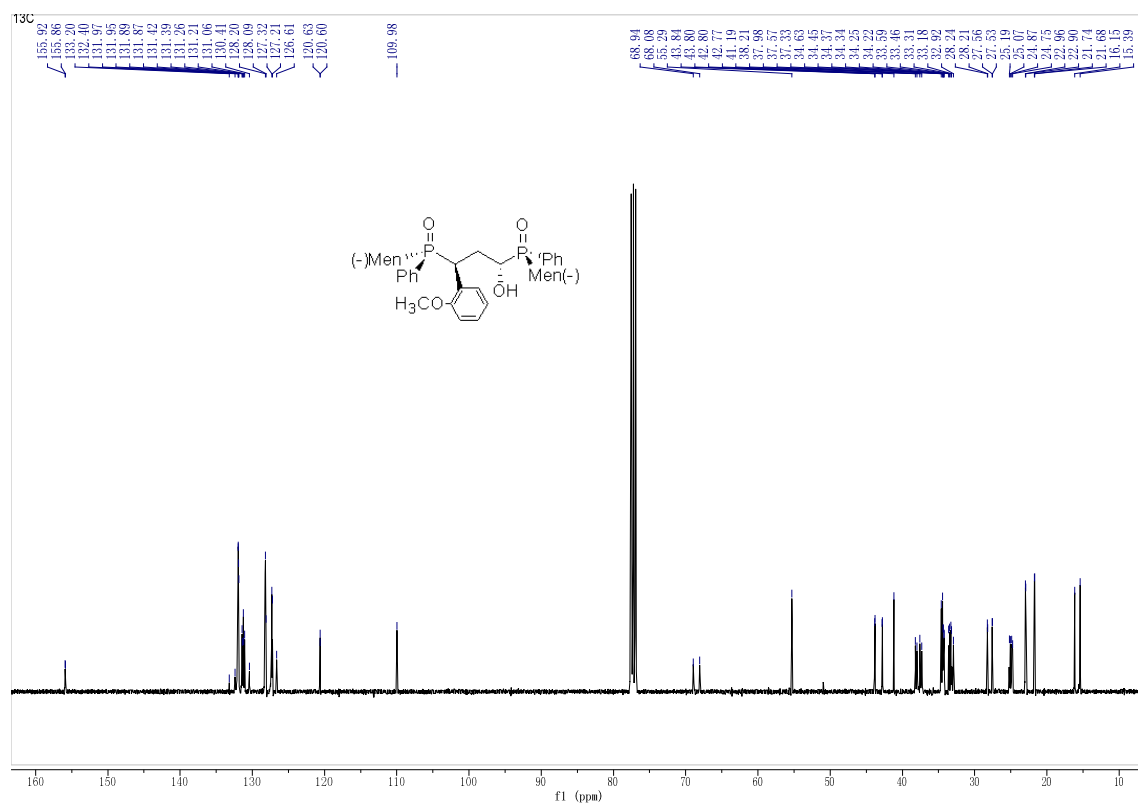
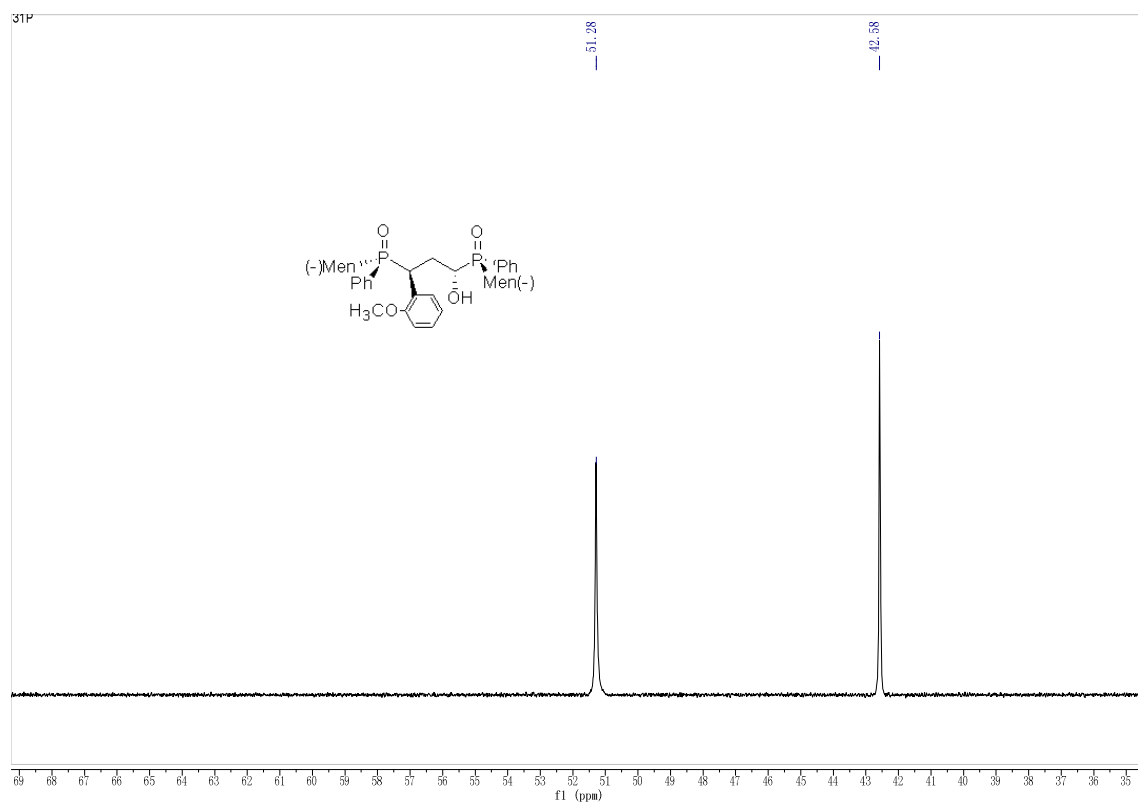
**Chemical structure of compound 10:**

COP(=O)(c1ccccc1)C[C@H](c2ccccc2)C[C@@H](c3ccccc3)P(=O)(c4ccccc4)C

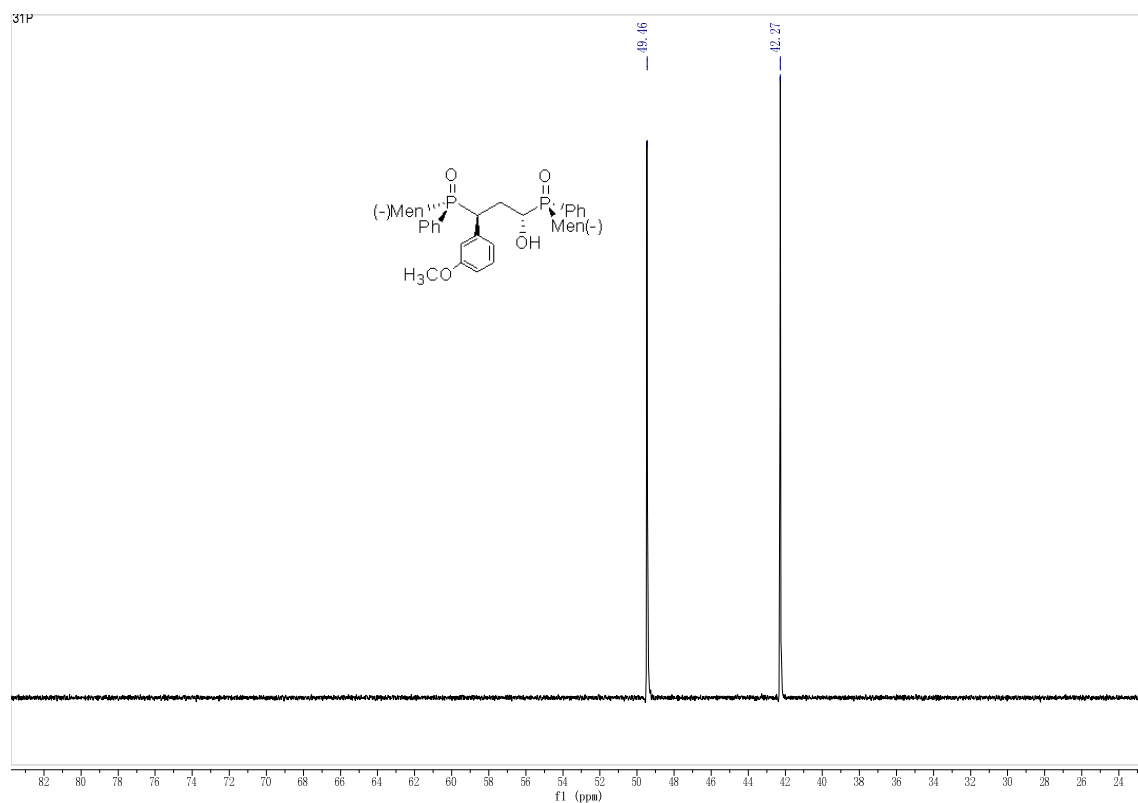
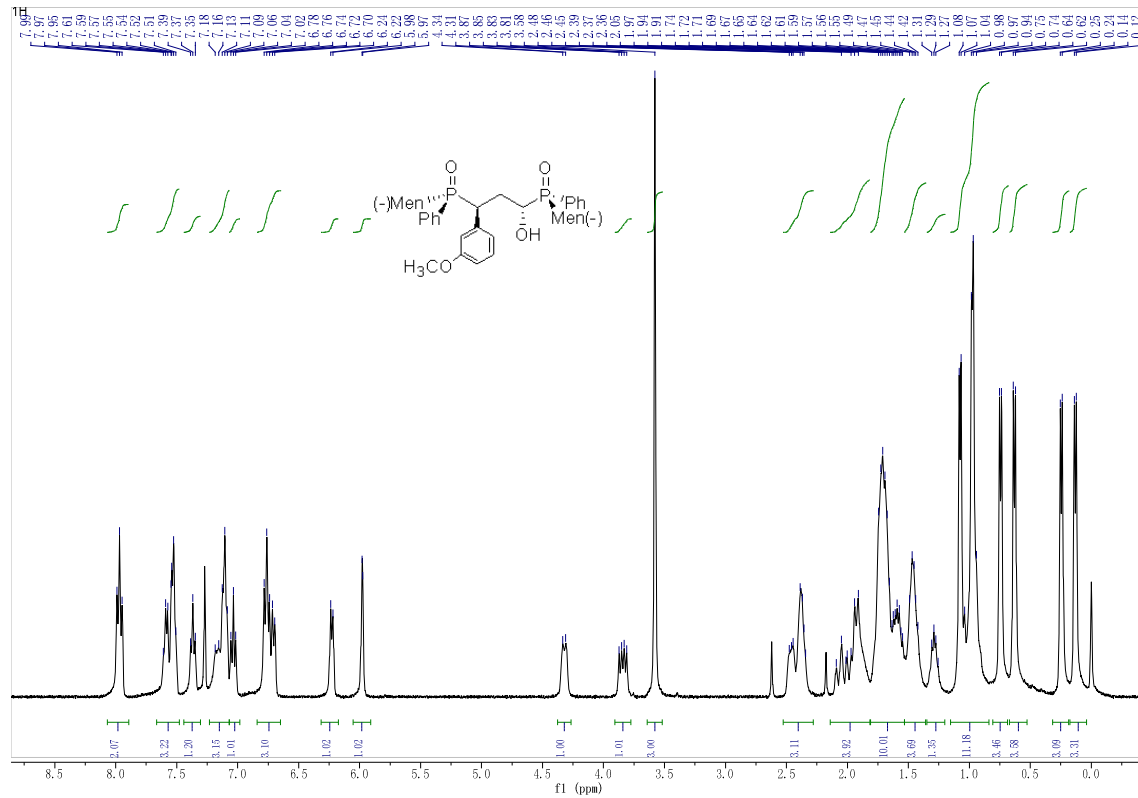
**<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>):**

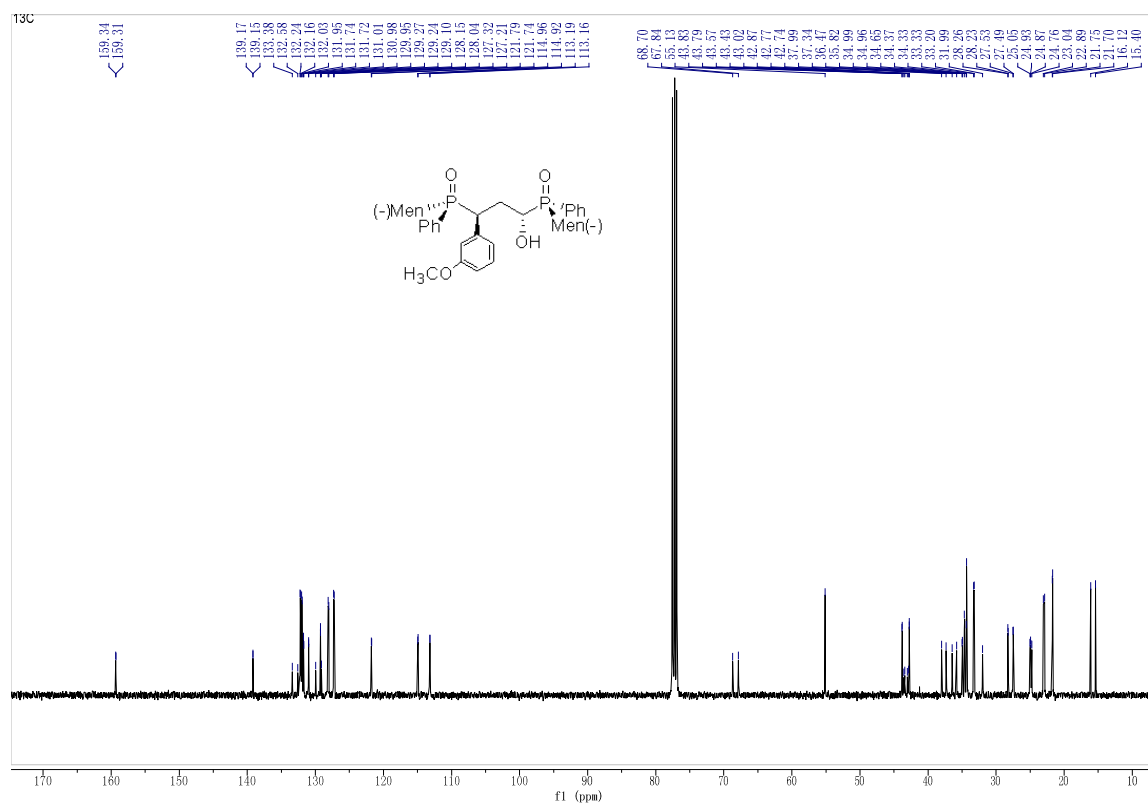
Chemical Shift (ppm)	Integration
8.50	1.00
8.00	1.00
7.50	1.00
7.00	1.00
6.50	1.00
6.00	1.00
4.50	1.00
4.00	1.00
3.50	1.00
3.00	1.00
2.50	1.00
2.00	1.00
1.50	1.00
1.00	1.00
0.50	1.00
0.10	1.00



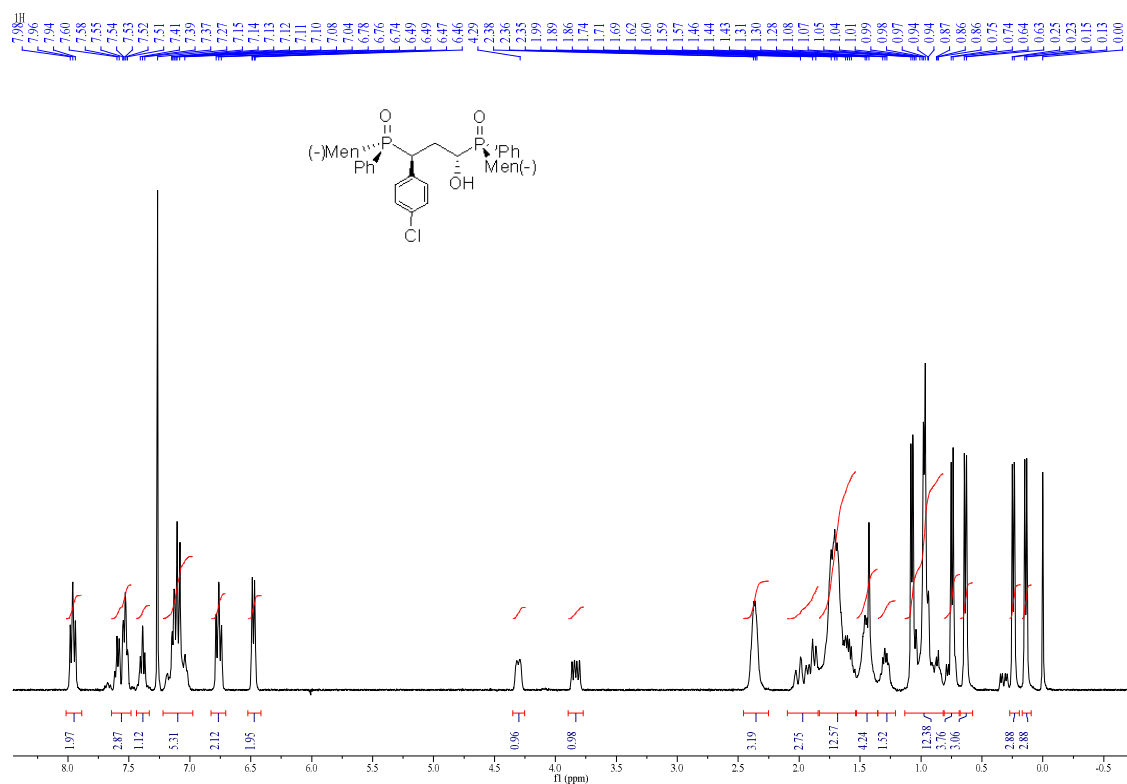


**(1*S*,3*S*,*R*<sub>α-P</sub>,*S*<sub>γ-P</sub>)-1-*m*-Methoxyphenyl-3-hydroxypropane-1,3-diylbismenthylphenylphosphine oxide, 3e**

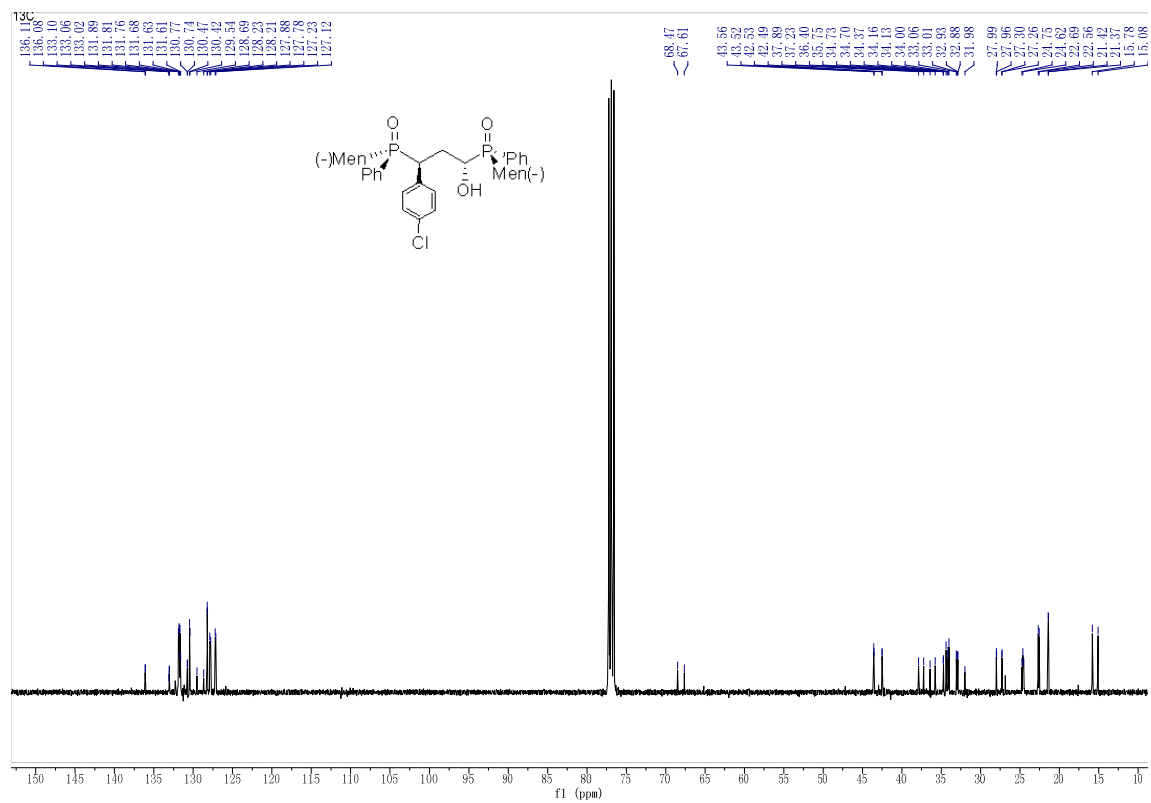
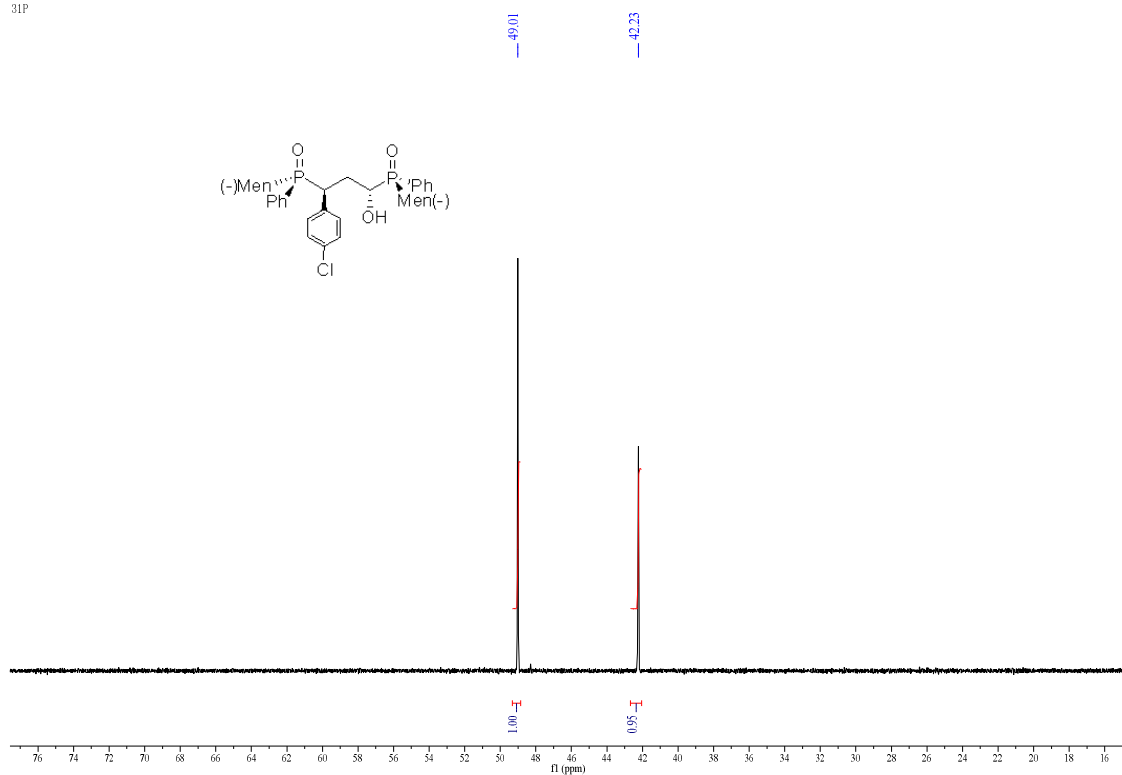




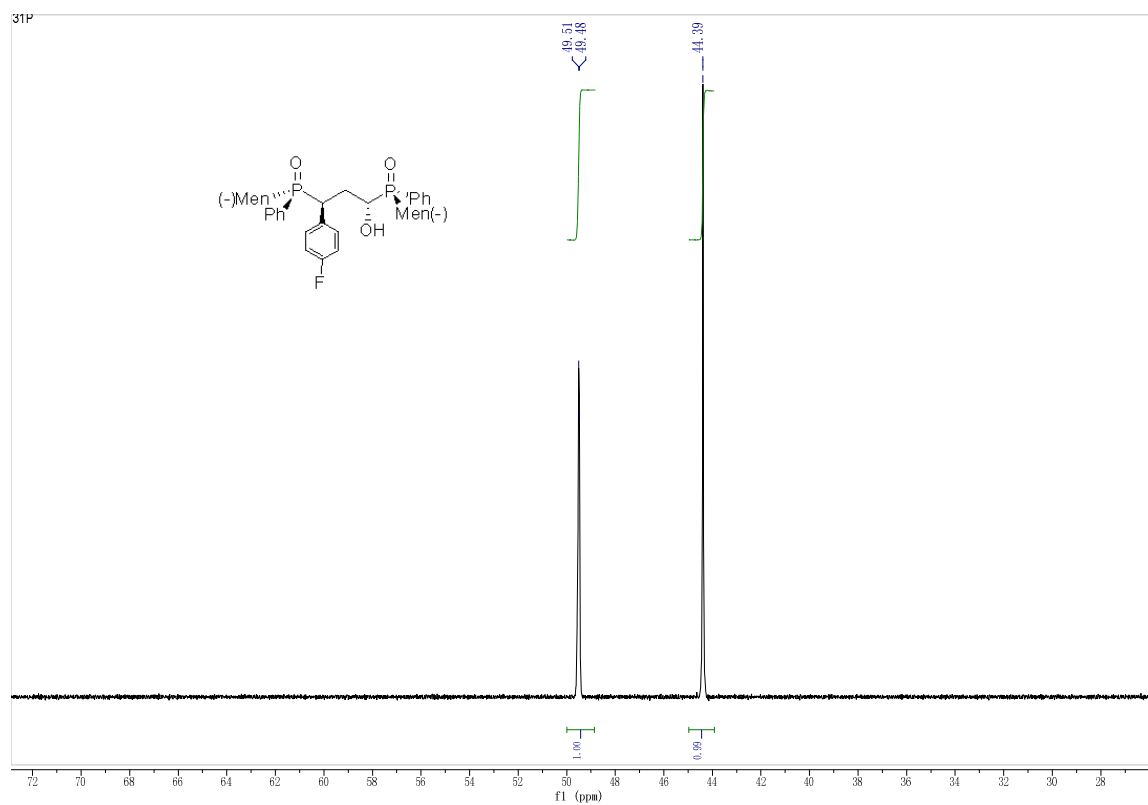
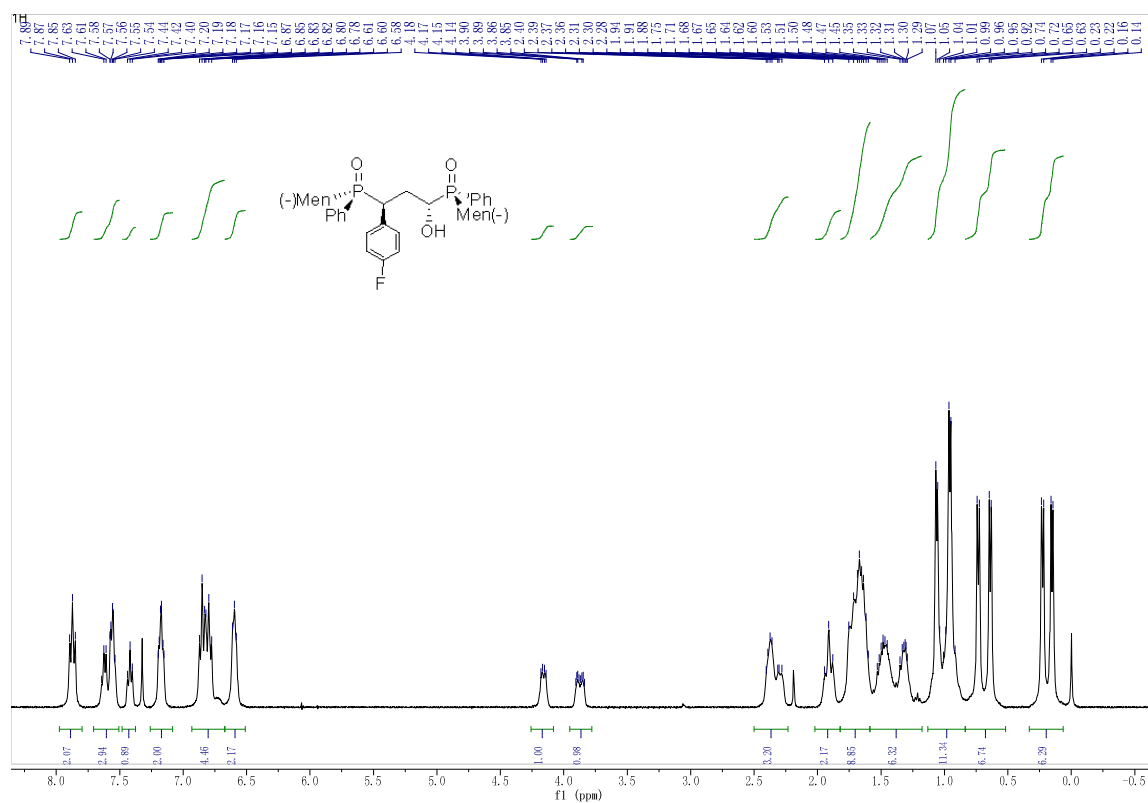
**(1*S*,3*S*,*R*<sub>α-P</sub>,*S*<sub>γ-P</sub>)-1-*p*-Chlorophenyl-3-hydroxypropane-1,3-diylbismenthylphenylphosphine oxide, 3f**

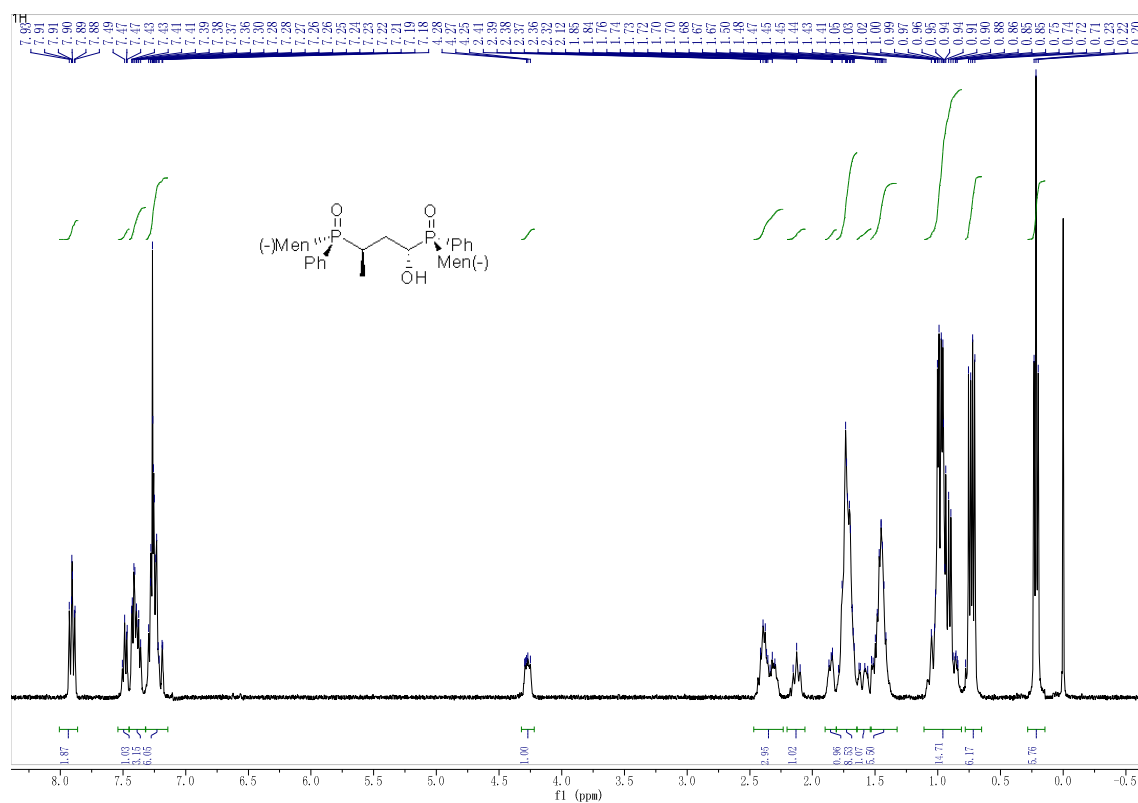
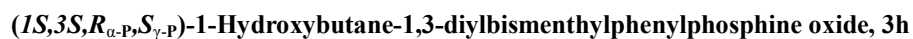


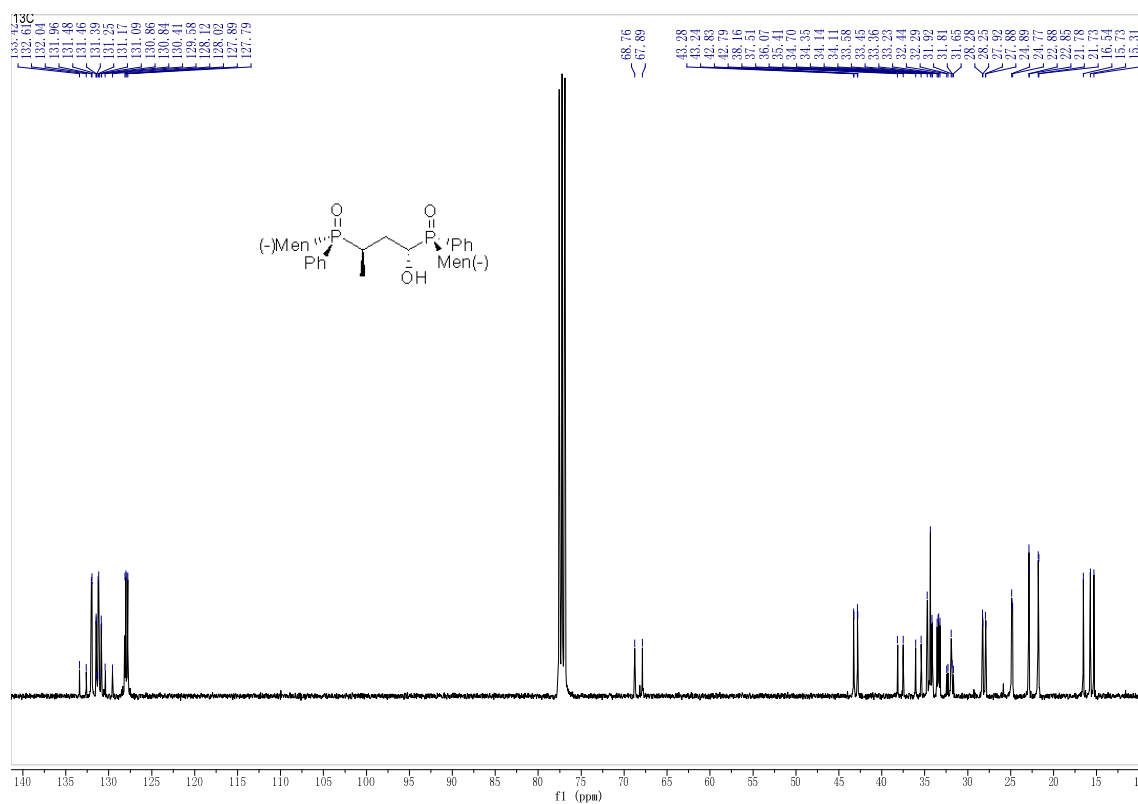
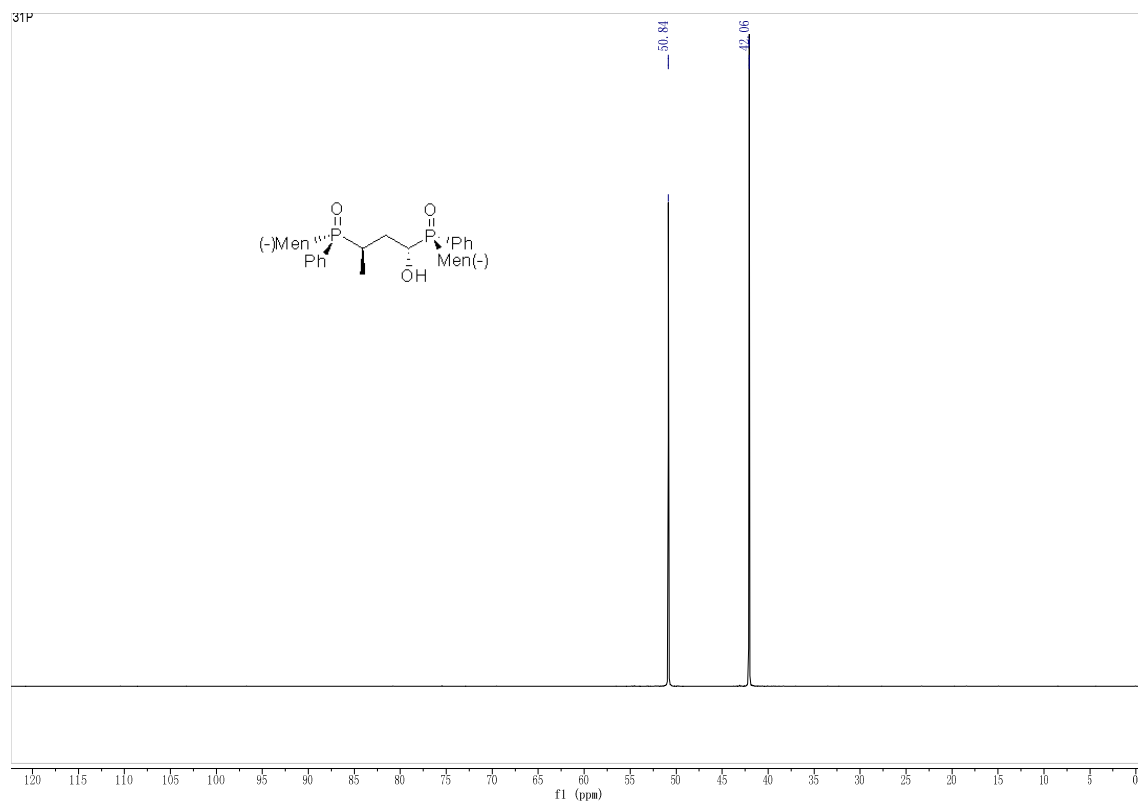
31P



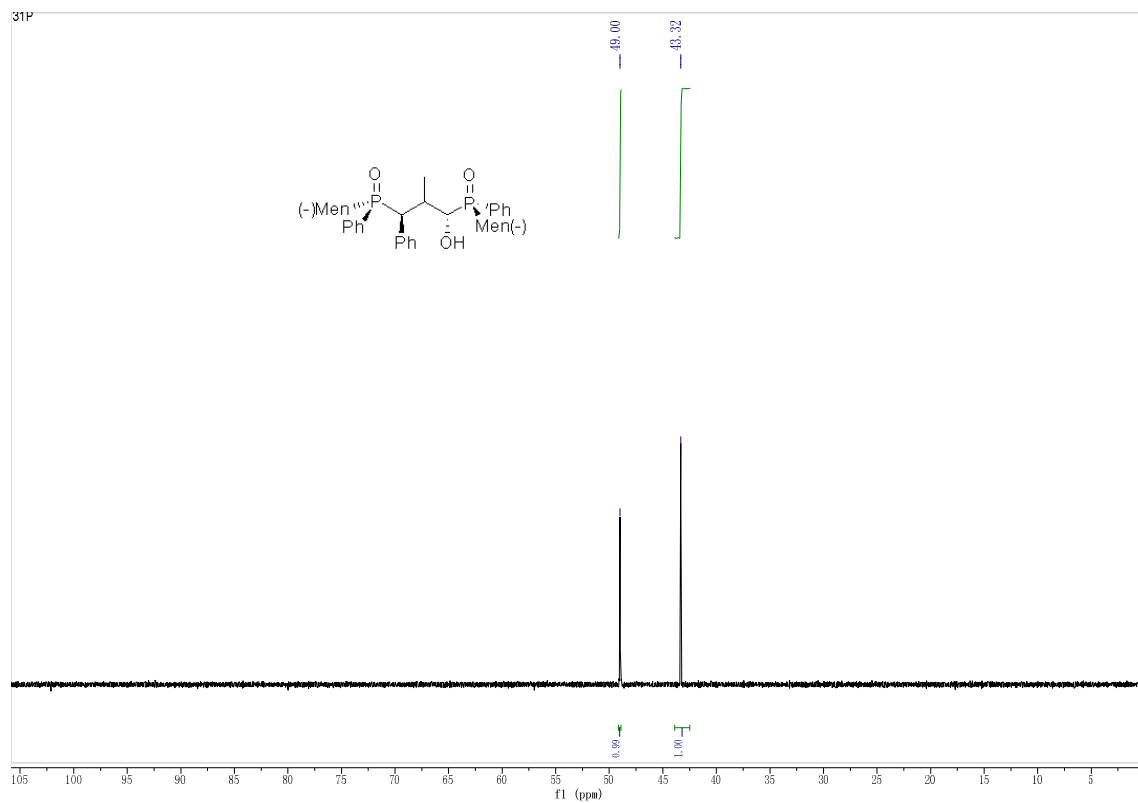
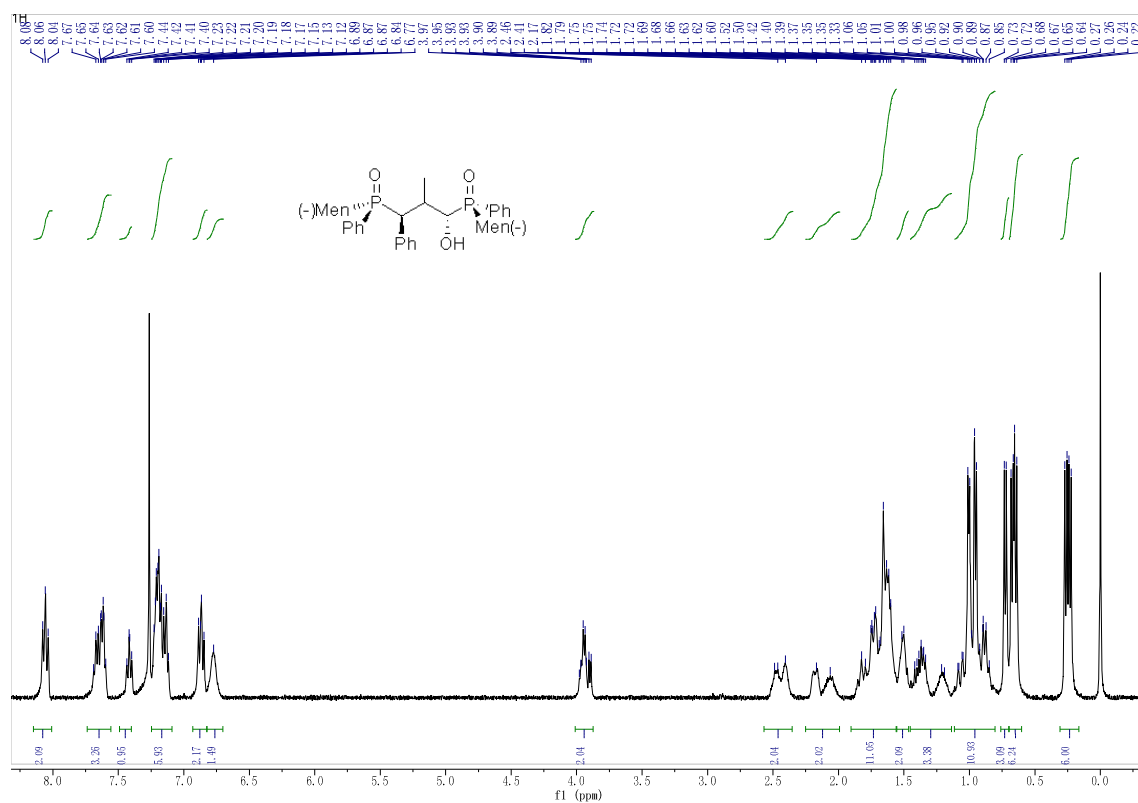
**(1*S*,3*S*,*R*<sub>α-P</sub>,*S*<sub>γ-P</sub>)-1-*p*-Fluorophenyl-3-hydroxypropane-1,3-diylbismenthylphenylphosphine oxide, 3g**



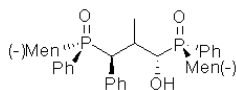




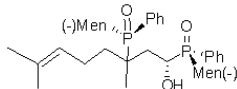
**(1*S*,3*S*,*R*<sub>α-P</sub>,*S*<sub>γ-P</sub>)-1-Phenyl-2-methyl-3-hydroxypropane-1,3-diylbismenthylphenylphosphine oxide, 3i**

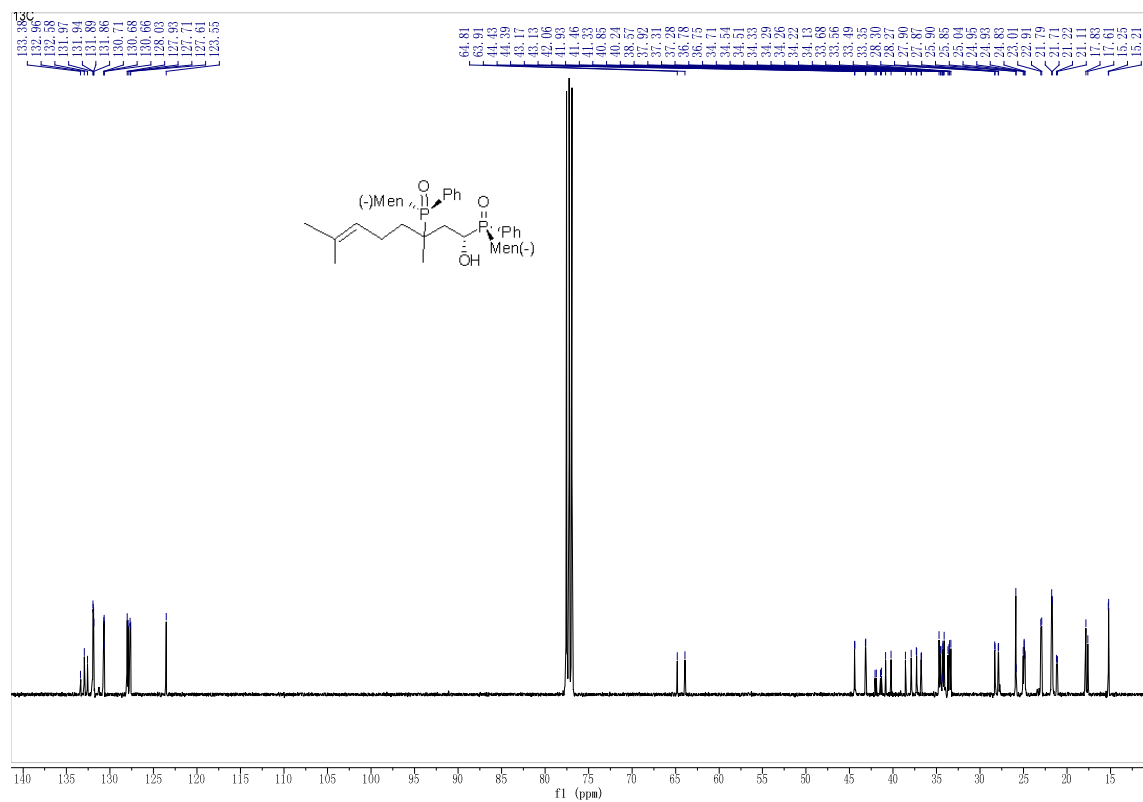
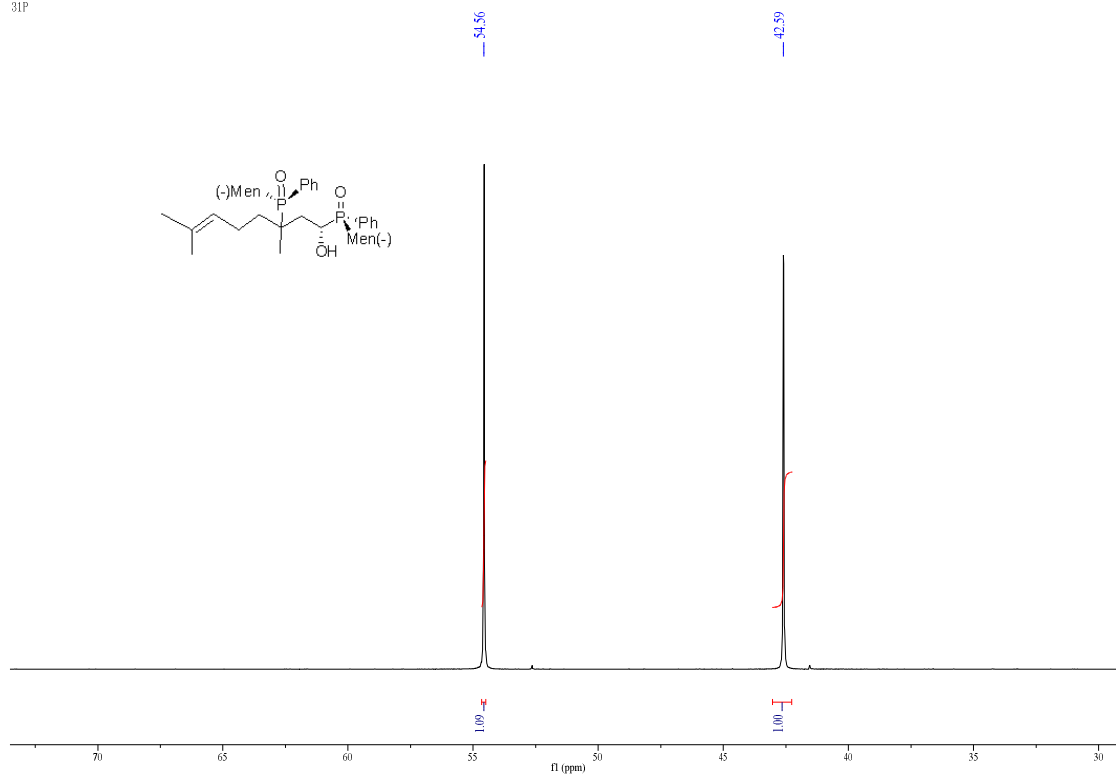




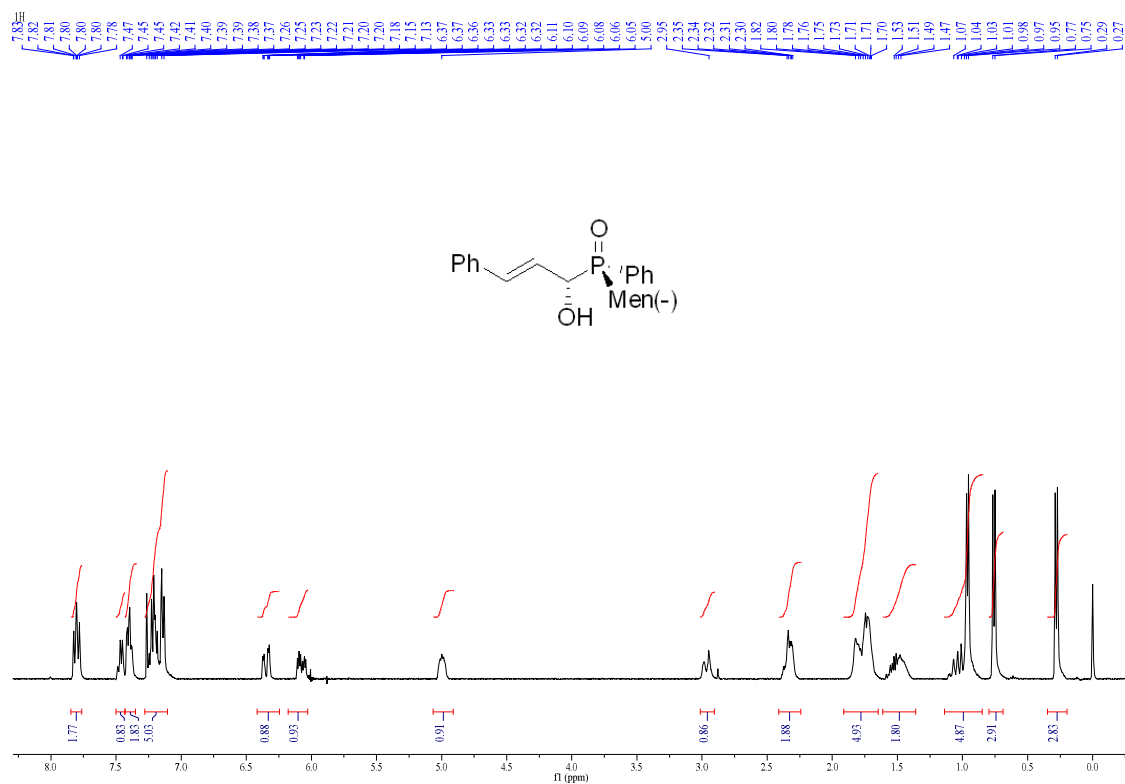


7.92	7.91	7.90	7.89	7.88	7.87	7.86	7.85	7.84	7.83	7.82	7.81	7.80	7.79	7.78	7.77	7.76	7.75	7.74	7.73	7.72	7.71	7.70	7.69	7.68	7.67	7.66	7.65	7.64	7.63	7.62	7.61	7.60	7.59	7.58	7.57	7.56	7.55	7.54	7.53	7.52	7.51	7.50	7.49	7.48	7.47	7.46	7.45	7.44	7.43	7.42	7.41	7.40	7.39	7.38	7.37	7.36	7.35	7.34	7.33	7.32	7.31	7.30	7.29	7.28	7.27	7.26	7.25	7.24	7.23	7.22	7.21	7.20	7.19	7.18	7.17	7.16	7.15	7.14	7.13	7.12	7.11	7.10	7.09	7.08	7.07	7.06	7.05	7.04	7.03	7.02	7.01	7.00	6.99	6.98	6.97	6.96	6.95	6.94	6.93	6.92	6.91	6.90	6.89	6.88	6.87	6.86	6.85	6.84	6.83	6.82	6.81	6.80	6.79	6.78	6.77	6.76	6.75	6.74	6.73	6.72	6.71	6.70	6.69	6.68	6.67	6.66	6.65	6.64	6.63	6.62	6.61	6.60	6.59	6.58	6.57	6.56	6.55	6.54	6.53	6.52	6.51	6.50	6.49	6.48	6.47	6.46	6.45	6.44	6.43	6.42	6.41	6.40	6.39	6.38	6.37	6.36	6.35	6.34	6.33	6.32	6.31	6.30	6.29	6.28	6.27	6.26	6.25	6.24	6.23	6.22	6.21	6.20	6.19	6.18	6.17	6.16	6.15	6.14	6.13	6.12	6.11	6.10	6.09	6.08	6.07	6.06	6.05	6.04	6.03	6.02	6.01	6.00	5.99	5.98	5.97	5.96	5.95	5.94	5.93	5.92	5.91	5.90	5.89	5.88	5.87	5.86	5.85	5.84	5.83	5.82	5.81	5.80	5.79	5.78	5.77	5.76	5.75	5.74	5.73	5.72	5.71	5.70	5.69	5.68	5.67	5.66	5.65	5.64	5.63	5.62	5.61	5.60	5.59	5.58	5.57	5.56	5.55	5.54	5.53	5.52	5.51	5.50	5.49	5.48	5.47	5.46	5.45	5.44	5.43	5.42	5.41	5.40	5.39	5.38	5.37	5.36	5.35	5.34	5.33	5.32	5.31	5.30	5.29	5.28	5.27	5.26	5.25	5.24	5.23	5.22	5.21	5.20	5.19	5.18	5.17	5.16	5.15	5.14	5.13	5.12	5.11	5.10	5.09	5.08	5.07	5.06	5.05	5.04	5.03	5.02	5.01	5.00	4.99	4.98	4.97	4.96	4.95	4.94	4.93	4.92	4.91	4.90	4.89	4.88	4.87	4.86	4.85	4.84	4.83	4.82	4.81	4.80	4.79	4.78	4.77	4.76	4.75	4.74	4.73	4.72	4.71	4.70	4.69	4.68	4.67	4.66	4.65	4.64	4.63	4.62	4.61	4.60	4.59	4.58	4.57	4.56	4.55	4.54	4.53	4.52	4.51	4.50	4.49	4.48	4.47	4.46	4.45	4.44	4.43	4.42	4.41	4.40	4.39	4.38	4.37	4.36	4.35	4.34	4.33	4.32	4.31	4.30	4.29	4.28	4.27	4.26	4.25	4.24	4.23	4.22	4.21	4.20	4.19	4.18	4.17	4.16	4.15	4.14	4.13	4.12	4.11	4.10	4.09	4.08	4.07	4.06	4.05	4.04	4.03	4.02	4.01	4.00	3.99	3.98	3.97	3.96	3.95	3.94	3.93	3.92	3.91	3.90	3.89	3.88	3.87	3.86	3.85	3.84	3.83	3.82	3.81	3.80	3.79	3.78	3.77	3.76	3.75	3.74	3.73	3.72	3.71	3.70	3.69	3.68	3.67	3.66	3.65	3.64	3.63	3.62	3.61	3.60	3.59	3.58	3.57	3.56	3.55	3.54	3.53	3.52	3.51	3.50	3.49	3.48	3.47	3.46	3.45	3.44	3.43	3.42	3.41	3.40	3.39
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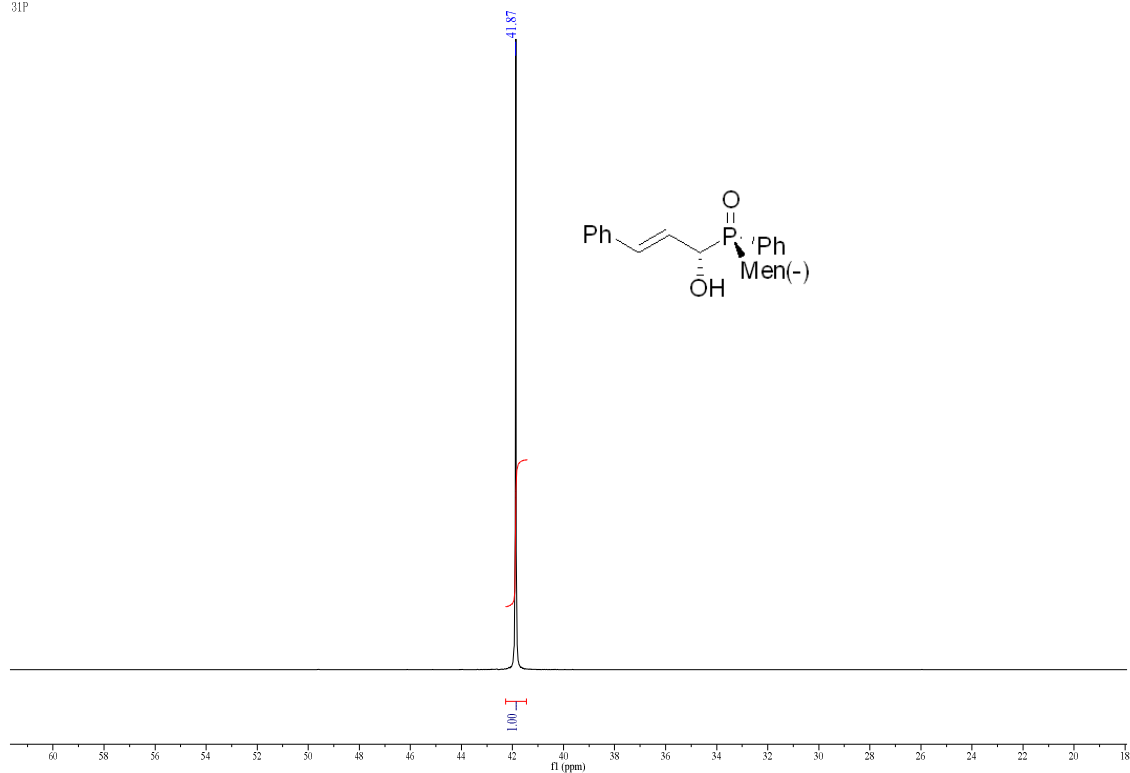


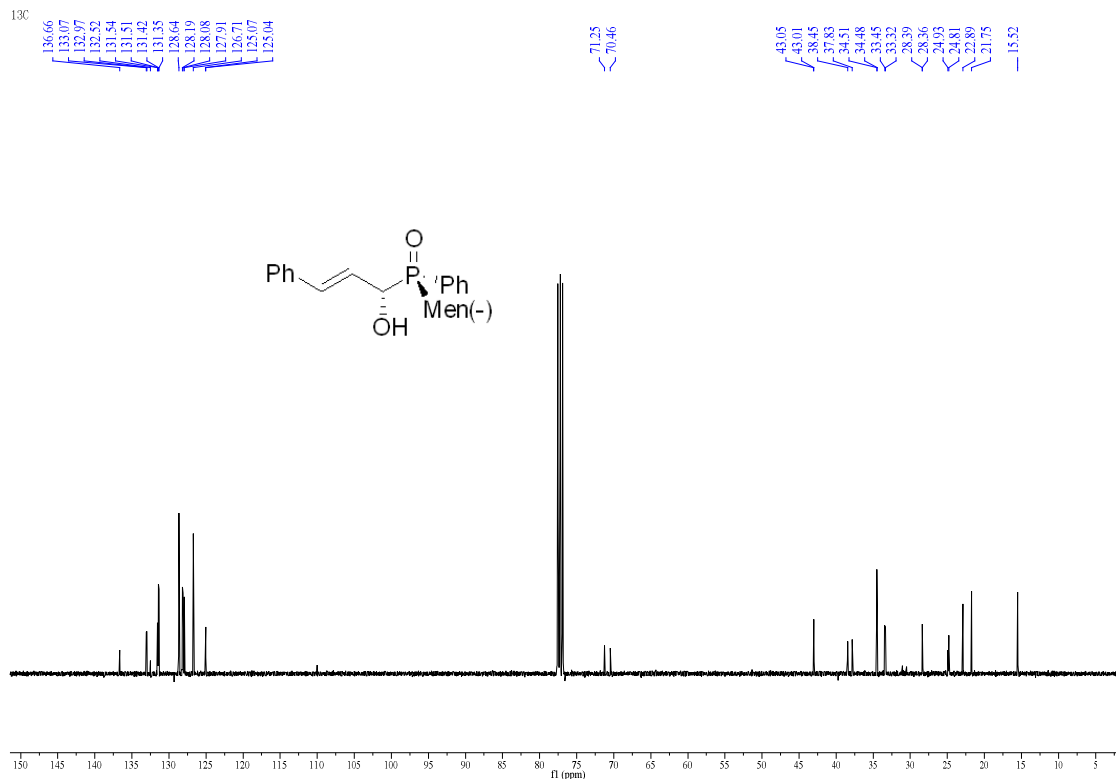


**(*R<sub>p</sub>*)-(-)-Menthyl[(*S,E*)-1-hydroxy-3-phenylallyl]phenylphosphine oxide, *S<sub>C</sub>*-4a**

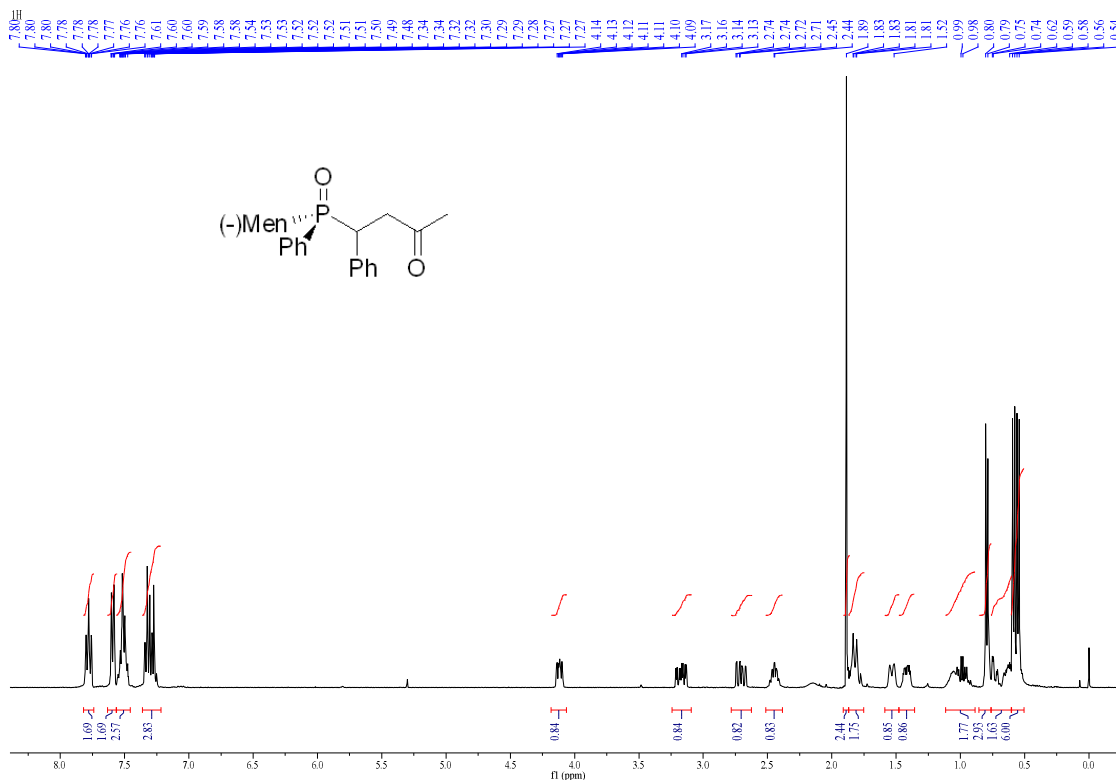


<sup>31</sup>P



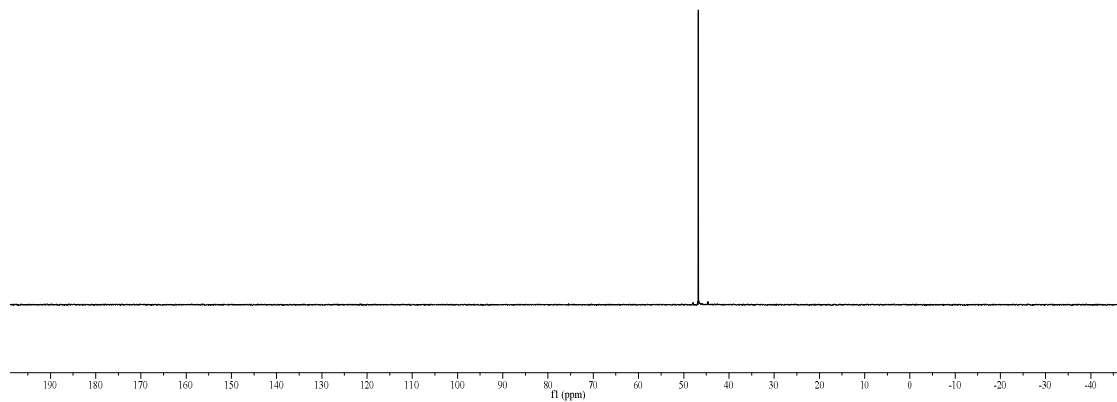
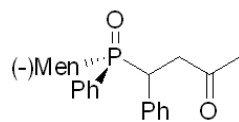


**(*S<sub>P</sub>*)-4-[(*R*)-(-)-Menthylphenylphosphoryl]-4-phenylbutan-2-one, *R<sub>C</sub>*-7**



31P

46.75



13C

206.08  
203.95

137.55  
137.50  
133.80  
132.96  
131.59  
131.52  
131.35  
131.28  
130.30  
130.25  
128.73  
128.73  
128.75  
128.66  
127.55  
127.53

45.89  
43.22  
43.28  
42.59  
41.95  
38.77  
38.66  
35.04  
34.58  
34.56  
33.37  
33.23  
30.95  
28.02  
28.07  
25.21  
25.08  
22.75  
21.40  
16.00

