The Construction of Three C-P Bonds of P-Stereogenic Tertiary Phosphines Containing (*L*)-Menthyl

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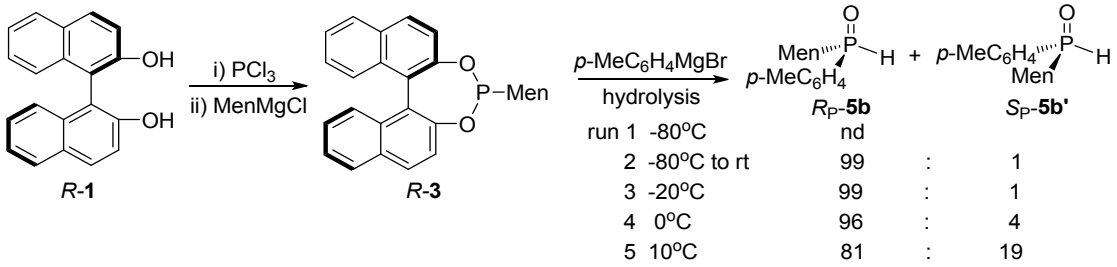
General Chemistry:

^{1}H NMR spectrum were recorded on a 400-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 101 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 162 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. 0.8 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 optimization of temperature for the stereoselective formation of R_P-5b/S_P-5b'.



The preparation of binaphthoxy phosphorochloridate *R*-2

A 100 mL, single-necked round-bottomed flask charged with (*R*)-(+)-1,1'-bi(2-naphthol) (2.29 g, 8 mmol) and toluene (10 mL) followed by *N*, *N*-dimethylformamide (20 μL, 0.26 mmol) under dry air, then the flask was cooled with ice-water added dropwise phosphorus trichloride (2 mL, 24 mmol). The mixture was stirred at 50 °C in an oil bath for 2 hours, during which time it became a colorless homogeneous solution. Toluene and excess phosphorus trichloride were removed via vacuum distillation and the DMF was azeotropically removed with toluene (2 × 10 mL) under high vacuum to afford the phosphochloridite *R*-**2** as an oily foam compound.

The preparation of binaphthoxy menthylphosphonites *R*-3

The above obtained *R*-**2** (2.8 g, 8 mmol) was dissolved in tetrahydrofuran (15 mL) under the atmosphere of N_2. To the ice-water cooled solution, menthyl magnesium chloride (0.8 M solution in THF, 15 mL, 12 mol) was added. After warming to room temperature and stirring for 6 hours, the solution of ***R*-3** (0.27 mol/L) was obtained, which was used in situ in the subsequent procedures. The subsequent preparation of *R*-**10a** from *R*-**2** confirmed the yield was near to completely (vide infra).

Typical procedure for the reaction of 3 with 4b:

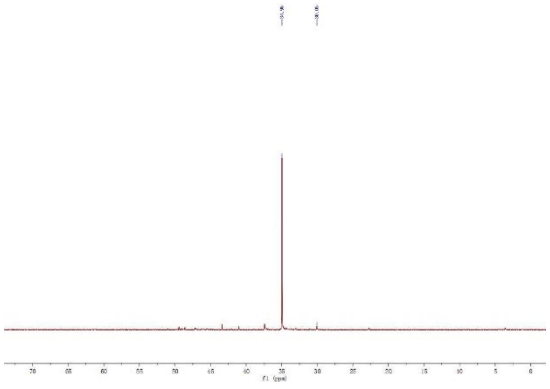
Run 1

Under the atmosphere of N_2, the solution of ***R*-3** (3 mL, 0.8 mmol) was cooled to -80 °C, then a solution of *p*-tolyl magnesium bromide **4b** (0.8 M solution in THF, 1.2 mL, 0.96 mmol) was added dropwise. After the mixture was stirred at -80 °C for 4 hours, diluted hydrochloric acid (7%, 1 mL) was added, and the mixture was heated with stirring at 50 °C for 6 hours. The mixture was extracted with ether (20 mL), washed with water (3 × 10 mL), dried over magnesium sulfate. The solution was analyzed with ^{31}P NMR spectrum (ca. 0.5 mL solution was transferred to a NMR

tube with syringe under nitrogen). No effective peak of **5b** was detected on NMR spectrum.

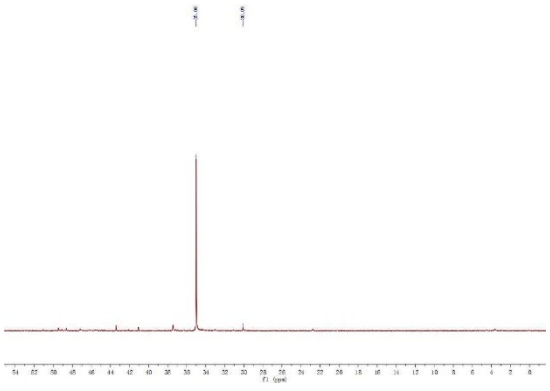
Run 2

Under the atmosphere of N_2, the solution of ***R*-3** (3 mL, 0.8 mmol) was cooled to -80 °C, then a solution of **4b** (0.8 M solution in THF, 1.2 mL, 0.96 mmol) was added dropwise. The mixture was stirred and warmed to room temperature within 4 hours, diluted hydrochloric acid (7%, 1 mL) was added. After stirred at 50 °C for 6 hours, the mixture was extracted with ether (20 mL), washed with water (3 × 10 mL), dried over magnesium sulfate. The solution was analyzed with ^{31}P NMR spectrum, and two peaks at 34.96 (s, 99%) and 30.05 ppm (s, 1%) were observed.



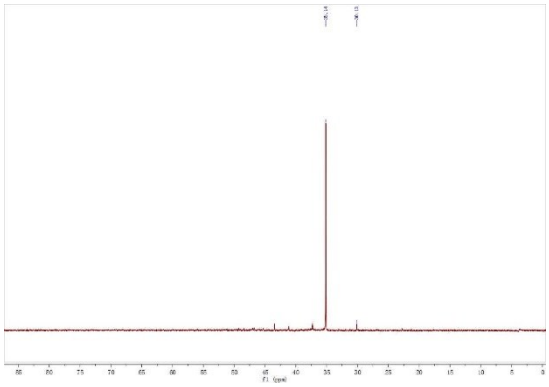
Run 3

The reaction was carried out under similar procedure to Run 2, except **4b** was added at -20 °C. The solution was analyzed with ^{31}P NMR spectrum, and two peaks at 34.96 (s, 99%) and 30.05 ppm (s, 1%) was observed.



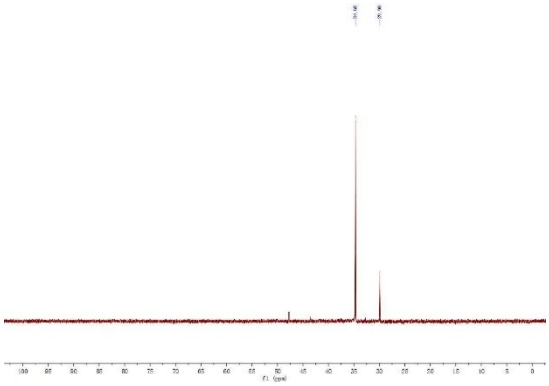
Run 4

The reaction was carried out under similar procedure to Run 2, except **4b** was added at 0 °C. The solution was analyzed with ^{31}P NMR spectroscopy, and two peaks at 35.00 (s, 96%) and 30.09 ppm (s, 4%) were observed.

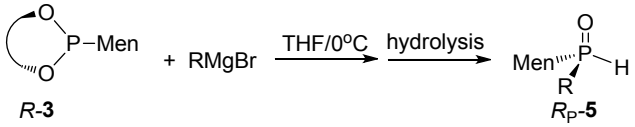


Run 5

The reaction was carried out under similar procedure to Run 2, except **4b** was added at 10 °C. The solution was analyzed with ^{31}P NMR spectroscopy, and two peaks at 34.68 (s, 81%) and 29.90 ppm (s, 19%) was observed on ^{31}P NMR spectrum.



Part 2. Preparation of R_P-5 form the substitution of *R*-3 with Grignard reagents.

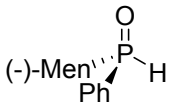


R-**3** R_P-**5**

Typical procedure:

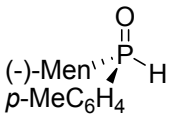
Under atmosphere of N_2, the solution of ***R*-3** (3 mL, 0.8 mmol) was cooled to 0 °C, then a solution of **4a** (0.8 M solution in THF, 1.2 mL, 0.96 mmol) was added dropwise. The mixture was stirred at the same temperature for 4 hours, then diluted hydrochloric acid (7%, 1mL) was added, and the mixture was stirred at 50 °C for 6 hours. After cooling to room temperature, the mixture was extracted with ether (20 mL), washed with water (3 × 10 mL), dried over magnesium sulfate. After removing solvent, the residue was analyzed with NMR spectrum, and purified with column chromatography on silica gel (petroleum ether/ ethyl acetate = 4/1) to afford **5a**.

***R*$_P$-(-)-Menthyl phenylphosphine oxide (5a)**



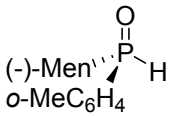
The crude **5a** was obtained from phenyl magnesium bromide (0.8 M solution in THF) in a ratio of 99:1 (estimated by ^{31}P-NMR spectrum), and the optically pure **5a** was obtained as a white solid (152.2 mg, 72%, >99:1 dr) from column chromatography, m.p.157.2 – 158.7 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 33.88 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.70 (dd, *J*=11.9, 7.4, 2H), 7.53 (dd, *J*=14.3, 6.2, 3H), 7.46 (d, *J*=115.0, 1H), 2.08 (dd, *J*=28.5, 17.4, 3H), 1.70 (s, 2H), 1.44 (d, *J*=11.5, 2H), 1.08 (dt, *J*=27.0, 11.0, 2H), 0.87 (dt, *J*=21.9, 10.8, 7H), 0.62 (d, *J*=6.7, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 132.03 (d, *J*=2.9), 130.96 (d, *J*=90.6), 130.13 (s), 130.02 (s), 128.69 (s), 128.57 (s), 42.68 (d, *J*=2.5), 40.76 (d, *J*=67.4), 34.89 (d, *J*=1.6), 34.10 (d, *J*=1.3), 32.96 (d, *J*=14.2), 28.60 (d, *J*=4.0), 24.25 (d, *J*=12.9), 22.34 (s), 21.29 (s), 15.09 (s); **HRMS (ESI$^+$)** Calcd. for $C_{16}H_{25}OP$ [M^+]: 264.1643, Found: 264.1620.

***R*$_P$-(-)-Menthyl *p*-tolylphosphine oxide (5b)**



The optically pure **5b** was obtained as a white solid (178.1 mg, 80%, >99:1 dr) from column chromatography and recrystallization with dichloromethane and petroleum ether (60-90 °C), m.p. 125.1 – 126.8 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 33.31 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.58 (dd, *J*=12.4, 7.9, 2H), 7.44 (d, *J*=115.0, 1H), 7.31 (d, *J*=6.8, 2H), 2.42 (s, 3H), 2.15 (dt, *J*=22.1, 11.1, 1H), 2.06 (dd, *J*=21.5, 10.7, 2H), 1.69 (dd, *J*=13.0, 6.4, 2H), 1.40 (dd, *J*=11.2, 3.2, 2H), 1.15 – 0.97 (m, 2H), 0.89 (t, *J*=6.7, 6H), 0.82 (dd, *J*=17.2, 7.7, 1H), 0.64 (d, *J*=6.8, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 142.52 (d, *J*=2.9), 130.21 (s), 130.10 (s), 129.46 (s), 129.34 (s), 127.55 (d, *J*=93.2), 42.76 (d, *J*=2.4), 40.82 (d, *J*=67.6), 34.72 (d, *J*=1.9), 34.19 (s), 33.00 (d, *J*=14.1), 28.56 (d, *J*=4.0), 25.66 (d, *J*=803.0), 24.32 (d, *J*=12.9), 22.35 (s), 21.30 (s), 15.16 (s); **HRMS (ESI$^+$)** Calcd. for $C_{17}H_{27}OPNa$ [M^++Na]: 301.1697, Found: 301.1694.

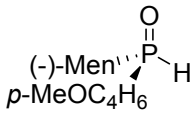
***R*$_P$-(-)-Menthyl *o*-tolylphosphine oxide (5c)**



The crude **5c** was obtained from *o*-tolyl magnesium bromide (0.8 M solution in THF) in a ratio of 99:1 (estimated by ^{31}P-NMR spectrum), and the optically pure **5c** was obtained as a pale yellow oil (106.8 mg, 48%, >99:1 dr) from column chromatography; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 38.03 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.73 (dd, *J*=14.1, 7.3, 1H), 7.43 (t, *J*=7.4, 1H), 7.37 – 7.22 (m, 2H), 7.34 (d, *J*=114.0, 1H), 2.52 (s, 3H), 2.36 – 2.25 (m, 1H), 2.02 (dd, *J*=18.3, 7.8, 1H), 1.80 – 1.65 (m, 4H), 1.23 (ddd,

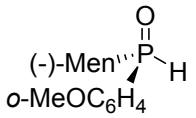
J=20.3, 12.9, 7.6, 1H), 1.08 – 1.00 (m, 1H), 0.89 (dd, *J*=13.9, 8.0, 8H), 0.50 (d, *J*=6.8, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 139.81 (d, *J*=10.0), 131.81 (d, *J*=2.6), 131.66 (d, *J*=10.3), 131.05 (d, *J*=10.1), 130.18(d, *J*=89.0), 125.95 (d, *J*=11.9), 43.25 (d, *J*=3.0), 40.20 (d, *J*=67.2), 36.51 (s), 34.14 (s), 33.16 (d, *J*=15.3), 28.71 (d, *J*=2.9), 24.39 (d, *J*=13.0), 22.42 (s), 21.48 (s), 20.31 (d, *J*=5.7), 15.09 (s); **HRMS (ESI$^+$)** Calcd. for $C_{17}H_{27}OPNa$ [M+Na $^+$]: 301.1697, Found: 301.1717.

R_P-(-)-Menthyl *p*-methoxyphenylphosphine oxide (5d)



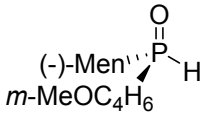
The crude **5d** was obtained from *p*-methoxyphenyl magnesium bromide (0.8 M solution in THF) in a ratio of 97:3 (estimated by ^{31}P-NMR spectrum), and the optically pure **5d** was obtained as a white solid (193.0 mg, 82%, 99:1 dr) from column chromatography, m.p. 115.6-120.2 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 32.92 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.73 – 7.54 (m, 2H), 7.44 (d, *J*=114.0, 1H), 7.02 (d, *J*=8.0, 2H), 3.87 (s, 3H), 2.09 (dd, *J*=30.5, 16.9, 3H), 1.70 (s, 2H), 1.40 (s, 2H), 1.15 – 0.96 (m, 2H), 0.85 (dt, *J*=23.9, 9.3, 7H), 0.66 (d, *J*=6.7, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 162.50 (s), 131.98 (s), 131.87 (s), 121.81 (d, *J*=96.0), 114.33 (s), 114.20 (s), 55.32 (s), 42.77 (d, *J*=2.3), 40.85 (d, *J*=68.1), 34.57 (s), 34.17 (s), 32.97 (d, *J*=14.1), 28.54 (d, *J*=4.0), 24.29 (d, *J*=12.9), 22.38 (s), 21.33 (s), 15.18 (s); **HRMS (ESI$^+$)** Calcd. for $C_{17}H_{28}O_2P$ [M+H$^+$]: 295.1827, Found: 295.1865.

R_P-(-)-Menthyl *o*-methoxyphenylphosphine oxide (5e)



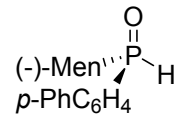
The crude **5e** was obtained from *o*-methoxyphenyl magnesium bromide (0.8 M solution in THF) in a ratio of 99:1 (estimated by ^{31}P-NMR spectrum), and the optically pure **5e** was obtained as a white solid (197.7 mg, 84%, >99:1 dr) from column chromatography, m.p. 89.5 – 94.0 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 29.83 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.84 (dd, *J*=12.7, 7.5, 1H), 7.51 (t, *J*=7.8, 1H), 7.36 (d, *J*=119.0, 1H), 7.12 (t, *J*=7.3, 1H), 6.91 (dd, *J*=8.2, 5.6, 1H), 3.89 (s, 3H), 2.16 – 1.93 (m, 3H), 1.72 (d, *J*=9.6, 3H), 1.39 (dd, *J*=11.8, 6.9, 2H), 1.01 (d, *J*=11.4, 1H), 0.93 (t, *J*=8.3, 4H), 0.85 (d, *J*=6.8, 3H), 0.37 (d, *J*=6.8, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 159.86 (d, *J*=4.9), 133.54 (s), 133.24 (d, *J*=5.0), 121.28 (d, *J*=10.7), 120.52 (s), 110.03 (d, *J*=6.0), 55.51 (s), 42.07 (d, *J*=3.5), 39.87 (d, *J*=70.1), 36.66 (s), 34.22 (s), 33.29 (d, *J*=15.8), 28.69 (d, *J*=3.5), 24.25 (d, *J*=13.2), 22.47 (s), 21.45 (s), 14.85 (s); **HRMS (ESI$^+$)** Calcd. for $C_{17}H_{28}O_2P$ [M+H$^+$]: 295.1827, Found: 295.1870.

R_P-(-)-Menthyl *m*-methoxyphenylphosphine oxide (5f)



The crude **5f** was obtained from *m*-methoxyphenyl magnesium bromide (0.8 M solution in THF) in a ratio of 99:1 (estimated by ^{31}P-NMR spectrum), and the optically pure **5f** was obtained as a pale yellow oil (157.7 mg, 67%, >99:1 dr) from column chromatography; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 34.41 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.42 – 7.32 (m, 1H), 7.37 (d, *J*=116.0, 1H), 7.18 (dd, *J*=11.9, 9.2, 2H), 7.02 (d, *J*=8.1, 1H), 3.79 (s, 3H), 2.11 (d, *J*=2.3, 1H), 2.00 (dd, *J*=12.5, 8.9, 2H), 1.67 (d, *J*=10.1, 2H), 1.42 (d, *J*=3.1, 2H), 1.11 – 0.94 (m, 2H), 0.85 (dd, *J*=6.6, 3.2, 6H), 0.81 – 0.73 (m, 1H), 0.58 (d, *J*=6.8, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 159.64 (d, *J*=14.6), 132.11 (d, *J*=89.6), 129.89 (d, *J*=14.3), 122.03 (d, *J*=10.8), 118.27 (d, *J*=2.7), 114.88 (d, *J*=11.1), 55.45 (s), 42.66 (d, *J*=2.3), 40.75 (d, *J*=67.2), 34.88 (s), 34.09 (s), 32.96 (d, *J*=14.3), 28.67 (d, *J*=3.9), 24.26 (d, *J*=13.0), 22.35 (s), 21.32 (s), 15.17 (s); **HRMS (ESI$^+$)** Calcd. for $C_{17}H_{28}O_2P$ [M+H$^+$]: 295.1827, Found: 295.1867.

R_P-(-)-Menthyl [1,1'-biphenyl]-4-ylphosphine oxide (5g)



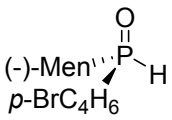
The optically pure **5g** was obtained as a white solid, m.p. 184.9 – 187.3 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 32.71 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.81 – 7.70 (m, 4H), 7.64 (d, *J*=7.9, 2H), 7.52 (d, *J*=115.0, 1H), 7.48 (t, *J*=7.5, 2H), 7.42 (d, *J*=7.4, 1H), 2.18 (dd, *J*=13.7, 6.9, 1H), 2.09 (d, *J*=10.0, 2H), 1.72 (d, *J*=10.3, 2H), 1.45 (dd, *J*=20.7, 9.2, 2H), 1.19 – 0.98 (m, 2H), 0.98 – 0.77 (m, 7H), 0.66 (d, *J*=6.8, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 145.12 – 144.49 (m), 139.96 – 139.58 (m), 130.74 (s), 130.63 (s), 129.97 – 129.84 (m), 128.96 (s, 2C), 128.20 (s), 127.37 (s), 127.23 (s, 3C), 42.76 (s), 40.87 (d, *J*=67.5), 34.77 (s), 34.16 (s), 33.04 (d, *J*=14.2), 28.69 (d, *J*=4.0), 24.33 (d, *J*=12.8), 22.39 (s), 21.35 (s), 15.21 (s); **HRMS (ESI$^+$)** Calcd. for $C_{22}H_{30}OP$ [M+H$^+$]: 341.2034, Found: 341.2069.

Preparation of 5g in gram scale

Under the atmosphere of N_2, the solution ***R*-3** (30 mL, 8.0 mmol) was cooled to -5 °C, then a solution of 1,1'-biphenyl-4-yl magnesium bromide (0.8 M solution in THF, 15 mL, 12 mmol) was added dropwise. After stirring at the same temperature for 6 hours, diluted hydrochloric acid (7%, 5 mL) was added, and the mixture was stirred at 50 °C for 6 hours. After cooling, the mixture was extracted with dichloromethane (3 × 50 mL), washed with water (3 × 30 mL), dried over magnesium sulfate. The residue was analyzed with NMR spectrum, and the crude product was

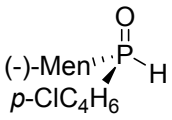
obtained in a ratio of 99:1 (estimated by ^{31}P-NMR spectrum). After recrystallization with ether, (*R*)-(+)-1,1'-bi(2-naphthol) (1.28 g, 56%) was recovered. The mother liquid was purified with column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1) to afford optically pure **5g** (1.77g, 65%, >99:1 dr), which had the same spectrum data to that obtained from the typical procedure.

R_P-(-)-Menthyl *p*-bromophenylphosphine oxide (5h)



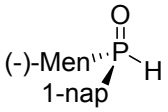
The crude **5h** was obtained from *p*-bromophenyl magnesium bromide (0.8 M solution in THF) in a ratio of 99:1 (estimated by ^{31}P-NMR spectrum), and the optically pure **5h** was obtained as a white solid (71.15 mg, 26%, >99:1 dr) from column chromatography, m.p. 135.7 – 138.4 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 31.96 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.64 (dd, J=8.4, 2.0, 2H), 7.55 (dd, J=11.9, 8.4, 2H), 7.41 (d, J=57, 1H), 2.03 (ddd, J=23.3, 10.1, 7.4, 3H), 1.75 – 1.64 (m, 2H), 1.47 – 1.32 (m, 2H), 1.12 – 0.97 (m, 2H), 0.88 (t, J=6.3, 6H), 0.84 – 0.78 (m, 1H), 0.61 (d, J=6.8, 3H) ; **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ =132.07 (s), 131.95 (s), 131.70 (s), 131.59 (s), 130.43 (s), 129.53 (s), 127.08 (d, J=3.5), 42.72 (d, J=2.5), 40.75 (d, J=67.6), 34.82 (s), 34.07 (s), 32.98 (d, J=14.3), 28.73 (d, J=4.0), 24.27 (d, J=13.0), 22.33 (s), 21.30 (s), 15.17 (s); **HRMS (ESI^+)** Calcd. for $C_{16}H_{25}BrOP$ [M+H^+]: 343.0826, Found: 343.0846.

R_P-(-)-Menthyl *p*-chlorophenylphosphine oxide (5i)



The crude **5i** was obtained from *p*-chlorophenyl magnesium bromide (0.8 M solution in THF) in a ratio of 99:1 (estimated by ^{31}P-NMR spectrum), and the optically pure **5i** was obtained as a white solid (159.8 mg, 67%, >99:1 dr) from column chromatography, m.p. 127.9 – 131.9 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 31.96 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.64 (dd, J=11.9, 8.4, 2H), 7.50 (dd, J=8.3, 1.8, 2H), 7.44 (d, J=116, 1H), 2.06 (dd, J=22.7, 9.5, 3H), 1.71 (t, J=10.1, 2H), 1.51 – 1.34 (m, 2H), 1.15 – 0.98 (m, 2H), 0.90 (t, J=6.3, 6H), 0.87 – 0.78 (m, 1H), 0.63 (d, J=6.8, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 138.58 (s), 131.58 (s), 131.47 (s), 129.95 (s), 129.15 (s), 129.02 (s), 42.75 (d, J=2.6), 40.80 (d, J=67.7), 34.88 (s), 34.09 (s), 32.99 (d, J=14.3), 28.71 (d, J=4.0), 24.28 (d, J=13.0), 22.32 (s), 21.29 (s), 15.16 (s); **HRMS (ESI^+)** Calcd. for $C_{16}H_{25}ClOP$ [M+H^+]: 299.1332, Found: 299.1346.

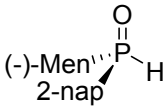
R_P-(-)-Menthyl 1-naphthalenylphosphine oxide (5j)



After added the 1-naphthalenyl magnesium bromide (0.4 M solution in THF,

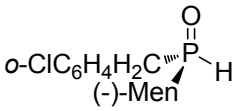
2.4mL, 0.96mmol), the mixture was stirred at the 0 °C for 4 hours, then warmed to the room temperature and stirred for 12 hours. The crude **5j** was obtained in a ratio of 99:1 (estimated by ^{31}P-NMR spectrum), and the optically pure **5j** was obtained as a white solid (145.8 mg, 58%, >99:1 dr) from column chromatography, m.p. 126.1 – 130.6 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 39.05 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 8.25 (d, *J*=8.4, 1H), 8.08 – 7.92 (m, 3H), 7.69 – 7.53 (m, 3H), 7.66 (d, *J*=111.0, 1H), 2.41 (d, *J*=6.6, 1H), 2.23 (d, *J*=10.0, 1H), 1.74 (dd, *J*=21.9, 8.8, 4H), 1.23 (dd, *J*=20.7, 12.2, 1H), 0.99 (d, *J*=13.5, 2H), 0.88 (dd, *J*=18.8, 6.5, 7H), 0.42 (d, *J*=6.7, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 133.39 (d, *J*=8.8), 132.84 (d, *J*=2.9), 132.63 (d, *J*=9.5), 131.61 (d, *J*=9.9), 129.30 (s), 127.92 (d, *J*=87), 127.53 (s), 126.51 (s), 124.85 (d, *J*=13.6), 124.40 (d, *J*=6.7), 43.40 (d, *J*=2.9), 40.83 (d, *J*=67.1), 36.53 (s), 34.11 (s), 33.04 (d, *J*=15.3), 28.74 (d, *J*=3.0), 24.37 (d, *J*=13.2), 22.40 (s), 21.48 (s), 15.16 (s); **HRMS (ESI^{+})** Calcd. for $C_{20}H_{28}OP$ [M+H^{+}]: 315.1878, Found: 315.1918.

R_P-(-)-Menthyl 2-naphthalenylphosphine oxide (5k)



Under similar procedure to **5j**, the crude **5k** was obtained from 2-naphthalenyl magnesium bromide (0.4 M solution in THF) in a ratio of 99:1 (estimated by ^{31}P-NMR spectrum), and the optically pure **5k** was obtained as a white solid (173.4 mg, 69%, >99:1 dr) from column chromatography, m.p. 145.7 – 148.1 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 32.89 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 8.31 (d, *J*=14.4, 1H), 8.00 – 7.83 (m, 3H), 7.71 – 7.51 (m, 3H), 7.60 (d, *J*=115.0, 1H), 2.29 – 1.98 (m, 3H), 1.71 (d, *J*=10.2, 2H), 1.41 (s, 1H), 1.27 – 0.95 (m, 3H), 0.90 (d, *J*=6.6, 6H), 0.80 (dd, *J*=18.6, 8.3, 1H), 0.61 (dd, *J*=6.7, 1.6, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 134.84 (d, *J*=2.4), 132.55 (d, *J*=13.1), 132.19 (d, *J*=9.3), 128.72 (s), 128.49 (d, *J*=12.0), 128.13 (s), 127.94 (s), 127.67 (s), 127.02 (s), 124.78 (d, *J*=11.7), 42.75 (d, *J*=2.5), 40.81 (d, *J*=67.4), 34.99 (s), 34.11 (s), 33.02 (d, *J*=14.3), 28.73 (d, *J*=3.9), 24.32 (d, *J*=12.9), 22.36 (s), 21.33 (s), 15.21 (s); **HRMS (ESI^{+})** Calcd. for $C_{20}H_{28}OP$ [M+H^{+}]: 315.1878, Found: 315.1918.

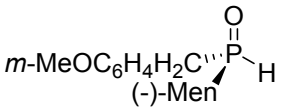
(R_P/S_P)-(-)-Menthyl 2- chlorobenzylphosphine oxide (5l/5l')



The crude **5l/5l'** was obtained from *p*-chlorobenzyl magnesium chloride (0.8 M solution in Et_2O) in a ratio of 38:62 (estimated by ^{31}P-NMR spectrum). After isolation with column chromatography, **5l/5l'** was obtained as a pale yellow oil (199.8 mg, 80%, 14:86 dr), **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 35.03

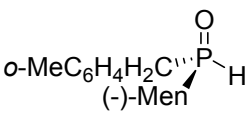
(s, 14%), 33.67 (s, 86%); **^{1}H NMR (400 MHz, $CDCl_3$)** ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 – 7.38 (m, 1H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.02 (dt, *J* = 115 Hz, 3.8 Hz, 1H), 3.52 – 3.36 (m, 1H), 3.33 (dt, *J* = 6.7, 4.2 Hz, 1H), 2.20 (dd, *J* = 13.1, 6.3 Hz, 1H), 1.93 (d, *J* = 7.3 Hz, 1H), 1.77 (d, *J* = 11.1 Hz, 2H), 1.68 (d, *J* = 7.7 Hz, 2H), 1.38 (d, *J* = 17.1 Hz, 1H), 1.35 – 1.21 (m, 1H), 1.06 (d, *J* = 12.3 Hz, 1H), 0.94 (dd, *J* = 16.0, 6.6 Hz, 7H), 0.85 (d, *J* = 6.8 Hz, 1H), 0.64 (d, *J* = 6.8 Hz, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 133.68 (s), 131.64 (d, *J*=5.1), 130.33 (d, *J*=6.9), 129.87 (d, *J*=2.8), 128.63 (d, *J*=3.3), 127.41 (d, *J*=2.8), 77.18 (d, *J*=32.0), 77.02 – 76.79 (m), 76.71 (s), 41.66 (d, *J*=3.6), 39.36 (s), 38.72 (s), 34.32 (s), 32.63 (dd, *J*=14.0, 8.2), 31.96 (s), 31.39 (s), 28.07 (d, *J*=4.9), 24.35 (d, *J*=11.9), 22.44 (d, *J*=13.8), 21.28 (s), 15.40 (s), 15.07 (s); **HRMS (ESI$^+$)** Calcd. for $C_{17}H_{27}ClOP$ [M+H$^+$]: 313.1488, Found: 313.1526.

(R_P/S_P)-(-)-Menthyl 3-methoxybenzylphosphine oxide (5m/5m')



The crude **5m/5m'** was obtained from 3-methoxybenzyl magnesium bromide (0.8 M solution in Et_2O) in a ratio of 38:62 (estimated by ^{31}P-NMR spectrum). After isolation with column chromatography, **5m/5m'** was obtained as a pale yellow oil (207.1 mg, 84%, 39:61 dr), **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 41.46 (s, 38%), 37.15 (s, 62%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.24 (t, *J* =7.7, 1H), 6.88 (m, 1H), 6.80 (dd, *J*=19.1, 10.9, 3H), 3.78 (s, 2H), 3.57 (s, 2H), 3.32 (d, *J*=38.0, 1H), 3.15 – 3.00 (m, 1H), 2.04 – 1.83 (m, 3H), 1.70 (d, *J*=29.2, 2H), 1.47 (s, 1H), 1.38 – 1.16 (m, 2H), 1.10 – 0.99 (m, 1H), 0.97 – 0.80 (m, 9H), 0.61 (d, *J*=6.5, 1H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 159.97 (s), 133.14 (d, *J*=6.4), 130.00 (dd, *J*=7.2, 2.6), 121.57 (dd, *J*=17.5, 5.7), 114.96 (dd, *J*=21.1, 5.6), 112.61 (s), 77.41 (s), 77.10 (s), 76.78 (s), 55.21 (s), 50.39 (s), 43.24 (d, *J*=2.2), 41.50 (d, *J*=3.5), 39.41 (s), 38.79 (s), 38.21 (s), 37.56 (s), 35.14 (s), 34.43 (d, *J*=31.2), 34.20 – 34.10 (m), 34.07 (s), 33.50 (s), 32.78 (dd, *J*=30.5, 13.6), 32.30 (s), 28.58 (d, *J*=4.1), 27.90 (d, *J*=5.0), 24.34 (dd, *J*=23.6, 12.2), 22.40 (d, *J*=18.1), 21.32 (d, *J*=10.3), 15.49 (s), 15.11 (s); **HRMS (ESI$^+$)** Calcd. for $C_{18}H_{30}O_2P$ [M+H$^+$]: 309.1983, Found: 309.1998.

(R_P/S_P)-(-)-Menthyl 2-methylbenzylphosphine oxide (5n/5n')



The crude **5n/5n'** was obtained from 2-methylbenzyl magnesium bromide (0.8 M solution in Et_2O) in a ratio of 40:60 (estimated by ^{31}P-NMR spectrum). After isolation with column chromatography, **5n/5n'** was obtained as a pale yellow oil (137.9 mg, 59%, 35:65 dr), **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 38.50 (s, 35%), 35.16 (s,

65%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.16 (dd, *J*=10.1, 5.4, 4H), 6.92 (dt, *J*=113.0,4.0, 0.6H), 6.88 (dt, *J*=114.0 3.8, 0.4H), 3.40 – 3.21 (m, 1H), 3.11 (ddd, *J*=19.1, 13.2, 6.1, 1H), 2.38 (s, 1H), 2.36 (s, 2H), 2.24 – 2.15 (m, 1H), 2.09 – 1.97 (m, 1H), 1.92 (s, 1H), 1.76 (d, *J*=9.6, 2H), 1.65 (dd, *J*=22.9, 10.7, 1H), 1.37 (d, *J*=10.8, 1H), 1.33 – 1.20 (m, 1H), 1.13 – 0.99 (m, 1H), 0.98 – 0.89 (m, 7H), 0.86 (d, *J*=6.8, 1H), 0.60 (d, *J*=6.8, 2H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 136.45 (d, *J*=5.4), 130.96 – 130.51 (m), 130.42 (d, *J*=6.7), 130.01 (dd, *J*=10.7, 5.3), 127.27 (s), 126.53 (d, *J*=3.1), 77.36 (s), 77.04 (s), 76.73 (s), 43.40 (s), 41.62 (d, *J*=3.5), 39.98 (s), 39.36 (s), 38.83 (s), 38.19 (s), 34.33 (s), 33.16 – 32.36 (m), 31.62 (s), 31.05 (s), 28.57 (d, *J*=4.4), 27.95 (d, *J*=4.9), 24.41 (dd, *J*=18.8, 12.0), 22.45 (d, *J*=16.2), 21.35 (d, *J*=11.6), 20.16 (d, *J*=11.6), 15.48 (s), 15.06 (s); **HRMS (ESI$^+$)** Calcd. for $C_{18}H_{30}OP$ [M+H$^+$]: 293.2034, Found: 293.2084.

Part 3. Preparation of S_P-5' form the substitution of *S*-3a' with Grignard reagents.

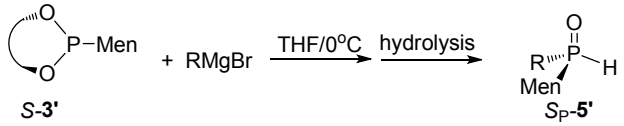
The preparation of binaphthoxy phosphorochloridate *S*-2'

A 100-mL, single-necked round-bottomed flask charged with ***S*-1** (2.29 g, 8 mmol) and toluene (10 mL) followed by *N*, *N*-dimethylformamide (20 μL, 0.26 mmol) under dry air, then the flask was cooled with ice-water added dropwise phosphorus trichloride (2 mL, 24 mmol). The mixture was stirred at 50 °C in an oil bath for 2 hours, during which time it became a colorless homogeneous solution. Toluene and excess phosphorus trichloride were removed via vacuum distillation and the DMF was azeotropically removed with toluene (2×10 mL) under high vacuum to afford the phosphochloridite ***S*-2'** as an oily foam compound.

The preparation of binaphthoxy menthylphosphonites *S*-3'

The above obtained *R*-**2'** (2.8 g, 8 mmol) was dissolved in tetrahydrofuran (15 mL) under the atmosphere of N_2. To the ice-cooled solution, menthyl magnesium chloride (0.8 M solution in THF, 15 mL, 12 mol) was added dropwise. After warming to room temperature and stirring for 6 hours, the solution of ***S*-3'** (0.27 mol/L) was used in situ in the subsequent procedures.

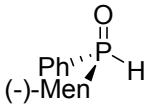
The substitution of *S*-3' with Grignard reagents to afford S_P-5'.



S-3' S_P-5'

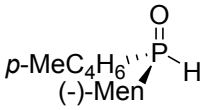
Typical procedure: Under the atmosphere of N_2, the solution of ***S*-3** (3 mL, 0.8 mmol) was cooled to 0 °C, a solution of phenyl magnesium bromide (0.8 M solution in THF, 1.2 mL, 0.96 mmol) was added dropwise. After stirring at the same temperature for 4 hours, diluted hydrochloric acid (7%, 1 mL) was added, and the mixture was stirred at 50 °C for 6 hours. After cooling to room temperature, the mixture was extracted with ether (3×20 mL), washed with water (3×10 mL), dried over magnesium sulfate. After removing solvent, the residue was analyzed with NMR spectroscopy, then was purified with column chromatography on silica gel (petroleum ether/ ethyl acetate = 4/1) to afford **5a'**.

***S*$_P$-(-)-Menthyl phenylphosphine oxide 5a'**



The crude **5a'** was obtained in a ratio of 1:99 (estimated by ^{31}P-NMR spectrum), and the optically pure **5a'** was obtained as a white solid (143.7 mg, 68%, <1:99 dr) from column chromatography, m.p. 94.3–97.2 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 27.95 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** 7.67 (dd, *J*=12.0, 7.4, 2H), 7.62 (d, *J*=115.0, 1H)7.61 – 7.46 (m, 3H), 2.48 (d, *J*=6.1, 1H), 2.05 (s, 1H), 1.86 – 1.64 (m, 4H), 1.48 (s, 1H), 1.25 (s, 1H), 1.18 – 1.05 (m, 2H), 1.01 (dd, *J*=6.7, 1.4, 3H), 0.92 (dd, *J*=13.1, 11.6, 3H), 0.82 (dd, *J*=6.3, 1.2, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 132.06 (s), 130.32 (s), 130.22 (s), 128.80 (s), 129.92 (d, *J*=93.0) 128.68 (s), 41.75 (d, *J*=3.4), 41.08 (d, *J*=68.7), 34.31 (s), 32.72 (d, *J*=14.1), 31.97 (s), 28.16 (d, *J*=4.8), 24.31 (d, *J*=12.3), 22.37 (s), 21.41 (s), 15.55 (s); **HRMS (ESI$^+$)** Calcd. for $C_{16}H_{25}OPNa$ [M+Na$^+$]: 287.1541, Found: 287.1584.

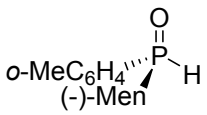
***S*$_P$-(-)-Menthyl *p*-tolylphosphine oxide (5b')**



The crude **5b'** was obtained from *p*-tolyl magnesium bromide (0.8 M solution in THF) in a ratio of 1:99 (estimated by ^{31}P-NMR spectrum), and the optically pure **5b'** was obtained as a pale yellow solid (164.5 mg, 74%, <1:99 dr) from column chromatography, m.p. 81.0 – 87.1 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 28.27 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.60, (d, *J*=115 Hz, 1H), 7.55 (dd, *J*=12.4, 7.8 Hz, 2H), 7.33 (d, *J*=6.3 Hz, 2H), 2.43 (s, 3H), 1.83 – 1.61 (m, 5H), 1.48 (d, *J*=7.1 Hz, 1H), 1.25 (s, 1H), 1.17 – 1.02 (m, 2H), 0.98 (t, *J*=8.2 Hz, 3H), 0.93 (d, *J*=6.8 Hz, 4H), 0.82 (d, *J*=6.4 Hz, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 142.50 (s), 130.32 (s), 130.21 (s), 129.55 (s), 129.42 (s), 126.52 (d, *J*=96.0), 41.78 (d, *J*=3.3), 41.16 (d, *J*=68.8), 34.33 (s), 32.74 (d, *J*=14.2), 32.00 (s), 28.13 (d, *J*=4.8), 24.32 (d, *J*=12.3), 22.37 (s), 21.66 (s), 21.40 (s), 15.55 (s); **HRMS (ESI$^+$)** Calcd. for $C_{17}H_{27}OPNa$ [M+Na$^+$]:

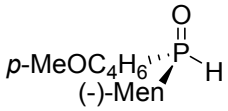
301.1697, Found: 301.1690.

S_P-(-)-Menthyl *o*-tolylphosphine oxide (5c')



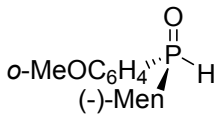
The crude **5c'** was obtained from *o*-tolyl magnesium bromide (0.8 M solution in THF) in a ratio of 1:99 (estimated by ^{31}P-NMR spectrum), and the optically pure **5c'** was obtained as a pale yellow oil (191.4 mg, 86%, <1:99 dr) from column chromatography; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 21.52 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.84 (d, *J*=114.0, 1H), 7.79 (dd, *J*=13.2, 7.5, 1H), 7.45 (t, *J*=7.5, 1H), 7.36 (t, *J*=7.5, 1H), 7.24 (d, *J*=7.0, 1H), 2.47 (s, 3H), 1.93 – 1.68 (m, 5H), 1.34 (s, 1H), 1.25 (dt, *J*=11.9, 5.4, 2H), 1.10 (s, 1H), 1.05 (d, *J*=6.8, 3H), 0.99 (d, *J*=10.3, 1H), 0.92 (d, *J*=6.9, 3H), 0.80 (d, *J*=5.8, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 139.42 (d, *J*=10.0), 132.55 (d, *J*=8.8), 131.79 (d, *J*=2.6), 131.03 (d, *J*=10.2), 128.15 (d, *J*=91.8), 126.09 (d, *J*=11.4), 41.79 (d, *J*=3.6), 40.06 (d, *J*=69.1), 34.34 (s), 32.82 (d, *J*=13.6), 31.76 (d, *J*=3.7), 27.98 (d, *J*=5.1), 24.31 (d, *J*=12.0), 22.37 (s), 21.52 (s), 20.13 (d, *J*=6.2), 15.74 (s); **HRMS (ESI$^+$)** Calcd. for $C_{17}H_{27}OPNa$ [M+Na$^+$]:301.1697, Found: 301.1701.

S_P-(-)-Menthyl *p*-methoxyphenylphosphine oxide (5d')



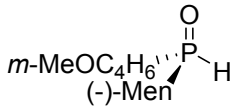
The crude **5d'** was obtained from *p*-methoxyphenyl magnesium bromide (0.8 M solution in THF) in a ratio of 4:96 (estimated by ^{31}P-NMR spectrum), and the optically pure **5d'** was obtained as a pale yellow solid (200.0 mg, 85%, 3:97 dr) from column chromatography, m.p. 37.5 – 42.7 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 32.62 (s, 3%), 28.24 (s, 97%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.72 (d, *J*=89.0, 1H), 7.59 (dd, *J*=12.0, 8.7, 2H), 7.03 (dd, *J*=8.7, 1.8, 2H), 3.87 (s, 3H), 2.48 (dd, *J*=6.5, 4.1, 1H), 1.76 (ddd, *J*=24.9, 12.4, 9.2, 4H), 1.50 (s, 1H), 1.26 (s, 1H), 1.12 – 1.04 (m, 2H), 0.99 (d, *J*=6.8, 3H), 0.91 (dd, *J*=13.8, 9.3, 4H), 0.83 (d, *J*=6.4, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 162.56 (d, *J*=2.7), 132.09 (s), 131.97 (s), 120.83 (d, *J*=98.5), 114.43 (s), 114.30 (s), 55.33 (s), 41.84 (d, *J*=3.3), 41.27 (d, *J*=69.5), 34.35 (s), 32.76 (d, *J*=14.1), 32.09 (s), 28.13 (d, *J*=4.7), 24.34 (d, *J*=12.2), 22.38 (s), 21.40 (s), 15.56 (s); **HRMS (ESI$^+$)** Calcd. for $C_{17}H_{28}O_2P$ [M+H$^+$]: 295.1827, Found: 295.1874.

S_P-(-)-Menthyl *o*-methoxyphenylphosphine oxide (5e')



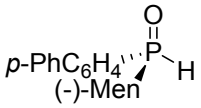
The crude **5e'** was obtained from *o*-methoxyphenyl magnesium bromide (0.8 M solution in THF) in a ratio of 1:99 (estimated by ^{31}P-NMR spectrum), and the optically pure **5e'** was obtained as a pale yellow oil (190.6 mg, 81%, <1:99 dr) from column chromatography; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 16.83 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.83 (ddd, *J*=12.1, 7.4, 1.6, 1H), δ = 7.83 (d, *J*=120.0, 1H), 7.52 (dd, *J*=11.3, 4.3, 1H), 7.13 (t, *J*=7.1, 1H), 6.92 (dd, *J*=7.9, 5.7, 1H), 3.86 (s, 3H), 2.50 – 2.38 (m, 1H), 2.08 – 1.92 (m, 1H), 1.90 – 1.68 (m, 3H), 1.34 (s, 1H), 1.22 (dd, *J*=14.8, 9.2, 2H), 1.14 – 1.06 (m, 1H), 1.03 (d, *J*=6.7, 3H), 0.94 (d, *J*=6.9, 4H), 0.83 – 0.73 (m, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 159.38 (d, *J*=4.7), 134.23 (d, *J*=4.1), 133.52 (d, *J*=1.8), 121.15 (d, *J*=10.6), 117.63 (d, *J*=93.8), 110.07 (d, *J*=6.1), 55.40 (s), 41.35 (d, *J*=3.5), 39.16 (d, *J*=71.1), 34.44 (s), 32.60 (d, *J*=14.0), 31.69 (d, *J*=3.9), 28.02 (d, *J*=5.6), 24.26 (d, *J*=12.5), 22.35 (s), 21.38 (s), 15.31 (s); **HRMS (ESI$^+$)** Calcd. for $C_{17}H_{28}O_2P$ [M+H$^+$]: 295.1827, Found: 295.1869.

S_P-(-)-Menthyl *m*-methoxyphenylphosphine oxide (5f')



The crude **5f'** was obtained from *m*-methoxyphenyl magnesium bromide (0.8 M solution in THF) in a ratio of 1:99 (estimated by ^{31}P-NMR spectrum), and the optically pure **5f'** was obtained as a pale yellow oil (190.62 mg, 81%, <1:99 dr) from column chromatography; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 27.84 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.60 (d, *J*=115.0 1H), 7.47 – 7.38 (m, 1H), 7.29 – 7.14 (m, 2H), 7.09 (d, *J*=8.1, 1H), 3.87 (s, 3H), 2.48 (s, 1H), 1.87 – 1.63 (m, 4H), 1.49 (s, 1H), 1.25 (s, 1H), 1.11 (dd, *J*=21.7, 9.2, 2H), 1.01 (d, *J*=6.7, 3H), 0.92 (t, *J*=12.5, 4H), 0.82 (d, *J*=6.3, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 159.73 (d, *J*=15.0), 131.40 (d, *J*=91.0), 129.96 (d, *J*=14.4), 121.95 (d, *J*=10.8), 118.16 (d, *J*=2.7), 115.27 (d, *J*=10.9), 55.47 (s), 41.74 (s), 41.12 (d, *J*=68.5), 34.31 (s), 32.72 (d, *J*=14.2), 32.01 (s), 28.17 (d, *J*=4.9), 24.32 (d, *J*=12.3), 22.36 (s), 21.41 (s), 15.54 (s); **HRMS (ESI$^+$)** Calcd. for $C_{17}H_{28}O_2P$ [M+H$^+$]: 295.1827, Found: 295.1869.

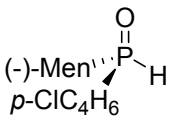
S_P-(-)-Menthyl [1,1'-biphenyl]-4-ylphosphine oxide (5g')



The crude **5g'** was obtained from [1,1'-biphenyl]-4-yl magnesium bromide (0.8 M solution in THF) in a ratio of 1:99 (estimated by ^{31}P-NMR spectrum), and the optically pure **5g'** was obtained as a white solid (145.0 mg, 54%, <1:99 dr) from column chromatography, m.p. 157.9-161.3 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 27.83 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 8.25 (s, 0.5H), 7.73 (dd, *J*=9.9, 6.9, 4H), 7.67 – 7.60 (m, 2H), 7.48 (t, *J*=7.4,

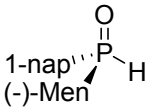
2H), 7.41 (t, *J*=7.3, 1H), 7.10 (s, 0.5H), 2.51 (dd, *J*=8.6, 4.6, 1H), 1.90 – 1.80 (m, 1H), 1.79 – 1.66 (m, 3H), 1.54 (s, 1H), 1.27 (d, *J*=7.0, 1H), 1.13 (ddd, *J*=14.8, 9.9, 4.5, 2H), 1.02 (d, *J*=6.8, 3H), 0.95 (d, *J*=6.8, 3H), 0.90 (s, 1H), 0.84 (d, *J*=6.4, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 144.90 – 144.81 (m), 139.87 – 139.79 (m), 130.85 (s), 130.75 (s), 128.97 (s, 2C), 128.18 (s), 128.04 (s), 127.47 (s), 127.35 (s), 127.25 (s, 2C), 41.80 (d, *J*=3.3), 41.20 (d, *J*=68.9), 34.33 (s), 32.77 (d, *J*=14.2), 32.05 (s), 28.21 (d, *J*=4.9), 24.35 (d, *J*=12.2), 22.39 (s), 21.43 (s), 15.59 (s); **HRMS (ESI$^+$)** Calcd. for $C_{22}H_{30}OP$ [M+H$^+$]: 341.2034, Found: 341.2071.

***S*$_P$-(-)-Menthyl *p*-chlorophenylphosphine oxide (5i')**



The crude **5i'** was obtained from *p*-chlorophenyl magnesium bromide (0.8 M solution in THF) in a ratio of 1:99 (estimated by ^{31}P-NMR spectrum). After isolation, **5i'** was obtained as a white solid (207.5 mg, 87%, 5:99 dr) from column chromatography, m.p. 99.4-101.9 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 31.97 (s, 5%), 26.91 (s, 95%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 8.20 (s, 0.5H), 7.61 (dd, J=11.9, 8.4, 2H), 7.51 (dd, J=8.3, 2.0, 2H), 7.04 (s, 0.5H), 2.45 (d, J=2.6, 1H), 1.87 – 1.62 (m, 5H), 1.44 (s, 1H), 1.31 – 1.20 (m, 1H), 1.16 – 1.05 (m, 2H), 1.00 (d, J=6.8, 3H), 0.93 (d, J=6.9, 3H), 0.83 (d, J=6.4, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 138.61 (s), 131.73 (s), 131.62 (s), 129.23 (s), 129.11 (s), 128.93 – 127.89 (m), 41.80 (d, J=3.5), 41.12 (d, J=69.2), 34.27 (s), 32.73 (d, J=14.2), 31.99 (d, J=2.7), 28.22 (d, J=4.8), 24.31 (d, J=12.4), 22.32 (s), 21.37 (s), 15.55 (s); **HRMS (ESI$^+$)** Calcd. for $C_{16}H_{25}ClOP$ [M+H$^+$]: 299.1332, Found: 299.1343.

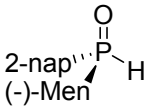
***S*$_P$-(-)-Menthyl 1-naphthalenylphosphine oxide (5j')**



After addition of 1-naphthalenyl magnesium bromide (0.4 M solution in THF, 2.4 mL, 0.96 mmol), the mixture was stirred at the 0 °C for 4 hours, then warmed to the room temperature and stirred for 12 hours. The crude **5j'** was obtained in a ratio of 1:99 (estimated by ^{31}P-NMR spectrum), and the optically pure **5j'** was obtained as a white solid (113.1 mg, 45%, <1:99 dr) from column chromatography, m.p. 110.6 – 106.1 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 22.54 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 8.20 (d, *J*=115.0, 1H), 8.16 (d, *J*=8.1, 1H), 8.11 – 7.99 (m, 2H), 7.94 (s, 1H), 7.62 – 7.54 (m, 3H), 2.59 (d, *J*=6.4, 1H), 1.95 (s, 2H), 1.82 (d, *J*=9.3, 1H), 1.69 (d, *J*=12.3, 1H), 1.23 (d, *J*=17.4, 2H), 1.08 (dd, *J*=6.1, 3.3, 5H), 1.01 (dt, *J*=11.1, 5.6, 3H), 0.97 – 0.88 (m, 1H), 0.74 – 0.62 (m, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 133.32 (d, *J*=8.9), 132.77 (d, *J*=2.9), 132.66 (d, *J*=9.6), 132.43 (d, *J*=8.4), 129.33 (s), 127.41 (s), 126.45

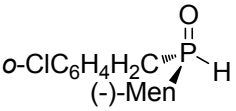
(s), 125.81 (d, *J*=90.8), 125.04 (d, *J*=13.0), 123.80 (d, *J*=7.3), 41.95 (d, *J*=3.5), 40.95 (d, *J*=69.4), 34.28 (s), 32.59 (d, *J*=13.6), 32.06 (d, *J*=3.6), 28.08 (d, *J*=5.1), 24.27 (d, *J*=12.1), 22.29 (s), 21.55 (s), 15.97 (s); **HRMS (ESI$^+$)** Calcd. for $C_{20}H_{28}OP$ [M+H$^+$]:315.1878, Found: 315.1918.

S_P-(-)-Menthyl 2-naphthalenylphosphine oxide (5k')



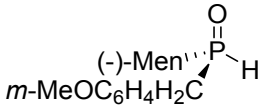
Under the similar procedure to prepare **5j'**, the crude **5k'** was obtained from 2-naphthalenyl magnesium bromide (0.4 M solution in THF) in a ratio of 1:99 (estimated by ^{31}P-NMR spectrum), and the optically pure **5k'** was obtained as a white solid (165.9 mg, 66%, <1:99 dr) from column chromatography and recrystallization with dichloromethane/petroleum ether (60-90 ^{o}C), m.p. 138.4 – 141.3 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 27.23 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 8.30 (d, *J*=14.3, 1H), 7.94 (dd, *J*=21.7, 7.5, 3H), 7.78 (d, *J*=115.0, 1H), 7.67 – 7.54 (m, 3H), 2.67 – 2.46 (m, 1H), 1.88 (d, *J*=11.7, 1H), 1.81 – 1.63 (m, 3H), 1.49 (s, 1H), 1.34 – 1.10 (m, 3H), 1.01 (dd, *J*=17.6, 6.8, 6H), 0.91 (d, *J*=11.7, 1H), 0.78 (d, *J*=6.0, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 134.89 (s), 132.72 (s), 132.63 (s), 128.70 (s), 128.60 (d, *J*=12.1), 128.11 (s), 127.97 (s), 127.05 (s), 124.69 (s), 124.57 (s), 41.80 (d, *J*=3.1), 41.11 (d, *J*=68.0), 34.34 (s), 32.74 (d, *J*=14.1), 31.99 (s), 28.21 (d, *J*=4.9), 24.35 (d, *J*=12.2), 22.33 (s), 21.44 (s), 15.63 (s); **HRMS (ESI$^+$)** Calcd. for $C_{20}H_{28}OP$ [M+H$^+$]: 315.1878, Found: 315.1921.

(R_P/S_P)-(-)-Menthyl 2- chlorobenzylphosphine oxide (5l/5l')



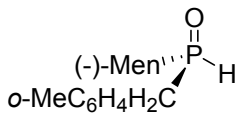
The crude **5l/5l'** in a ratio of 84:16 (estimated by ^{31}P-NMR spectrum). After isolation, **5l/5l'** was obtained as a pale yellow oil (89.9 mg, 36%, 26:74 dr) from column chromatography. **^{31}P NMR (162 MHz, $CDCl_3$)** δ =35.01 (s, 26%), 37.08 (s, 74%). Other spectrum data of the compound was similar to that obtained from ***R*$_P$-3**. **HRMS (ESI$^+$)** Calcd. for $C_{18}H_{30}OP$ [M+Na$^+$]: 335.1307, Found: 335.1285.

(R_P/S_P)-(-)-Menthyl 3-methoxybenzylphosphine oxide (5m/5m')



The crude **5m/5m'** was obtained from 3-methoxybenzyl magnesium bromide (0.8 M solution in Et_2O) 72:28 (estimated by ^{31}P-NMR spectrum). After isolation, **5m/5m'** was obtained as a pale yellow oil (202.2 mg, 82%, 75:25 dr) from column chromatography; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 41.38 (s, 75%), 37.08 (s, 25%). Other spectrum data of the compound was similar to that obtained from ***R*$_P$-3**. **HRMS (ESI$^+$)** Calcd. for $C_{18}H_{30}OP$ [M+Na$^+$]: 331.1803, Found: 331.1784.

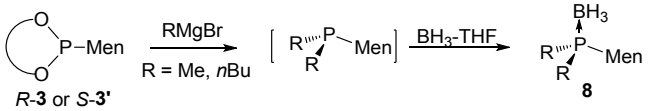
(R_P/S_P)-(-)-Menthyl 2-methylbenzylphosphine oxide (5n/5n')



The crude **5n/5n'** was obtained from 2-methylbenzyl magnesium bromide (0.8 M solution in Et_2O) in a ratio of 80:20 (estimated by ^{31}P-NMR spectrum). After isolation, **5o/5o'** was obtained as a pale yellow oil (177.7 mg, 76%, 80:20 dr); **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 38.58 (s, 80%), 35.26 (s, 20%); **^{1}H NMR (400 MHz, $CDCl_3$)** 7.18 (dt, *J*=8.1, 4.2, 4H), 6.94 (dt, *J*=115.0, 3.7, 0.2H), 6.90 (dt, *J*=114.0 4.7, 0.4H), 3.38 – 3.21 (m, 1H), 3.15 – 3.04 (m, 1H), 2.39 (s, 2H), 2.38 (s, 1H), 2.10 (d, *J*=9.3, 1H), 2.03 (dd, *J*=16.9, 6.5, 1H), 1.84 – 1.72 (m, 2H), 1.58 – 1.49 (m, 1H), 1.42 (dd, *J*=14.8, 7.2, 1H), 1.21 (t, *J*=7.0, 1H), 1.07 (dt, *J*=15.9, 10.0, 2H), 0.99 – 0.90 (m, 7H), 0.87 (d, *J*=6.9, 2.64H), 0.61 (d, *J*=6.8, 0.66H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 136.52 (d, *J*=5.1), 130.72 (dd, *J*=11.9, 5.3), 130.07 (d, *J*=5.2), 128.81 (s), 127.28 (d, *J*=3.3), 126.47 (d, *J*=2.9), 77.38 (s), 77.06 (s), 76.74 (s), 43.42 (s), 39.95 (s), 39.34 (s), 34.30 (d, *J*=9.1), 32.84 (dd, *J*=32.6, 16.4), 32.10 (s), 31.53 (s), 28.57 (d, *J*=4.3), 27.98 (s), 24.50 (d, *J*=12.3), 22.46 (d, *J*=16.3), 21.35 (d, *J*=11.6), 20.17 (d, *J*=11.9), 15.49 (s), 15.07 (s); **HRMS (ESI$^+$)** Calcd. for $C_{18}H_{30}OP$ [M+Na$^+$]: 315.1854, Found: 315.1832.

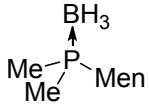
Part 4. The reaction of aliphatic Grignard reagent with *R*-3 or *S*-3'.

The reaction of *R*-3 with methyl magnesium bromide, formation of 8a

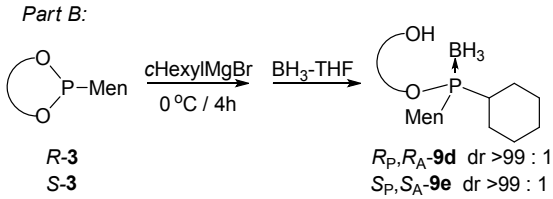


Under the atmosphere of N_2, the solution of ***R*-3** (3 mL, 0.8 mmol) was cooled to 0 °C. A solution of methyl magnesium bromide (3.0 M solution in diethyl ether, 0.32mL, 0.96mmol) was added dropwise. The mixture was stirred at 0 °C for 4 hours. After warmed to room temperature, the solution of BH_3-THF (1.0 M solution in THF, 1 mL, 1 mmol) was added dropwise, and the mixture was stirred for 6 hours. Diluted hydrochloric acid (7%, 1 mL) was added to quench the reaction, and the solvent was removed in vacuo. The mixture was extracted with ether (20 mL), washed with water (3×10 mL), dried over magnesium sulfate. After removing solvent, the residue was purified with column chromatography on silica gel (petroleum ether/ dichloromethane = 2/1) to afford **8a**.

Dimethyl menthyl phosphine oxide 8a



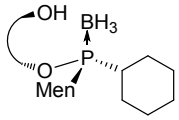
The compound **8a** was obtained as a white solid (73.7 mg, 43%), m.p. 91.3 – 94.4 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 8.42 – 7.40 (broad m); **^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$)** δ = 2.23 – 2.09 (m, 1H), 1.74 (d, *J* = 9.2 Hz, 3H), 1.70 – 1.65 (m, 1H), 1.48 – 1.38 (m, 1H), 1.34 (d, *J* = 9.8 Hz, 3H), 1.25 (d, *J* = 9.9 Hz, 3H), 1.04 (d, *J* = 10.5 Hz, 1H), 1.01 – 0.97 (m, 1H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.89 – 0.84 (m, 1H), 0.78 (d, *J* = 6.8 Hz, 3H), 0.45 (dd, *J* = 138.6, 45.7 Hz, 2H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 44.38 (s), 36.31 (d, *J*=32.1), 35.99 (s), 34.27 (s), 33.28 (d, *J*=10.7), 28.39 (d, *J* =3.9), 24.75 (d, =10.9), 22.47 (s), 21.34 (s), 15.43 (s), 12.92 (d, *J*=36.6), 10.71 (d, *J*=37.9); **HRMS (ESI^{+})** Calcd. for $C_{12}H_{22}P$ [M-BH_3+H^{+}]: 201.1727, Found: 201.1769.



The reaction of *R*-3 with cyclohexyl magnesium bromide, protected with borane.

Under the atmosphere of N_2, the solution of ***R*-3** (3 mL, 0.8 mmol) was cooled to 0 °C. A solution of *cyclo*-hexyl magnesium bromide (0.8 M solution in ether, 1.2 mL, 0.96 mmol) was added dropwise. The mixture was stirred at 0 °C for 4 hours, then warmed to room temperature. The solution of BH_3-THF (1.0 M solution in THF, 1 mL, 1 mmol) was added dropwise. After stirred for 6 hours, diluted hydrochloric acid (7%, 1 mL) was added. The mixture was extracted with ether (20 mL), washed with water (3 × 10 mL), dried over magnesium sulfate. After removing solvent in vacuo, the residue was analyzed with NMR spectrum, and was purified with column chromatography on silica gel (petroleum ether/ dichloromethane = 2/1) to afford **9d**.

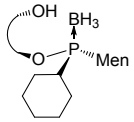
***$R_A R_P$*- (-)-Menthyl cyclohexyl (2'-hydroxyl-1,1'-binaphthalen-2-yloxy) phosphine borane, 9d**



The crude **9d** was formed in a ratio of 99:1 (estimated by ^{1}H-NMR spectrum), the optically pure **9d** was obtained as a pale yellow oil (256.3 mg, 58%, >99:1 dr); **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 138.47 – 138.11 (broad m); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 8.00 (d, *J*=9.1, 1H), 7.92 (t, *J*=8.7, 2H), 7.86 (d, *J*=9.3, 2H), 7.48 – 7.40 (m, 1H), 7.38 – 7.28 (m, 4H), 7.27 – 7.20 (m, 1H), 7.10 (d, *J*=8.4, 1H), 4.88 (s, 1H), 2.08 – 1.92 (m, 2H), 1.80 (s, 1H), 1.73 – 1.58 (m, 4H), 1.44 (dd, *J*=40.5, 21.3, 5H), 1.22 (d, *J*=24.6, 2H), 0.96 (ddd, *J*=47.2, 22.5, 11.9, 7H), 0.82 (d, *J*=6.5, 3H), 0.76 (d, *J*=6.8, 3H), 0.65 (d, *J*=6.7, 3H), 0.55 – 0.32 (m, 2H); **^{13}C {^{1}H}**

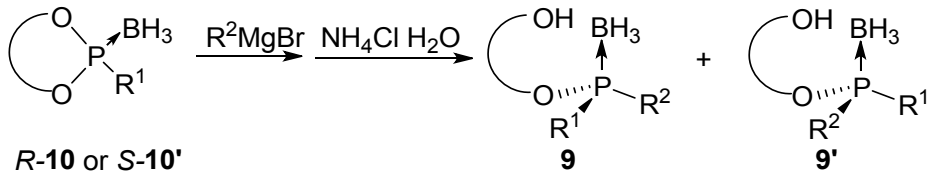
NMR (101 MHz, $CDCl_3$) δ = 151.27 (s), 151.07 – 150.96 (m), 133.66 (s), 133.34 (s), 130.56 (s), 130.39 (s), 130.03 (s), 129.06 (s), 128.32 (s), 127.99 (s), 127.51 (s), 126.33 (s), 125.30 (s), 124.94 (s), 124.76 (s), 123.40 (s), 120.33 (s), 118.75 – 118.45 (m), 117.67 (s), 114.56 (s), 43.32 (s), 39.95 (d, *J*=27.4), 38.60 (s), 35.24 (s), 34.16 (s), 33.34 (d, *J*=11.6), 28.60 (s), 26.60 (s), 26.37 (d, *J*=10.4), 26.01 (s), 25.41 (s), 24.85 (d, *J*=11.0), 24.33 (s), 22.42 (s), 21.21 (s), 15.64 (s); **HRMS (ESI^+)** Calcd. for $C_{36}H_{42}O_2P$ [M - BH_4]: 537.2922, Found: 537.3430.

S_AS_P- (-)-Menthyl cyclohexyl (2'-hydroxyl-1,1'-binaphthalen-2-yloxy) phosphine borane, 9e



Under similar procedure to **9d**, the crude **9e** was obtained from the reaction of *cyclo*-hexyl magnesium bromide (0.8 M solution in ether) with ***S*-3**, in a ratio of 1:99 (estimated by ^{1}H-NMR spectrum), and the optically pure **9e** was obtained as a pale yellow oil (137.0 mg, 31%, <99:1 dr) from column chromatography; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 139.83 – 139.24 (broad m); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 8.00 (d, *J*=9.1, 1H), 7.92 (dd, *J*=8.3, 5.7, 2H), 7.85 (d, *J*=8.1, 1H), 7.76 (d, *J*=9.1, 1H), 7.44 (dd, *J*=10.6, 4.0, 1H), 7.37 – 7.27 (m, 4H), 7.26 – 7.20 (m, 1H), 7.13 (d, *J*=8.4, 1H), 4.94 (s, 1H), 2.20 – 2.07 (m, 1H), 1.94 (dd, *J*=21.1, 10.0, 1H), 1.63 (d, *J*=8.4, 6H), 1.54 (d, *J*=12.7, 2H), 1.36 (d, *J*=13.0, 1H), 1.26 (s, 1H), 1.05 (d, *J*=13.8, 3H), 1.00 – 0.90 (m, 5H), 0.88 (d, *J*=6.7, 4H), 0.79 (t, *J*=6.3, 3H), 0.66 (d, *J*=6.7, 3H), 0.47 (d, *J*=12.4, 2H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 151.20 (s), 150.44 (d, *J*=5.8), 133.64 (s), 133.38 (s), 130.69 (s), 130.29 (s), 130.03 (s), 129.04 (s), 128.28 (s), 127.90 (s), 127.48 (s), 126.61 (s), 125.39 (s), 125.32 (s), 125.06 (s), 123.49 (s), 120.99 (s), 119.27 – 119.01 (m), 117.81 (s), 114.68 (s), 43.41 (s), 40.03 (d, *J*=28.9), 37.18 (d, *J*=36.6), 35.38 (s), 34.11 (s), 33.10 (d, *J*=10.8), 28.68 (d, *J*=2.9), 26.55 (d, *J*=13.6), 26.37 (d, *J*=9.9), 25.33 (s), 25.22 (s), 24.94 (d, *J*=11.0), 24.78 (d, *J*=4.7), 22.43 (s), 21.43 (s), 15.99 (s); **HRMS (ESI^+)** Calcd. for $C_{36}H_{42}O_2P$ [M - BH_4]: 537.2922, Found: 537.2845.

Part 5. The reaction of borane-complex 10 or 10' with Grignard reagent.

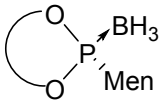


R-**10** or *S*-**10'** **9** **9'**

The preparation of 10, typical procedure:

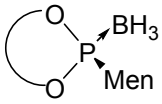
To the ice-water cooled solution of ***S*-2** (2.80 g, 8 mmol) in tetrahydrofuran (15 mL), was added dropwise the solution of menthyl magnesium chloride (0.8 M solution in THF, 15 mL, 12 mmol). The mixture was stirred and warmed to room temperature within 4 hours. BH_3-THF (1.0 M solution in THF, 10 mL, 10 mmol) was added, and the mixture was stirred for 2 hours. Diluted hydrochloric acid (7%, 5 mL) was added to quench the reaction, and then the mixture was extracted with ether (3 × 50 mL), washed with water (3 × 30 mL), dried over magnesium sulfate. After removing solvents, the residue was analyzed with NMR spectroscopy, and purified with recrystallization or column chromatography (dichloromethane/petroleum ether = 1:4) to afford **10a'**.

***S*-Binaphthoxy menthylphosphonites borane, 10a'**



The crude **10a'** was obtained in 99% yield based on ***S*-2** (estimated by **^{31}P-NMR** spectrum, only one peak at 185.51 – 185.11 ppm was observed). The pure compound was obtained from recrystallization as a white solid (2.52 g, 69%), m.p. 186.4 – 193.3 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 185.46 – 185.06 (broad m); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 8.01 (d, *J*=8.8, 2H), 7.95 (t, *J*=7.9, 2H), 7.55 – 7.48 (m, 2H), 7.48 – 7.44 (m, 2H), 7.37 (d, *J*=8.9, 1H), 7.30 (dd, *J*=13.7, 6.1, 1H), 7.25 (t, *J*=5.0, 2H), 2.44 (dd, *J*=3.7, 2.8, 1H), 2.36 – 2.27 (m, 1H), 2.06 – 1.88 (m, 1H), 1.78 (d, *J*=9.3, 3H), 1.40 (dd, *J*=7.4, 3.1, 2H), 1.04 (d, *J*=5.4, 3H), 0.99 (dt, *J*=19.6, 9.7, 4H), 0.93 – 0.83 (m, 1H), 0.63 (dd, *J*=6.7, 2.8, 3H), 0.56 – 0.15 (m, 2H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 147.65 (s), 147.55 (d, *J*=4.2), 132.62 (d, *J*=21.3), 131.64 (d, *J*=54.4), 130.71 (s), 128.47 (d, *J*=22.2), 127.15 (d, *J*=39.3), 126.63 (d, *J*=20.5), 125.66 (d, *J*=16.2), 122.75 (s), 122.54 (s), 121.85 (s), 120.18 (s), 43.45 (s), 41.02 (d, *J*=28.1), 35.00 (s), 34.51 (s), 32.85 (d, *J*=12.4), 29.09 (s), 24.49 (d, *J*=13.4), 22.76 (s), 21.72 (s), 15.53 (s). **HRMS (ESI^+)** Calcd. for $C_{30}H_{32}O_2P$ [M-BH_3]: 455.2140, Found: 455.2129.

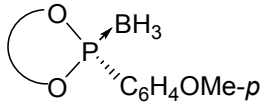
***R*-Binaphthoxy menthylphosphonites borane, 10a**



The crude **10a** was obtained in 99% yield based on ***R*-2** (estimated by **^{31}P-NMR** spectrum, only one peak at 186.00 – 185.47 ppm was observed). The pure compound was obtained from recrystallization as a white solid (2.03 g, 56%), m.p. 121.8– 127.4 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 186.00 – 185.47 (broad m); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 8.06 – 7.98 (m, 2H), 7.95 (dd, *J*=7.9, 3.8, 2H), 7.57 – 7.42 (m, 4H), 7.38 – 7.20 (m, 4H), 2.56 – 2.38 (m, 1H), 2.13 – 1.96 (m, 2H), 1.87 – 1.67 (m, 4H), 1.32 – 1.19 (m, 2H), 1.10 – 1.00 (m, 8H),

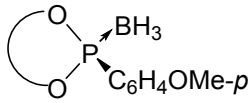
0.97 – 0.87 (m, 4H), 0.78 – 0.12 (m, 1H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 152.78 (s), 147.47 (d, *J*=9.0), 132.62 (d, *J*=33.3), 131.68 (d, *J*=38.3), 130.54 (d, *J*=24.6), 128.44 (d, *J*=24.7), 127.01 (d, *J*=55.5), 126.68 (d, *J*=38.3), 125.62 (d, *J*=18.9), 124.12 (d, *J*=41.8), 122.80 (s), 121.48 (d, *J*=136.5), 117.86 (s), 110.64 (d, *J*=130.5), 42.03 (d, *J*=7.0), 39.57 (d, *J*=27.3), 34.63 (s), 34.01 (s), 32.62 (d, *J*=10.5), 28.96 (s), 24.60 (d, *J*=14.8), 22.41 (s), 21.58 (s), 17.16 (s). **HRMS (ESI$^+$)** Calcd. for $C_{30}H_{32}O_2P$ [M-BH_3]: 455.2159, Found: 455.2140.

***S*-Binaphthoxy *p*-methyoxyphenylphosphonites borane, 10b'**



The crude **10b'** was obtained in 99% yield based on ***S*-2** (estimated by **^{31}P-NMR** spectrum, only one peak at 157.08 – 156.53 ppm was observed). The pure compound was obtained from column chromatography as a white solid (2.13 g, 61%), m.p. 97.1– 103.4 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 157.30 – 156.95 (broad m); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 8.06 (d, *J*=8.8, 1H), 7.97 (d, *J*=8.2, 1H), 7.91 (d, *J*=8.1, 1H), 7.79 (d, *J*=8.8, 1H), 7.61 (d, *J*=8.8, 1H), 7.55 (t, *J*=9.3, 2H), 7.52 – 7.41 (m, 3H), 7.33 (t, *J*=9.0, 2H), 7.28 (d, *J*=8.4, 1H), 6.89 (d, *J*=8.8, 1H), 6.84 (d, *J*=7.0, 2H), 3.81 (s, 3H), 1.26 – 0.67 (m, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 164.02 (d, *J*=1.8), 147.22 (s), 147.13 (d, *J*=3.4), 133.65 (d, *J*=15.2), 132.54 (d, *J*=4.3), 131.78 (d, *J*=43.1), 130.68 (d, *J*=59.2), 128.55 (d, *J*=8.0), 127.06 (d, *J*=15.2), 126.64 (d, *J*=3.9), 125.67 (d, *J*=3.3), 122.90 (d, *J*=2.7), 122.52 (d, *J*=2.9), 121.76 (d, *J*=2.2), 121.18 (d, *J*=1.2), 119.66 (d, *J*=66.4), 114.73 (d, *J*=11.5), 114.02 (d, *J*=12.1), 55.41 (s). **HRMS (ESI$^+$)** Calcd. for $C_{27}H_{19}O_3PNa$ [M-BH_3+Na^+]: 445.0970, Found: 445.0977.

***R*-Binaphthoxy *p*-methyoxyphenylphosphonites borane, 10b**



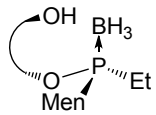
The crude **10b'** was obtained in 99% yield based on ***R*-2** (estimated by **^{31}P-NMR** spectrum, only one peak at 157.21 – 156.66 ppm was observed). The pure compound was obtained from column chromatography as a white solid (1.89 g, 56%), m.p. 124.5 – 130.2 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 157.15 – 156.60 (broad m); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 8.06 (d, *J*=8.9, 1H), 7.98 (d, *J*=8.1, 1H), 7.92 (d, *J*=7.8, 1H), 7.80 (d, *J*=8.8, 1H), 7.64 – 7.53 (m, 3H), 7.48 (dd, *J*=13.9, 7.0, 2H), 7.44 (s, 1H), 7.37 – 7.27 (m, 3H), 6.90 (d, *J*=8.8, 1H), 6.85 (dd, *J*=8.8, 1.9, 2H), 3.83 (s, 3H), 1.15 – 0.85 (m, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 164.03 (d, *J*=2.0), 147.22 (s), 147.12 (d, *J*=4.3), 133.66 (d, *J*=15.1), 132.54 (d, *J*=4.7), 131.79 (d, *J*=42.4), 131.01 (s), 130.44 (s), 128.58 (d, *J*=7.1), 127.06 (d, *J*=14.4), 126.68 (d, *J*=4.2), 125.71 (d, *J*=3.9), 122.90 (d, *J*=2.8), 122.53 (d, *J*=2.9), 121.78 (s), 121.19 (s),

119.60 (d, *J*=66.4), 114.04 (d, *J*=12.1), 55.43 (s). **HRMS (ESI$^+$)** Calcd. for $C_{27}H_{19}P$ [M-BH_3]: 423.1150, Found: 423.1155.

The reaction of 10 or 10' with Grignard reagent, typical procedure:

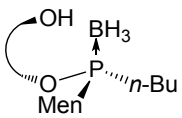
To the ice-water cooled solution of ***R*-10a** (93.7 mg, 0.2 mmol), was add a solution of ethyl magnesium bromide (0.1 mL, 3.0 M solution in ether) was added. After the mixture was warmed and stirred at 50 °C for 6 hours, saturated solution of ammonium chloride (3 mL) was added. The mixture was extracted with ether (3 × 10 mL), washed with water (3 × 5 mL), dried over magnesium sulfate. After removing solvents, the residue was analyzed with NMR spectrum, and purified with flash chromatography on silica gel (petroleum ether/dichloromethane = 2/1) to afford **9a**.

***R*$_A$,*R*$_P$-(-)-Menthyl ethyl (2'-hydroxyl-1,1'-binaphthalen-2-oxy)phosphine borane, 9a**



The crude **9a** was obtained in 99:1 dr (estimated by ^{1}H-NMR spectrum), and the optically pure **9a** was obtained as a white solid (61 mg, 61%, >99:1 dr), m.p. 82.5 – 85.5 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 139.17 – 138.42 (broad m); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 8.01 (d, *J*=8.9, 1H), 7.92 (dd, *J*=12.6, 8.7, 2H), 7.85 (d, *J*=8.0, 1H), 7.72 (d, *J*=9.0, 1H), 7.46 (t, *J*=7.0, 1H), 7.35 (dd, *J*=14.5, 9.3, 4H), 7.29 – 7.23 (m, 1H), 7.12 (d, *J*=8.1, 1H), 4.92 (s, 1H), 2.06 – 1.87 (m, 2H), 1.79 (s, 1H), 1.58 (d, *J*=13.9, 4H), 1.45 (dd, *J*=14.0, 7.1, 2H), 1.26 (s, 2H), 1.13 (s, 1H), 0.95 (dd, *J*=23.9, 11.5, 2H), 0.81 (d, *J*=6.5, 3H), 0.73 – 0.62 (m, 9H), 0.58 – 0.40 (m, 2H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 151.24 (s), 150.11 (s), 133.61 (s), 133.22 (s), 130.97 (s), 130.51 (s), 130.24 (s), 129.03 (s), 128.36 (s), 127.99 (s), 127.55 (s), 126.49 (s), 125.54 (s), 125.10 (s), 124.89 (s), 123.46 (s), 121.09 (d, *J*=2.9), 120.11 – 119.90 (m), 117.58 (s), 114.46 (s), 43.35 (d, *J*=2.7), 39.89 (d, *J*=31.5), 35.02 (s), 34.17 (s), 33.17 (d, *J*=12.6), 28.18 (d, *J*=2.5), 24.72 (d, *J*=10.4), 22.28 (s), 21.15 (s), 20.22 (d, *J*=35.5), 15.67 (s), 5.73 (s). **HRMS (ESI$^+$)** Calcd. for $C_{32}H_{38}O_2P$ [M-BH_3+H^+]: 485.2609, Found: 485.2649.

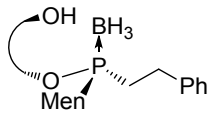
***R*$_A$,*R*$_P$-(-)-Menthyl butyl (2'-hydroxyl-1,1'-binaphthalen-2-oxy) phosphine borane, 9b**



The crude **9b** was obtained from butyl magnesium bromide (0.8 M solution in ether) in 99:1r (estimated by ^{1}H-NMR spectra), and the optically pure **9b** was obtained as a white solid (63 mg, 60%, >99:1 dr) from recrystallization with dichloromethane/petroleum ether (60-90 ^{o}C); m.p. 166.2– 170.2 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 137.33 – 137.02 (broad m); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 8.01 (d, *J*=9.1, 1H), 7.92 (dd,

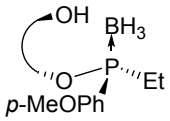
J=11.5, 8.7, 2H), 7.85 (d, *J*=7.8, 1H), 7.68 (d, *J*=9.0, 1H), 7.45 (t, *J*=7.0, 1H), 7.33 (d, *J*=8.7, 4H), 7.26 (t, *J*=7.0, 1H), 7.12 (d, *J*=8.4, 1H), 4.90 (s, 1H), 1.99 (d, *J*=10.7, 2H), 1.84 (s, 1H), 1.64 (d, *J*=12.1, 2H), 1.42 – 1.24 (m, 4H), 1.17 (s, 1H), 1.04 (dd, *J*=14.0, 6.9, 3H), 0.96 (d, *J*=7.5, 3H), 0.83 (d, *J*=6.4, 4H), 0.75 – 0.64 (m, 10H), 0.52 (dd, *J*=12.2, 5.7, 1H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 151.27 (s), 150.12 (d, *J*=6.0), 133.37 (d, *J*=40.4), 130.98 (s), 130.38 (d, *J*=25.8), 129.00 (s), 128.37 (s), 127.78 (d, *J*=44.1), 126.45 (s), 125.34 (d, *J*=45.5), 124.17 (d, *J*=143.4), 121.21 (d, *J*=3.0), 120.10 (d, *J*=4.4), 117.65 (s), 114.47 (s), 43.47 (d, *J*=2.6), 40.22 (d, *J*=31.2), 35.17 (s), 34.21 (s), 33.23 (d, *J*=12.9), 28.19 (d, *J*=2.5), 26.77 (d, *J*=35.6), 24.75 (d, *J*=10.1), 24.20 (d, *J*=14.4), 23.36 (s), 22.35 (s), 21.17 (s), 15.68 (s), 13.32 (s). **HRMS (ESI$^+$)** Calcd. for $C_{34}H_{44}BNaO_2P$ [M+Na$^+$]: 549.3070, Found: 549.3079.

R_A,R_P-(-)-Menthyl □-phenylethyl (2'-hydroxyl-1,1'-binaphthalen-2-oxy)phosphine borane, 9c



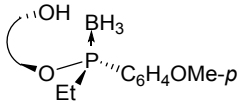
The crude **9c** was obtained from phenylethyl magnesium bromide (0.8 M solution in THF) in 99:1 dr (estimated by ^{1}H-NMR spectra), and the optically pure **9c** was obtained as a white solid (80 mg, 72%, >99:1 dr) from flash chromatography), m.p. 75.1 – 79.2 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 136.70 – 136.28 (broad m); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 8.04 (d, *J*=9.1, 1H), 7.95 (d, *J*=8.2, 1H), 7.83 (t, *J*=8.4, 2H), 7.73 (d, *J*=9.1, 1H), 7.46 (d, *J*=8.2, 1H), 7.35 (t, *J*=6.9, 3H), 7.31 – 7.22 (m, 4H), 7.17 (dd, *J*=12.9, 7.2, 2H), 6.86 (d, *J*=7.6, 2H), 4.93 (s, 1H), 2.48 (d, *J*=8.1, 1H), 2.12 (dd, *J*=30.3, 15.5, 2H), 1.89 (s, 1H), 1.72 – 1.53 (m, 4H), 1.35 – 1.10 (m, 4H), 0.98 (dd, *J*=23.7, 11.1, 1H), 0.87 (d, *J*=6.8, 1H), 0.82 (d, *J*=6.3, 3H), 0.69 (dd, *J*=15.4, 6.6, 6H), 0.63 – 0.39 (m, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 151.28 (s), 149.90 (s), 141.16 (s), 133.40 (d, *J*=31.3), 130.98 (s), 130.48 (d, *J*=18.9), 129.03 (s), 128.45 – 128.30 (m), 128.09 (s), 128.01 (s), 127.63 (s), 126.30 (d, *J*=29.9), 125.37 (d, *J*=48.9), 124.84 (s), 123.52 (d, *J*=2.1), 120.79 – 120.47 (m), 117.74 (d, *J*=2.1), 114.34 (s), 43.53 (d, *J*=3.8), 40.98 (d, *J*=30.4), 35.36 – 35.16 (m), 34.38 – 33.90 (m), 33.34 (s), 33.26 – 33.18 (m), 28.22 – 28.13 (m), 27.46 – 27.21 (m), 24.76 (d, *J*=9.8), 22.32 (dd, *J*=3.9, 2.3), 21.19 (dd, *J*=4.1, 1.8), 15.81 (dd, *J*=3.4, 1.6). **HRMS (ESI$^+$)** Calcd. for $C_{38}H_{44}BNaO_2P$ [M+Na$^+$]: 597.3070, Found: 597.3083.

(R_P/S_P)-(-)-*p*-Methyoxyphenyl ethyl (2'-hydroxyl-1,1'-binaphthalen-2-oxy)phosphine borane, 9f/9f'



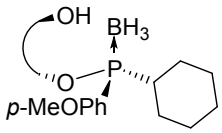
The crude **9f/9f'** was obtained from **10b** and ethyl magnesium bromide (3.0 M solution in ether) in a ratio of 63:37 (estimated by ^{1}H-NMR spectrum, based on the peak of *para*-MeO on phenyl around 3.8 ppm). After isolation, **9f/9f'** was obtained as a white solid (81mg, 73%, 60:40 dr); **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 121.33 – 120.64 (broad m); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.98 – 7.85 (m, 3H), 7.80 (dd, *J* = 8.0, 3.4 Hz, 2H), 7.42 (dd, *J* = 7.9, 4.3 Hz, 2H), 7.35 (d, *J* = 8.9 Hz, 2H), 7.28 (d, *J* = 6.8 Hz, 2H), 7.17 (t, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.81 – 6.75 (m, 1H), 6.73 – 6.70 (m, 1H), 3.82 (s, 1H), 3.79 (s, 2H), 1.80 – 1.44 (m, 3H), 0.72 – 0.56 (m, 4H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 162.57 (s), 151.41 (d, *J*=10.9), 149.77 (d, *J*=5.6), 133.77 – 133.31 (m), 132.70 (t, *J*=12.0), 131.13 (s), 130.48 (d, *J*=3.4), 130.14 (d, *J*=8.9), 128.98 (s), 128.27 (d, *J*=4.7), 127.86 (d, *J*=6.4), 127.37 (d, *J*=8.6), 126.68 (s), 126.43 (s), 125.76 – 125.32 (m), 125.11 (d, *J*=9.3), 124.21 (s), 123.48 (s), 123.24 (s), 121.65 (s), 121.32 – 120.92 (m), 120.64 (s), 117.78 (s), 117.48 (s), 114.14 (dd, *J*=22.6, 13.3), 55.27 (d, *J*=8.0), 29.68 (s), 25.10 (s), 24.62 (s), 24.15 (s), 5.70 (s).

(R_P/S_P)-(-)-*p*-Methyoxyphenyl ethyl (2'-hydroxyl-1,1'-binaphthalen-2-yloxy)phosphine borane, 9g/9g'



The crude **9g/9g'** was obtained from **10b'** and ethyl magnesium bromide (3.0 M solution in ether) in a ratio of 51:49 (estimated by ^{1}H-NMR spectrum, based on the peak of *para*-MeO on phenyl around 3.8 ppm). After isolation, **9g/9g'** was obtained as a white solid (57 mg, 60%, 51:49 dr); m.p. 66.7 – 72.3 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 121.05 – 120.58 (broad m); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.94 – 7.86 (m, 2H), 7.80 (dd, *J*=11.0, 5.5, 1H), 7.53 (d, *J*=9.0, 1H), 7.42 (d, *J*=10.7, 2H), 7.39 – 7.33 (m, 2H), 7.33 – 7.26 (m, 3H), 7.21 (d, *J*=6.2, 1H), 7.16 (dd, *J*=10.9, 5.1, 1H), 6.97 (d, *J*=8.1, 1H), 6.77 (d, *J*=8.5, 1H), 6.71 (d, *J*=8.5, 1H), 3.81 (s, 1H), 3.79 (s, 2H), 1.80 – 1.61 (m, 1H), 1.51 (ddd, *J*=30.3, 15.2, 7.5, 1H), 0.88 (s, 1H), 0.64 (ddd, *J*=25.3, 16.5, 7.6, 4H). **HRMS (ESI$^+$)** Calcd. for $C_{29}H_{28}BNaO_3P$ [M+Na^+]: 489.1767, Found: 489.1771.

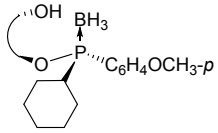
R_A-(-)-*p*-Methyoxyphenyl *cyclo*hexyl (2'-hydroxyl-1,1'-binaphthalen-2-yloxy)phosphine borane, 9h



During the reaction of **10b** with *cyclo*-hexyl magnesium bromide (0.8 M solution in ether), crude **9h/9h'** was observed in yield of 11% and in 99:1dr as seen the peaks on **^{31}P-NMR** spectrum at δ = 157.34 – 156.85 (broad m,

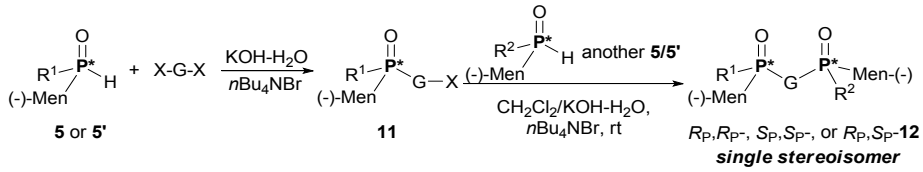
89%, assigned as **10b**), 121.42 – 121.30 (broad m, 11%). Pure product wass not isolated because of the low yield.

S_A-(-)-*p*-Methyoxyphenyl *cyclo*hexyl (2'-hydroxyl-1,1'-binaphthalen-2-yloxy)phosphine borane, 9i



During the reaction of **10b'** with *cyclo*-hexyl magnesium bromide (0.8 M solution in ether), crude **9i/9i'** was observed in yield of 29% and in 99:1 dr as seen the peaks on **^{31}P-NMR** spectrum at δ = 157.43 – 157.05 (broad m, 71%, assigned as **10b'**), 121.36 – 121.05 (broad m, 29%).After isolation, **9i/9i'** was obtained as a white solid (25 mg, 24%, >99:1 dr), m.p. 75.6– 78.9 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 121.61 – 121.13 (broad m); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.90 (d, *J*=9.1, 2H), 7.83 (dd, *J*=7.9, 2.8, 2H), 7.46 (d, *J*=9.0, 1H), 7.44 – 7.40 (m, 2H), 7.37 (d, *J*=6.7, 1H), 7.35 – 7.29 (m, 3H), 7.19 (t, *J*=7.0, 1H), 6.89 – 6.79 (m, 2H), 4.83 (s, 1H), 3.84 (s, 3H), 1.57 (s, 1H), 1.43 (d, *J*=17.1, 3H), 1.26 (s, 4H), 1.14 (s, 1H), 0.81 (d, *J*=5.8, 4H), 0.62 (s, 1H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 162.68 – 162.14 (m), 151.43 – 150.74 (m), 133.44 (s), 132.98 (d, *J*=11.8), 130.90 (s), 130.24 (d, *J*=37.2), 129.06 (s), 127.87 (d, *J*=87.2), 127.29 (d, *J*=97.1), 125.49 (s), 125.29 (s), 123.55 (s), 120.83 (d, *J*=4.0), 120.82 (d, *J*=55.1), 120.02 (d, *J*=4.7), 117.32 (s), 114.34 (s), 114.06 (d, *J*=11.0), 55.31 (s), 40.06 (d, *J*=44.8), 29.70 (s), 26.07 (d, *J*=13.6), 25.44 (s), 24.60 (d, *J*=22.6), 14.14 (s). **HRMS (ESI$^+$)** Calcd. for $C_{33}H_{34}BNaO_3P$ [M+Na$^+$]: 543.2236, Found: 543.2244.

Part 6. The preparation of 12 from the alkylation of 5 and/or 5'.

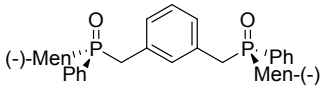


Typical procedure for preparation of 12a:

The reaction could be carried out under air. To the solution of ***R*$_P$-5a** (50 mg, 0.190 mmol) and tetra(n-butyl)ammonium bromide (6 mg, 0.019 mmol, 10% mol) in dichloromethane (0.2 mL), 1,3-dichloromethylbenzene (0.014 ml, 0.095 mmol) was added. The potassium hydroxide solution in water (50%, 0.5 mL) was added and the mixture was stirred at room temperature for 10 h, with the monitoring by TLC (silica gel, petroleum ether/ethyl acetate = 1/1 as eluent, **11a**, Rf = 0.7; **12a**,

Rf = 0.3). After the reaction was completed, the mixture was extracted with dichloromethane (3×10 mL), washed with water (3×5 mL), dried over magnesium sulfate. After removing the solvents, the residue was purified with flash chromatography on silica gel (petroleum ether/ethyl acetate = 1/1) to afford **12a**.

(R_P,R_P)-1,3-Phenylenebis(methylene) bis[(−)-menthylphenylphosphine oxide], 12a

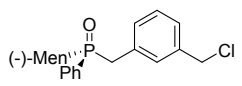


The pure compound **12a** was obtained as a white solid (43 mg, 71%, >99:1 dr), m.p. 121.3 – 123.6 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 40.06 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.50 – 7.41 (m, 4H), 7.35 (d, *J*=6.3, 2H), 7.33 – 7.27 (m, 4H), 6.91 (s, 1H), 6.71 (dd, *J*=27.7, 7.3, 3H), 3.40 (t, *J*=15.6, 2H), 2.93 (dd, *J*=14.1, 7.8, 2H), 2.13 – 1.99 (m, 5H), 1.92 (s, 2H), 1.72 (s, 6H), 1.41 – 1.24 (m, 4H), 0.95 (t, *J*=8.2, 9H), 0.76 (d, *J*=6.6, 6H), 0.35 (d, *J*=6.6, 6H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 133.73 (d, *J*=89.6), 132.26 (t, *J*=5.1), 131.66 – 131.41 (m), 130.68 (s), 130.52 (d, *J*=8.7), 127.98 (s), 127.87 (s), 127.58 (s) 43.41 (s), 40.73 (d, *J*=66.0), 35.82 (s), 35.44 (s), 35.22 (s), 34.25 (s), 33.22 (d, *J*=13.1), 28.12 (s), 24.64 (d, *J*=12.2), 22.61 (s), 21.42 (s), 15.17 (s). **HRMS (ESI^+)** Calcd. for $C_{40}H_{57}O_2P_2$ [$M+H^+$]: 631.3834, Found: 631.3858.

The preparation of 11a

The reaction could be carried out under air. To the solution of ***R_P*-5a** (300 mg, 1.136 mmol) and *tetra*(*n*-butyl)ammonium bromide (36 mg, 0.1136 mmol, 10% mol) in dichloromethane (1.2 mL), 1,3-dichloromethylbenzene (0.33 ml, 2.27 mmol) was added. Then the potassium hydroxide solution in water (50%, 3 mL) was added and the mixture was stirred at room temperature for 7 h, with the monitoring by TLC (**11a**, Rf = 0.7; **12a**, Rf = 0.3, petroleum ether/ethyl acetate = 1/1). After the reaction was finished, the mixture was extracted with dichloromethane (3×20 mL), washed with water (3 × 10 mL), dried over magnesium sulfate. After removing the solvents, the residue was purified with flash chromatography on silica gel (petroleum ether/ethyl acetate = 1/1) to afford **11a**.

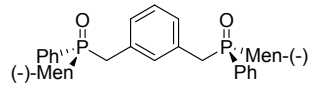
***R_P*-(-)-Menthyl phenyl (3-chloromethylbenzyl) phosphine oxide, 11a**



The optically pure **11a** was obtained as a white solid (300 mg, 66%, >99:1 dr); m.p. 154.1– 163.8 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 39.88 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.50 (dd, *J*=9.4, 8.0, 2H), 7.41 – 7.30 (m, 3H), 7.13 – 7.05 (m, 2H), 6.98 – 6.89 (m, 2H), 4.39 (q, *J*=11.5, 2H), 3.51 (dd, *J*=16.9, 14.4, 1H), 3.01 (dd, *J*=14.2, 7.5, 1H),

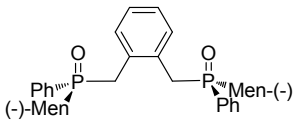
2.12 (d, *J*=4.1, 1H), 2.00 (dd, *J*=11.9, 6.3, 2H), 1.78 (d, *J*=28.6, 4H), 1.46 (dd, *J*=20.6, 8.5, 2H), 0.98 (d, *J*=5.7, 4H), 0.77 (d, *J*=6.8, 3H), 0.30 (d, *J*=6.7, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 137.01 (s), 133.72 (d, *J*=89.4), 132.47 (d, *J*=7.6), 130.87 (d, *J*=2.8), 130.39 (s), 130.31 (s), 130.06 (d, *J*=4.8), 128.28 (s), 128.04 (d, *J*=11.2), 126.45 (d, *J*=2.5), 46.03 (s), 43.32 (d, *J*=3.7), 40.37 (d, *J*=66.3), 36.27 (d, *J*=60.0), 35.20 (s), 34.18 (d, *J*=4.0), 33.30 (t, *J*=8.3), 28.13 (d, *J*=7.2), 24.60 (t, *J*=7.3), 22.64 (s), 21.45 (d, *J*=2.1), 15.12 (d, *J*=2.1). **HRMS (ESI$^+$)** Calcd. for $C_{24}H_{33}ClOP_2$ [M+H$^+$]: 403.1958, Found: 403.1955.

(S_P,S_P)-(1,3-Phenylenebismethylene) bis[(−)-menthylphenylphosphine oxide], 12b



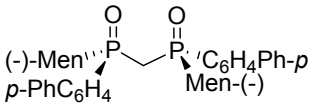
The pure compound **12b** was obtained as a white solid (41 mg, 70%, >99:1 dr); m.p. 181.0 – 184.4 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 42.47 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.57 (dd, *J*=9.3, 7.7, 4H), 7.41 (dq, *J*=12.2, 6.4, 6H), 7.14 (s, 1H), 6.91 (t, *J*=3.2, 3H), 3.45 (t, *J*=14.4, 2H), 3.21 (dd, *J*=14.5, 10.3, 2H), 2.67 – 2.55 (m, 2H), 2.05 – 1.94 (m, 2H), 1.84 (d, *J*=9.2, 2H), 1.66 (d, *J*=9.3, 4H), 1.38 – 1.13 (m, 5H), 1.11 – 1.01 (m, 2H), 0.95 (ddd, *J*=18.6, 12.4, 6.2, 3H), 0.86 (d, *J*=6.4, 6H), 0.82 (d, *J*=6.7, 6H), 0.77 (d, *J*=6.9, 6H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 132.24 (dd, *J*=9.2, 4.0), 131.77 (dd, *J*=7.5, 2.2), 131.13 (s), 131.05 (s), 130.92 (s), 128.16 (s), 128.05 (s), 127.94 (s), 43.39 (s), 41.11 (d, *J*=65.3), 36.40 (s), 34.28 (s), 33.10 (d, *J*=13.6), 28.38 (s), 24.69 (d, *J*=12.9), 22.63 (s), 21.46 (s), 15.77 (s). **HRMS (ESI$^+$)** Calcd. for $C_{40}H_{57}O_2P_2$ [M+H$^+$]: 631.3834, Found: 631.3849.

(S_P,S_P)-(1,2-Phenylenebismethylene) bis[(−)-menthyl phenyl phosphine oxide], 12c



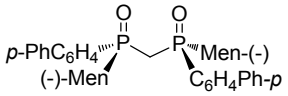
The pure compound **12c** was obtained as a white solid (43 mg, 72%, >99:1 dr); m.p. 199.5 – 201.2 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 43.09 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.58 (t, *J*=8.4, 4H), 7.39 (dd, *J*=15.3, 6.6, 6H), 6.59 (s, 2H), 6.40 (s, 2H), 4.55 (t, *J*=14.7, 2H), 3.22 (dd, *J*=14.7, 7.0, 2H), 2.60 (s, 2H), 2.18 – 2.09 (m, 2H), 1.91 (s, 2H), 1.73 (d, *J*=11.2, 4H), 1.39 (s, 4H), 1.16 – 1.06 (m, 3H), 0.96 (d, *J*=6.4, 6H), 0.85 (dd, *J*=24.8, 6.4, 15H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 132.64 (d, *J*=17.2), 132.63 (d, *J*=3.8), 131.89 (s), 131.26 – 131.07 (m), 130.97 (d, *J*=9.0), 128.11 – 127.89 (m), 125.67 (s), 43.60 (s), 42.17 (d, *J*=64.9), 36.57 (s), 35.38 (d, *J*=59.3), 34.44 (s), 33.60 – 33.13 (m), 28.59 (s), 24.83 (d, *J*=12.9), 22.57 (s), 21.50 (s), 15.88 (s). **HRMS (ESI$^+$)** Calcd. for $C_{40}H_{57}O_2P_2$ [M+H$^+$]: 631.3834, Found: 631.3849.

(R_P,R_P)-(−)-Methylene-bis[(−)-menthyl(biphenyl) phosphine oxide], 12d



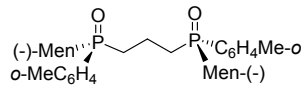
The pure compound **12d** was obtained as a white solid (34mg, 66%, >99:1 dr); m.p. 96.8 – 99.1 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 41.16 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.81 – 7.74 (m, 4H), 7.72 – 7.67 (m, 4H), 7.63 (d, *J*=7.2, 4H), 7.47 (t, *J*=7.4, 4H), 7.40 (d, *J*=7.3, 2H), 2.29 – 2.19 (m, 2H), 1.96 (dd, *J*=20.1, 8.9, 2H), 1.76 (s, 5H), 1.70 (s, 3H), 1.67 (s, 3H), 1.33 (s, 2H), 1.15 (dd, *J*=12.0, 6.6, 2H), 1.10 – 0.96 (m, 3H), 0.91 (d, *J*=6.3, 6H), 0.87 (d, *J*=6.8, 6H), 0.47 (d, *J*=6.7, 6H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 143.75 (d, *J*=2.9), 139.97 (d, *J*=0.7), 134.36 (d, *J*=92.4), 130.57 (d, *J*=9.1), 128.89 (s), 128.00 (s), 127.18 (s), 127.00 (d, *J*=11.4), 43.50 (s), 41.26 (d, *J*=69.1), 35.73 (s), 34.35 (s), 33.20 (d, *J*=13.6), 28.37 (s), 24.61 (d, *J*=12.3), 22.57 (s), 21.56 (s), 15.23 (s), 14.55 (s). **HRMS (ESI$^+$)** Calcd. for $C_{45}H_{59}O_2P_2$ [M+H$^+$]: 693.3990, Found: 693.3995.

(S_P,S_P)-(−)-Methylene-bis[(−)-menthyl(biphenyl) phosphine oxide], 12e



The pure compound **12e** was obtained as a white solid (33mg, 65%, >99:1 dr); m.p. 121.3 – 123.6 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 42.74 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.74 (dt, *J*=8.1, 6.9, 8H), 7.68 – 7.61 (m, 4H), 7.47 (t, *J*=7.4, 4H), 7.39 (t, *J*=7.3, 2H), 2.57 – 2.48 (m, 1H), 1.99 (t, *J*=10.6, 1H), 1.84 (s, 4H), 1.81 (s, 2H), 1.78 (s, 2H), 1.72 (d, *J*=2.9, 5H), 1.34 (s, 3H), 1.01 (ddd, *J*=18.5, 16.7, 8.5, 4H), 0.84 (dt, *J*=17.5, 8.3, 18H).; **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 143.92 (d, *J*=2.8), 139.95 (s), 132.40 (d, *J*=91.8), 130.96 (d, *J*=9.0), 128.91 (s), 128.03 (s), 127.20 (s), 127.04 (d, *J*=11.2), 43.48 (s), 41.98 (d, *J*=68.3), 36.28 (s), 34.32 (s), 33.19 (d, *J*=13.5), 28.60 (s), 24.66 (d, *J*=12.7), 22.54 (s), 21.50 (s), 16.55 (d, *J*=67.1), 15.64 (s). **HRMS (ESI$^+$)** Calcd. for $C_{45}H_{59}O_2P_2$ [M+H$^+$]: 693.3990, Found: 693.4045.

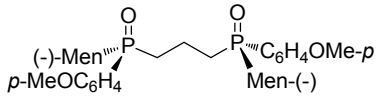
(R_P,R_P)-Propane-1,3-diylbis[(−)-menthyl 2-methylphenylphosphine oxide], 12f



The pure compound **12f** was obtained as a white solid (33mg, 61%, >99:1 dr) from flash chromatography (silica gel, petroleum ether/ethylacetate = 2/1 as eluent); m.p. 70.6 – 78.6 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 47.95 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.60 – 7.46 (m, 3H), 7.28 (s, 2H), 7.12 (dd, *J*=16.4, 9.4, 3H), 2.56 (d, *J*=4.3, 1H), 2.49 (s, 6H), 2.25 (d, *J*=7.4, 2H), 2.09 (dd, *J*=15.0, 7.6, 3H), 2.01 (s, 3H), 1.70 (s, 15H), 1.55 (s, 2H), 0.89 (d, *J*=6.2, 6H), 0.82 (d, *J*=6.7, 6H), 0.32 (dd, *J*=12.7, 5.6, 6H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 140.12 (d, *J*=8.5), 132.20 (d, *J*=8.7), 131.52 (s), 130.37 (d, *J*=84.8), 130.86 (d, *J*=2.6), 125.56 (d, *J*=10.8), 43.10 (d, *J*=3.4), 40.61 (d, *J*=66.1), 35.28 (s), 34.21 (s),

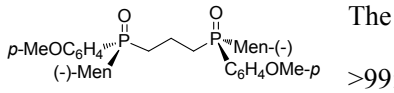
33.32 (d, *J*=13.1), 28.11 (d, *J*=2.7), 27.51 (s), 24.53 (d, *J*=12.0), 22.56 (s), 21.51 (s), 14.94 (s), 14.68 – 14.53 (m). **HRMS (ESI$^+$)** Calcd. for $C_{37}H_{59}O_2P_2$ [M+H$^+$]: 597.3990, Found: 597.4001.

(R_P,R_P)-Propane -1,3-diylbis[(−)-menthyl *p*-methoxyphenylphosphine oxide], 12g



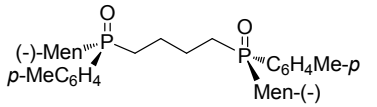
The pure compound **12g** was obtained as a white solid (35mg, 66%, >99:1 dr); m.p. 180.5 – 185.4 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 44.10 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.43 (t, *J*=9.3, 4H), 6.90 – 6.78 (m, 4H), 3.83 (s, 6H), 2.05 (dt, *J*=22.1, 7.4, 5H), 1.88 (s, 1H), 1.82 – 1.76 (m, 3H), 1.69 (d, *J*=11.1, 4H), 1.62 (s, 2H), 1.41 (s, 2H), 1.25 (s, 4H), 1.19 (d, *J*=6.5, 2H), 0.96 (s, 2H), 0.90 (t, *J*=7.6, 7H), 0.82 (d, *J*=6.8, 6H), 0.33 (d, *J*=6.7, 6H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 161.50 (d, *J*=2.5), 132.24 (d, *J*=9.7), 124.58 (dd, *J*=91.9, 1.5), 113.83 (d, *J*=11.9), 55.12 (s), 43.20 (d, *J*=3.4), 41.14 (d, *J*=67.6), 34.75 (d, *J*=105.6), 33.19 (d, *J*=12.9), 28.34 (d, *J*=10.2), 28.10 (d, *J*=3.0), 27.68 (d, *J*=9.0), 24.55 (d, *J*=11.8), 22.02 (d, *J*=100.6), 15.10 (s), 14.48 – 14.40 (m). **HRMS (ESI$^+$)** Calcd. for $C_{37}H_{59}O_4P_2$ [M+H$^+$]: 629.3889, Found: 629.3908.

(S_P,S_P)-Propane -1,3-diylbis[(−)-menthyl *p*-methoxyphenylphosphine oxide], 12h



The pure compound **12h** was obtained as a white solid (31mg, 52%, >99:1 dr); m.p. 223.0 – 224.7 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 45.44 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.49 (t, *J*=9.1, 4H), 6.90 (d, *J*=7.3, 4H), 3.84 (s, 6H), 2.62 – 2.50 (m, 2H), 2.24 (dd, *J*=14.5, 7.3, 2H), 2.11 – 2.01 (m, 2H), 1.94 (dd, *J*=24.2, 11.7, 2H), 1.71 (s, 6H), 1.64 (d, *J*=13.1, 4H), 1.27 (s, 2H), 1.02 (dd, *J*=23.1, 10.8, 4H), 0.86 – 0.80 (m, 12H), 0.73 (dd, *J*=22.1, 9.3, 8H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 161.78 (d, *J*=2.8), 132.74 (d, *J*=9.4), 122.03 (d, *J*=92.6), 113.91 (d, *J*=11.7), 55.19 (s), 43.31 (s), 41.76 (d, *J*=66.6), 35.21 (d, *J*=189.2), 33.12 (d, *J*=13.4), 29.24 (d, *J*=10.3), 28.59 (d, *J*=9.9), 28.36 (s), 24.62 (d, *J*=12.8), 22.02 (d, *J*=119.1), 15.73 (s), 14.86 – 14.68 (m). **HRMS (ESI$^+$)** Calcd. for $C_{37}H_{59}O_4P_2$ [M+H$^+$]: 629.3889, Found:629.3904.

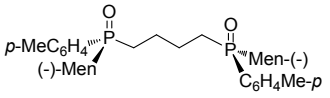
(R_P,R_P)-Butane-1,4-diylbis[(−)-menthyl *p*-tolylphosphine oxide], 12i



The pure compound **12i** was obtained as a white solid (35mg, 65%, >99:1 dr); m.p. 206.1 – 208.5 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 42.90 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.55 – 7.45 (m, 4H), 7.22 (d, *J*=7.4, 4H), 2.38 (s, 6H), 2.08 (dd, *J*=14.0, 7.7, 2H), 2.04 – 1.92 (m, 4H), 1.86 (s, 2H), 1.78 (s, 2H), 1.70 (d, *J*=11.5, 4H), 1.61 (s, 5H), 1.30 (s, 2H), 1.17 (dd, *J*=15.7, 9.2, 4H), 0.99 (d, *J*=10.8, 3H), 0.90 (d,

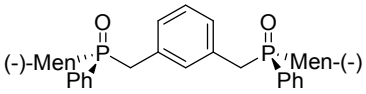
J=5.7, 6H), 0.82 (d, *J*=6.4, 6H), 0.36 (d, *J*=6.7, 6H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 141.29 (d, *J*=2.7), 130.56 (d, *J*=90.9), 130.46 (d, *J*=8.8), 129.16 (d, *J*=11.3), 43.26 (d, *J*=3.3), 40.91 (d, *J*=67.2), 35.33 (d, *J*=2.2), 34.23 (s), 33.66 (d, *J*=13.1), 33.22 (d, *J*=13.0), 32.79 (s), 28.17 (d, *J*=2.7), 26.87 (d, *J*=65.9), 24.58 (d, *J*=12.0), 22.61 (s), 21.54 (s), 20.19 (d, *J*=3.6), 15.19 (s). **HRMS (ESI$^+$)** Calcd. for $C_{38}H_{61}O_2P_2$ [M+H$^+$]: 611.4147, Found: 611.4153.

(S_P,S_P)-Butane-1,4-diylbis[(−)-menthyl *p*-tolylphosphine oxide], 12j



The pure compound **12i** was obtained as a white solid (37mg, 66%, >99:1 dr); m.p. 80.3 – 84.6 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 45.15 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.49 (dd, *J*=9.6, 8.4, 4H), 7.24 (d, *J*=6.7, 4H), 2.63 – 2.51 (m, 2H), 2.41 (d, *J*=9.8, 6H), 2.16 (s, 1H), 2.11 – 1.99 (m, 2H), 1.90 – 1.81 (m, 2H), 1.72 – 1.60 (m, 9H), 1.37 (dd, *J*=31.7, 26.9, 4H), 1.14 – 0.99 (m, 5H), 0.88 – 0.80 (m, 14H), 0.77 (q, *J*=5.5, 7H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 141.44 (d, *J*=2.5), 130.93 (d, *J*=8.5), 129.11 (d, *J*=11.1), 128.31 (d, *J*=88.9), 43.30 (d, *J*=2.9), 41.43 (d, *J*=66.1), 36.22 (s), 34.30 (s), 33.16 (d, *J*=13.3), 28.72 (s), 28.40 (s), 28.19 (s), 24.68 (d, *J*=12.6), 23.14 – 22.74 (m), 22.57 (s), 21.45 (d, *J*=11.7), 15.70 (s), 15.41 (d, *J*=59.6). **HRMS (ESI$^+$)** Calcd. for $C_{38}H_{61}O_2P_2$ [M+H$^+$]: 611.4147, Found: 611.4160.

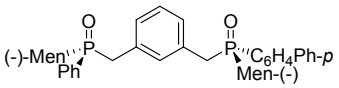
(R_P,S_P)-(1,3-Phenylenebismethylene) bis[(−)-menthylphenylphosphine oxide], 12k



The crude product **12k** was obtained from **11a** in a yield of 99% (estimated by **^{31}P-NMR** spectra), and the pure compound **12k** was obtained as a white solid (96mg, 81%, >99:1 dr); m.p. 199.5 – 201.2 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 42.42 (s), 40.25 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.61 – 7.54 (m, 2H), 7.50 – 7.42 (m, 3H), 7.41 – 7.34 (m, 3H), 7.31 (t, *J*=6.0, 2H), 6.89 – 6.79 (m, 3H), 6.70 (d, *J*=7.0, 1H), 3.26 (ddt, *J*=24.2, 14.6, 12.3, 3H), 2.94 (dd, *J*=14.4, 7.2, 1H), 2.60 – 2.50 (m, 1H), 2.01 (d, *J*=5.1, 4H), 1.92 (d, *J*=10.2, 1H), 1.81 (d, *J*=9.5, 1H), 1.70 (dd, *J*=27.4, 12.7, 5H), 1.40 – 1.28 (m, 3H), 1.20 (s, 1H), 1.09 – 0.93 (m, 7H), 0.85 (dd, *J*=19.2, 6.6, 6H), 0.76 (dd, *J*=9.2, 7.0, 6H), 0.30 (d, *J*=6.7, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 137.00 (d, *J*=2.2), 134.17 (s), 133.28 (s), 132.47 (d, *J*=7.6), 130.87 (d, *J*=2.8), 130.39 (s), 130.36 (s), 130.31 (s), 130.06 (d, *J*=4.8), 128.28 (s), 128.04 (d, *J*=11.2), 126.45 (d, *J*=2.5), 46.03 (s), 45.98 (s), 45.77 (s), 43.33 (d, *J*=3.6), 42.81 – 42.74 (m), 41.70 (s), 40.71 (s), 40.05 (s), 36.58 (s), 35.98 (s), 35.24 (s), 34.57 (s), 34.18 (s), 33.28 (d, *J*=13.0), 28.10 (s), 24.58 (d, *J*=11.9), 22.64 (s), 21.45 (s), 15.45 (s), 15.13 (s). **HRMS (ESI$^+$)**

Calcd. for $C_{40}H_{57}O_2P_2$ [M+H$^+$]: 631.3834, Found: 631.3848.

(R_P,R_P)-1,3-Di(menthyl phenyl phosphinylmethyl)benzene, 12l

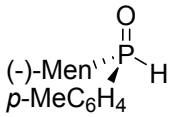


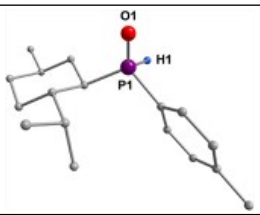
Under similar procedure to **12k**, The pure compound **12l** was obtained as a white solid (105mg, 79%, >99:1 dr); m.p. 111.1 – 114.8 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 40.51 (s), 39.97 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.57 (dd, *J*=14.3, 10.8, 7H), 7.45 – 7.41 (m, 2H), 7.37 (d, *J*=7.1, 3H), 7.22 (d, *J*=5.5, 2H), 6.91 (s, 1H), 6.82 – 6.75 (m, 2H), 6.59 (s, 1H), 3.42 (d, *J*=18.9, 2H), 3.00 (s, 1H), 2.88 (s, 1H), 2.03 (s, 3H), 1.92 (s, 2H), 1.72 (s, 7H), 1.36 (s, 3H), 0.95 (d, *J*=4.1, 9H), 0.77 (dd, *J*=13.8, 6.7, 8H), 0.41 (d, *J*=6.6, 3H), 0.31 (d, *J*=6.6, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ = 143.23 (s), 139.95 (s), 134.16 (s), 133.26 (dd, *J*=3.8, 2.1), 132.66 (s), 132.29 (t, *J*=4.8), 131.63 – 131.56 (m), 131.52 (dd, *J*=2.4, 1.3), 131.15 (d, *J*=8.5), 130.67 (s), 130.39 (d, *J*=8.5), 128.85 (s), 127.90 (s), 127.73 – 127.61 (m), 127.09 (s), 126.60 (d, *J*=11.4), 43.47 (d, *J*=3.2), 43.40 (d, *J*=4.0), 40.94 (d, *J*=65.8), 40.58 (d, *J*=65.6), 36.01 (d, *J*=1.5), 35.69 (s), 35.51 (s), 35.36 (s), 35.10 (s), 34.24 (s), 33.21 (d, *J*=13.0), 28.20 (s), 24.68 (d, *J*=12.2), 24.61 (d, *J*=11.8), 24.32 (s), 22.64 (s), 21.46 (d, *J*=3.0), 19.79 (d, *J*=1.5), 15.25 (d, *J*=15.0), 13.76 (s). **HRMS (ESI$^+$)** Calcd. for $C_{46}H_{60}O_2P_2Na$ [M+Na$^+$]: 729.3966, Found: 729.3996.

Part 7. Crystallographic information 5b, 5k' and 9b.

Table S-1. Crystallography data of R_P-(-)-Menthyl *p*-tolylphosphine oxide (5b)

The single crystal suited for the X-ray diffraction was obtained from the evaporation of the solution of **5b** in dichloromethane and petroleum ether (60-90 °C).

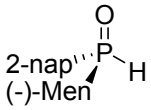


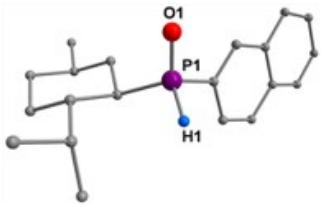


Empirical formula	C17 H27 O P
Crystal system	Monoclinic
space group	P2(1)
Formula weight	252.15
a, Å	12.8110(11)
b, Å	5.7207(5)
c, Å	12.9076(12)
α, deg	90
β, deg	114.493(3)
γ, deg	90
V, Å3	860.84(13)
Z	2
T, K	298(2)
λ, Å	0.71073
ρ, Mg m-3	0.973
Rint	0.0311
R1 [I N 2σ(I)]	0.0781
R1 (all data)	0.0959
wR2 [I N 2σ(I)]	0.2175
wR2 (all data)	0.2384
Absolute structure parameter	0.1(2)
CCDC	1828875

Table S-2. Crystallography data of S_P-(-)-Menthyl 2-naphthalenylphosphine oxide (5k')

The single crystal suited for the X-ray diffraction was obtained from the evaporation of the solution of **5k'** in dichloromethane and petroleum ether (60-90 °C).



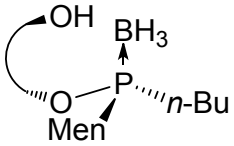


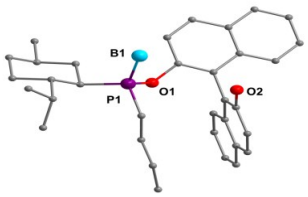
Empirical formula	C20 H27 O P
Crystal system	Orthorhombic
space group	P2(1)2(1)2(1)
Formula weight	314.39
a, Å	5.6725(4)
b, Å	16.4065(13)
c, Å	39.935(3)
α, deg	90
β, deg	90
γ, deg	90
V, Å3	3716.6(5)
Z	8
T, K	298(2)
λ, Å	0.71073
ρ, Mg m−3	1.124
Rint	0.0624
R1 [I N 2σ(I)]	0.0613
R1 (all data)	0.1237
wR2 [I N 2σ(I)]	0.1403
wR2 (all data)	0.1685
Absolute structure parameter	0.14(15)
CCDC	1828876

Table S-3. Crystallography data of

R_AR_P- (-)-menthyl butyl (2'-hydroxyl-1,1'-binaphthalen-2-yloxy) phosphine borane, 9b

The single crystal suited for the X-ray diffraction was obtained from the evaporation of the solution of **7b** in dichloromethane and petroleum ether (60-90 °C).

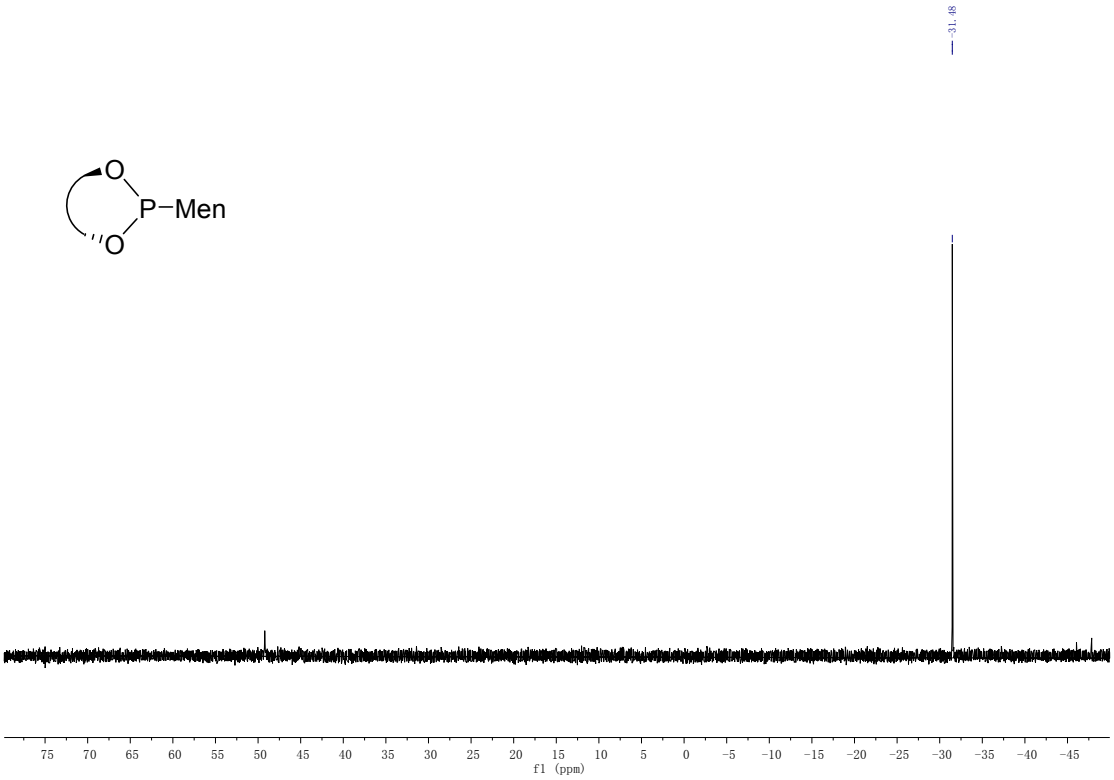




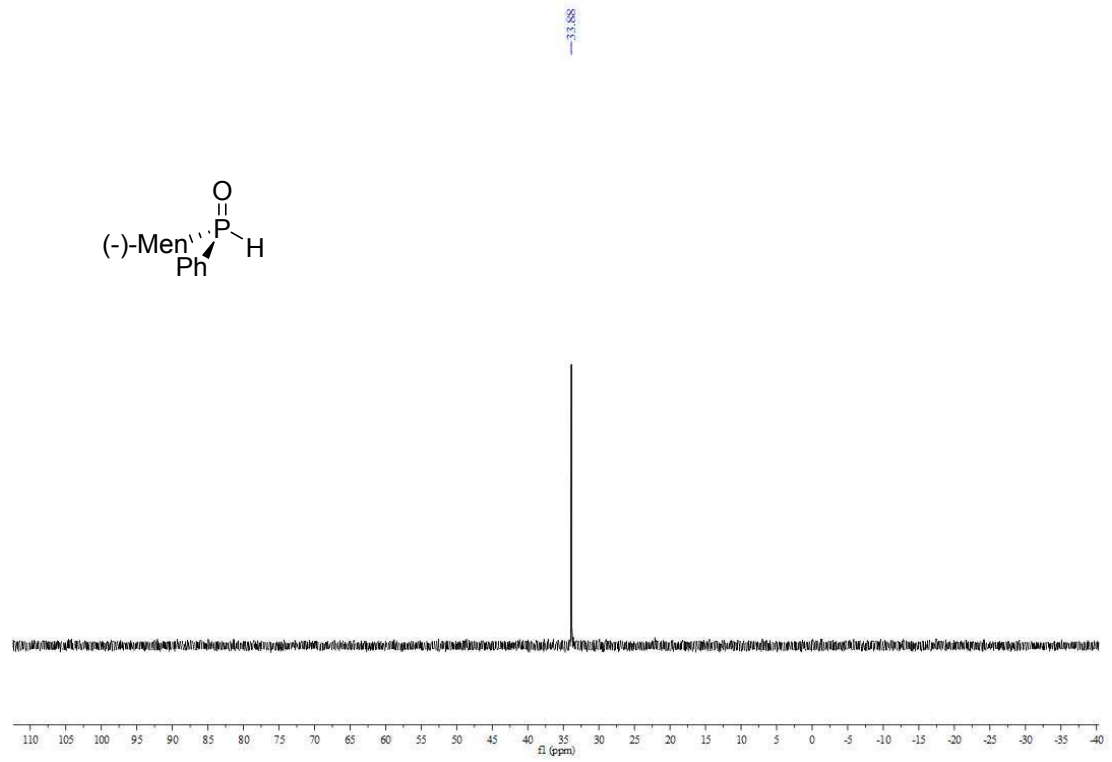
Empirical formula	C34 H44 B O2 P
Crystal system	triclinic
space group	P 1
Formula weight	526.47
a, Å	8.8610(7)
b, Å	8.9222(8)
c, Å	11.1927(9)
α, deg	76.371(2)
β, deg	78.494(2)
γ, deg	65.5380(10)
V, Å3	777.57(11)
Z	1
T, K	298(2)
λ, Å	0.71073
ρ, Mg m^{-3}	1.124
Rint	0.0218
R1 [I N 2σ(I)]	0.0474
R1 (all data)	0.0633
wR2 [I N 2σ(I)]	0.1023
wR2 (all data)	0.1106
Absolute structure parameter	0.28(13)
CCDC	1877581

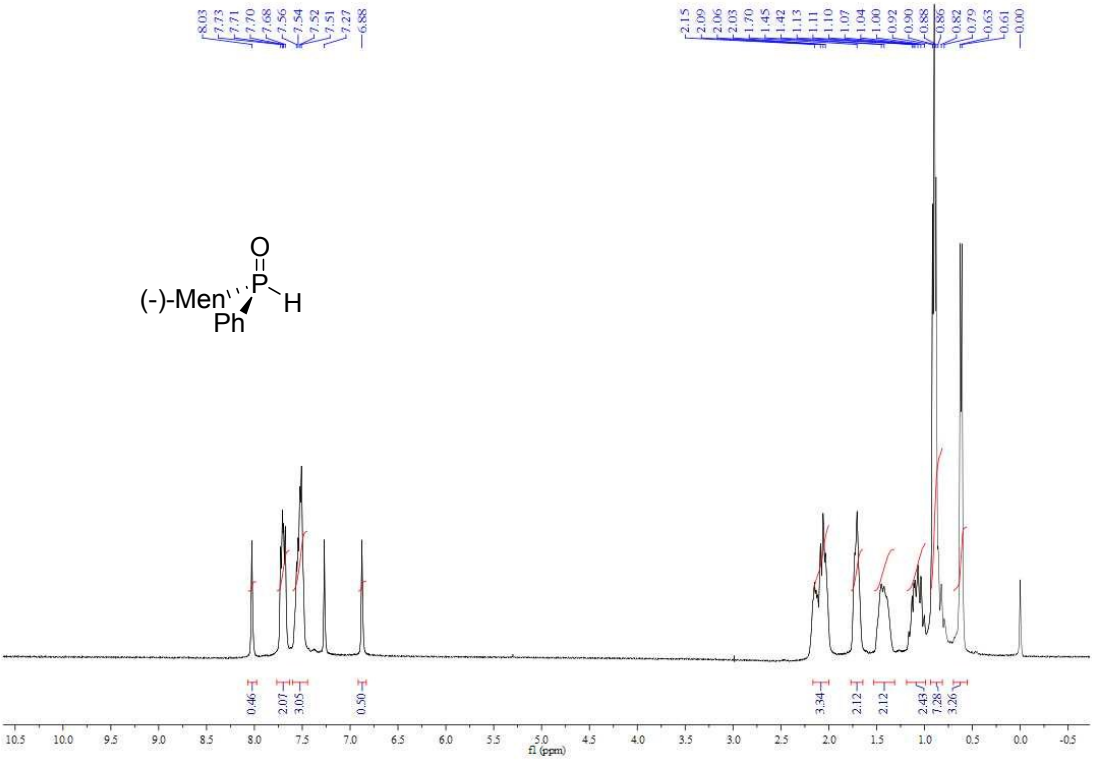
Part 8. Selected photocopies of ^{1}H, ^{31}P and ^{13}C NMR spectroscopy.

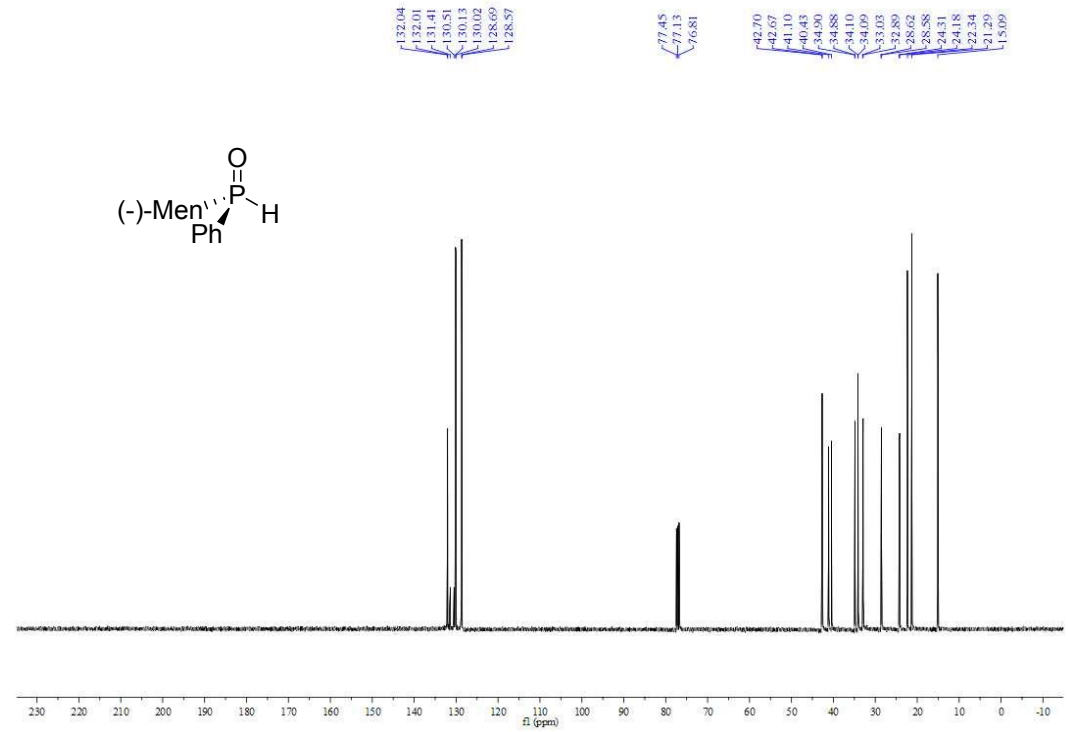
***R*-3 binaphthoxy menthylphosphonites**



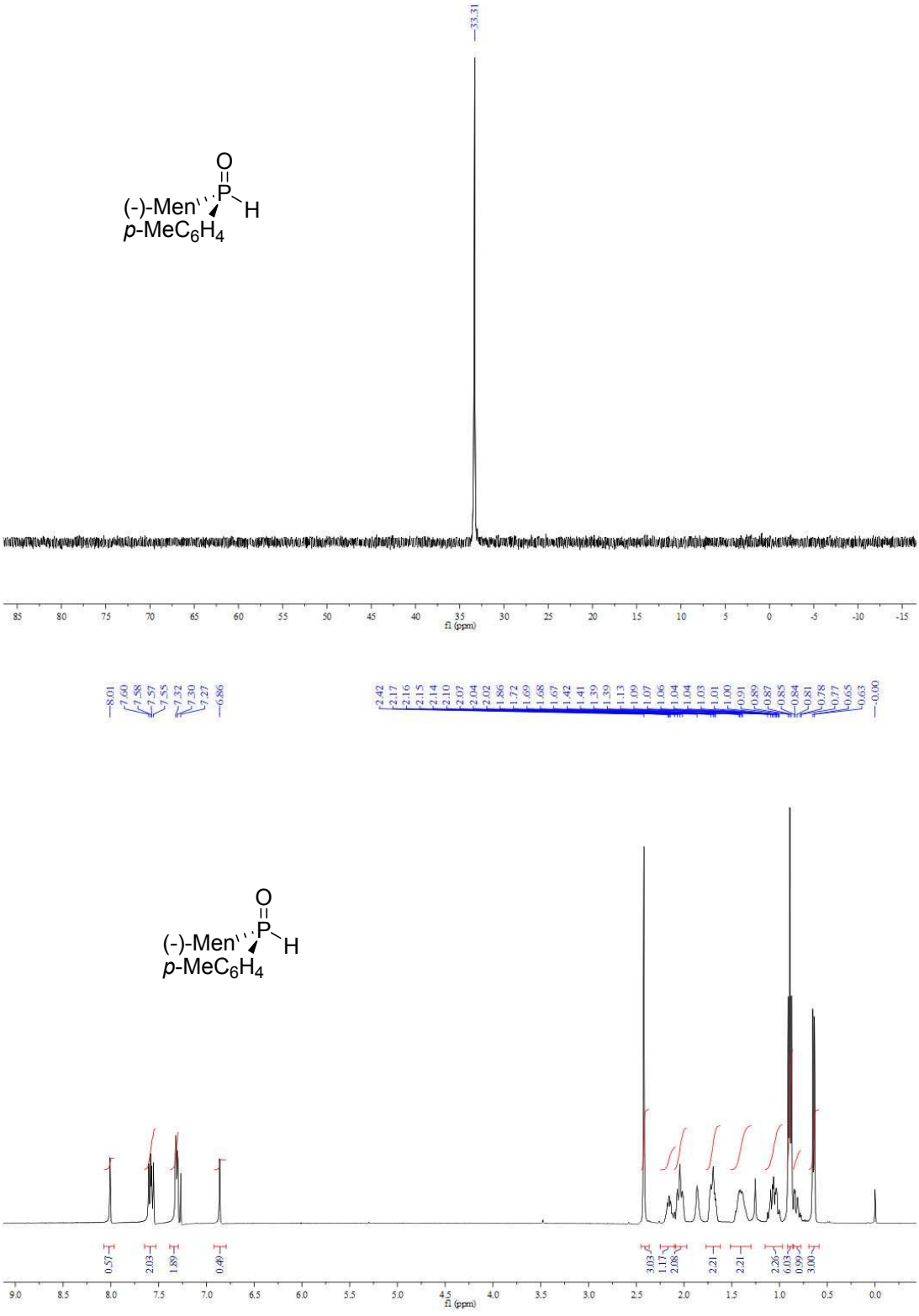
***R*$_P$-(-)-Menthyl phenylphosphine oxide (5a)**

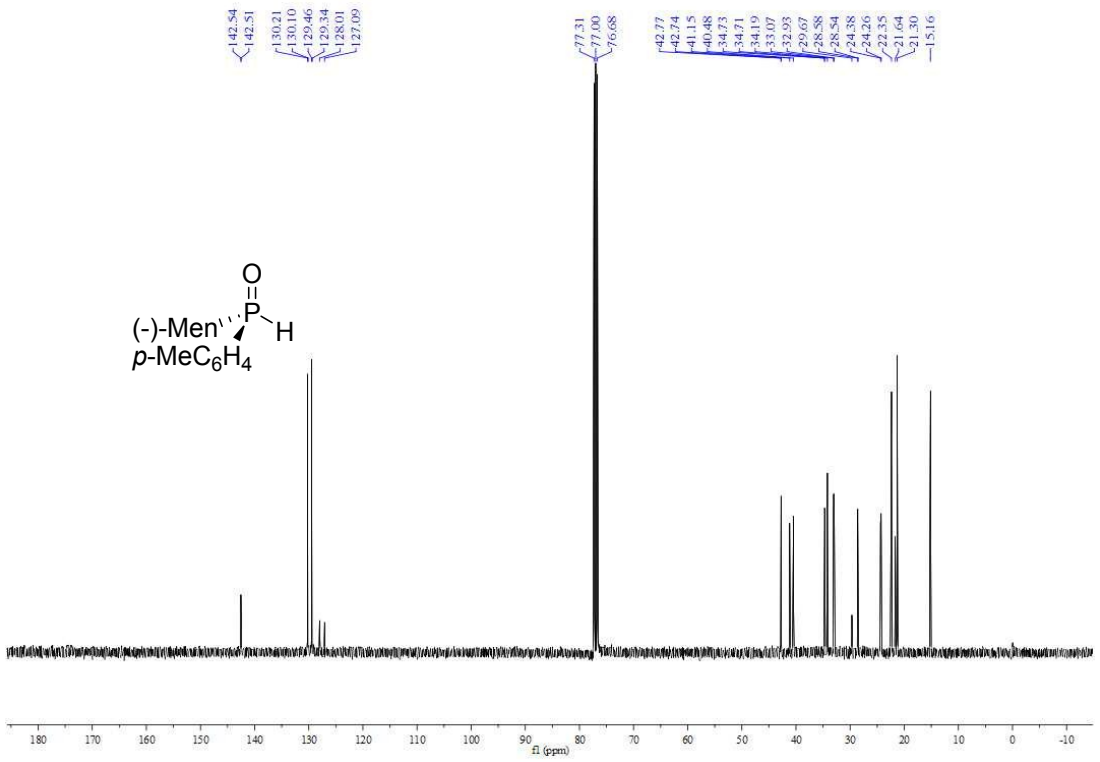



8.03
7.73
7.71
7.70
7.68
7.56
7.54
7.52
7.51
7.27
6.88
2.15
2.09
2.06
2.03
1.70
1.45
1.42
1.13
1.11
1.10
1.07
1.04
1.00
0.92
0.90
0.88
0.86
0.82
0.79
0.63
0.61
0.00
O
P
H
(-)-Men
Ph
0.46
2.07
3.05
0.50
3.34
2.12
2.12
2.43
7.28
3.26
f1 (ppm)

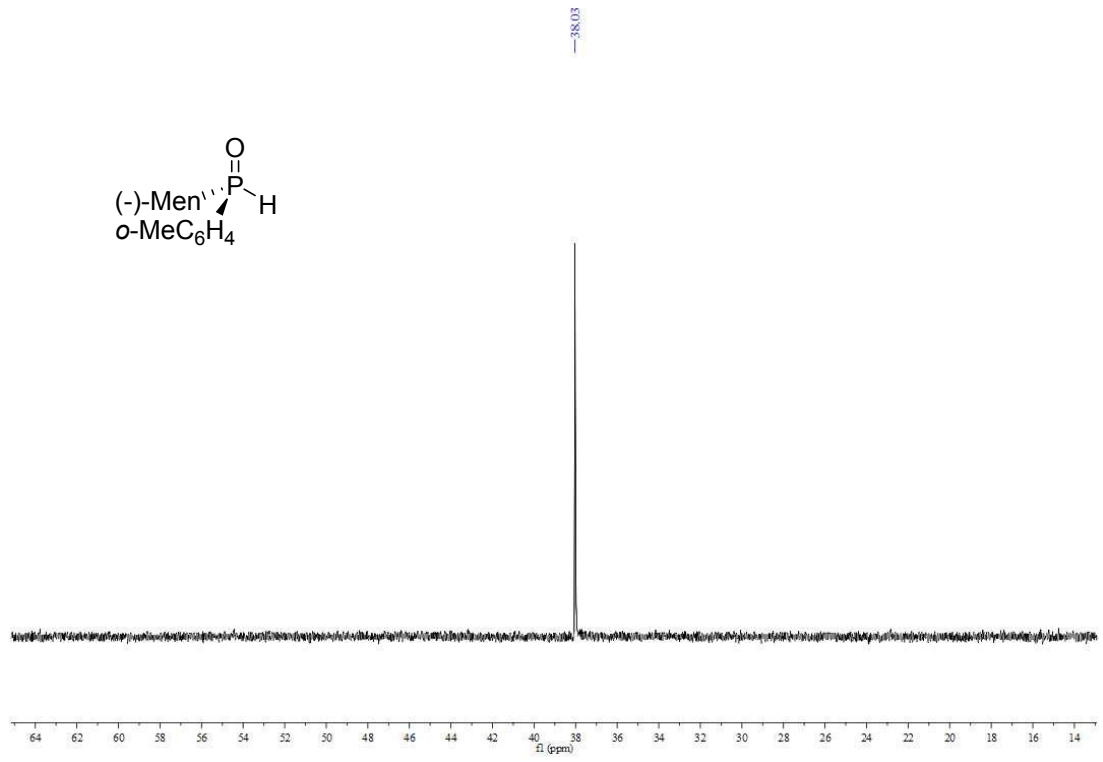

132.04
132.01
131.41
130.51
130.13
130.02
128.69
128.57
77.45
77.13
76.81
42.70
42.67
41.10
40.43
34.90
34.88
34.10
34.09
33.03
32.89
28.62
28.58
24.31
24.18
22.34
21.29
15.09
O
P
H
(-)-Men
Ph
f1 (ppm)

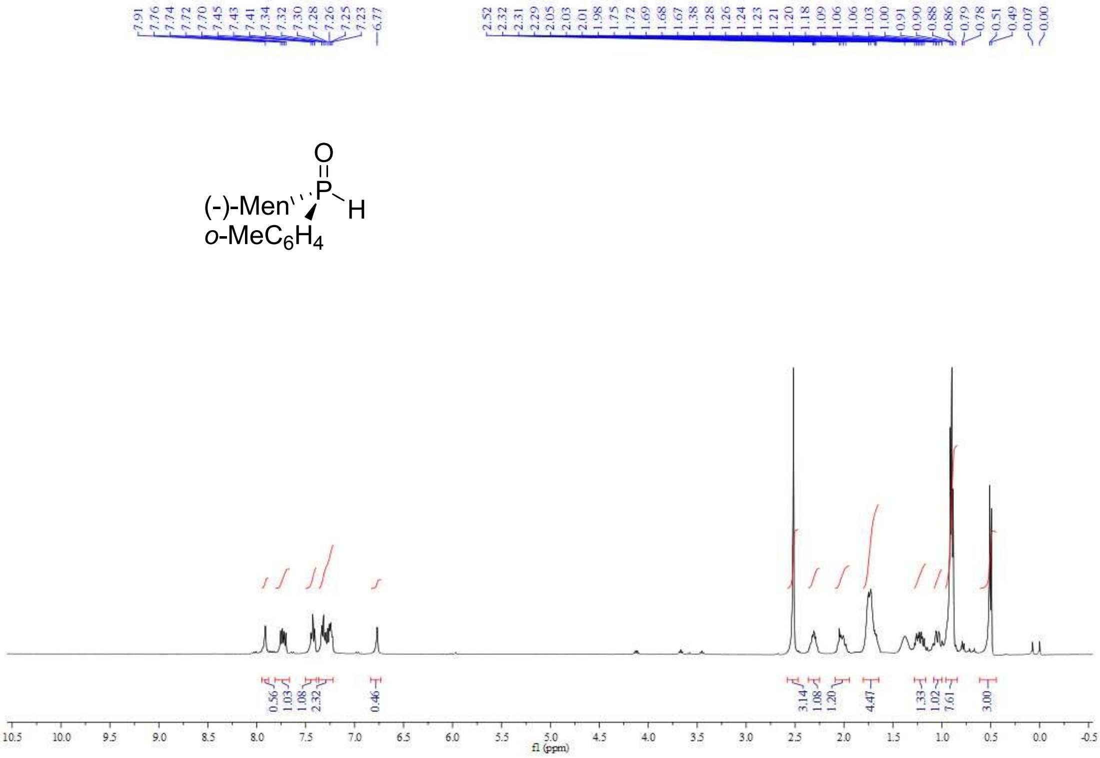
R_P-(-)-Menthyl *p*-tolylphosphine oxide (5b)

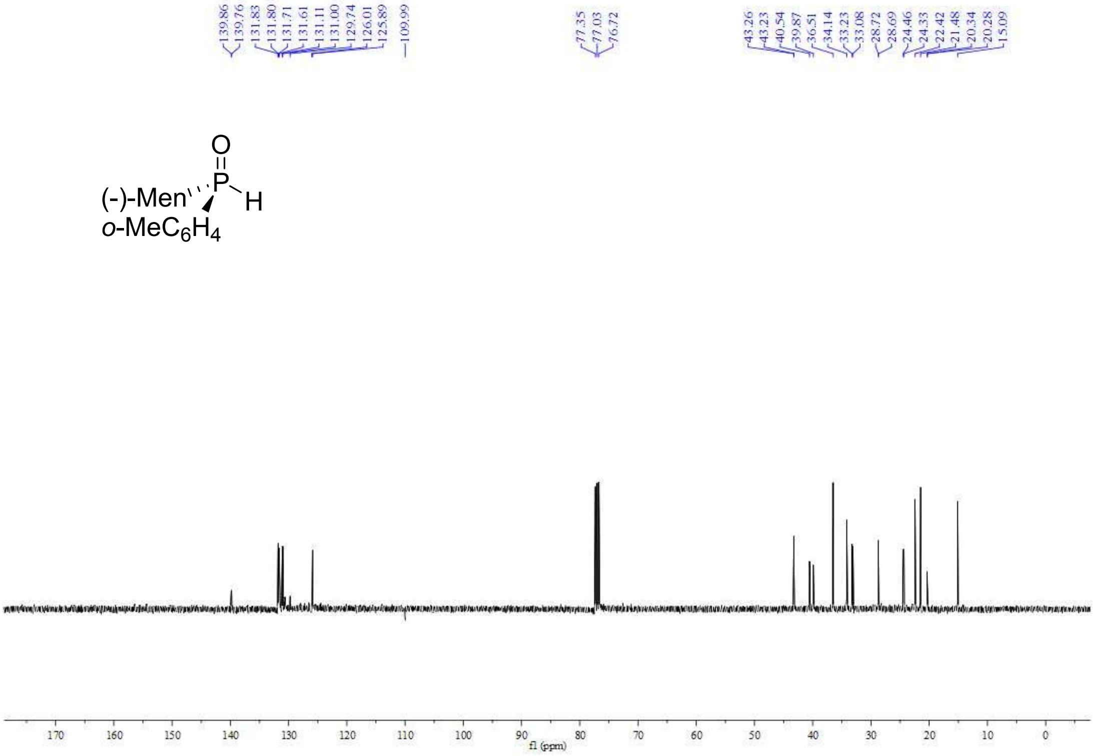




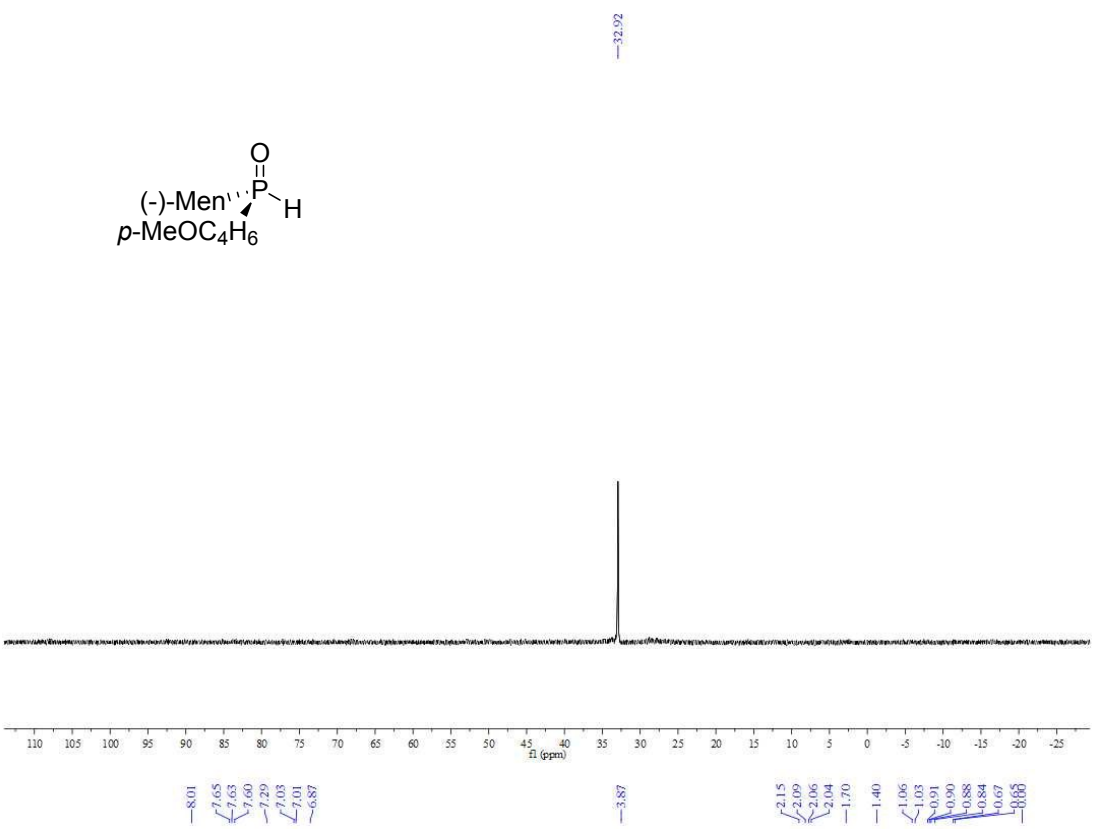
R_P-(-)-Menthyl *o*-tolylphosphine oxide (5c)

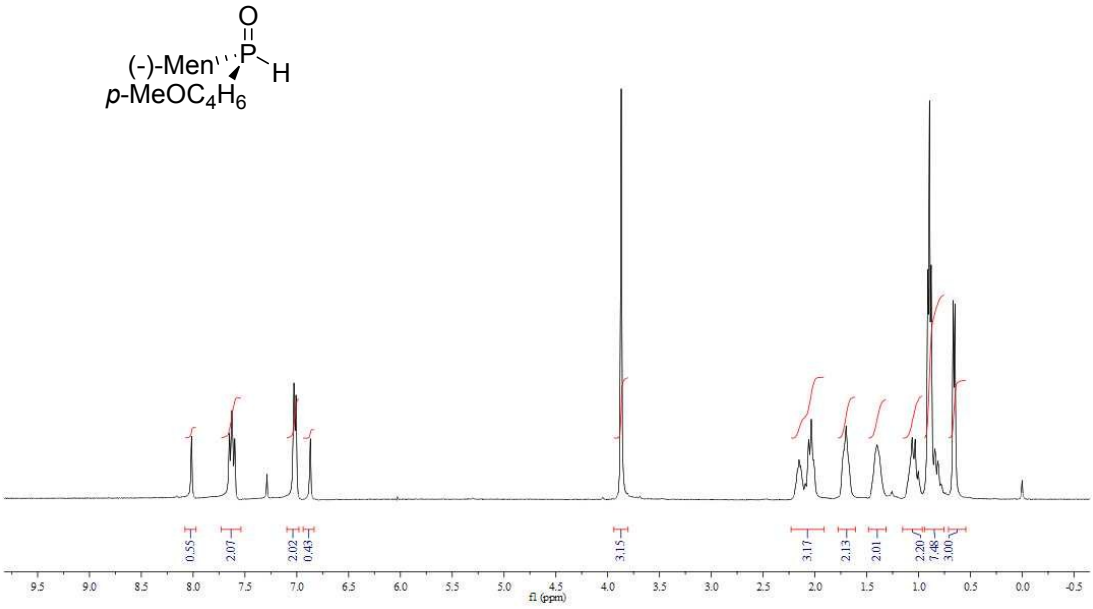


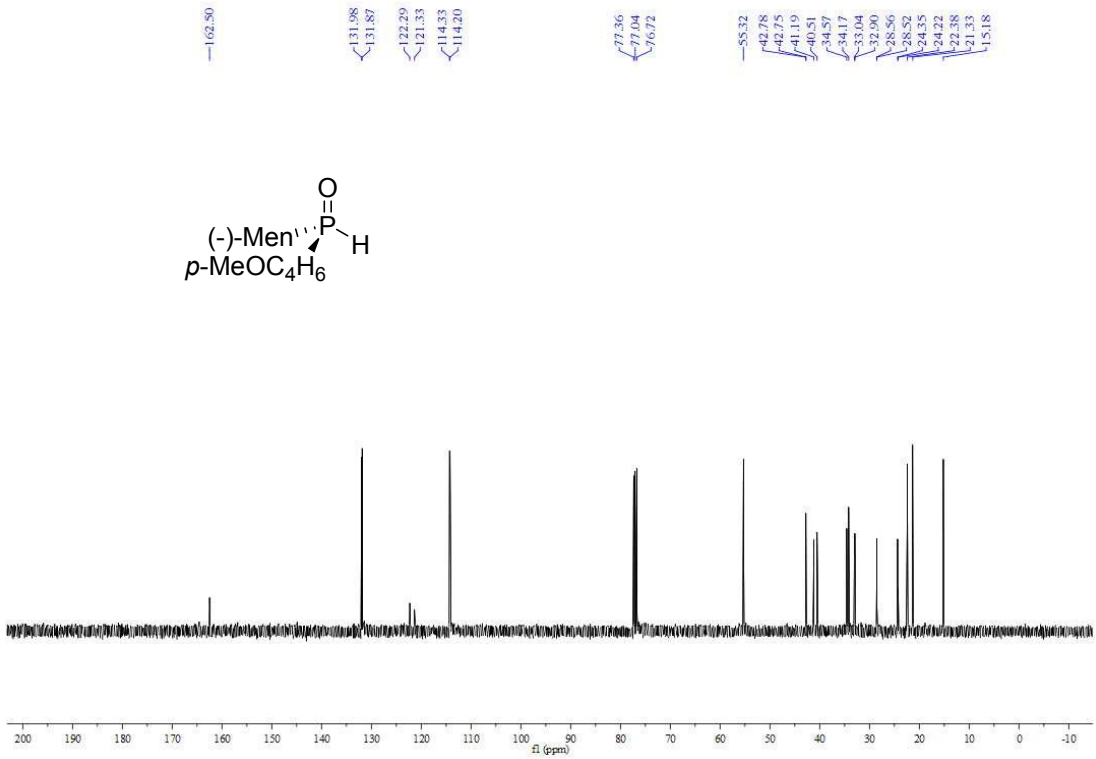

7.91 7.76 7.74 7.72 7.70 7.45 7.43 7.41 7.34 7.32 7.30 7.28 7.26 7.25 7.23 6.77
2.52 2.32 2.31 2.29 2.05 2.03 2.01 1.98 1.75 1.72 1.69 1.68 1.67 1.38 1.28 1.26 1.24 1.23 1.21 1.20 1.18 1.09 1.06 1.06 1.03 1.00 0.91 0.90 0.88 0.86 0.79 0.78 0.51 0.49 0.07 0.00
O
P
H
(-)-Men
o-MeC6H4
0.56 1.03 1.08 2.32 0.46
3.14 1.08 1.20 4.47 1.33 1.02 7.61 3.00
f1 (ppm)


139.86 139.76 131.83 131.80 131.71 131.61 131.11 131.00 129.74 126.01 125.89 109.99
77.35 77.03 76.72
43.26 43.23 40.54 39.87 36.51 34.14 33.23 33.08 28.72 28.69 24.46 24.33 22.42 21.48 20.34 20.28 15.09
O
P
H
(-)-Men
o-MeC6H4
f1 (ppm)

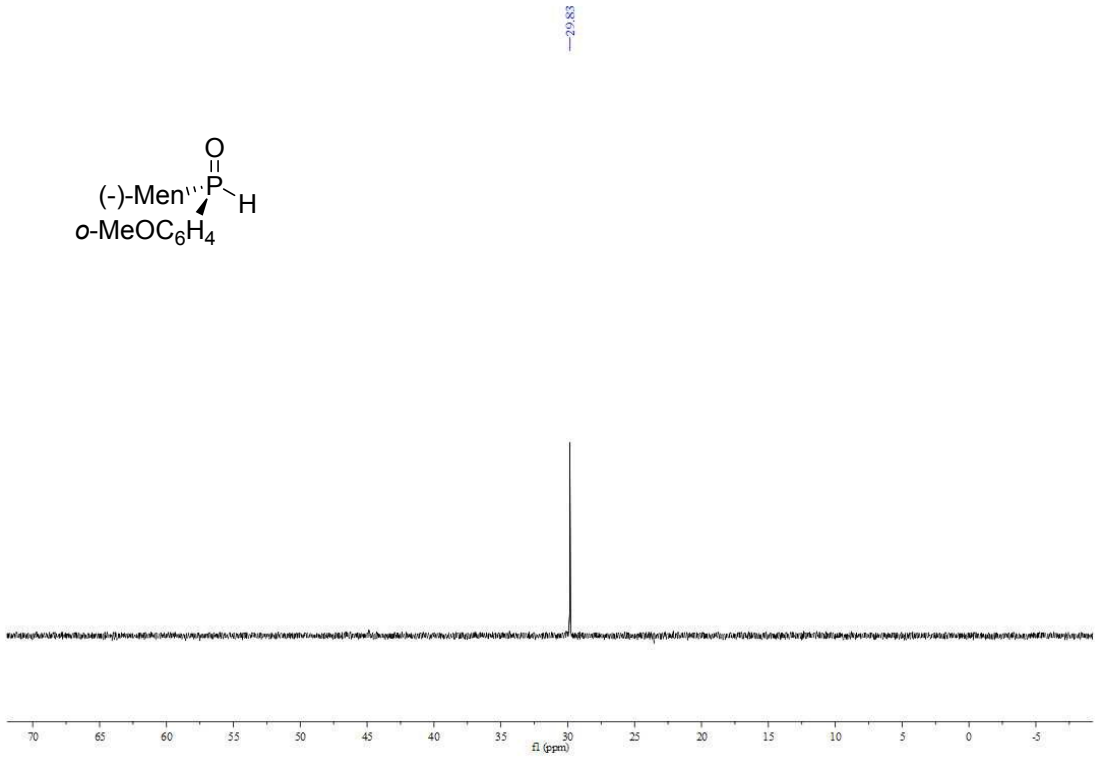
R_P-(-)-Menthyl *p*-methoxyphenylphosphine oxide (5d)

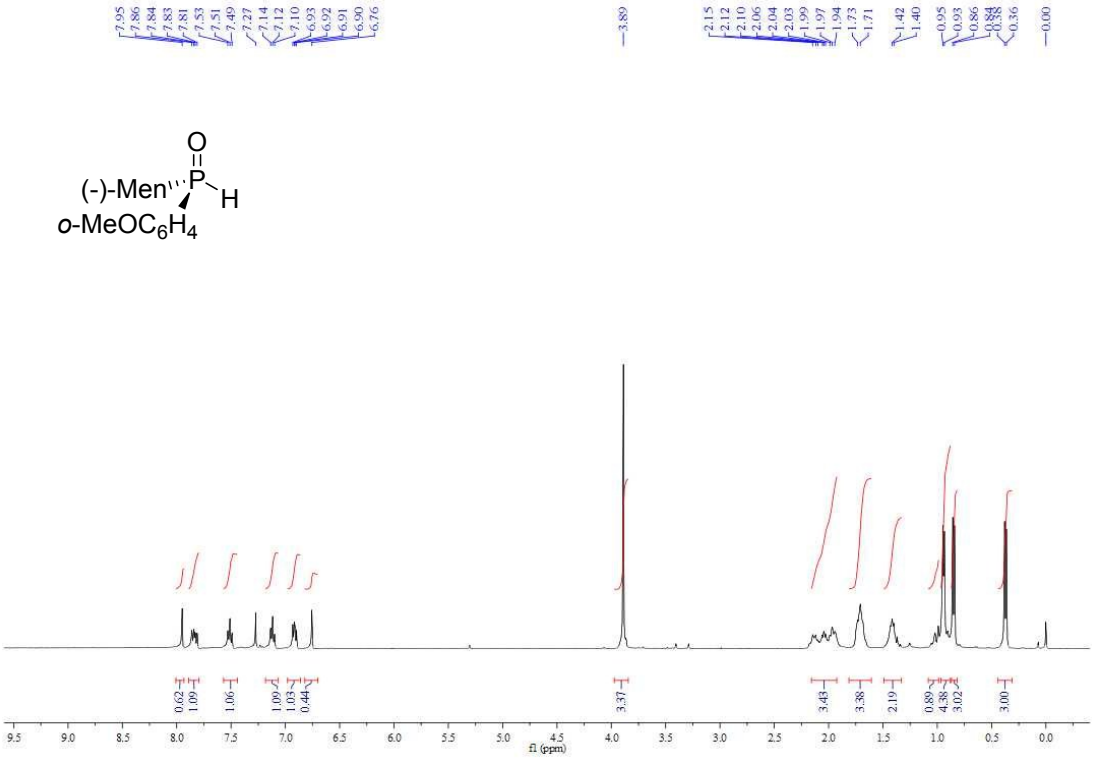


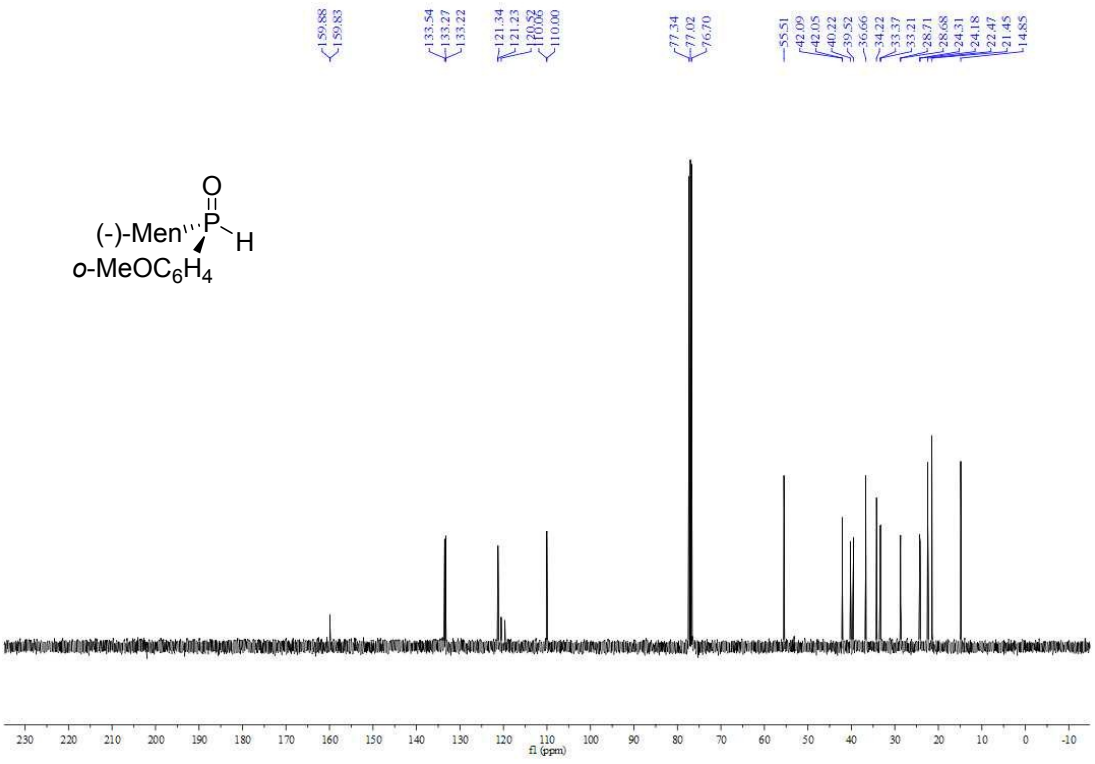




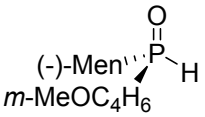
R_P-(-)-Menthyl *o*-methoxyphenylphosphine oxide (5e)

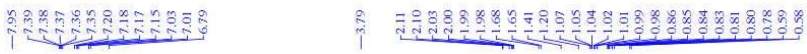


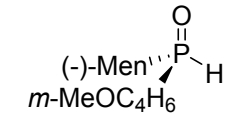

7.95
7.86
7.84
7.83
7.81
7.53
7.51
7.49
7.27
7.14
7.12
7.10
6.93
6.92
6.91
6.90
6.76
3.89
2.15
2.12
2.10
2.06
2.04
2.03
1.99
1.97
1.94
1.73
1.71
1.42
1.40
0.95
0.93
0.86
0.84
0.36
0.00
O
(-)-Men
P
H
o-MeOC6H4
0.62
1.09
1.06
1.09
1.03
0.44
3.37
3.48
3.38
2.19
0.89
4.38
3.02
3.00
f1 (ppm)

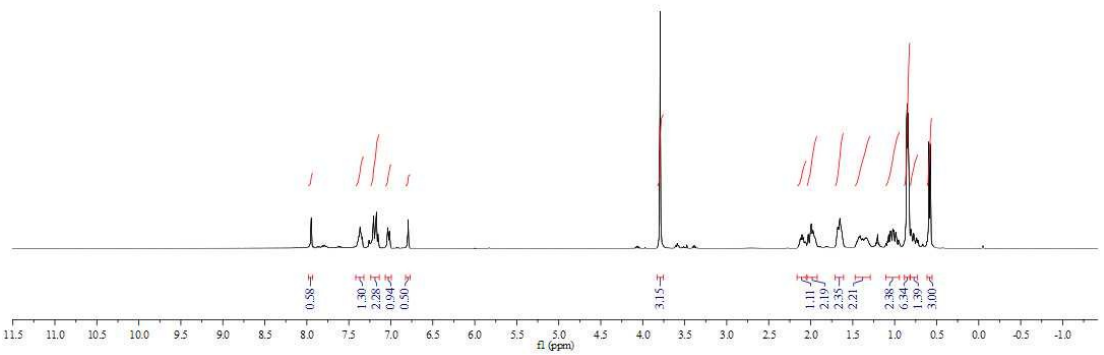

159.88
159.83
133.54
133.27
133.22
121.34
121.23
120.52
110.06
110.00
77.34
77.02
76.70
55.51
42.09
42.05
40.22
39.52
36.66
34.22
33.37
33.21
28.71
28.68
24.31
24.18
22.47
21.45
14.85
O
(-)-Men
P
H
o-MeOC6H4
f1 (ppm)

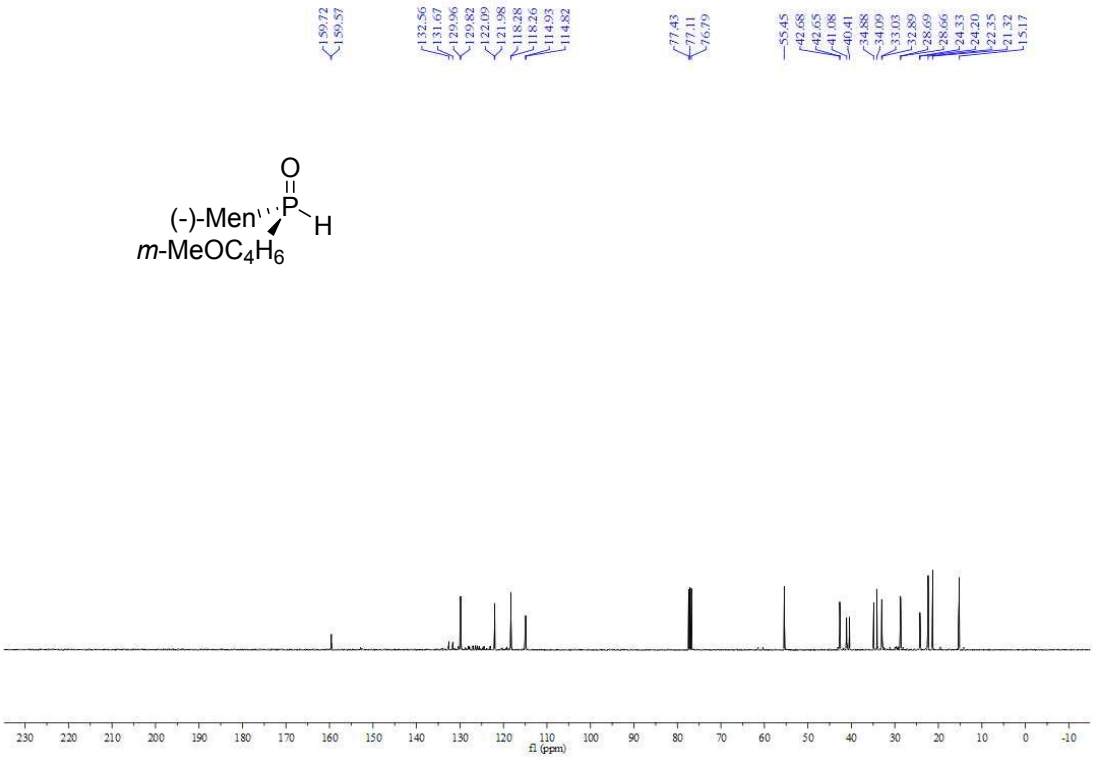
R_P-(-)-Menthyl *m*-methoxyphenylphosphine oxide (5f)



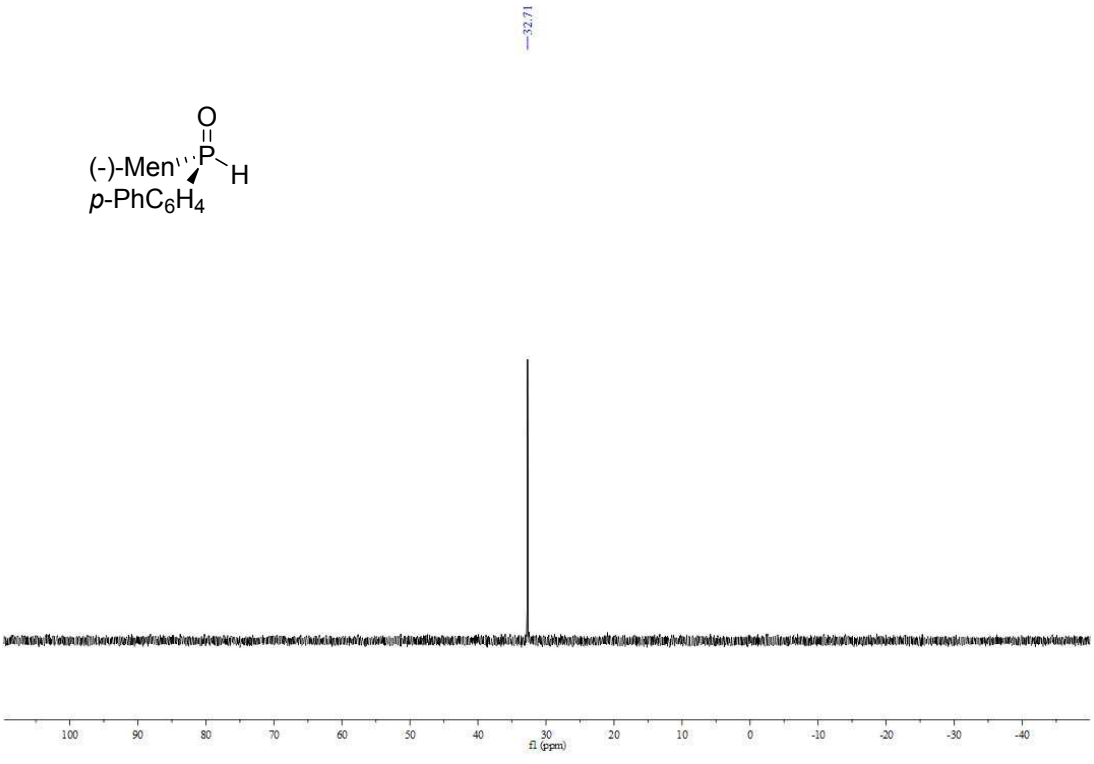


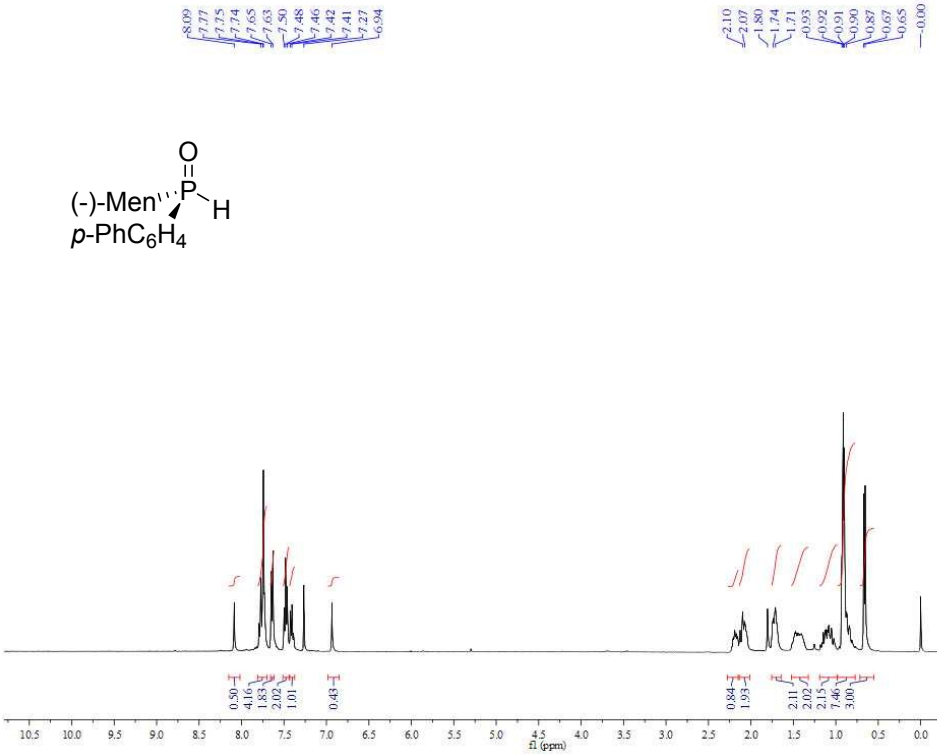


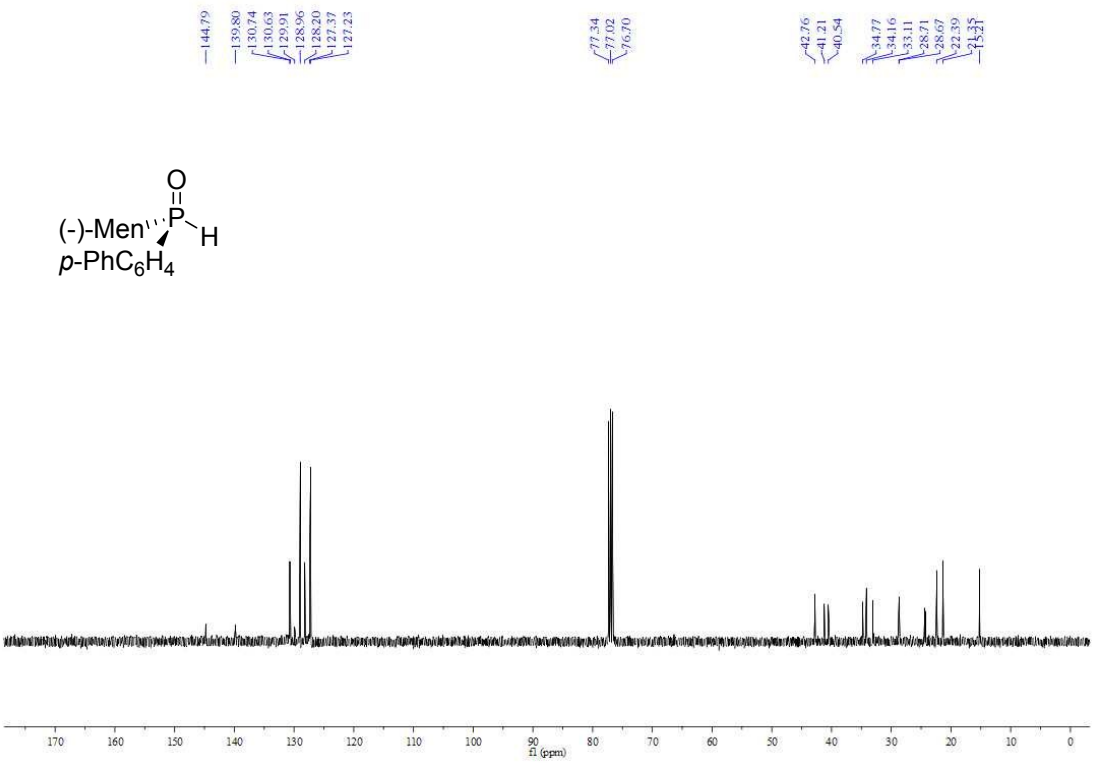




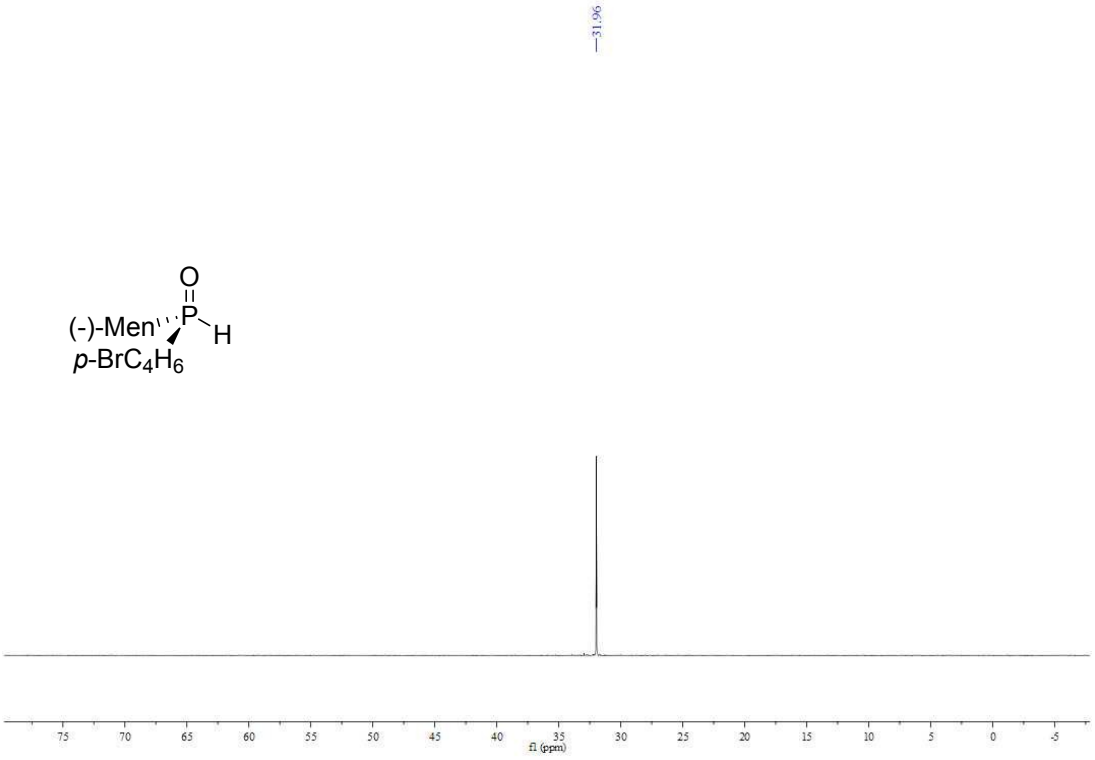
R_P-(-)-Menthyl [1,1'-biphenyl]-4-ylphosphine oxide (5g)

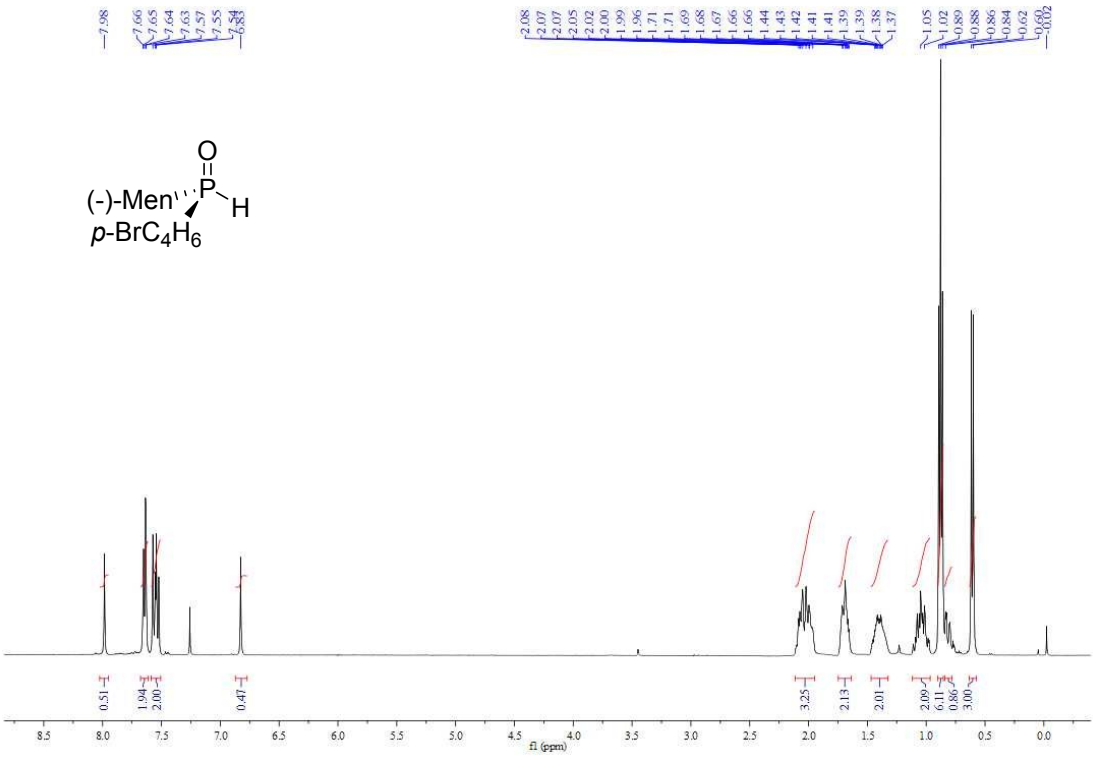


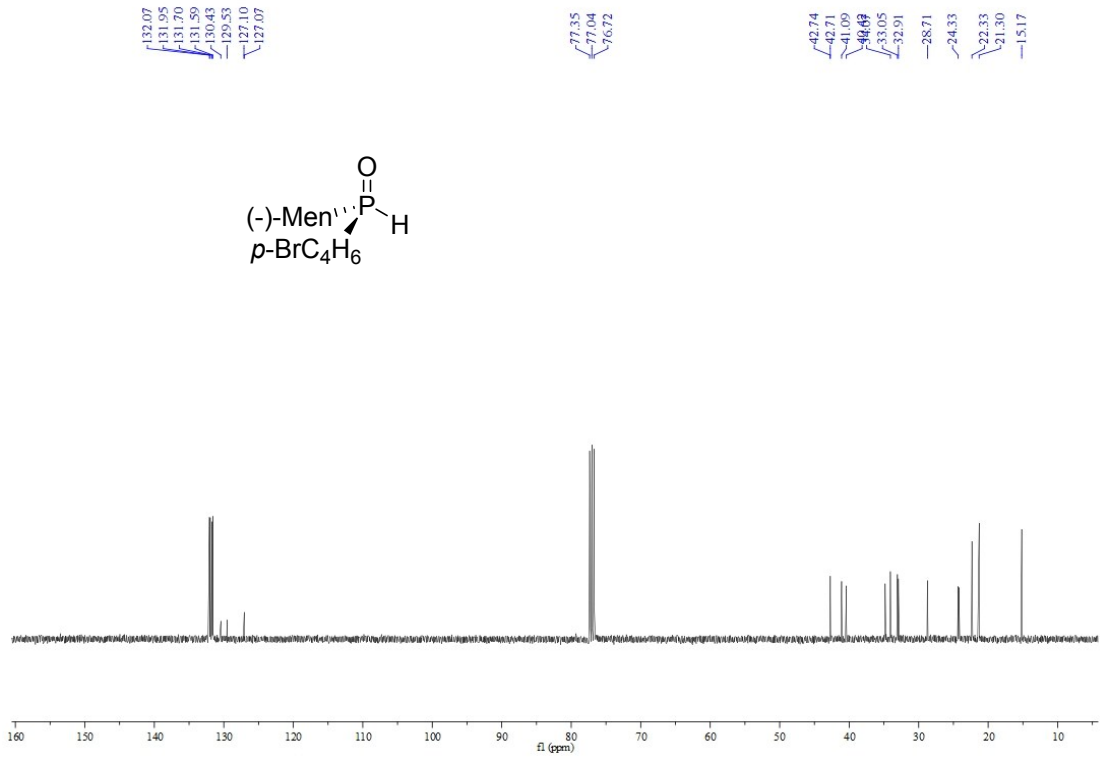

8.09
7.77
7.75
7.74
7.65
7.63
7.50
7.48
7.46
7.42
7.41
7.27
6.94
2.10
2.07
1.80
1.74
1.71
0.93
0.92
0.91
0.90
0.87
0.67
0.65
-0.00
O
P
H
(-)-Men
p-PhC6H4
0.50
4.16
1.83
2.02
1.01
0.43
0.84
1.93
2.11
2.02
2.15
7.46
3.00
f1 (ppm)


144.79
139.80
130.74
130.63
129.91
128.96
128.20
127.37
127.23
77.34
77.02
76.70
42.76
41.21
40.54
34.77
34.16
33.11
28.71
28.67
22.39
21.35
15.21
O
P
H
(-)-Men
p-PhC6H4
f1 (ppm)

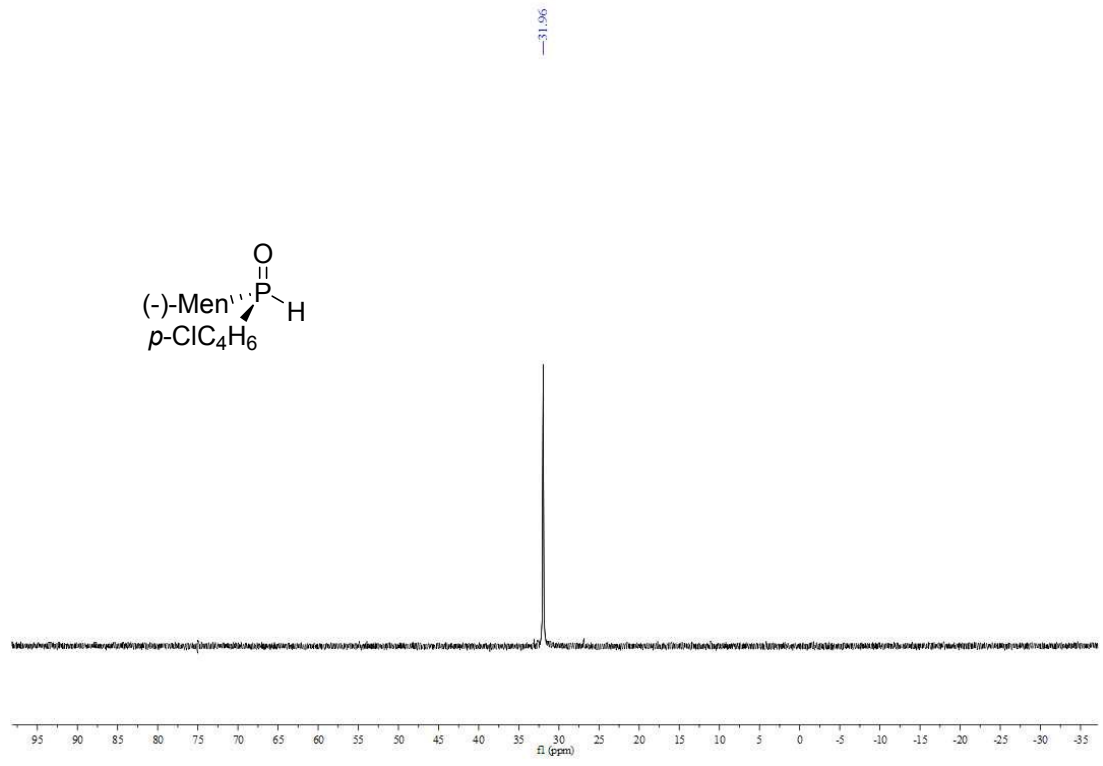
R_P-(-)-Menthyl *p*-bromophenylphosphine oxide (5h)

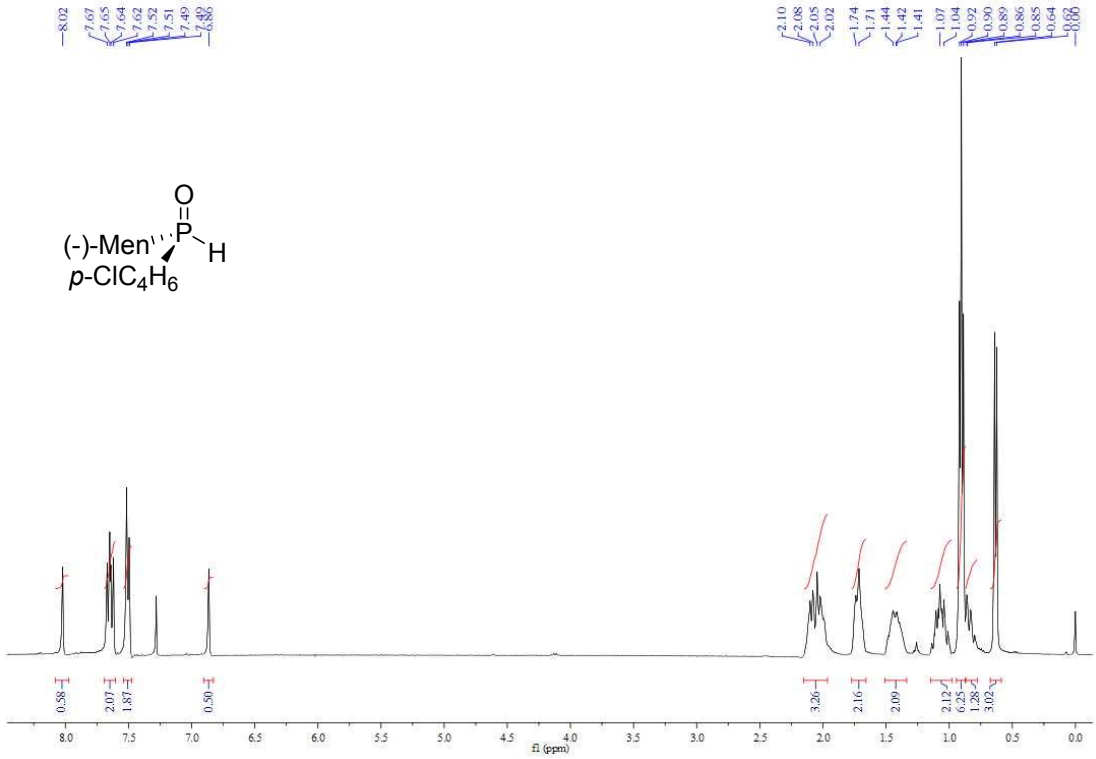


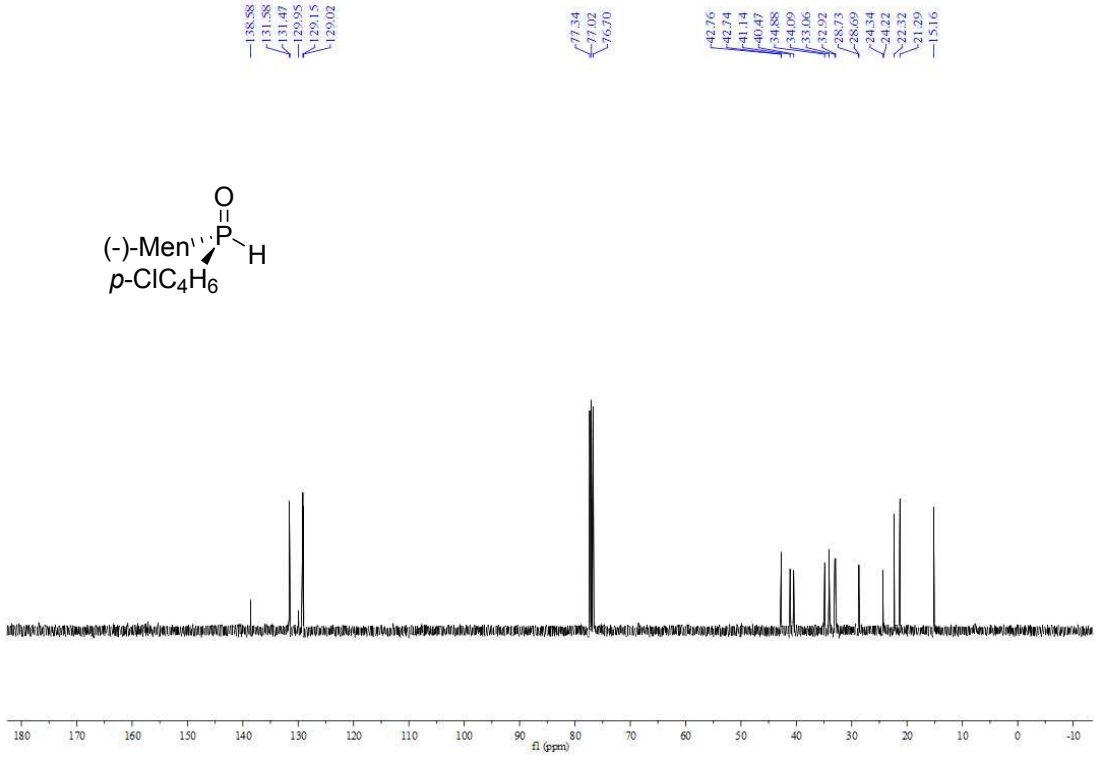




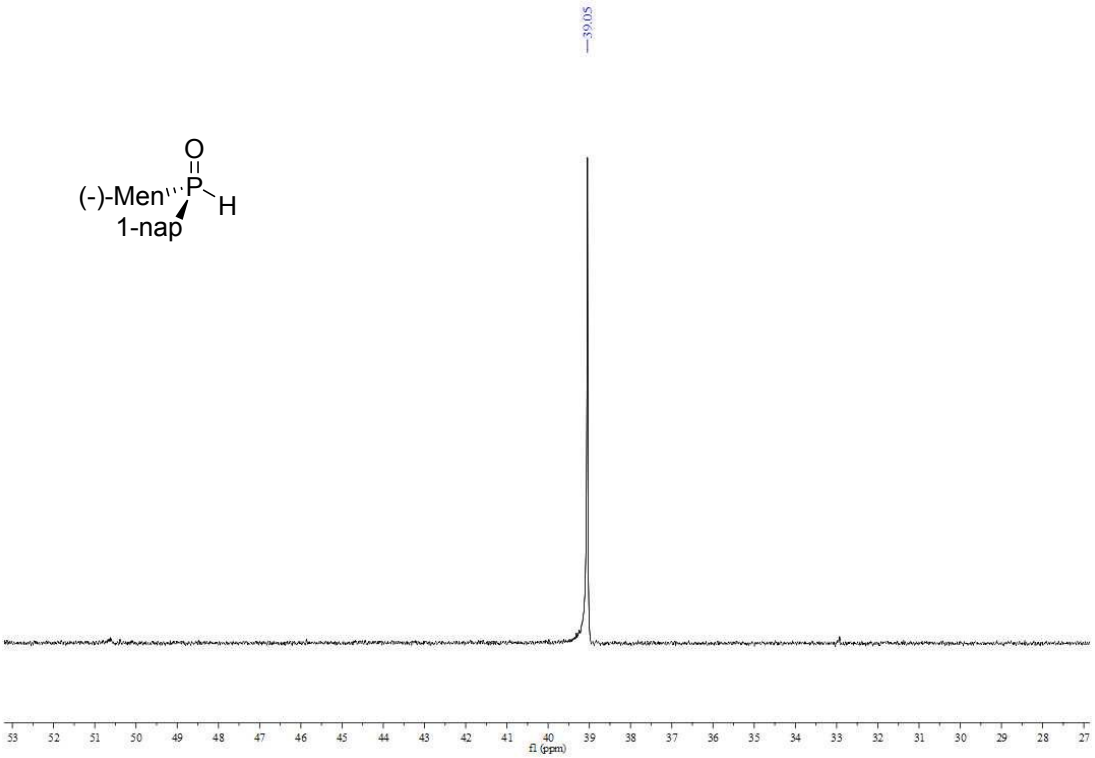
R_P-(-)-Menthyl *p*-chlorophenylphosphine oxide (5i)

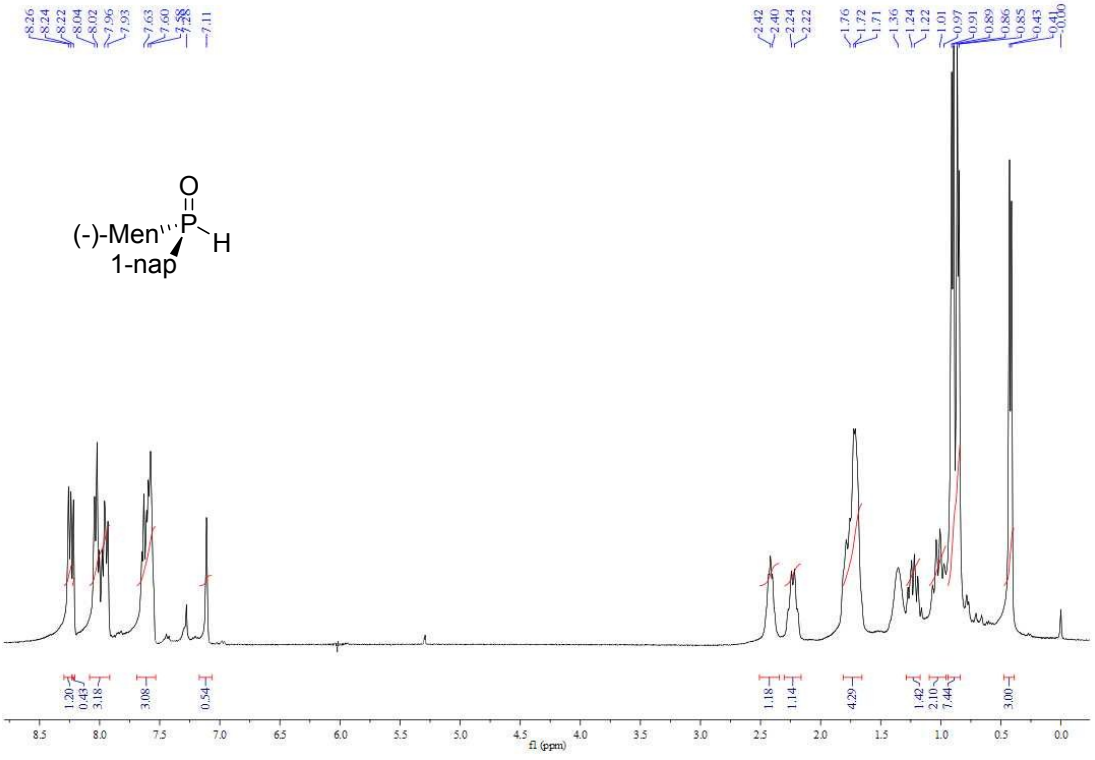


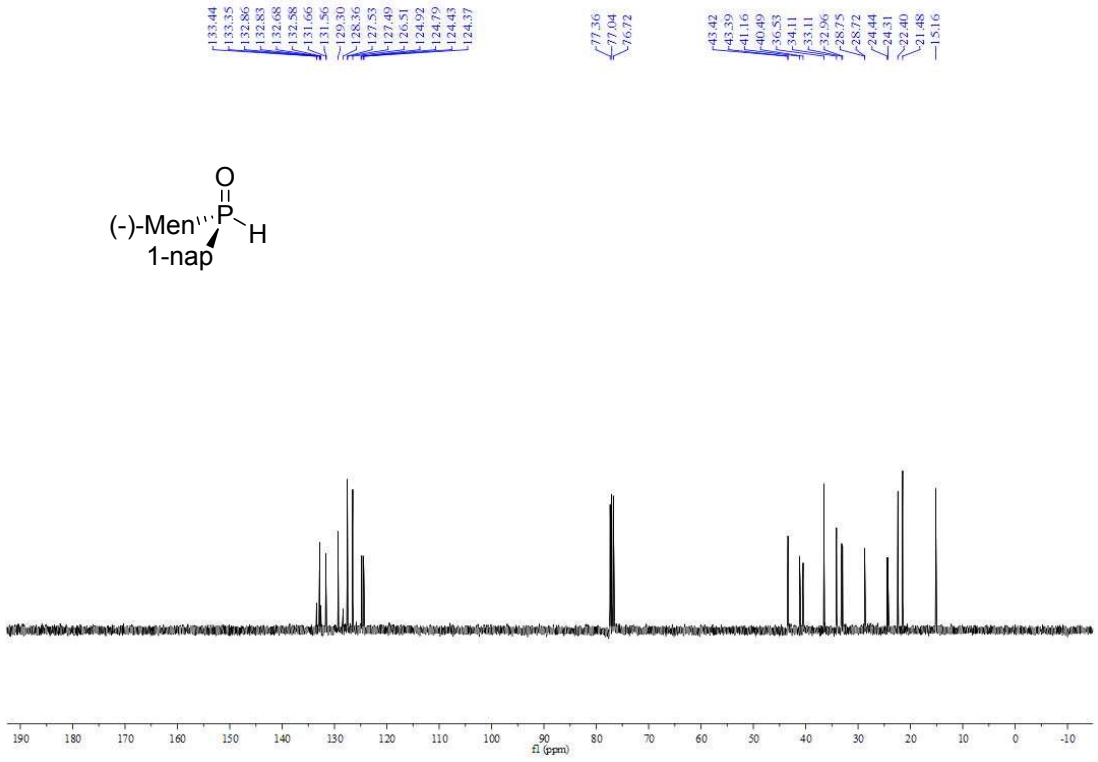

8.02
7.67
7.65
7.64
7.62
7.52
7.51
7.49
7.48
6.86
2.10
2.08
2.05
2.02
1.74
1.71
1.44
1.42
1.41
1.07
1.04
0.92
0.90
0.89
0.86
0.85
0.64
0.62
0.00
O
P
H
(-)-Men
p-ClC4H6
0.58
2.07
1.87
0.50
3.26
2.16
2.09
2.12
6.25
1.28
3.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


138.58
131.58
131.47
129.95
129.15
129.02
77.34
77.02
76.70
42.76
42.74
41.14
40.47
34.88
34.09
33.06
32.92
28.73
28.69
24.34
24.22
22.32
21.29
15.16
O
P
H
(-)-Men
p-ClC4H6
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

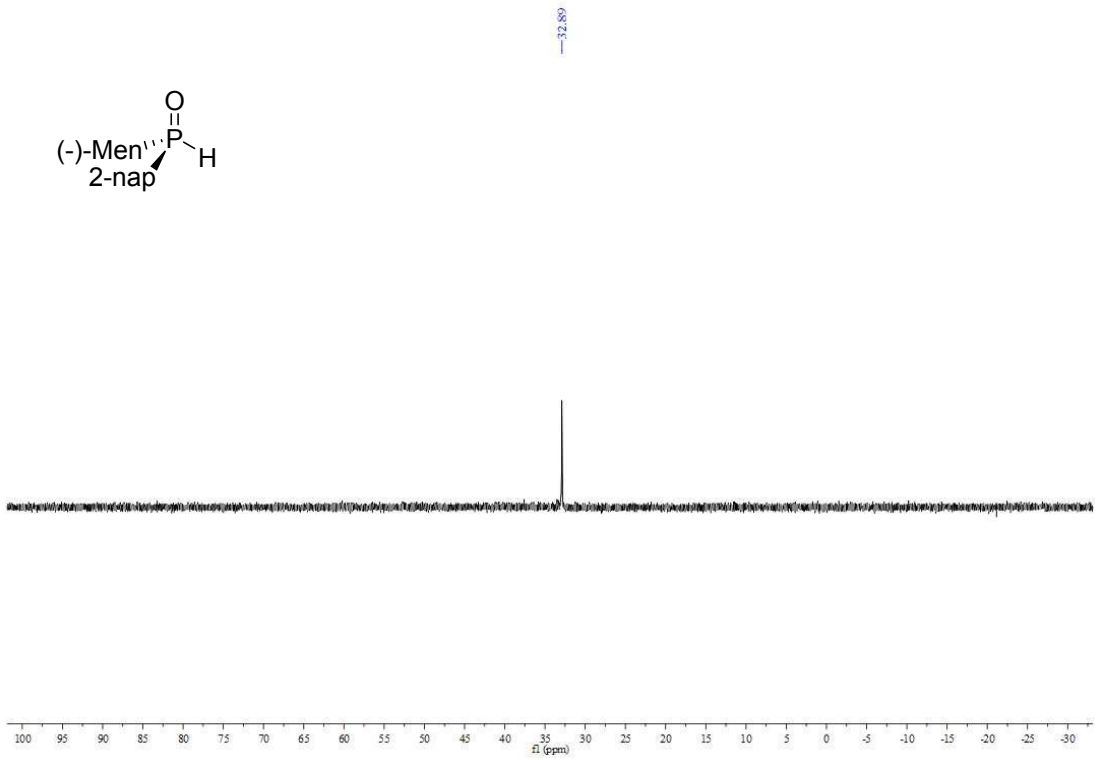
R_P-(-)-Menthyl 1-naphthalenylphosphine oxide (5j)

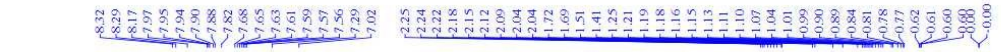


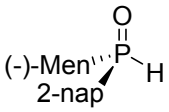


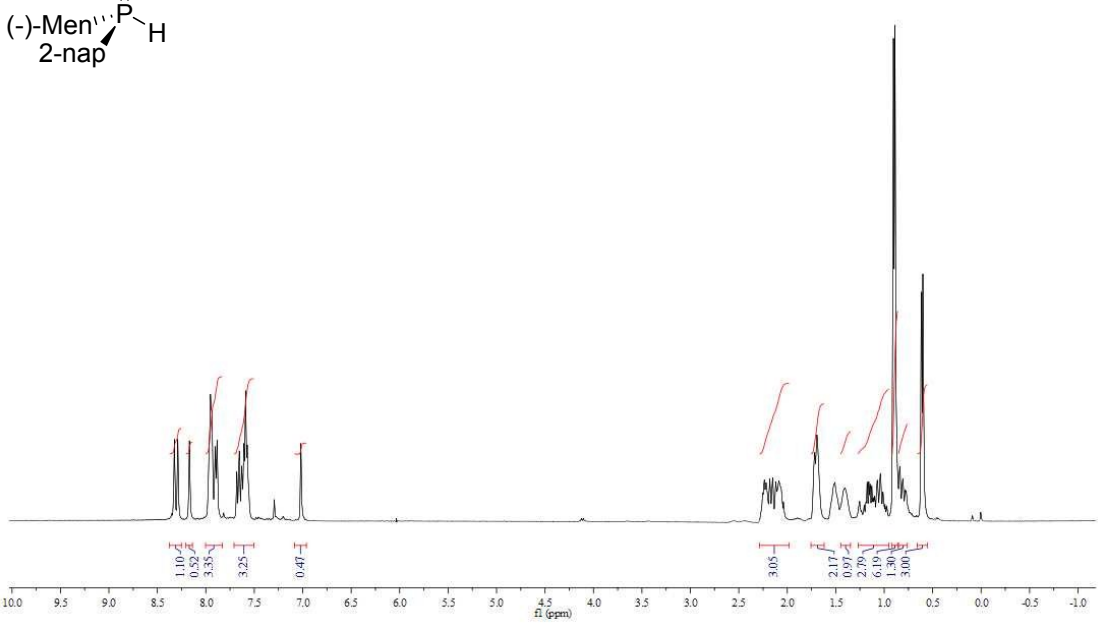


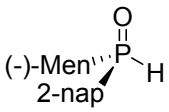
R_P-(-)-Menthyl 2-naphthalenylphosphine oxide (5k)

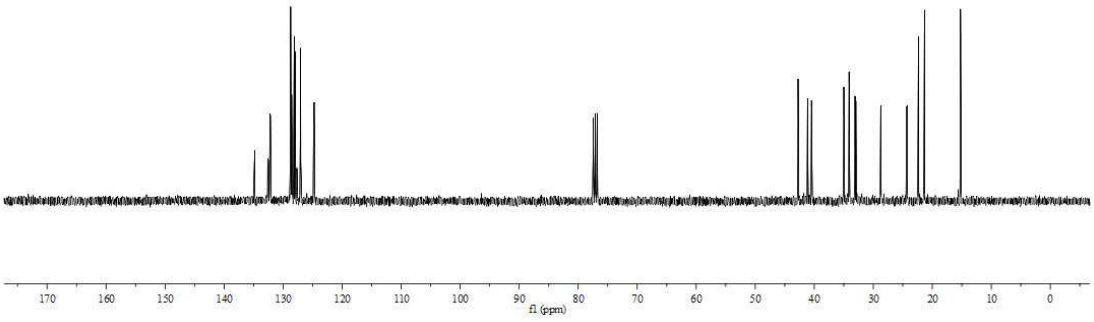




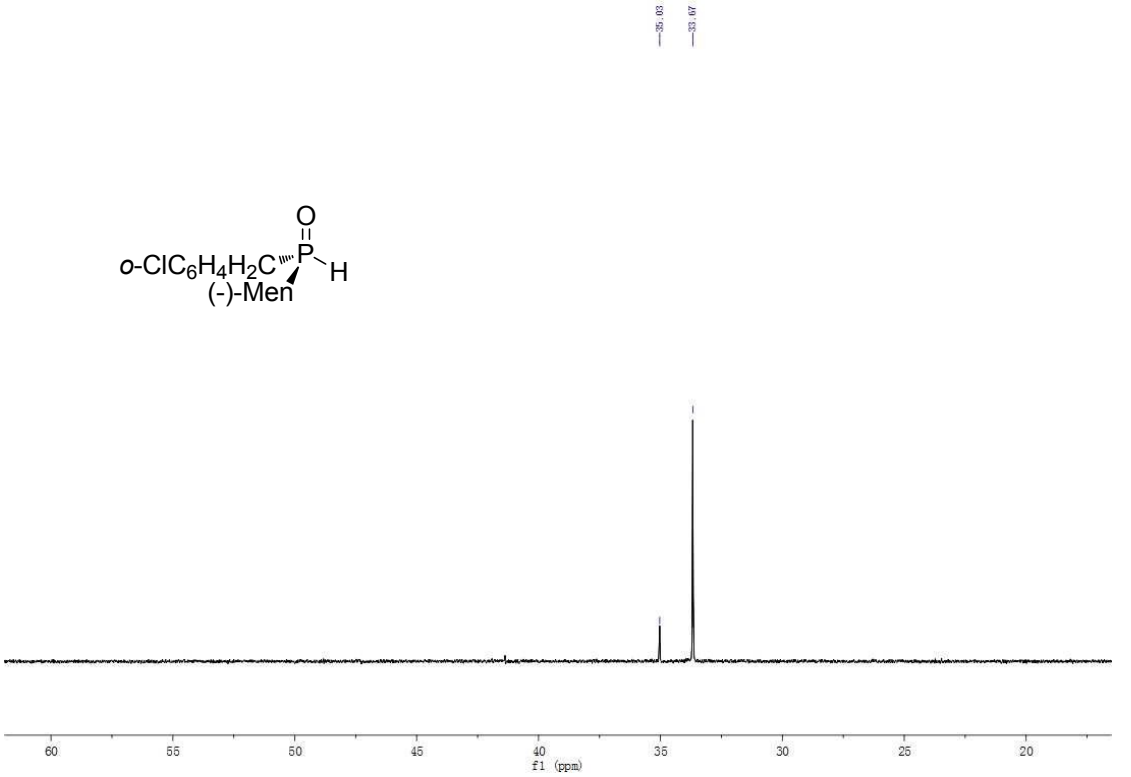

O
P
H
(-)-Men
2-nap

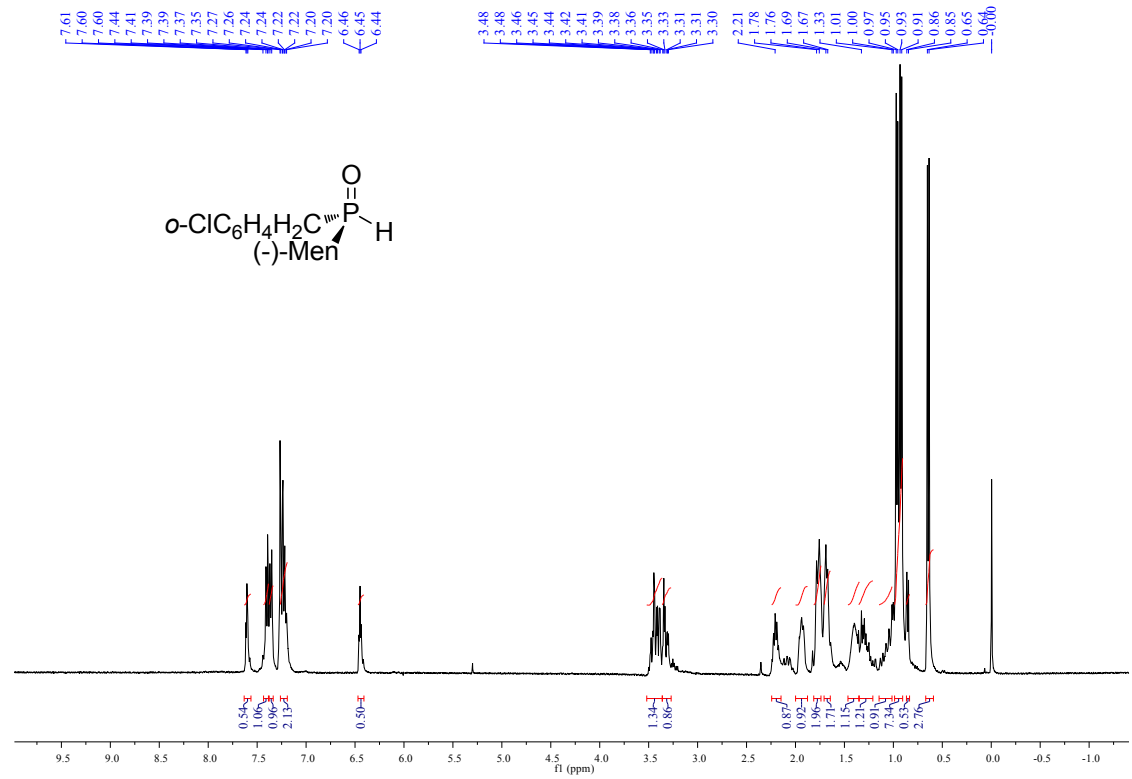

1.10
0.52
3.35
3.25
0.47
3.05
2.17
0.97
2.79
6.19
1.30
3.00
f1 (ppm)

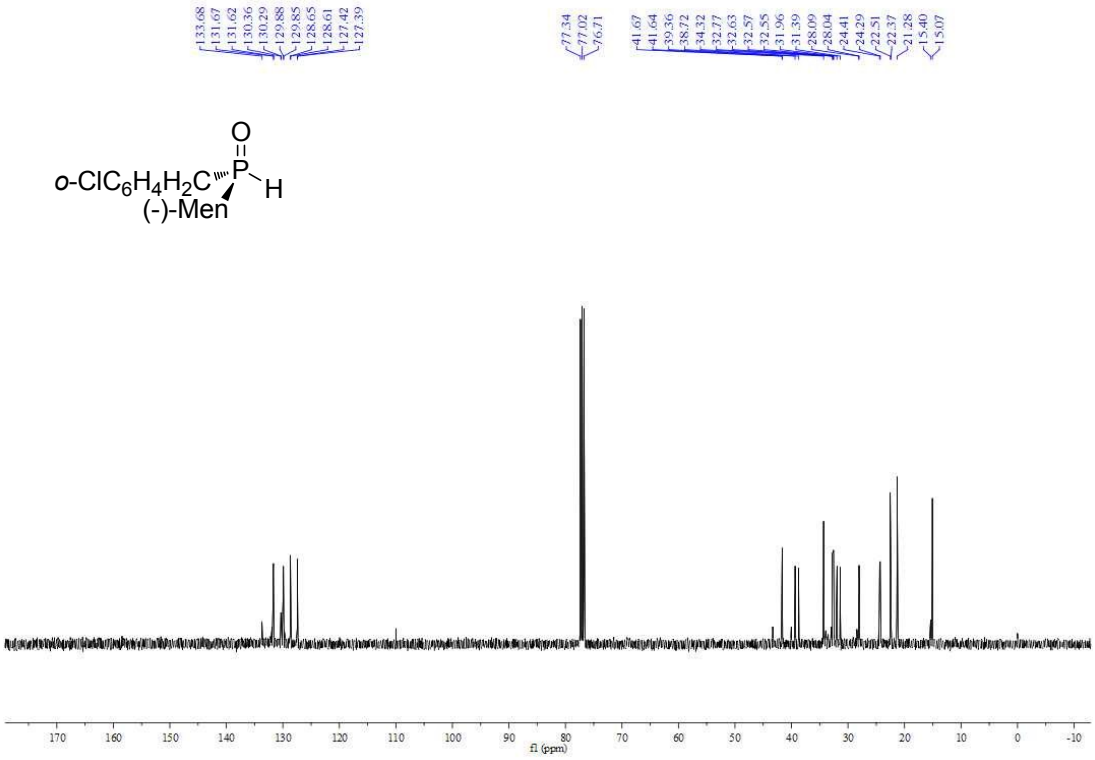

O
P
H
(-)-Men
2-nap


f1 (ppm)

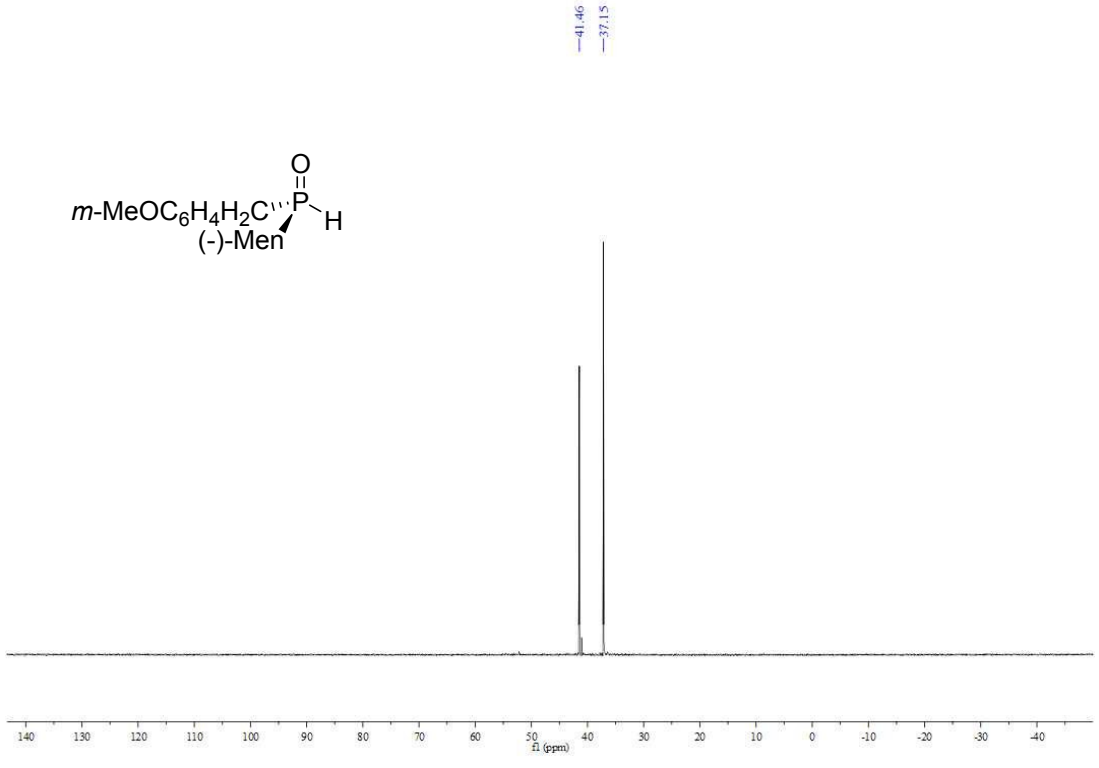
(R_P/S_P)-(-)-Menthyl 2- chlorobenzylphosphine oxide (5l/5l')

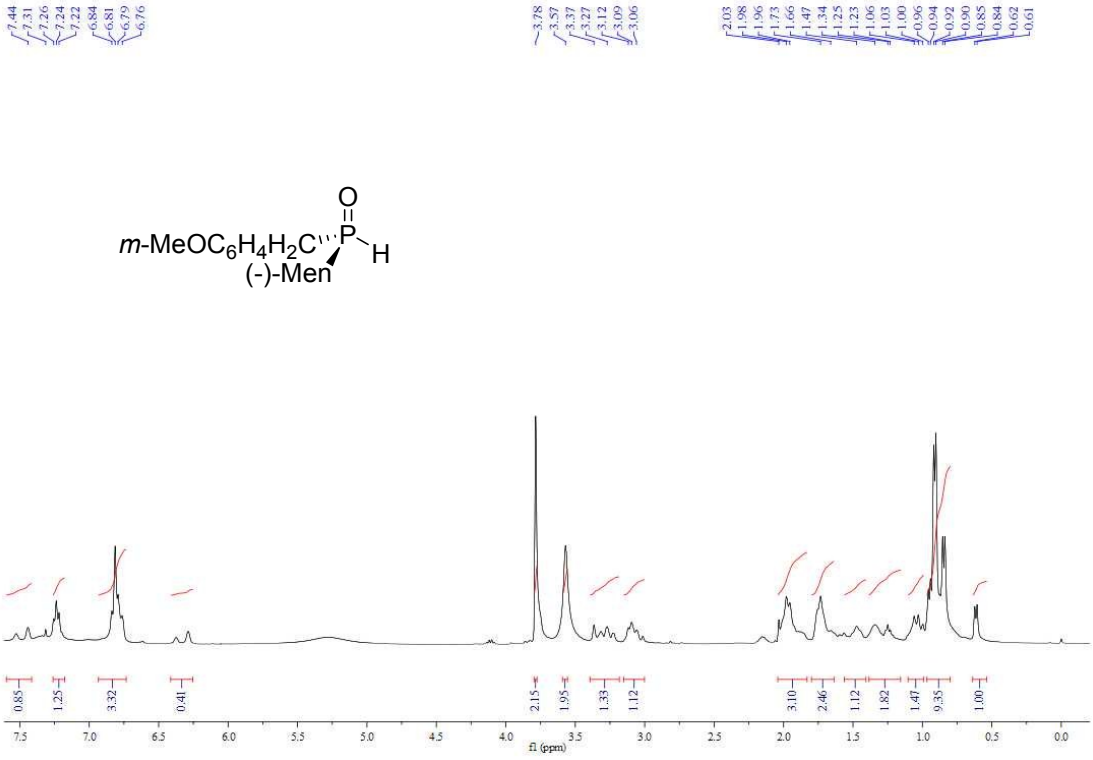


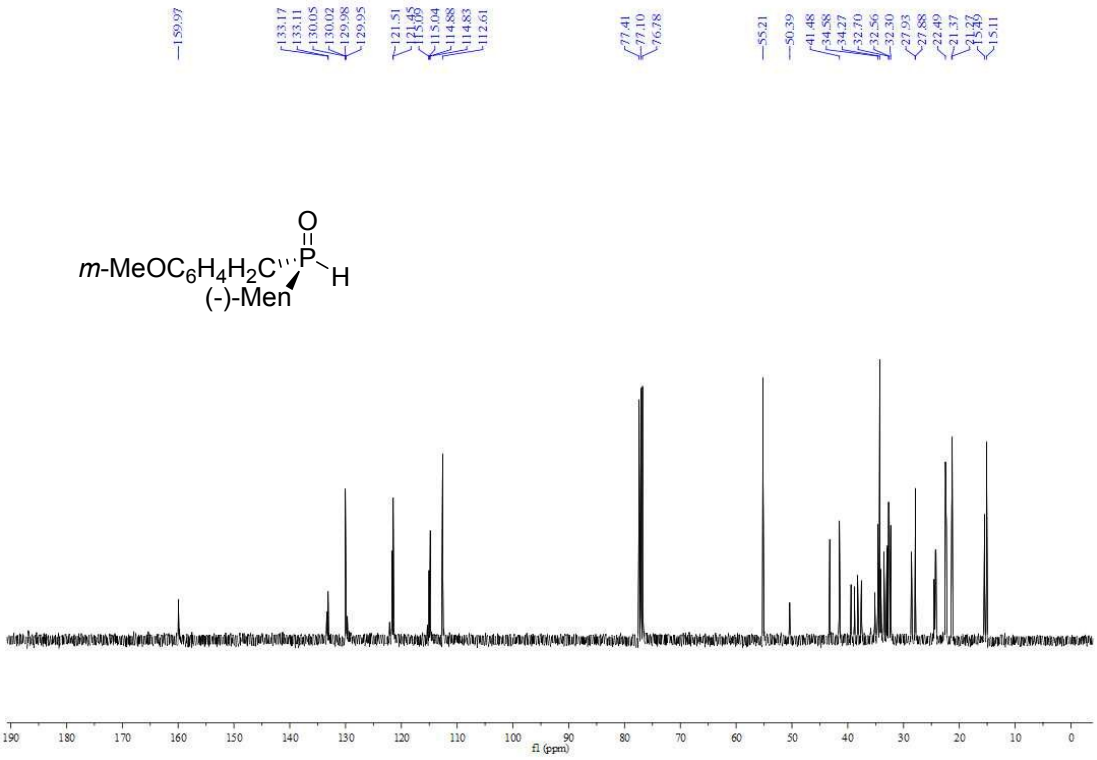




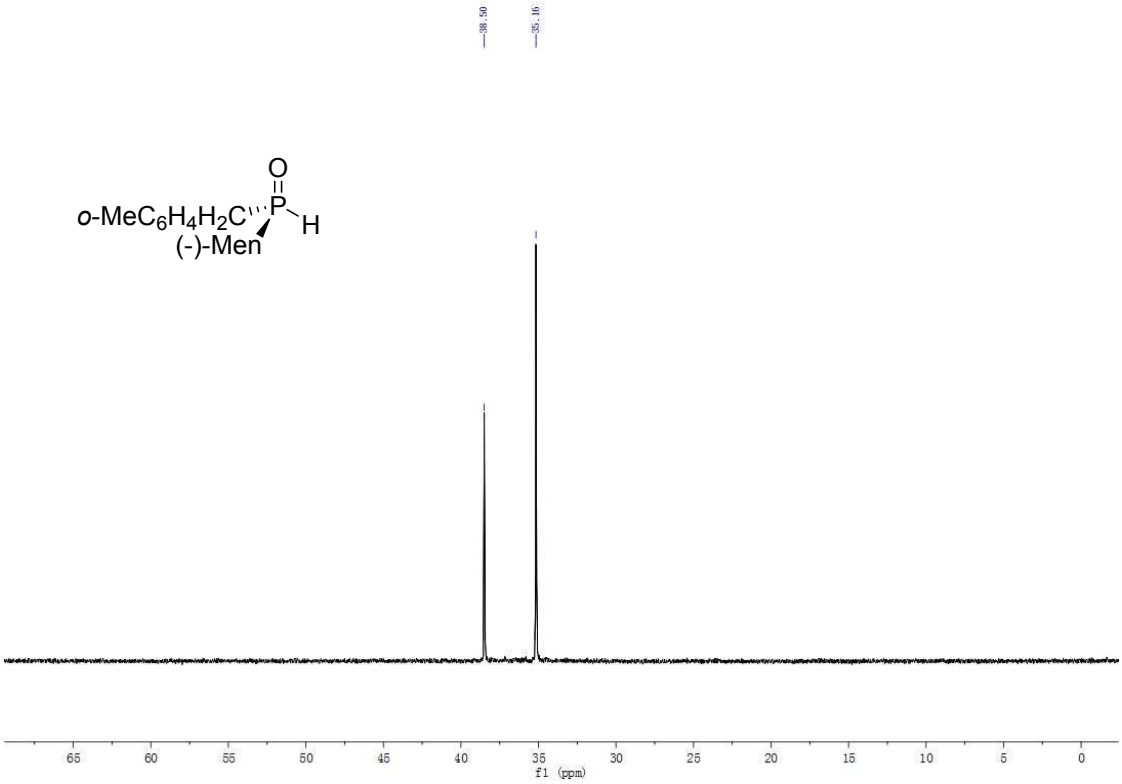
(R_P/S_P)-(-)-Menthyl 3-methoxybenzylphosphine oxide (5m/5m')

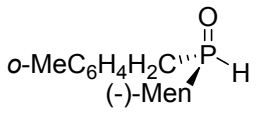


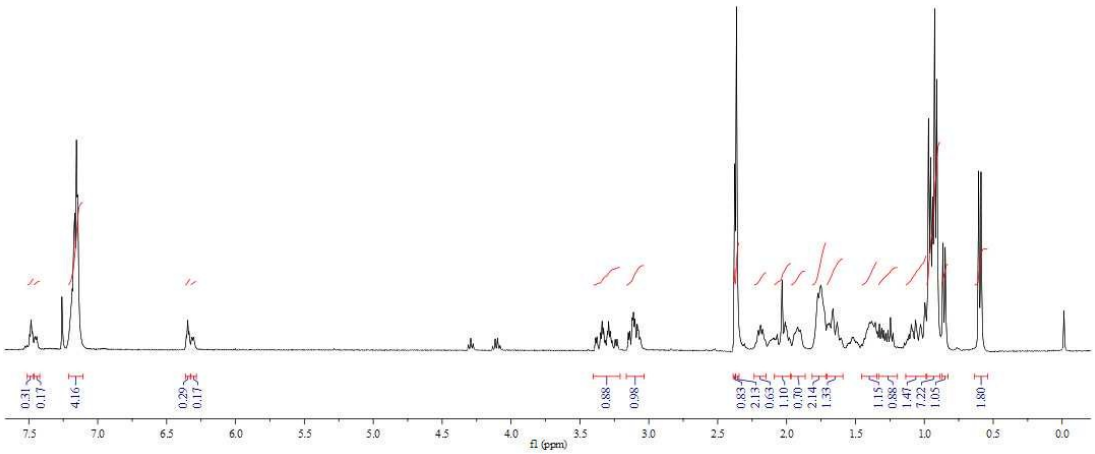

7.44
7.31
7.26
7.24
7.22
6.84
6.81
6.79
6.76
3.78
3.57
3.37
3.27
3.12
3.09
3.06
2.03
1.98
1.96
1.73
1.66
1.47
1.34
1.25
1.23
1.06
1.03
1.00
0.96
0.94
0.92
0.90
0.85
0.84
0.62
0.61
m-MeOC6H4H2C
P
O
H
(-)-Men
0.85
1.25
3.32
0.41
2.15
1.95
1.33
1.12
3.10
2.46
1.12
1.82
1.47
9.35
1.00
f1 (ppm)

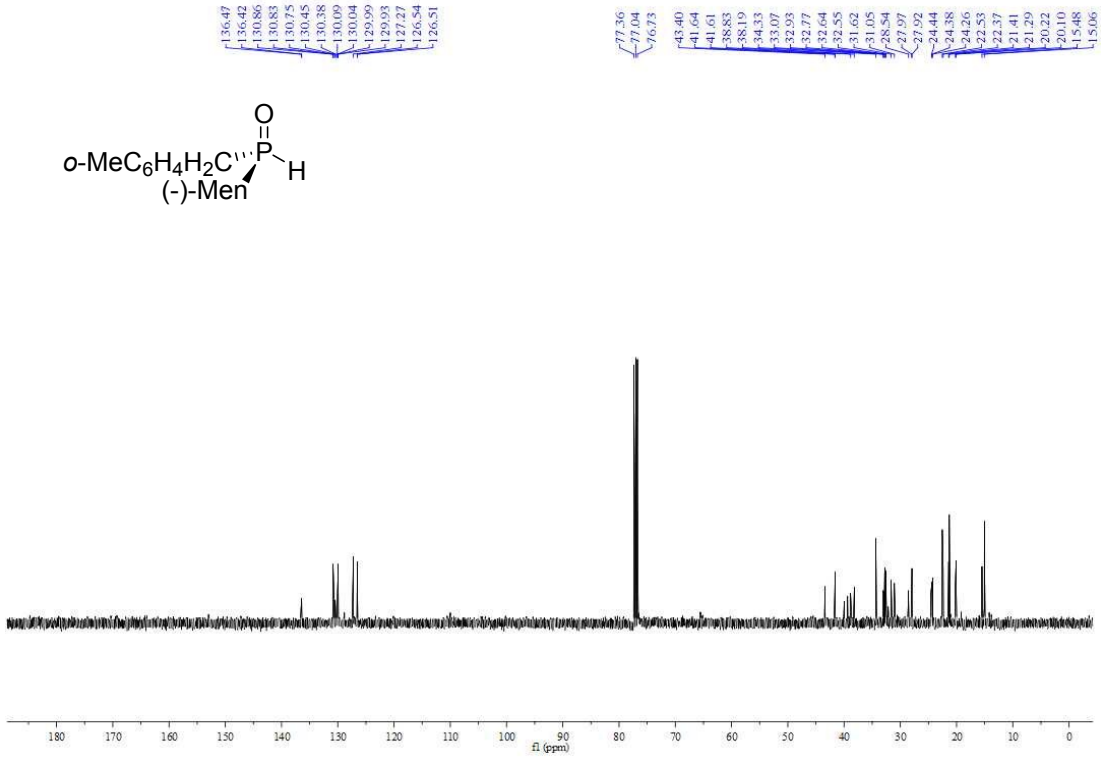

159.97
133.17
133.11
130.05
130.02
129.98
129.95
121.51
121.45
115.09
115.04
114.88
114.83
112.61
77.41
77.10
76.78
55.21
50.39
41.48
34.58
34.27
32.70
32.56
32.30
27.93
27.88
22.49
21.37
15.36
15.11
m-MeOC6H4H2C
P
O
H
(-)-Men
f1 (ppm)

(R_P/S_P)-(-)-Menthyl 2-methylbenzylphosphine oxide (5n/5n')

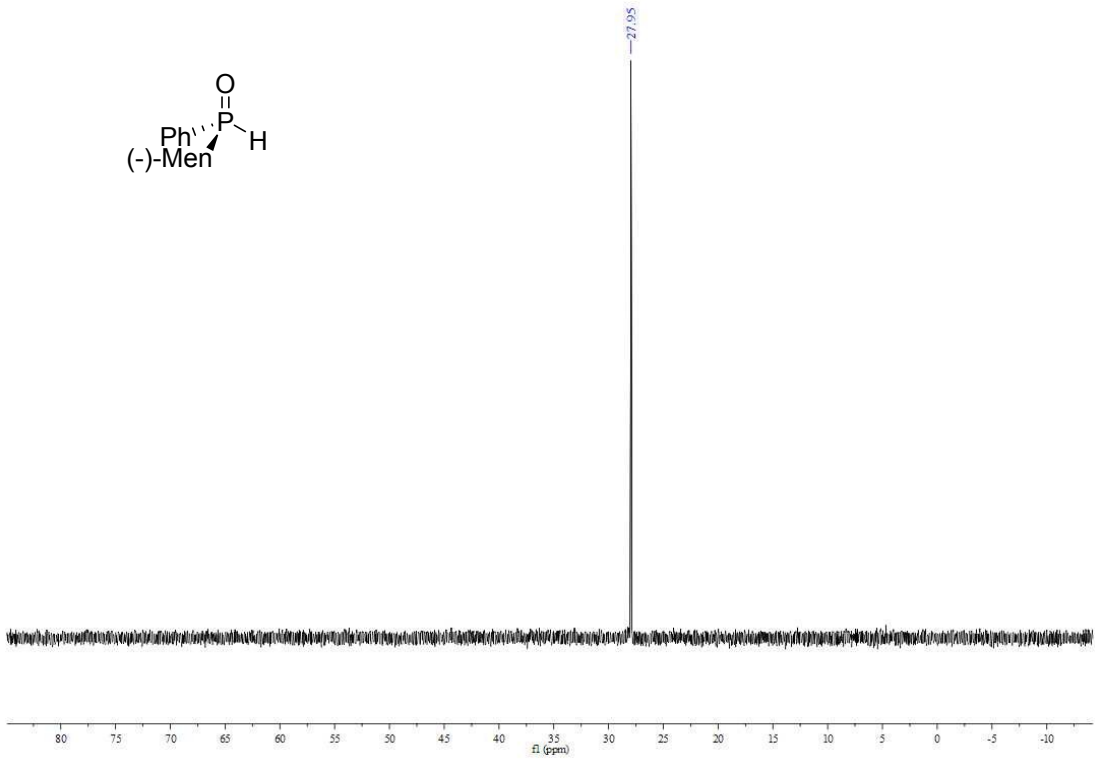


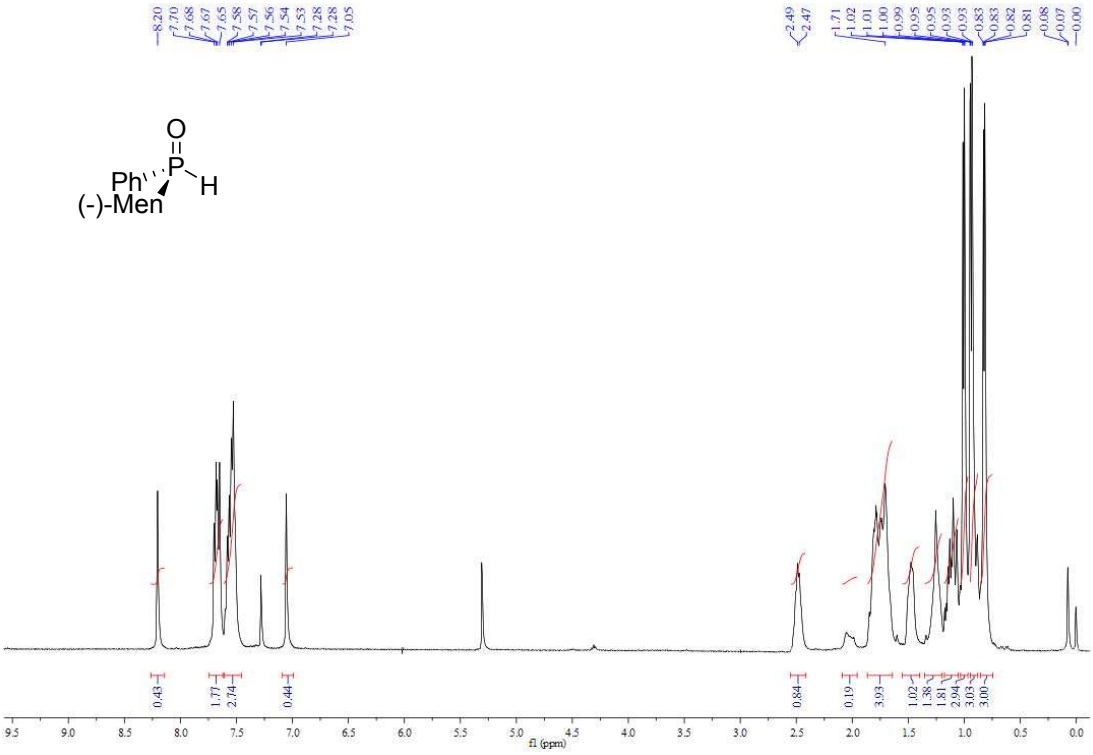


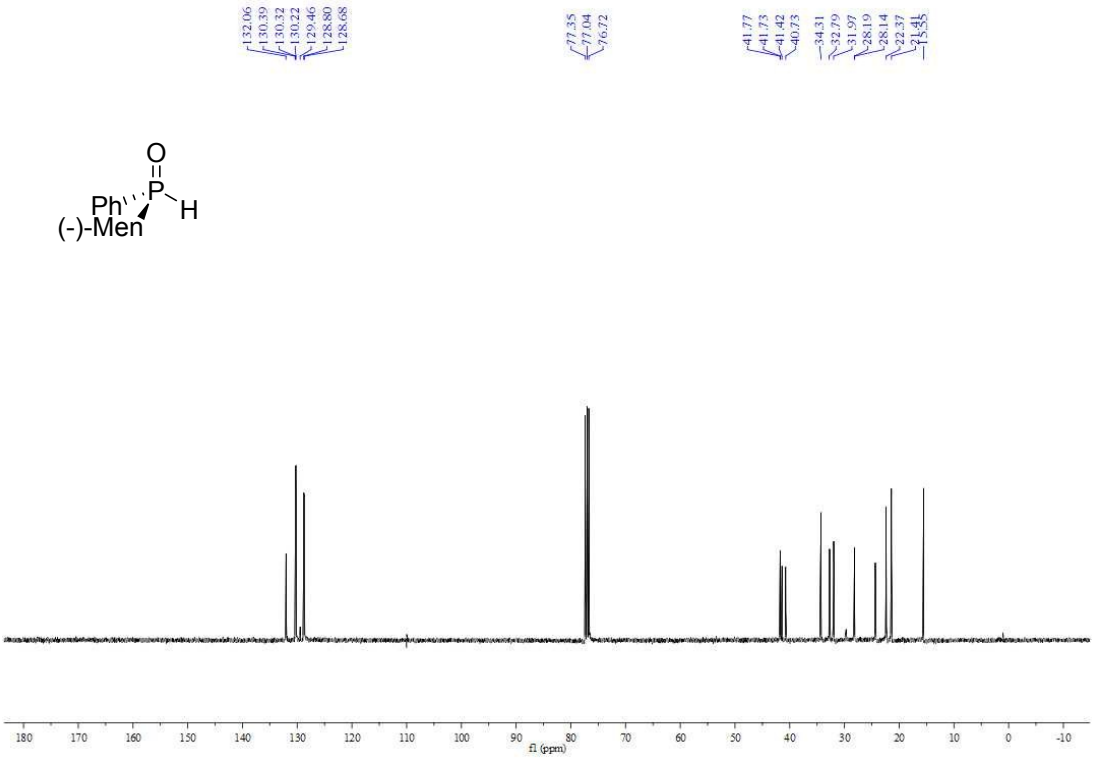




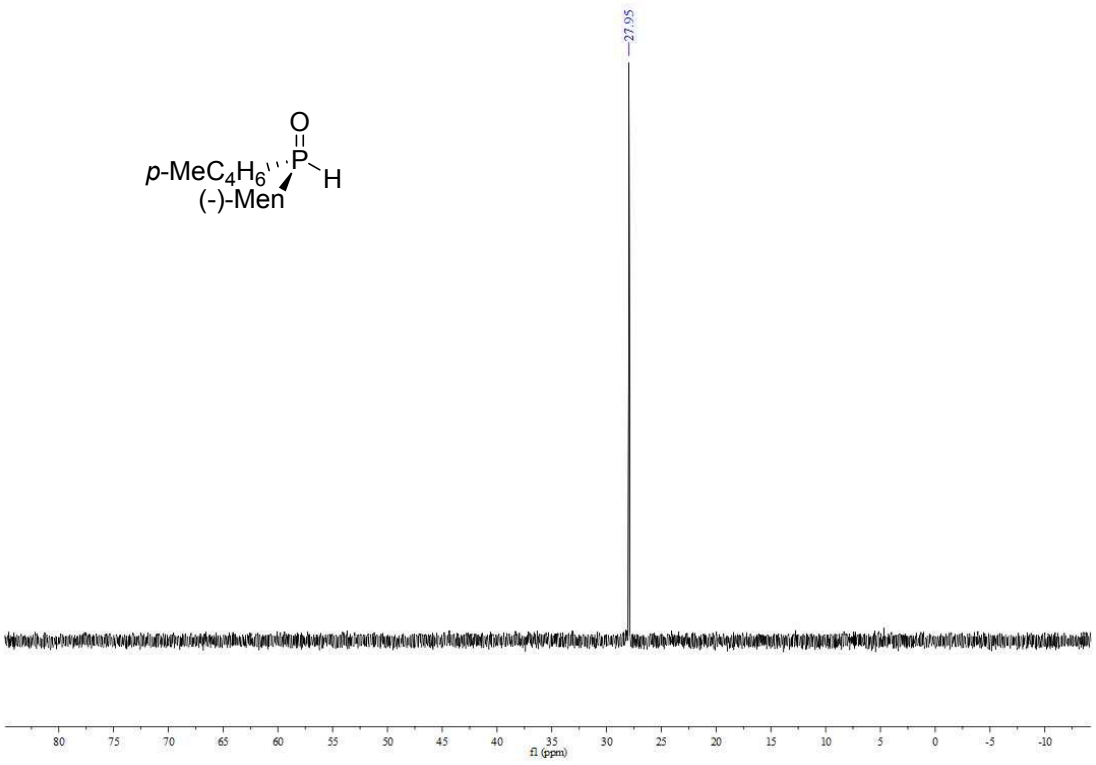
S_P-(-)-Menthylphenyl phosphine oxide 5a'

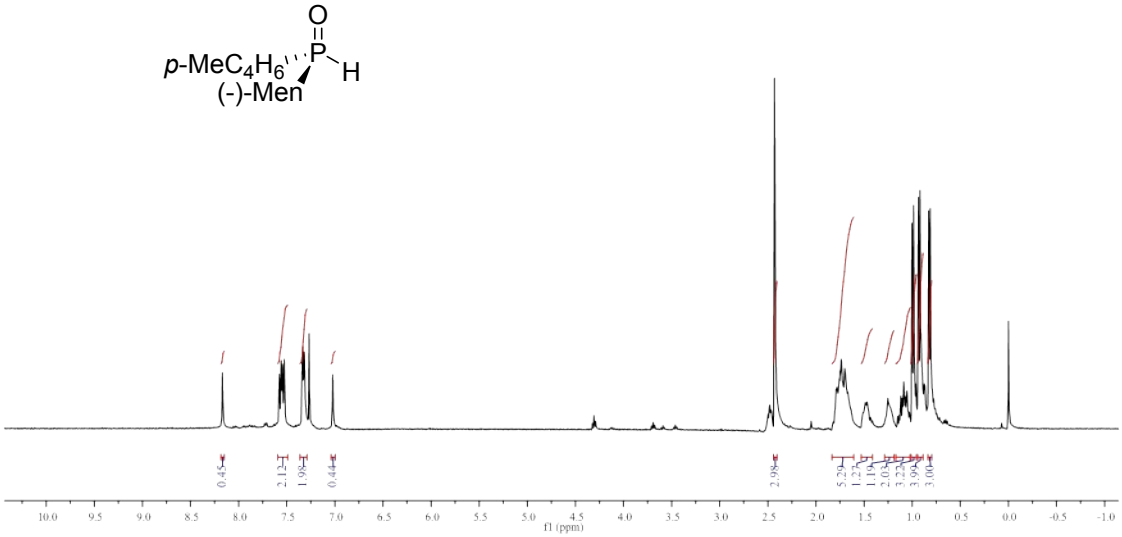


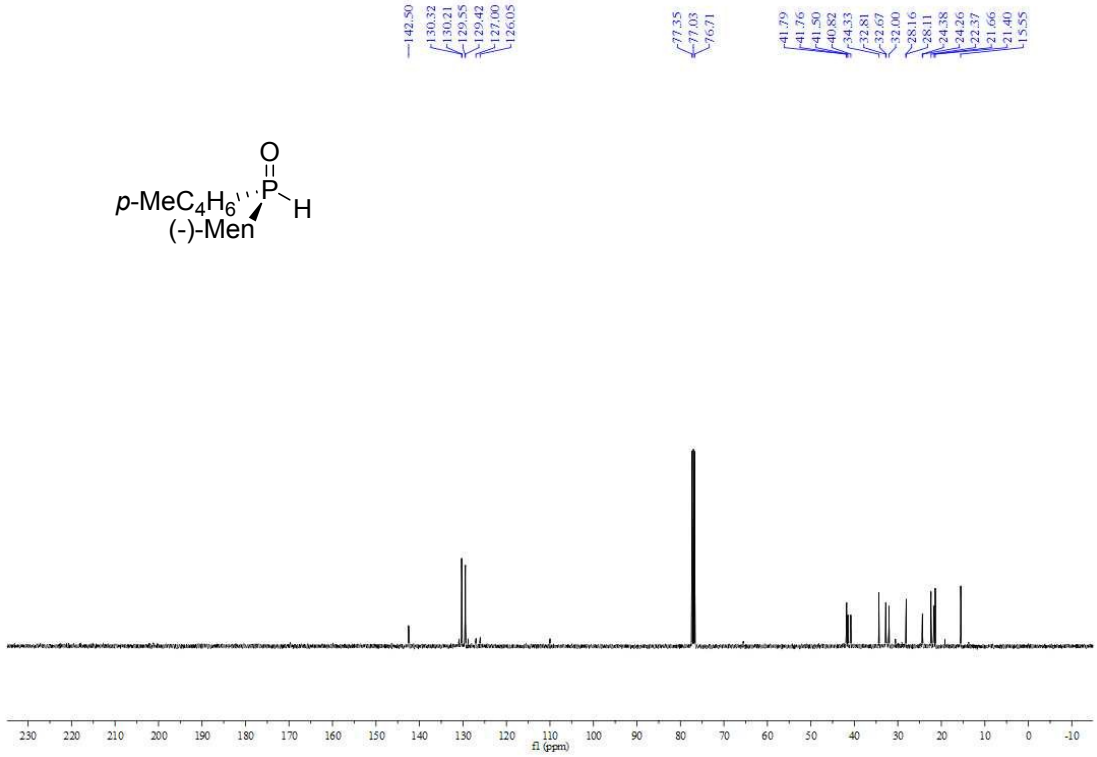

8.20
7.70
7.68
7.67
7.65
7.58
7.57
7.56
7.54
7.53
7.28
7.28
7.05
2.49
2.47
1.71
1.02
1.01
1.00
0.99
0.95
0.95
0.93
0.93
0.83
0.82
0.81
0.08
0.07
0.00
O
P
H
Ph
(-)-Men
0.43
1.77
2.74
0.44
0.84
0.19
3.93
1.02
1.38
1.81
2.94
3.03
3.00
fl (ppm)


132.06
130.39
130.32
130.22
129.46
128.80
128.68
77.35
77.04
76.72
41.77
41.73
41.42
40.73
34.31
32.79
31.97
28.19
28.14
22.37
21.41
15.35
O
P
H
Ph
(-)-Men
fl (ppm)

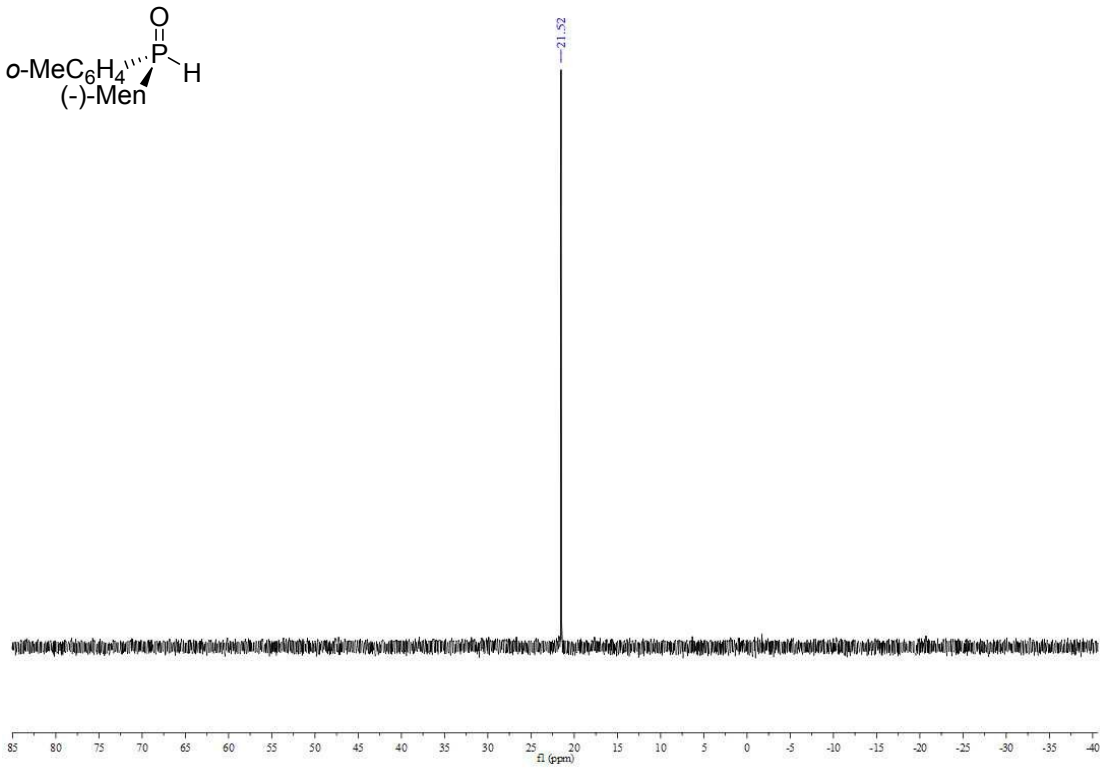
S_P-(-)-Menthyl *p*-tolylphosphine oxide (5b')

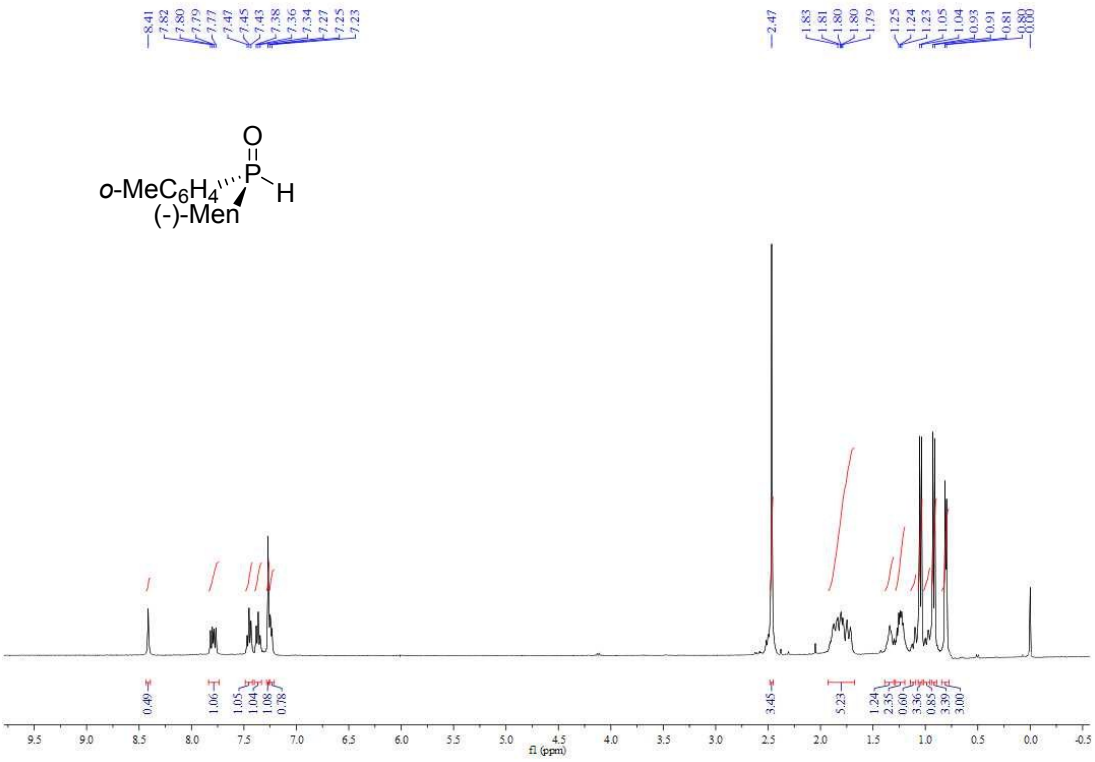


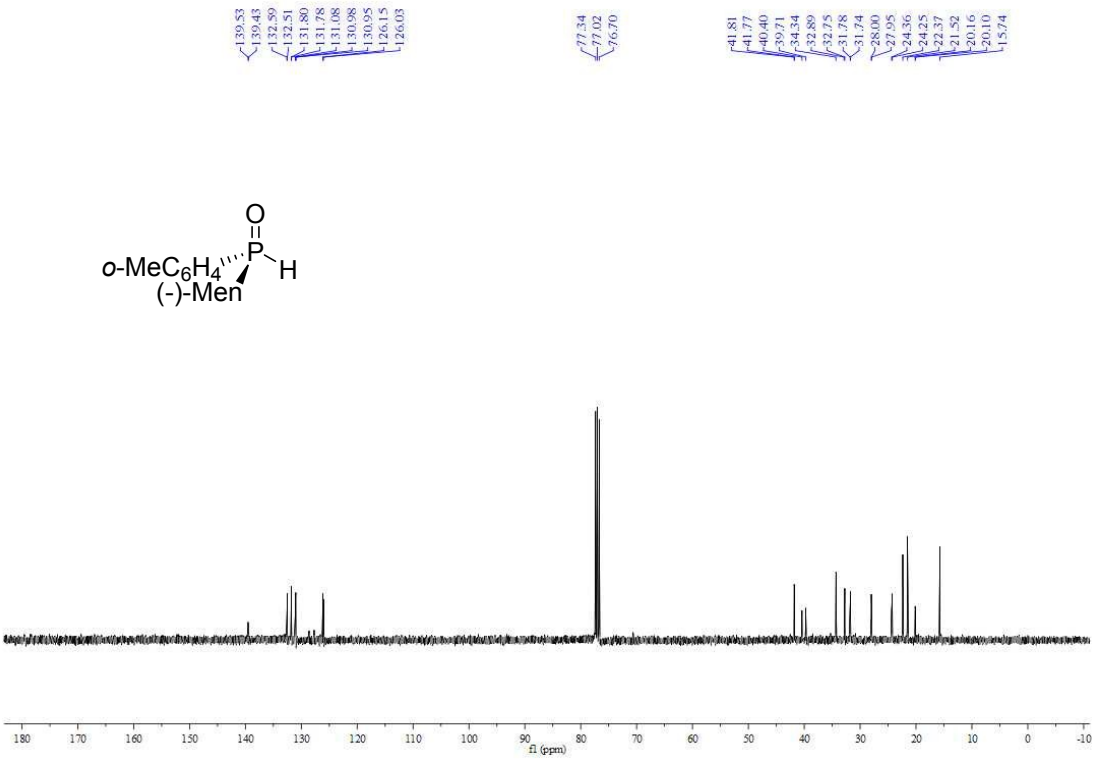




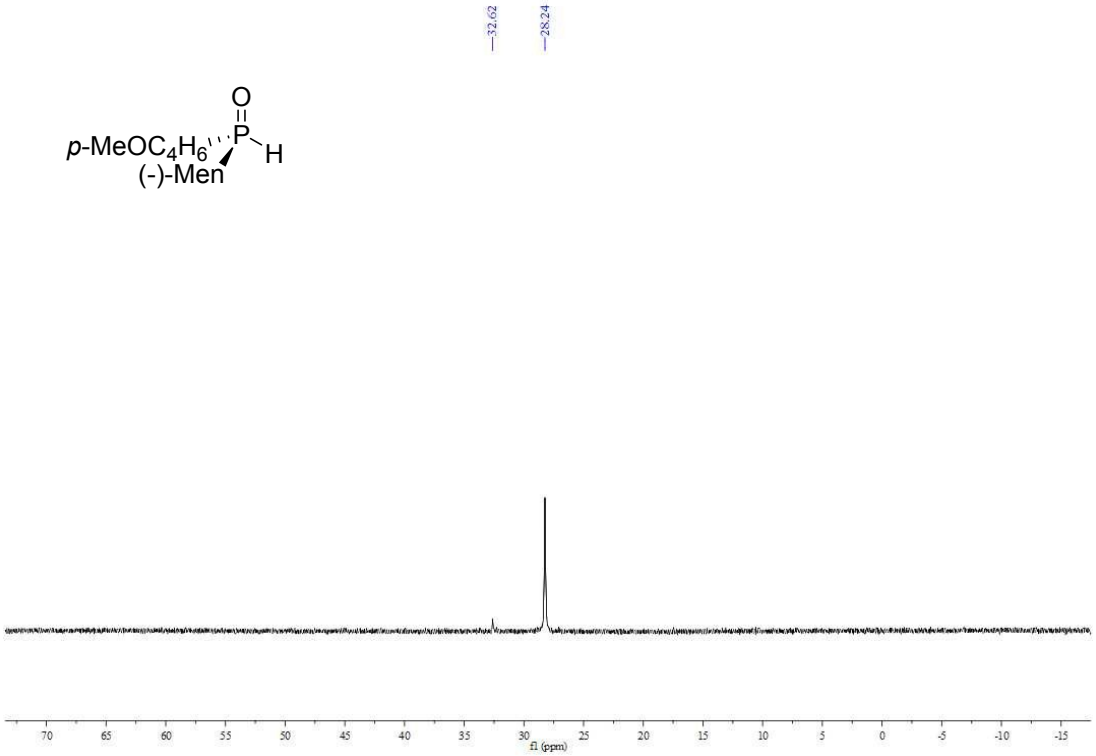
S_P-(-)-Menthyl *o*-tolylphosphine oxide (5c')

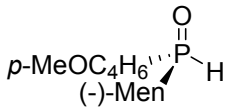


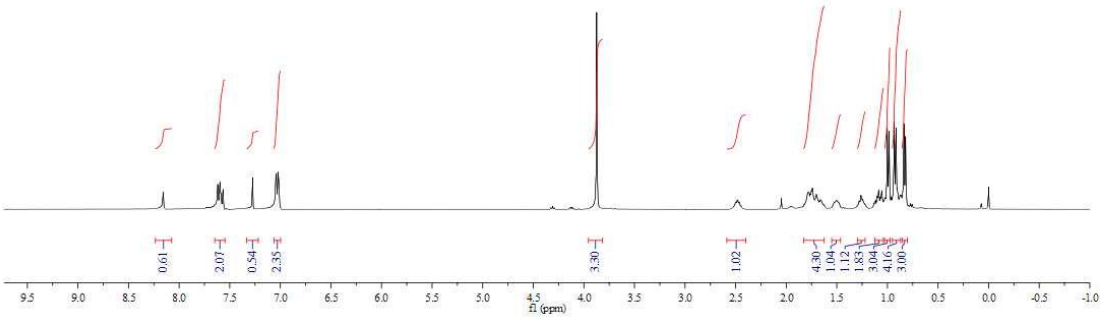

8.41
7.82
7.80
7.79
7.77
7.47
7.45
7.43
7.38
7.36
7.34
7.27
7.25
7.23
2.47
1.83
1.81
1.80
1.80
1.79
1.25
1.24
1.23
1.05
1.04
0.93
0.91
0.81
0.80
0.00
O
P
H
o-MeC6H4
(-)-Men
0.49
1.06
1.05
1.04
1.08
0.78
3.45
5.23
1.24
2.35
0.60
3.36
0.85
3.39
3.00
f1 (ppm)

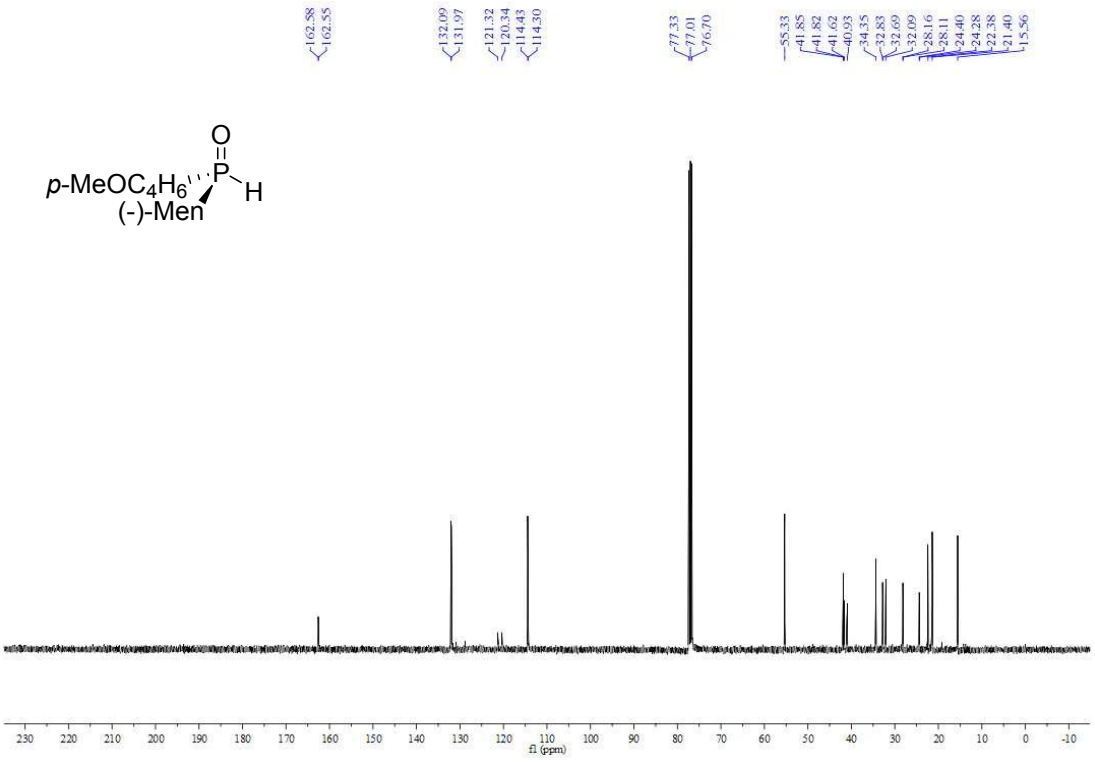

139.53
139.43
132.59
132.51
131.80
131.78
131.08
130.98
130.95
126.15
126.03
77.34
77.02
76.70
41.81
41.77
40.40
39.71
34.34
32.89
32.75
31.78
31.74
28.00
27.95
24.36
24.25
22.37
21.52
20.16
20.10
15.74
O
P
H
o-MeC6H4
(-)-Men
f1 (ppm)

S_P-(-)-Menthyl *p*-methoxyphenylphosphine oxide (5d')

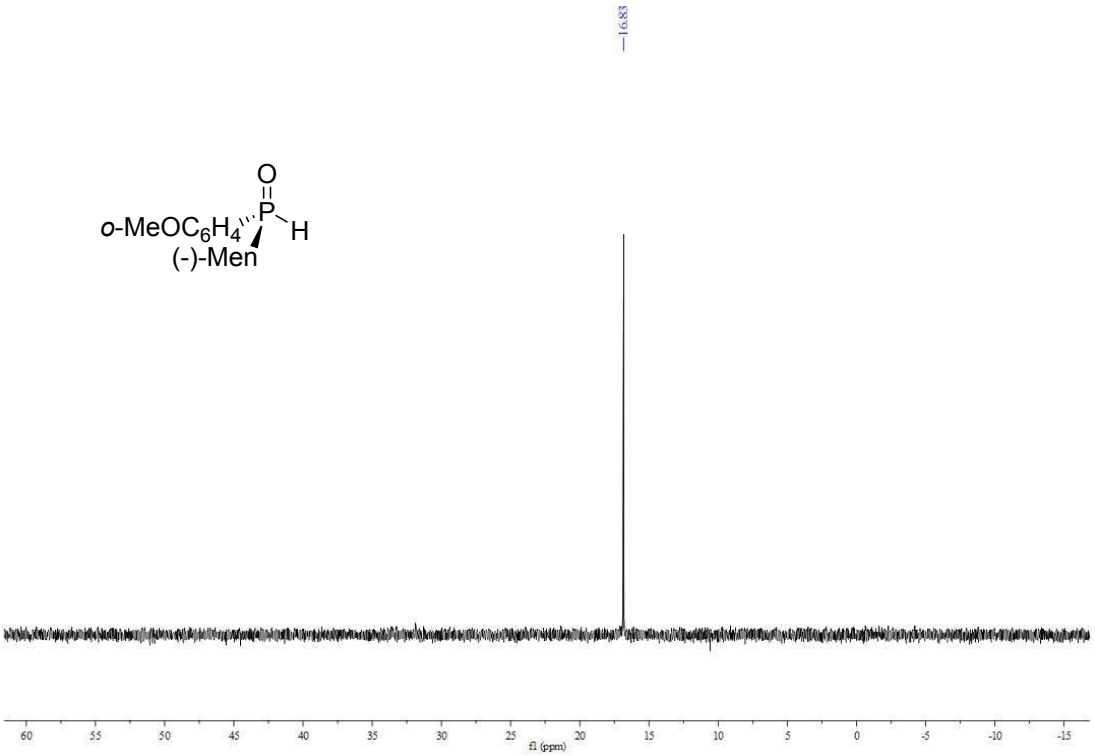


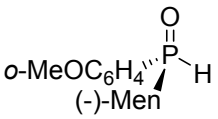


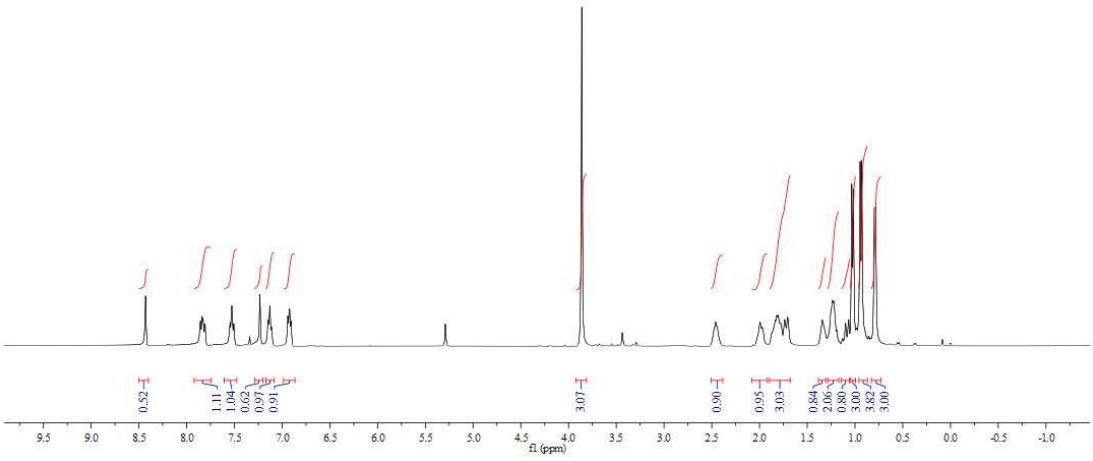


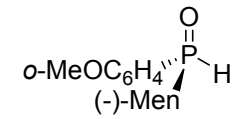


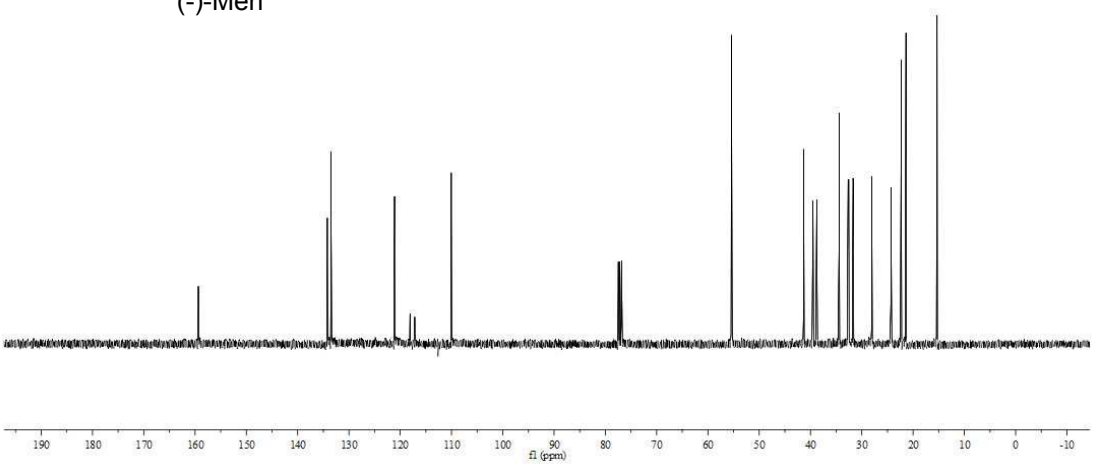
S_P-(-)-Menthyl *o*-methoxyphenylphosphine oxide (5e')



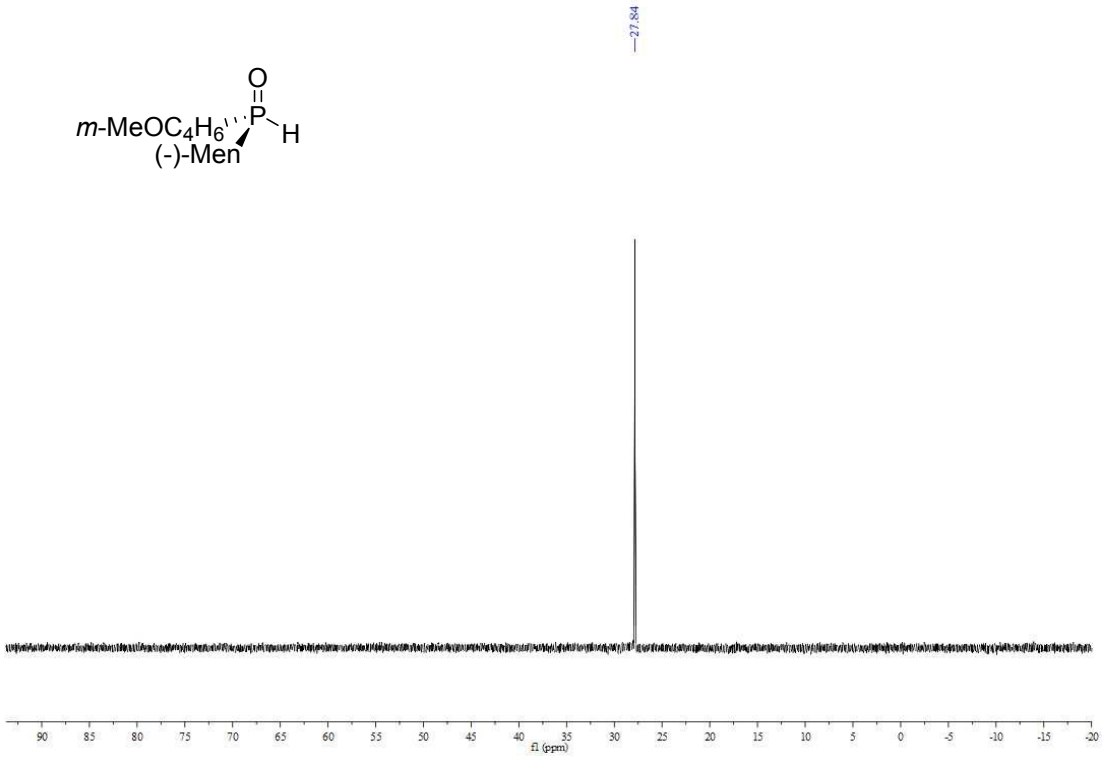

O
P
H
o-MeOC6H4
(-)-Men

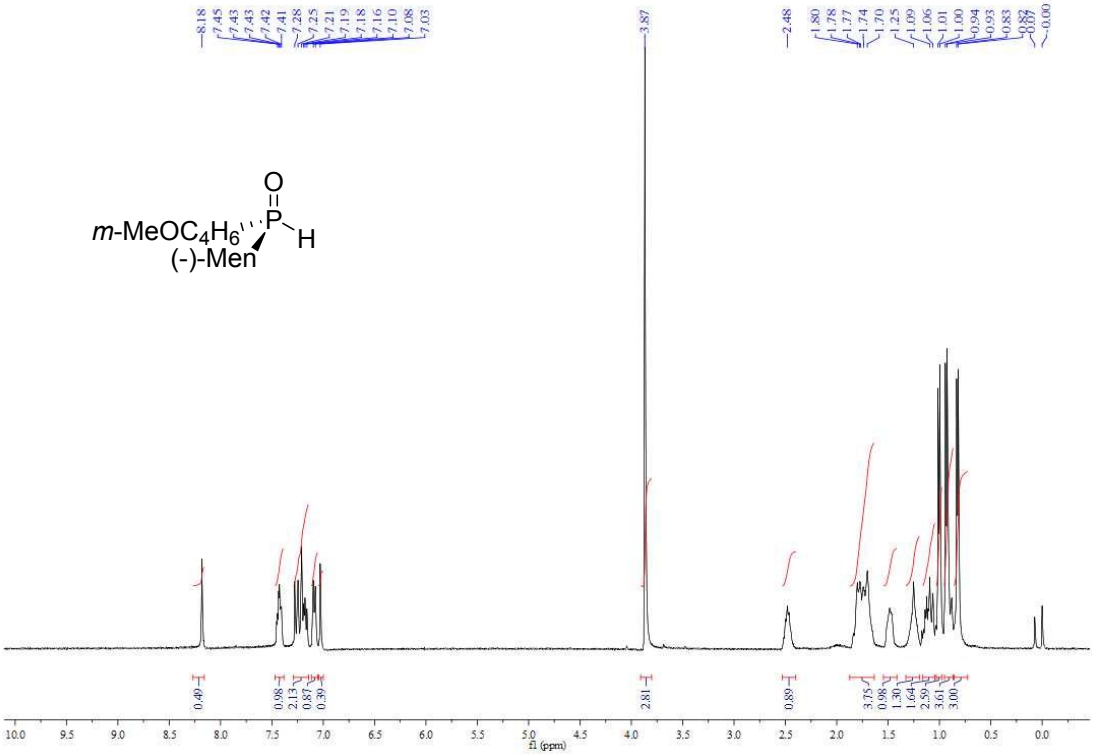

0.52
1.11
1.04
0.62
0.97
0.91
3.07
0.90
0.93
3.03
0.84
2.06
0.80
3.00
3.82
3.00
f1 (ppm)

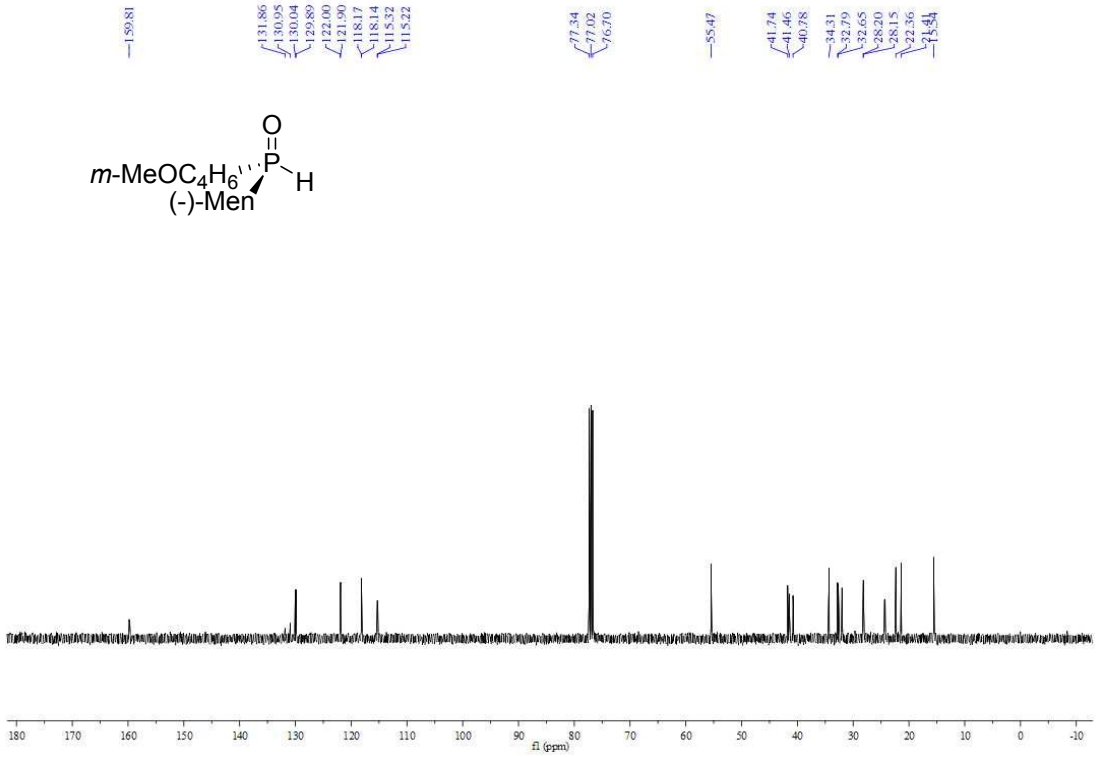

O
P
H
o-MeOC6H4
(-)-Men


f1 (ppm)

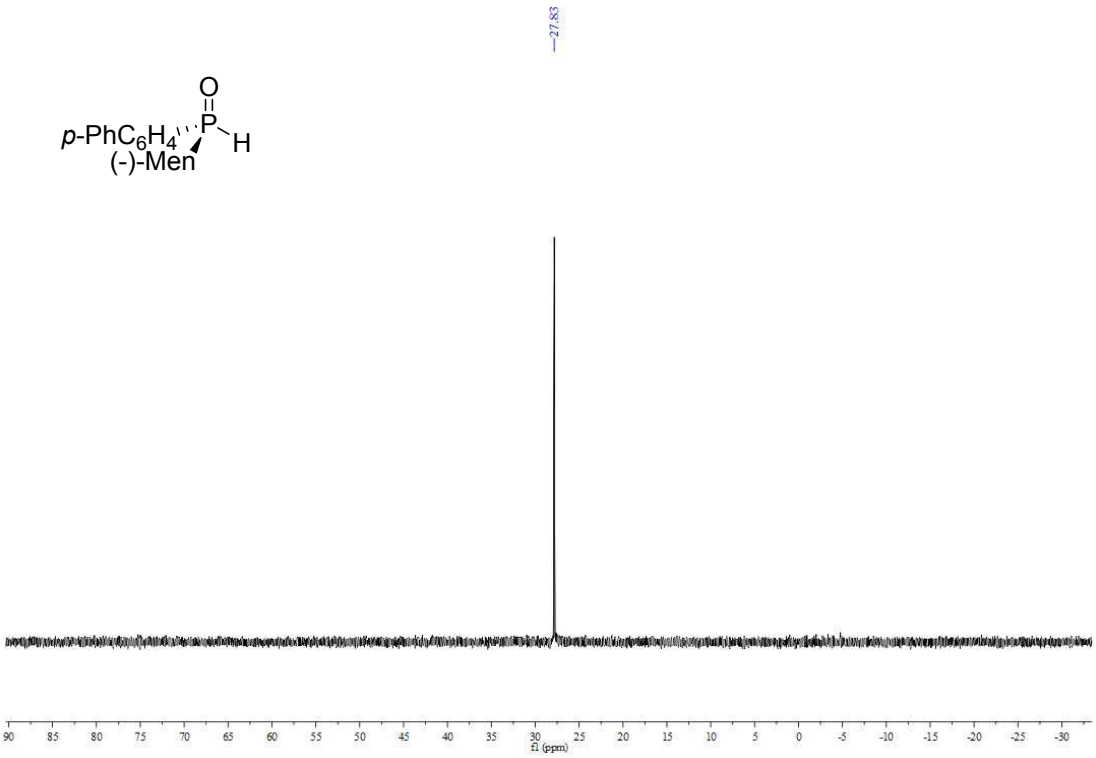
S_P-(-)-Menthyl *m*-methoxyphenylphosphine oxide (5f')

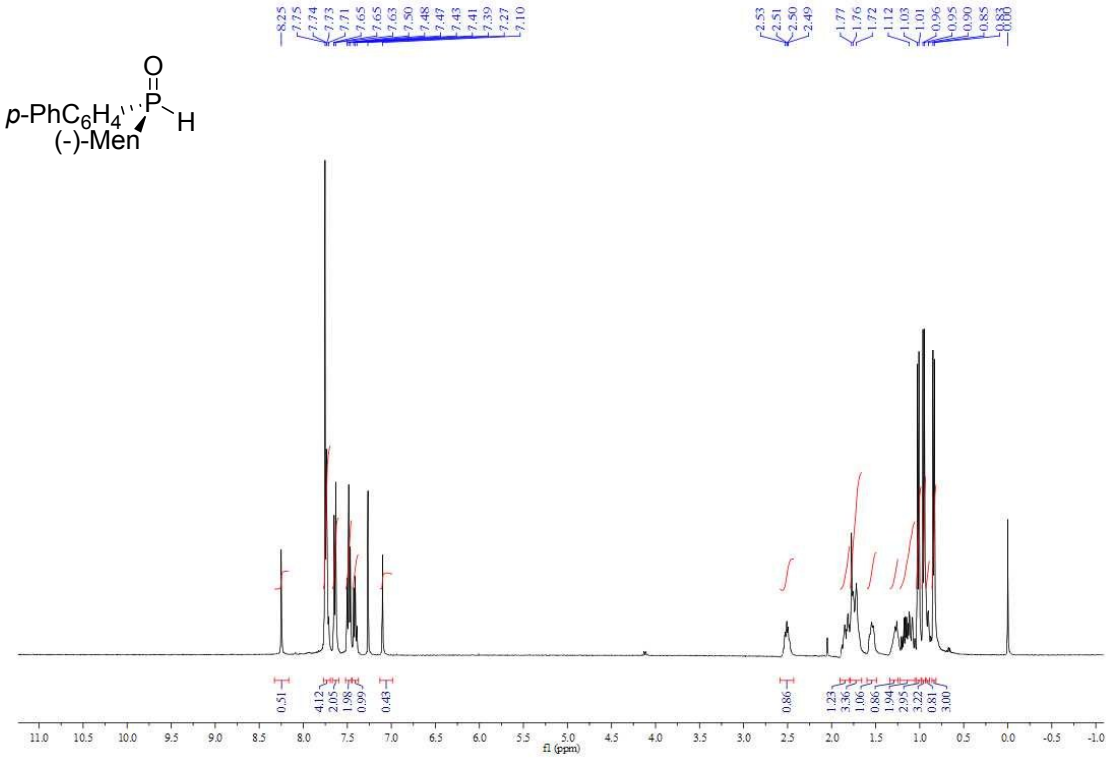


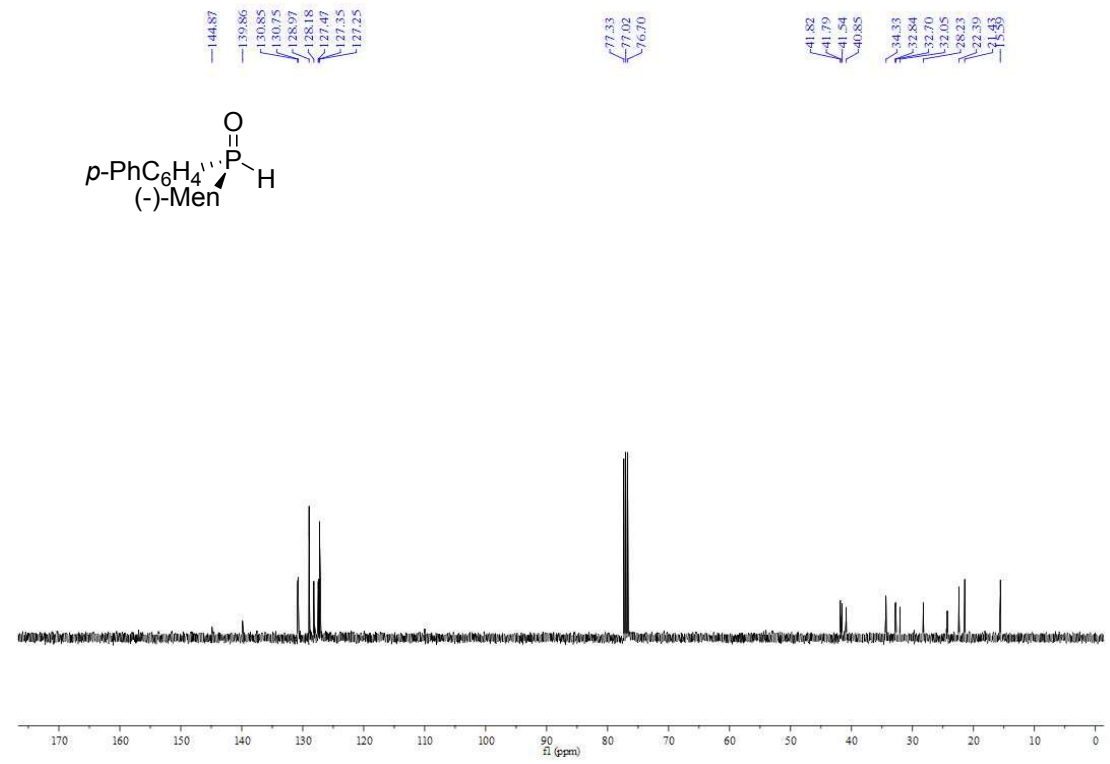




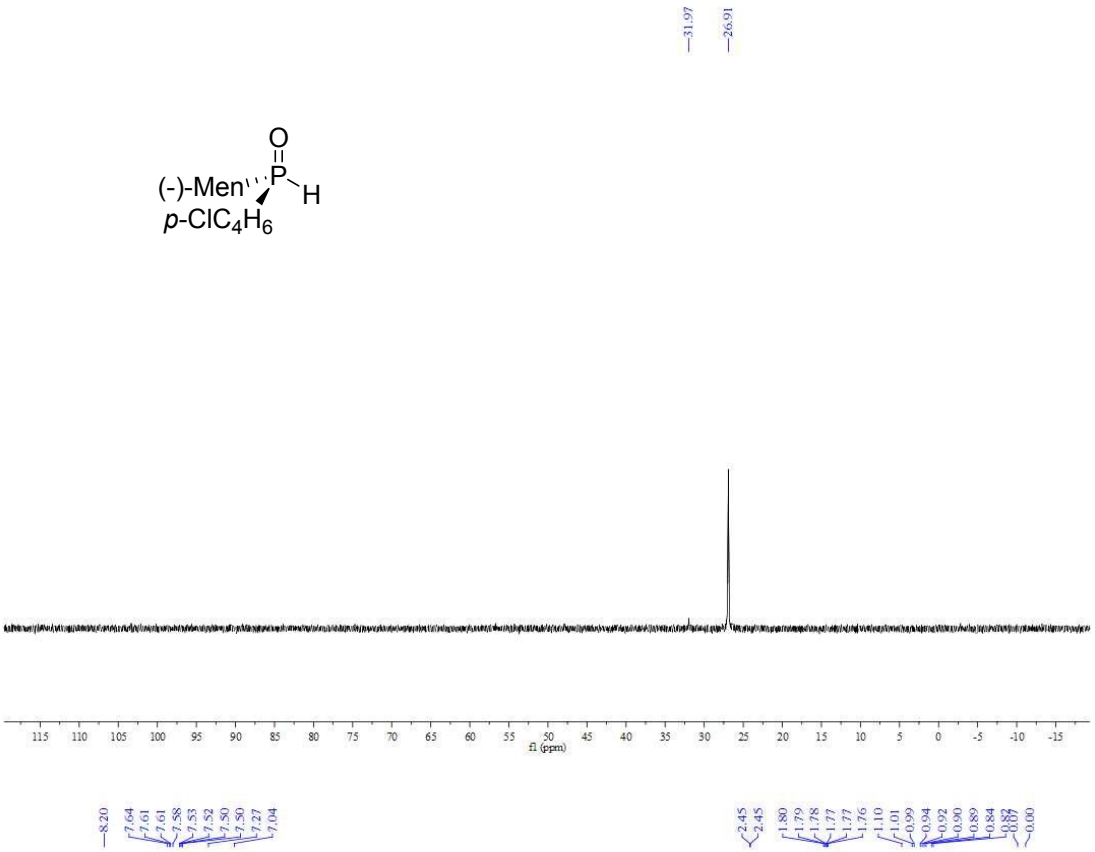
S_P-(-)-Menthyl [1,1'-biphenyl]-4-ylphosphine oxide (5g')

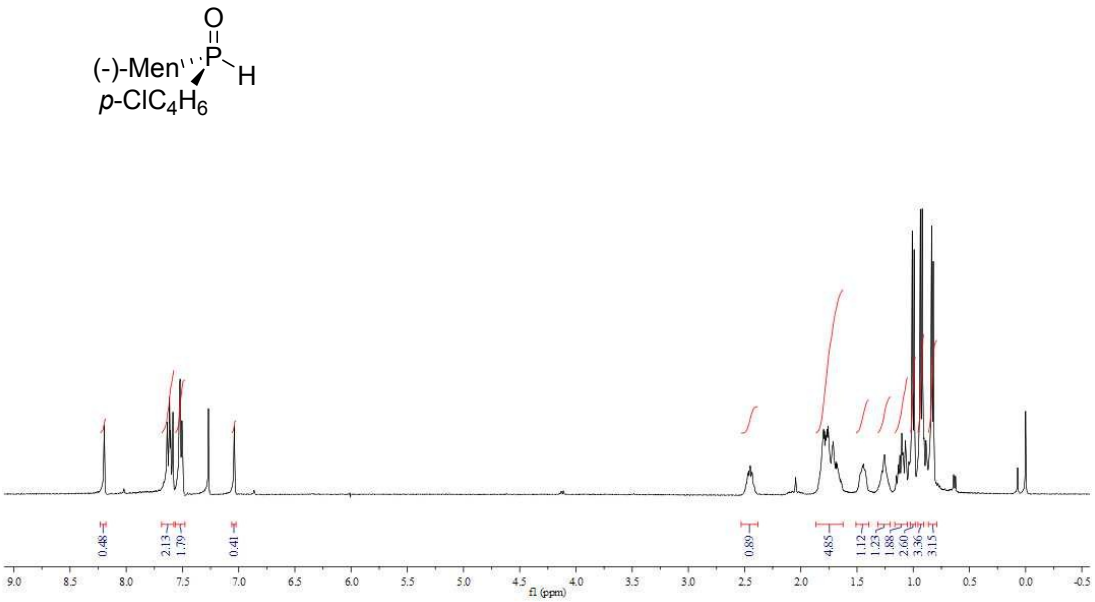


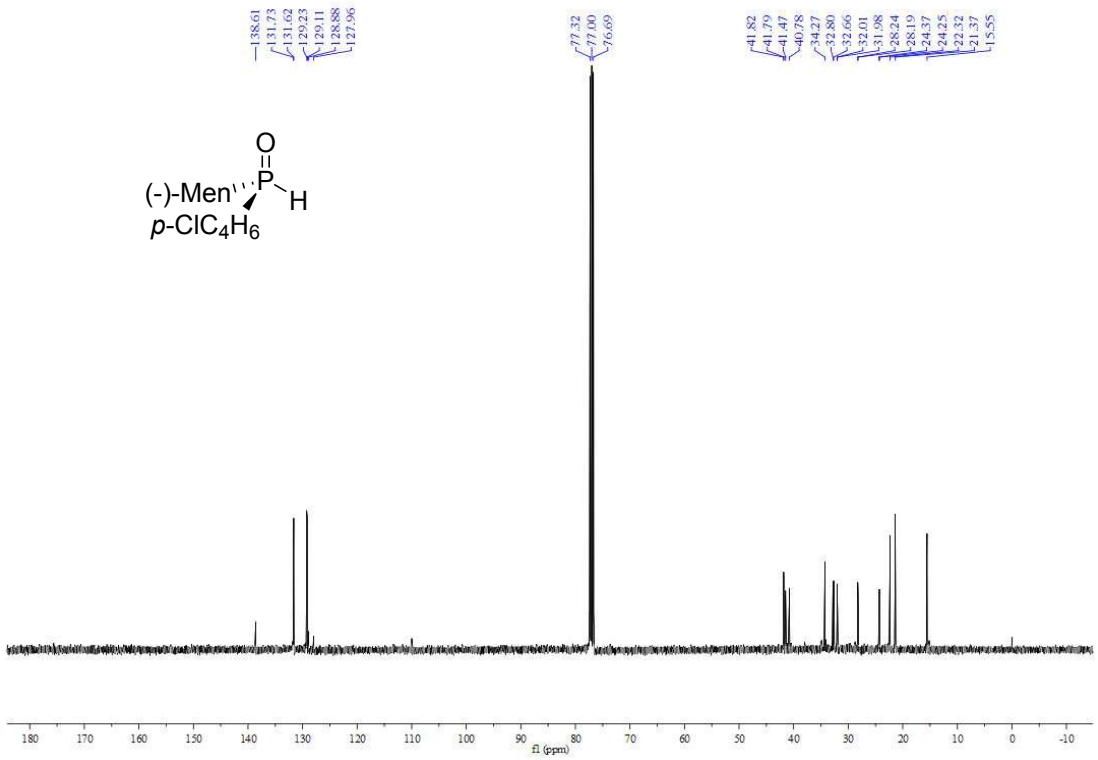

p-PhC6H4
(-)-Men
O
P
H
8.25
7.75
7.74
7.73
7.71
7.65
7.65
7.63
7.50
7.48
7.47
7.43
7.41
7.39
7.27
7.10
2.53
2.51
2.50
2.49
1.77
1.76
1.72
1.12
1.03
1.01
0.96
0.95
0.90
0.85
0.51
4.12
2.05
1.98
0.99
0.43
0.86
1.23
3.36
1.06
0.86
1.94
2.95
3.22
0.81
3.00
fl (ppm)


p-PhC6H4
(-)-Men
O
P
H
144.87
139.86
130.85
130.75
128.97
128.18
127.47
127.35
127.25
77.33
77.02
76.70
41.82
41.79
41.54
40.85
34.33
32.84
32.70
32.05
28.23
22.39
21.43
15.59
fl (ppm)

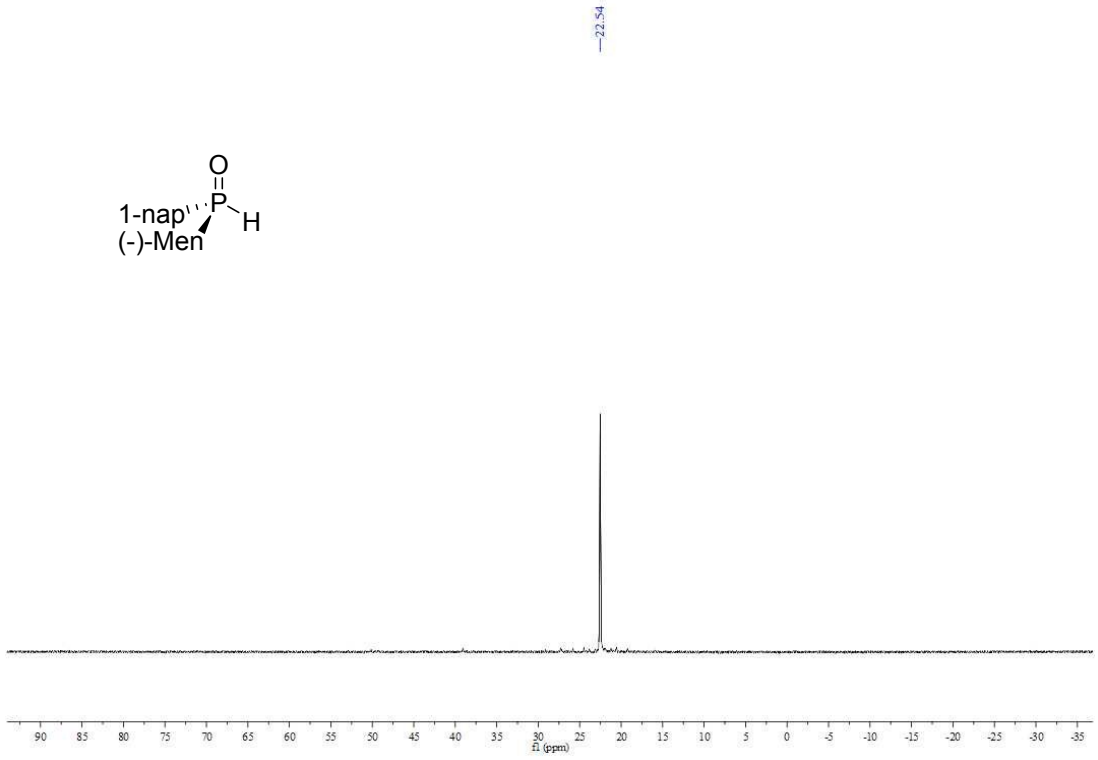
S_P-(-)-Menthyl *p*-chlorophenylphosphine oxide (5i')

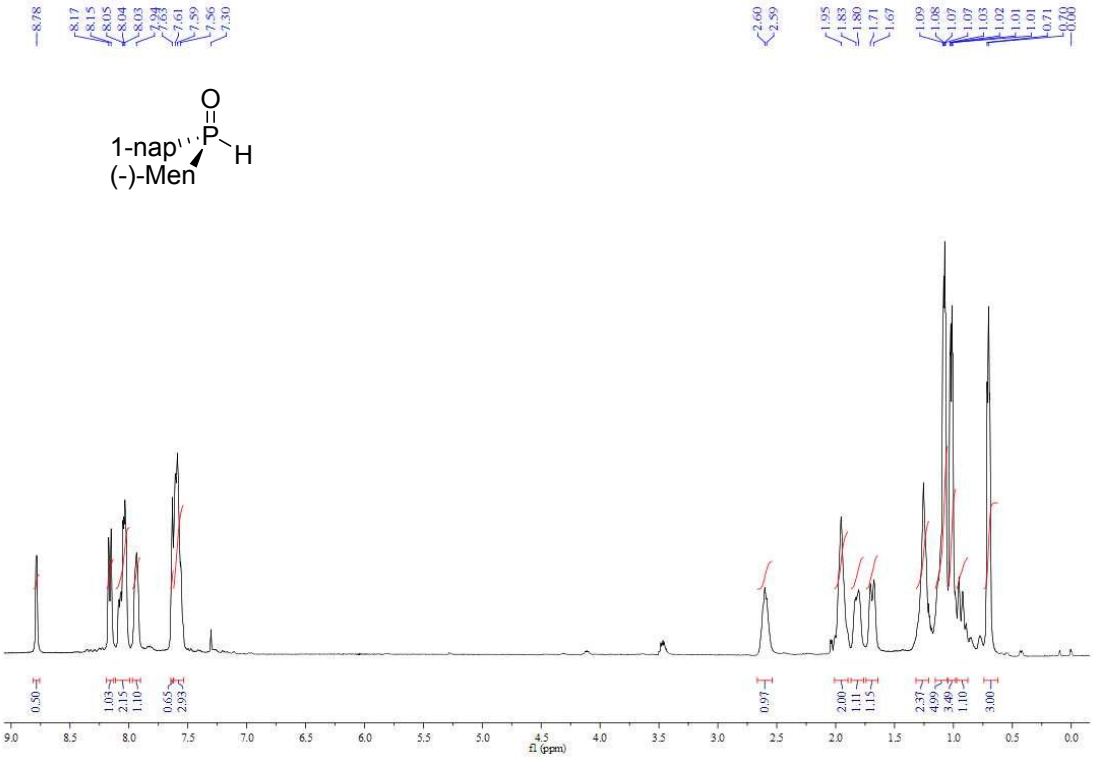


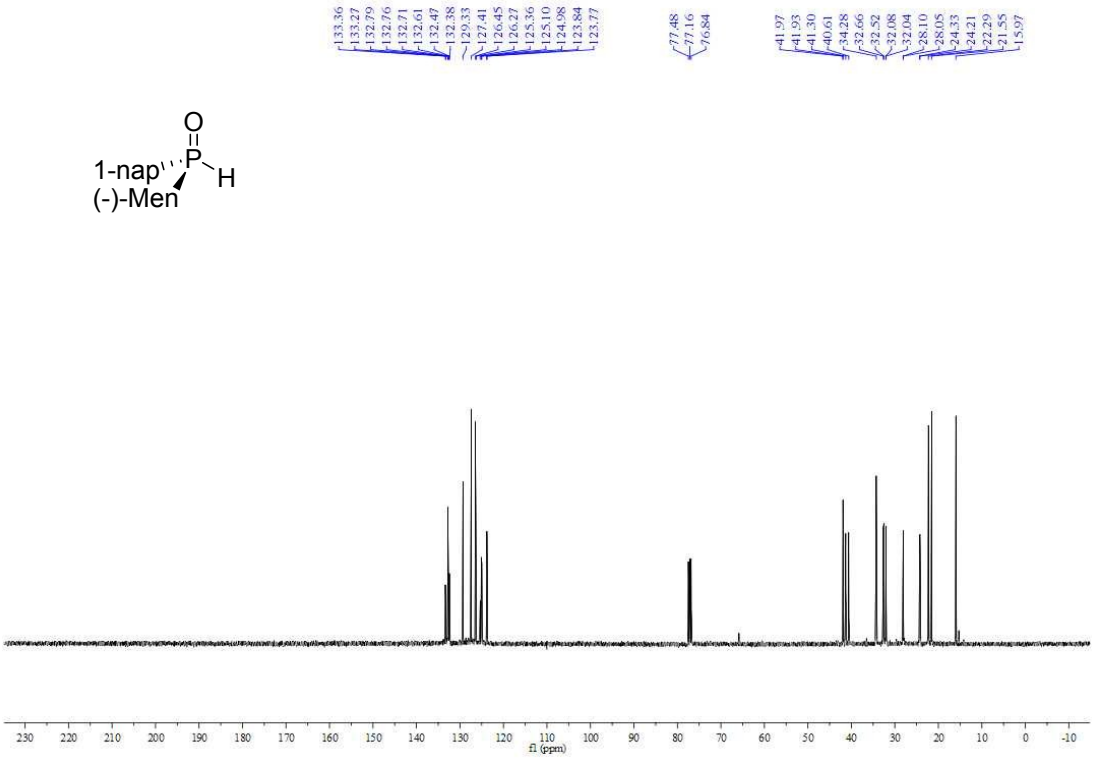




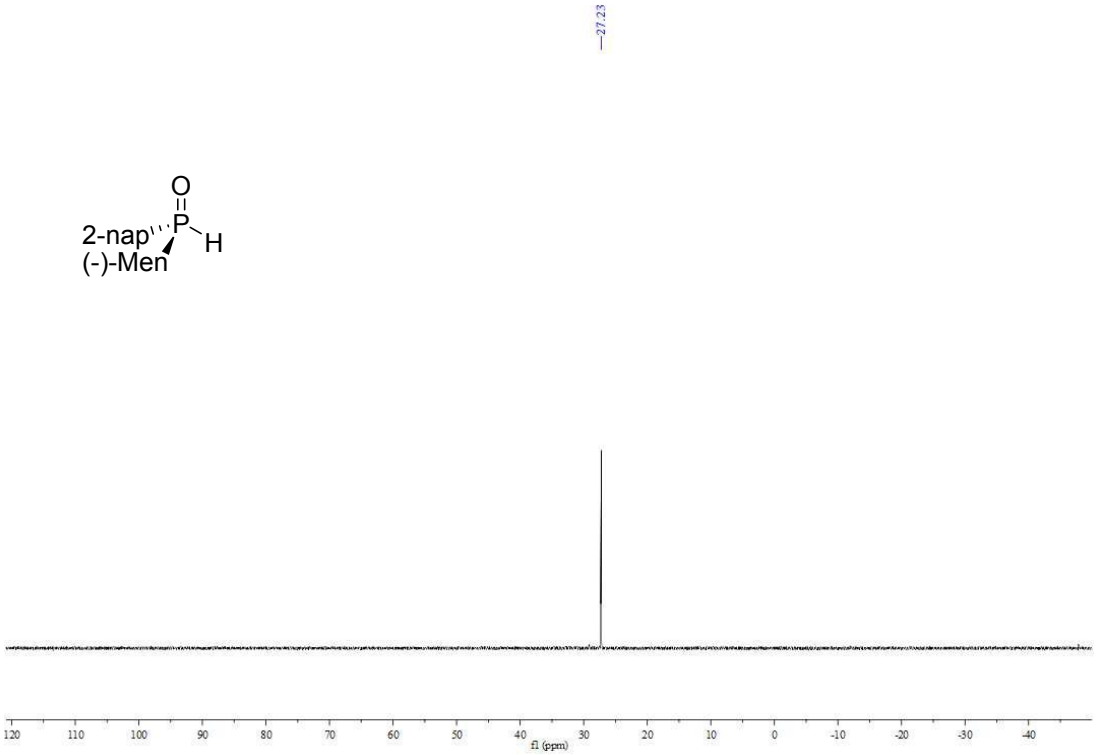
S_P-(-)-Menthyl 1-naphthalenylphosphine oxide (5j')

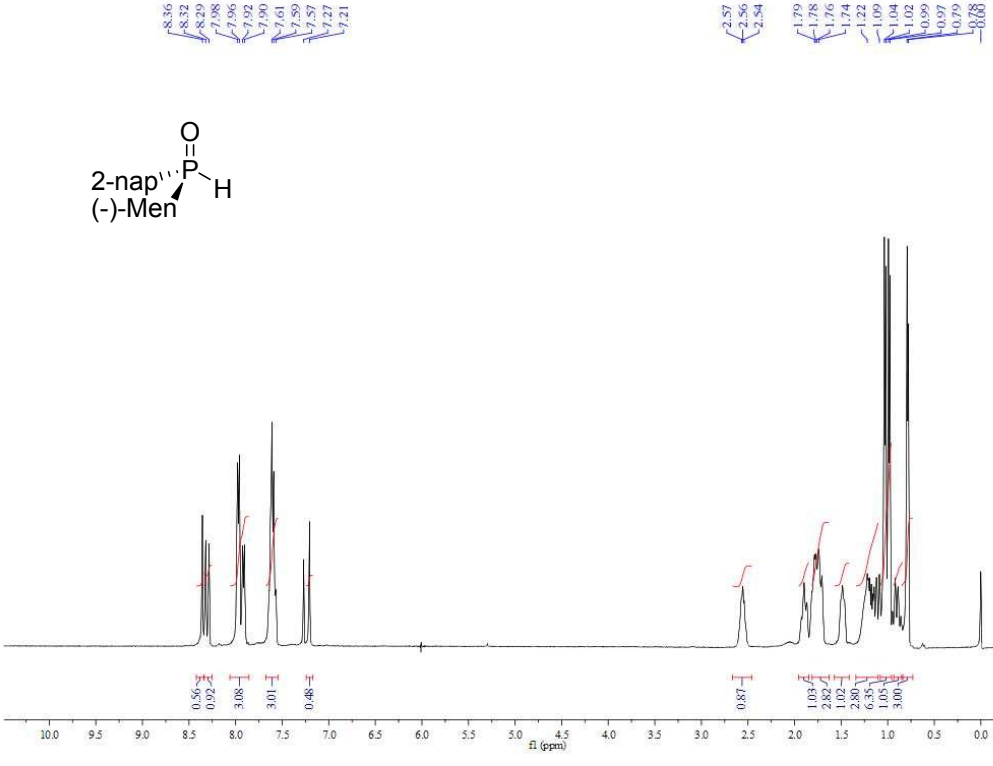


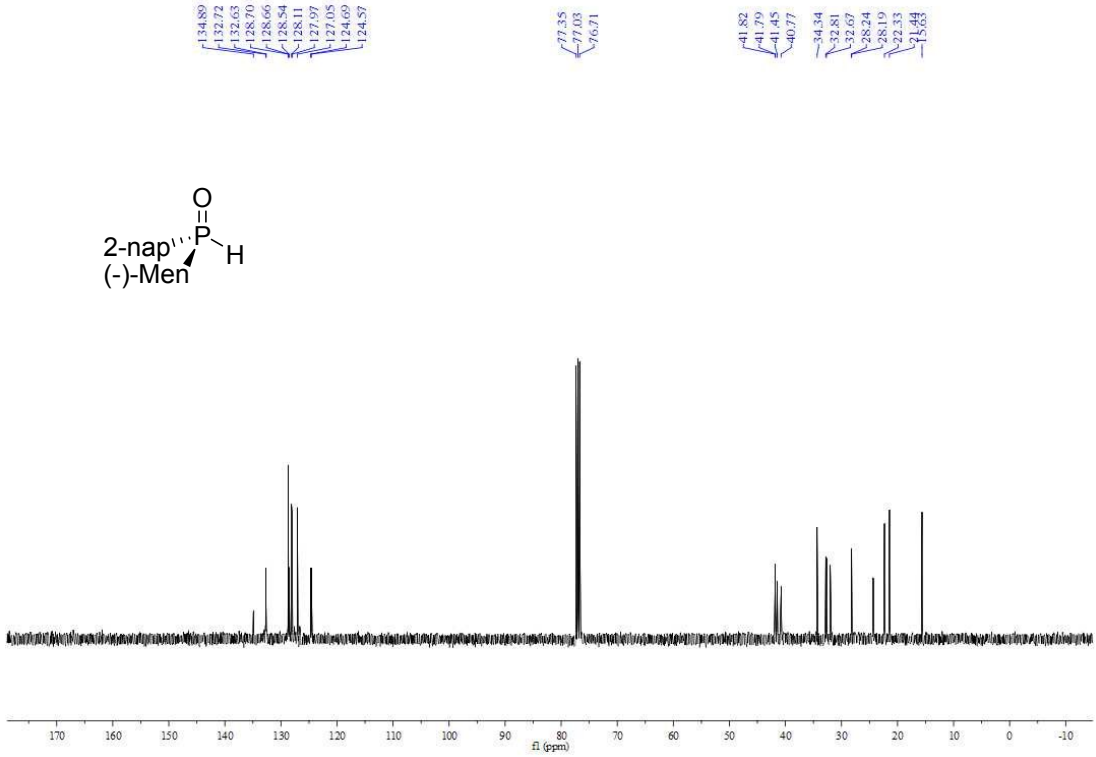

1-nap
(-)-Men
P
O
H
fl (ppm)


1-nap
(-)-Men
P
O
H
fl (ppm)

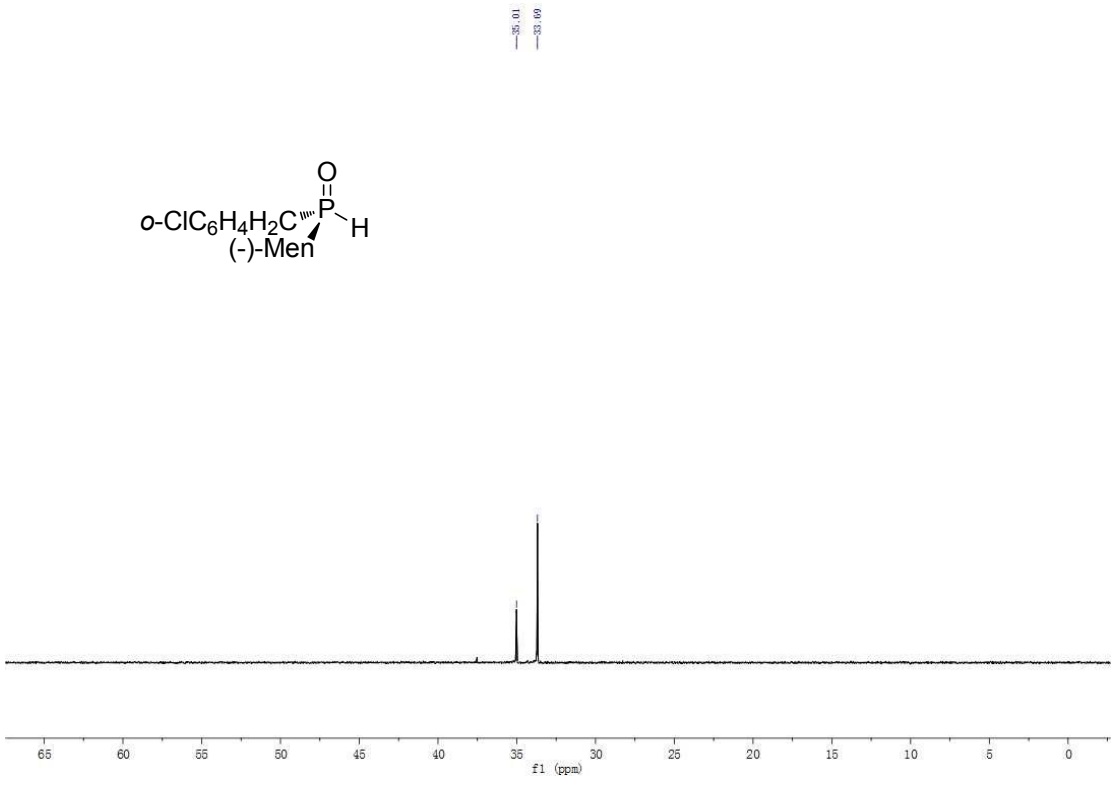
S_P-(-)-Menthyl 2-naphthalenylphosphine oxide (5k')



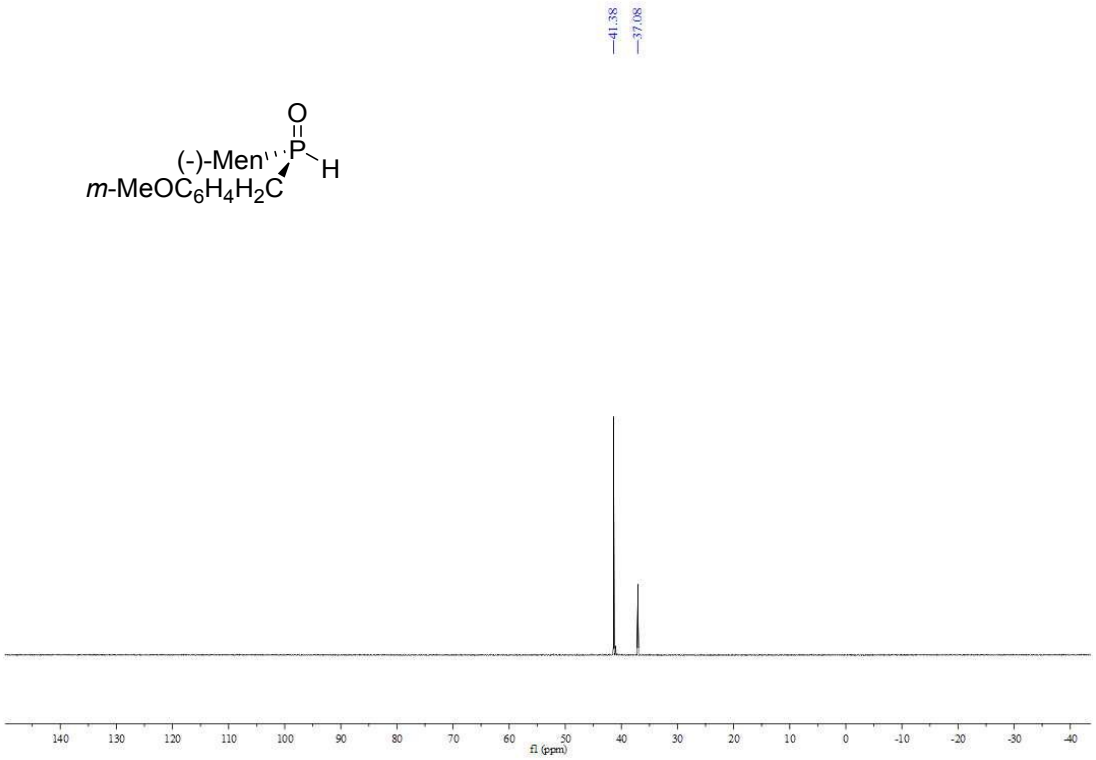




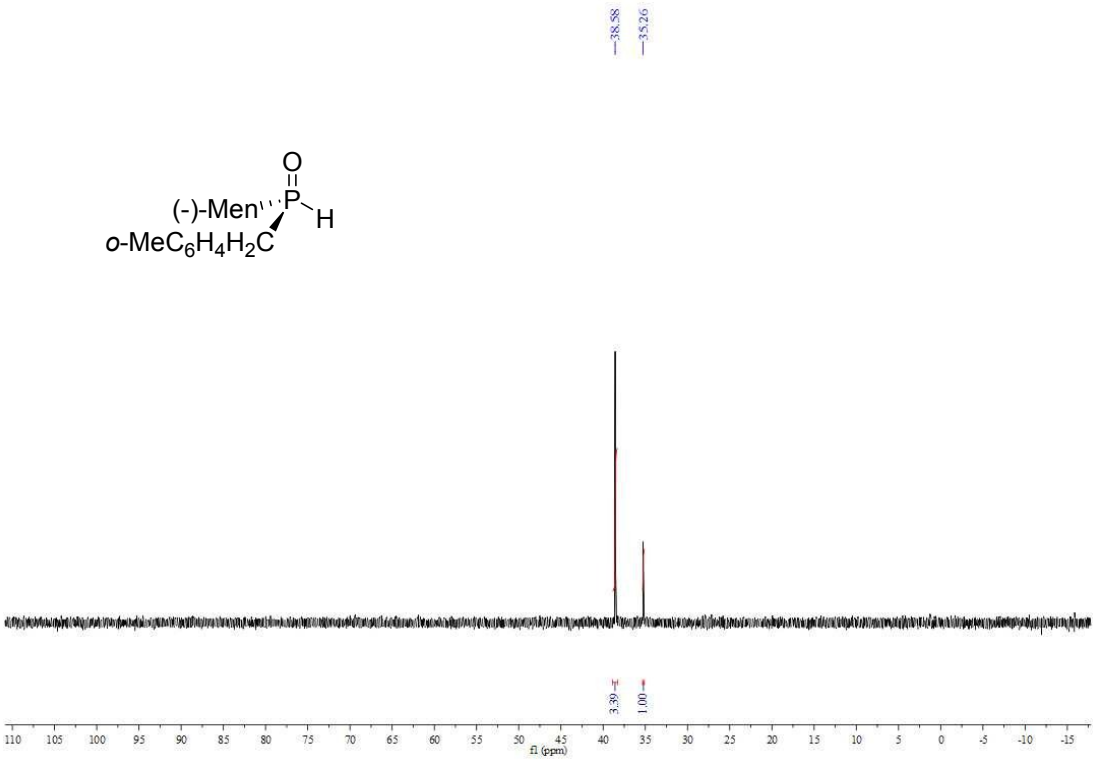
(R_P/S_P)-(-)-Menthyl 2- chlorobenzylphosphine oxide (5l/5l')

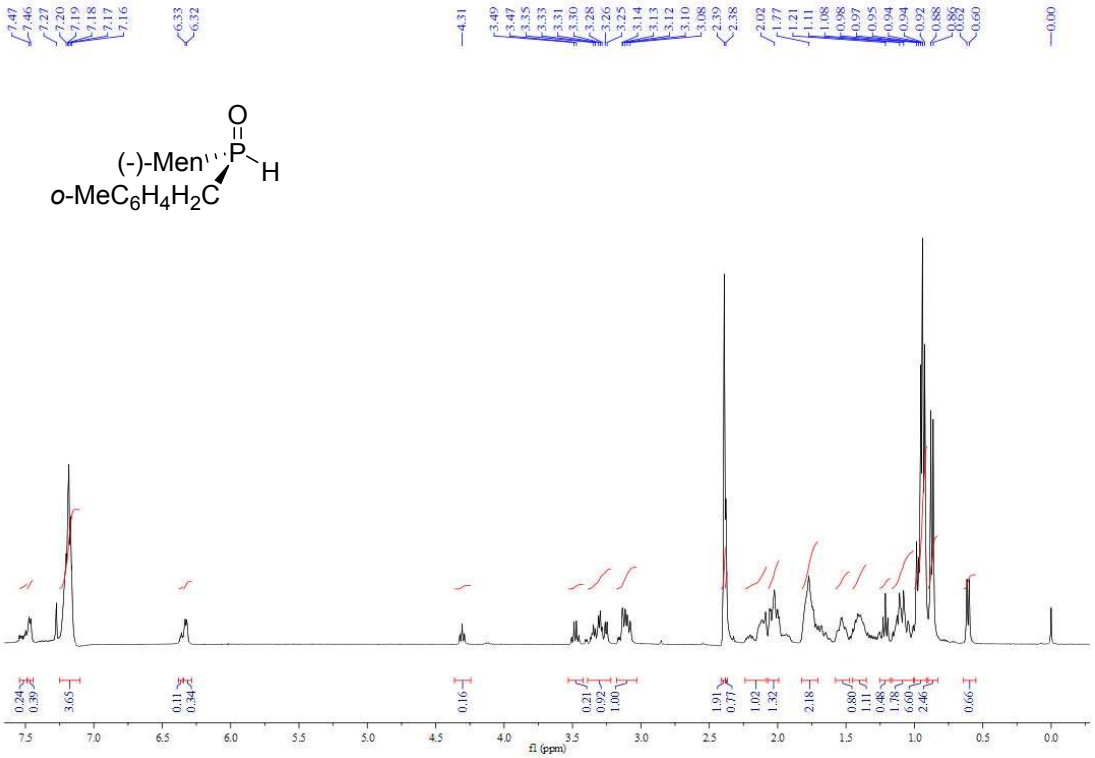


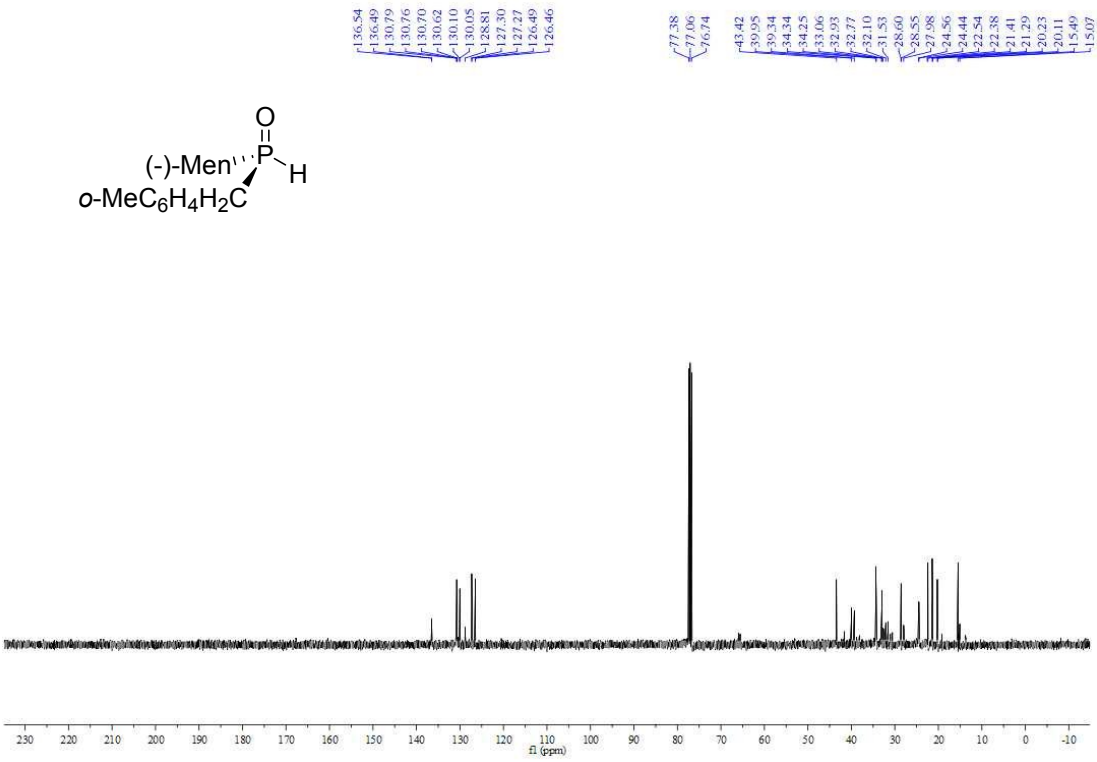
(R_P/S_P)-(-)-Menthyl 3-methoxybenzylphosphine oxide (5m/5m')



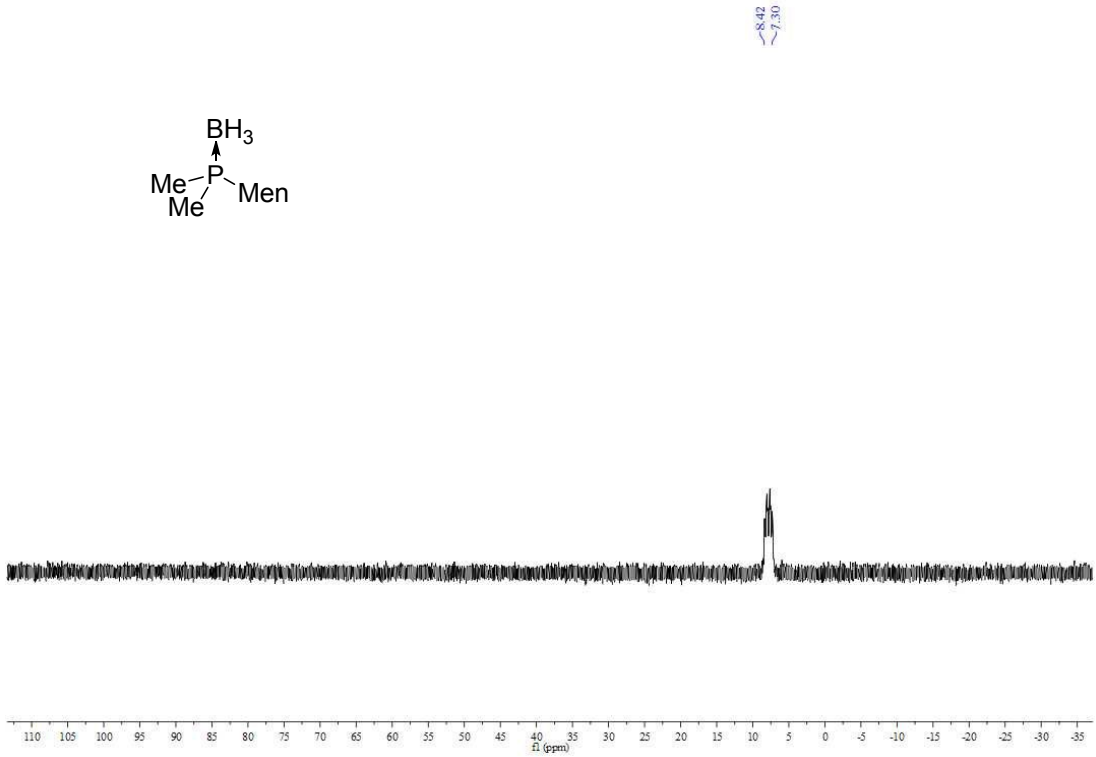
(R_P/S_P)-(-)-Menthyl 2-methylbenzylphosphine oxide (5n/5n')

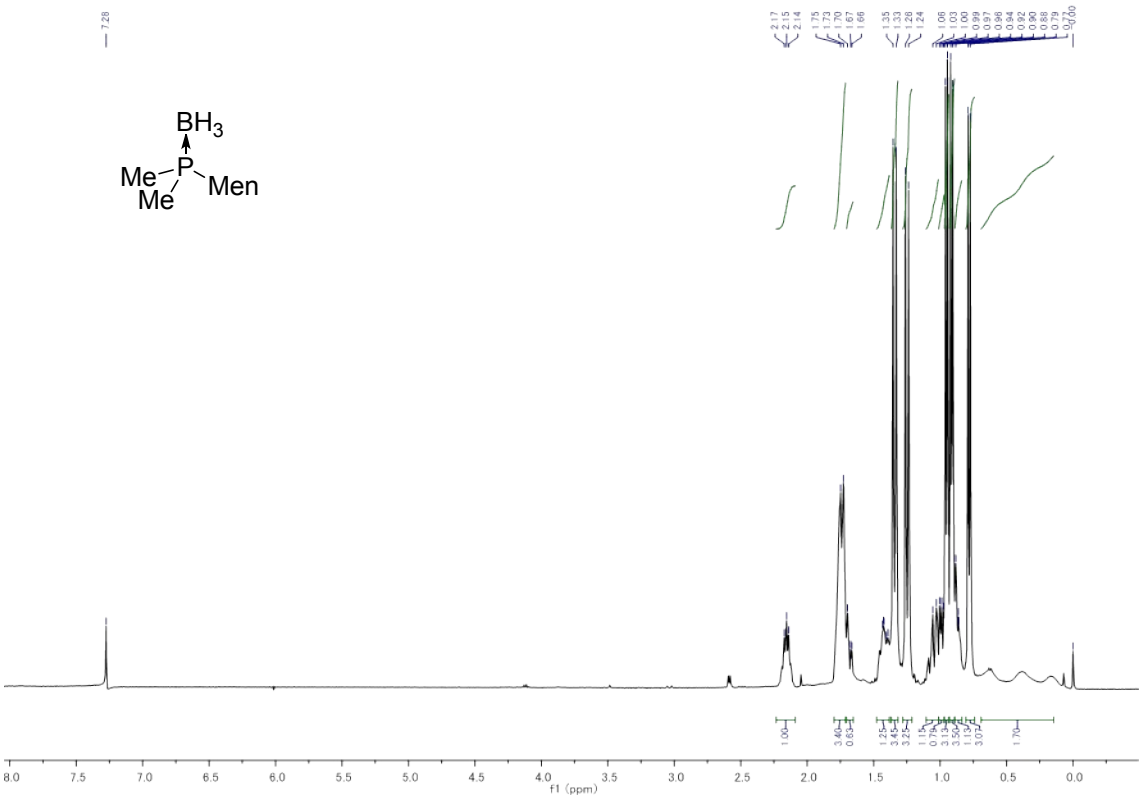


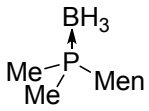

(-)-Men
o-MeC6H4H2C
f1 (ppm)

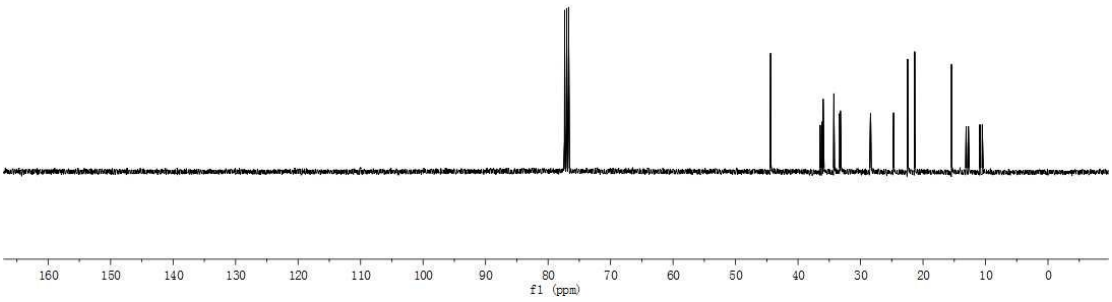

(-)-Men
o-MeC6H4H2C
f1 (ppm)

Dimethyl menthyl phosphine oxide 8a

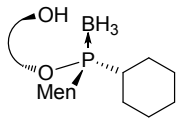


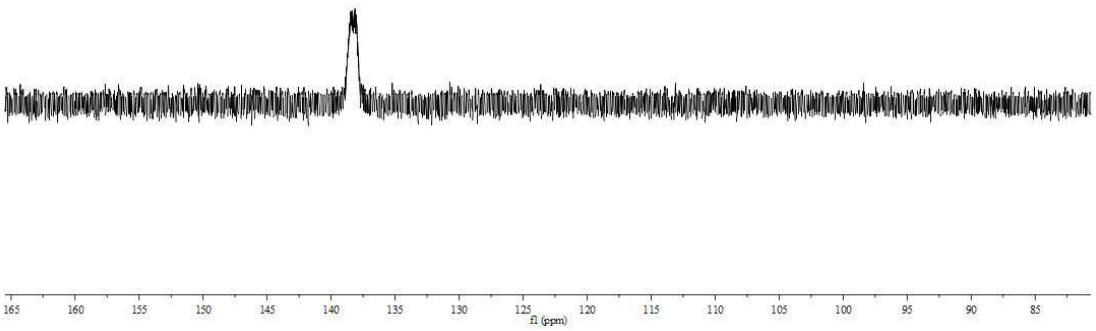


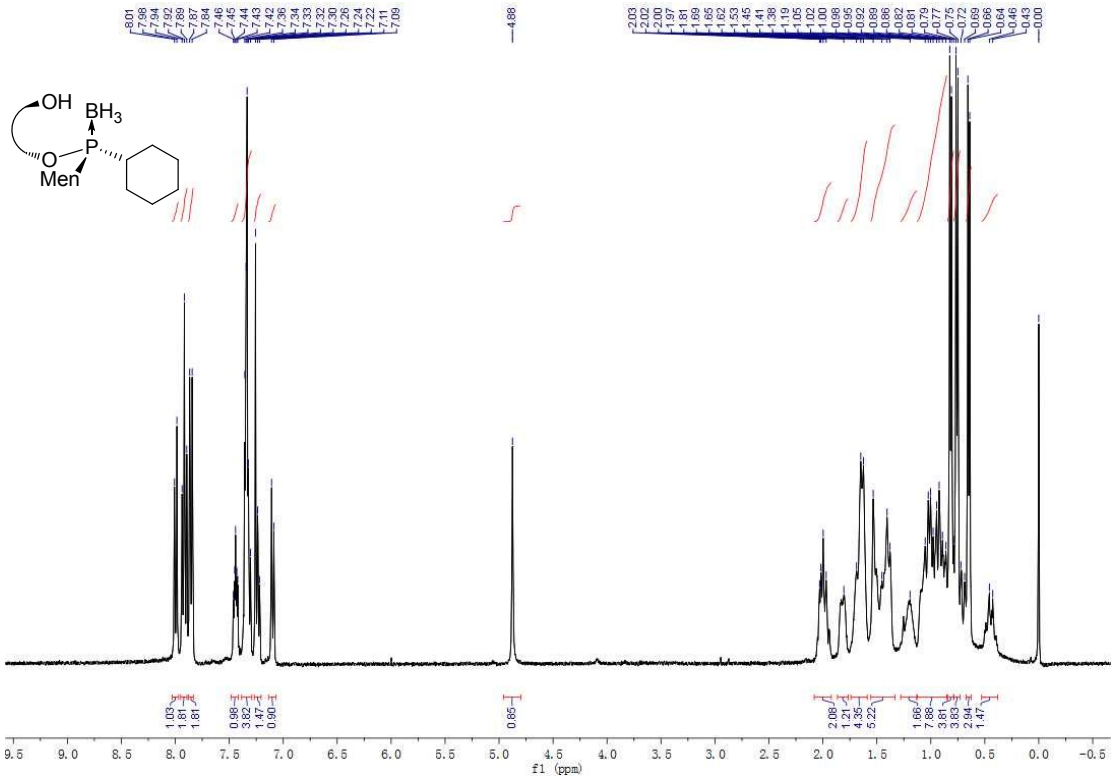


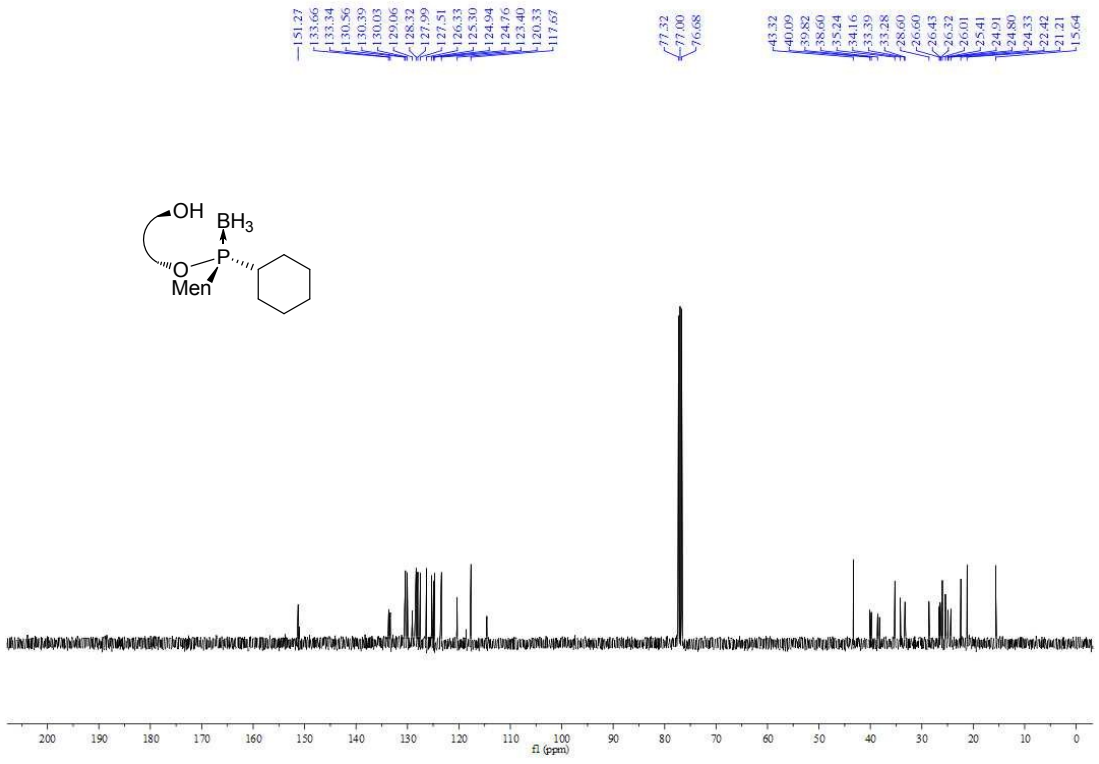


R_AR_P- (-)-menthyl cyclohexyl (2'-hydroxyl-1,1'-binaphthalen-2-yloxy) phosphine borane, 9d

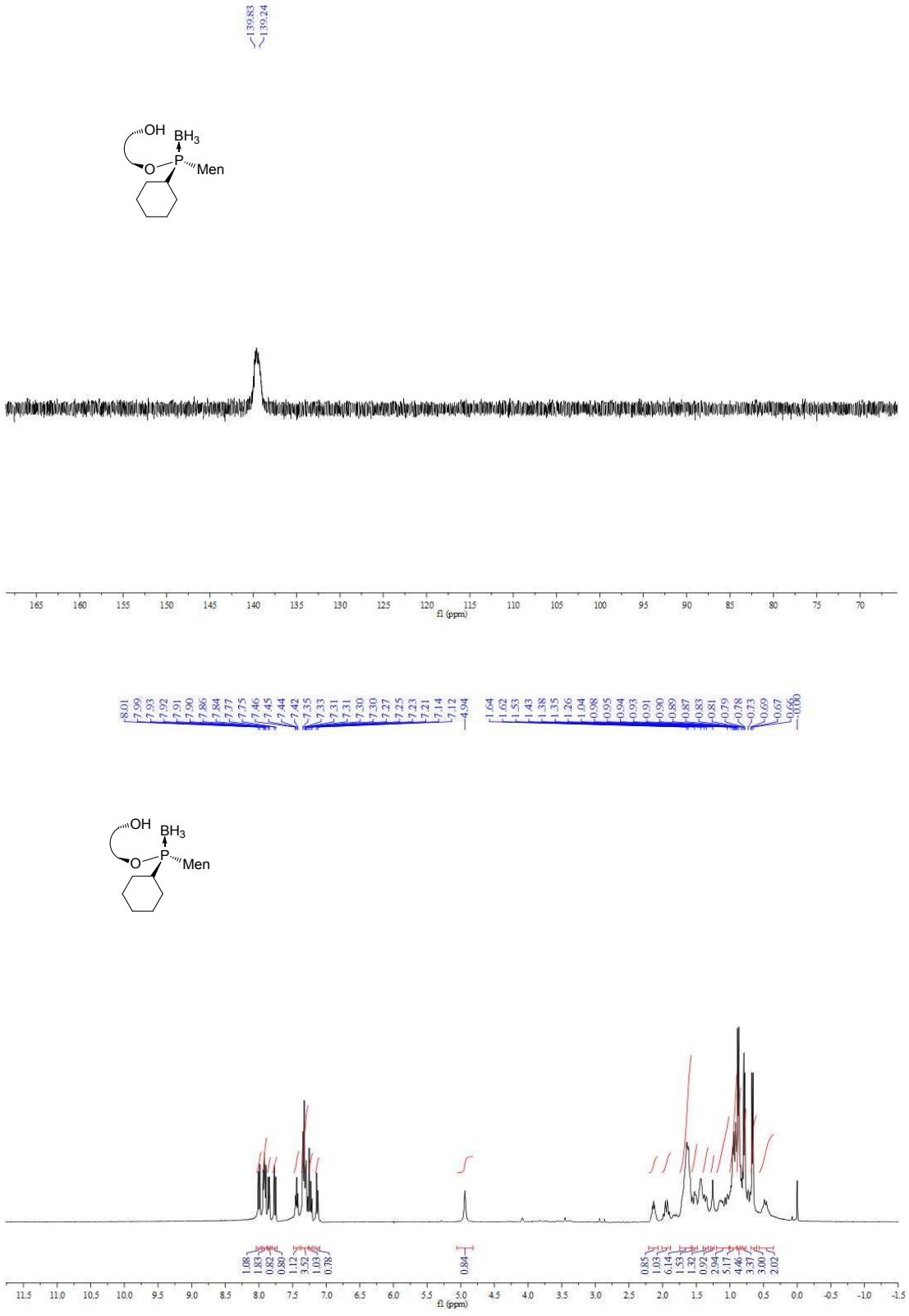


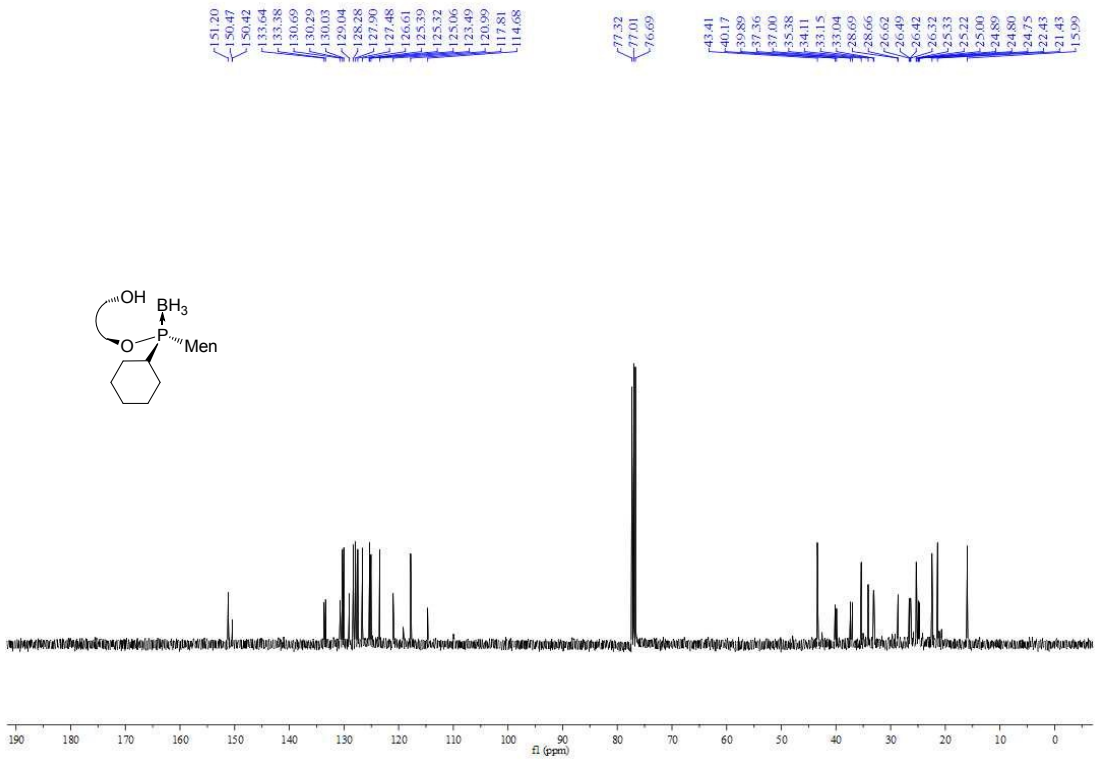



OH
BH3
O
P
Men
f1 (ppm)

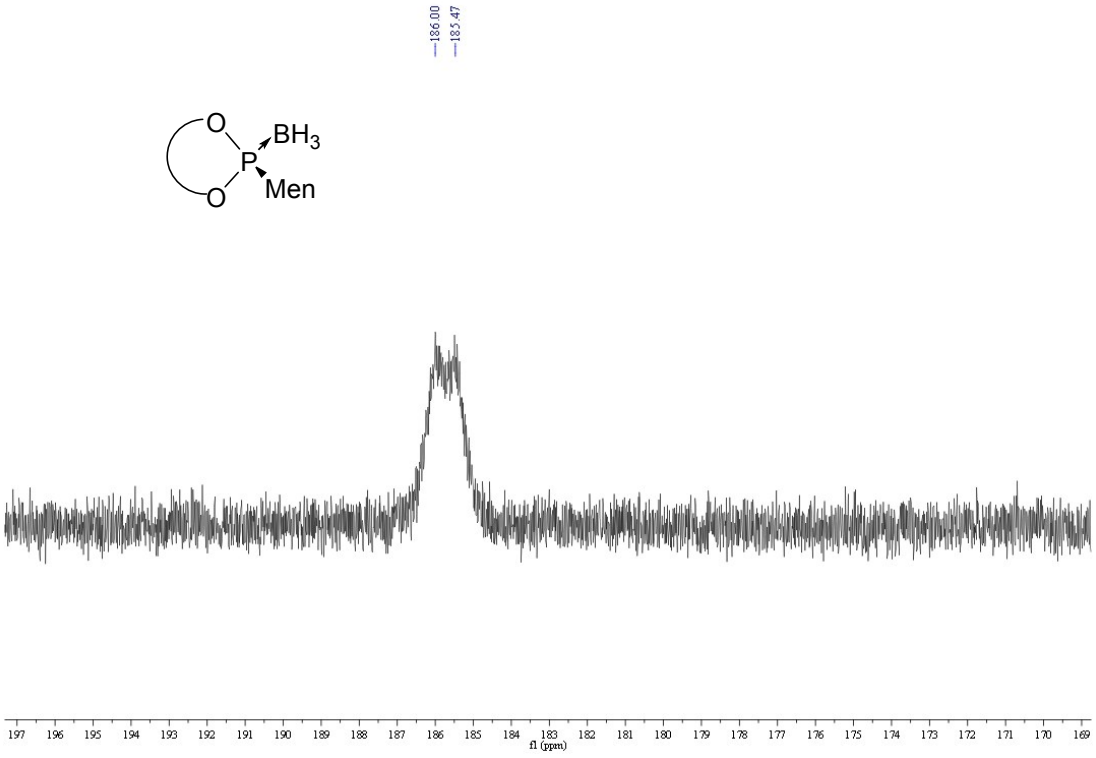

OH
BH3
O
P
Men
f1 (ppm)

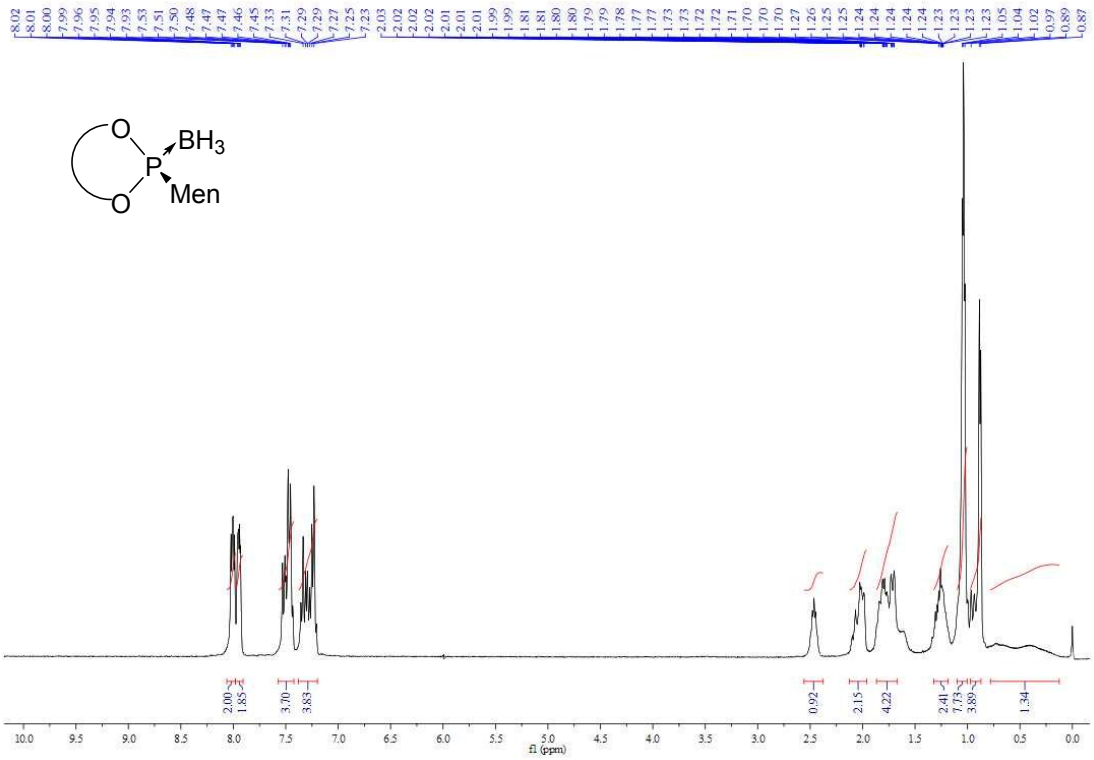
S_AS_P- (-)-menthyl cyclohexyl (2'-hydroxyl-1,1'-binaphthalen-2-yloxy) phosphine borane, 9e

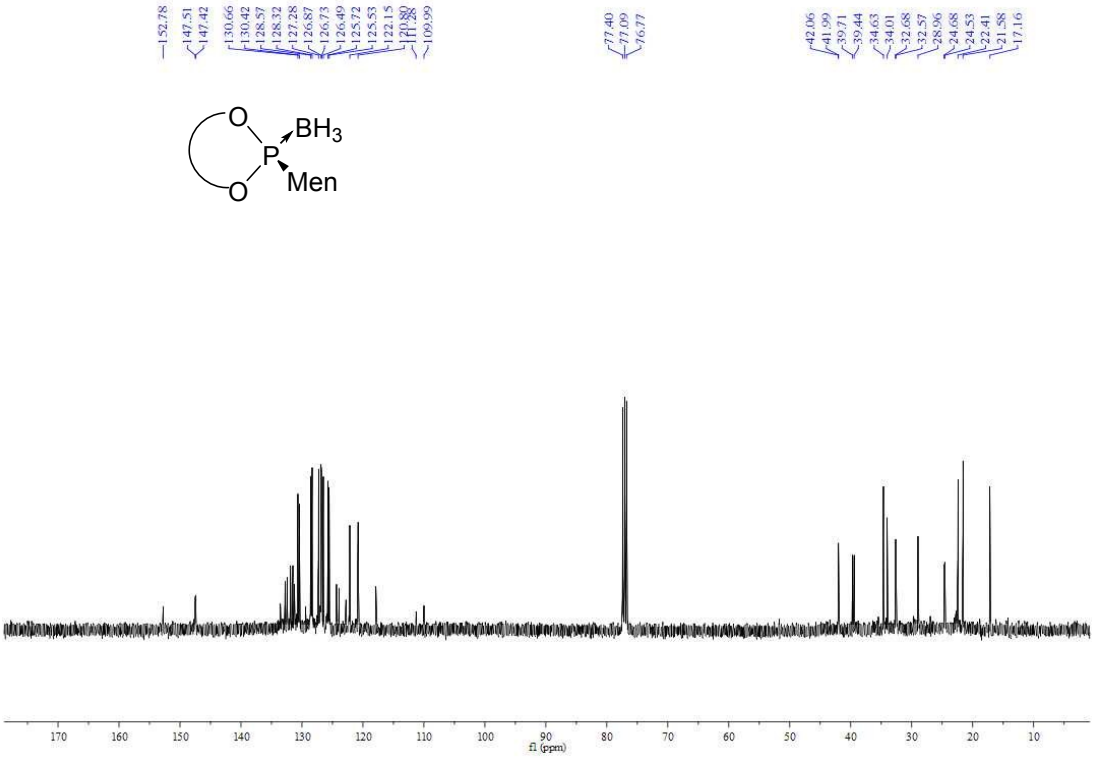




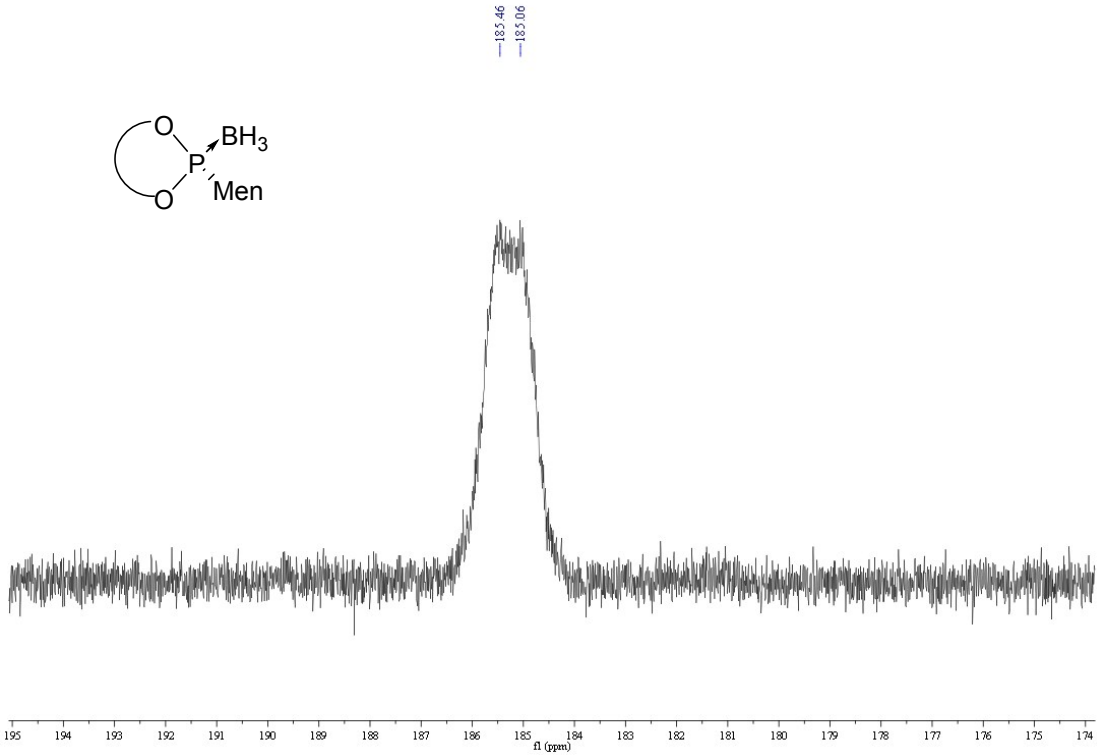
***R*-(-)-menthylbinaphthoxy phosphonites borane, 10a**

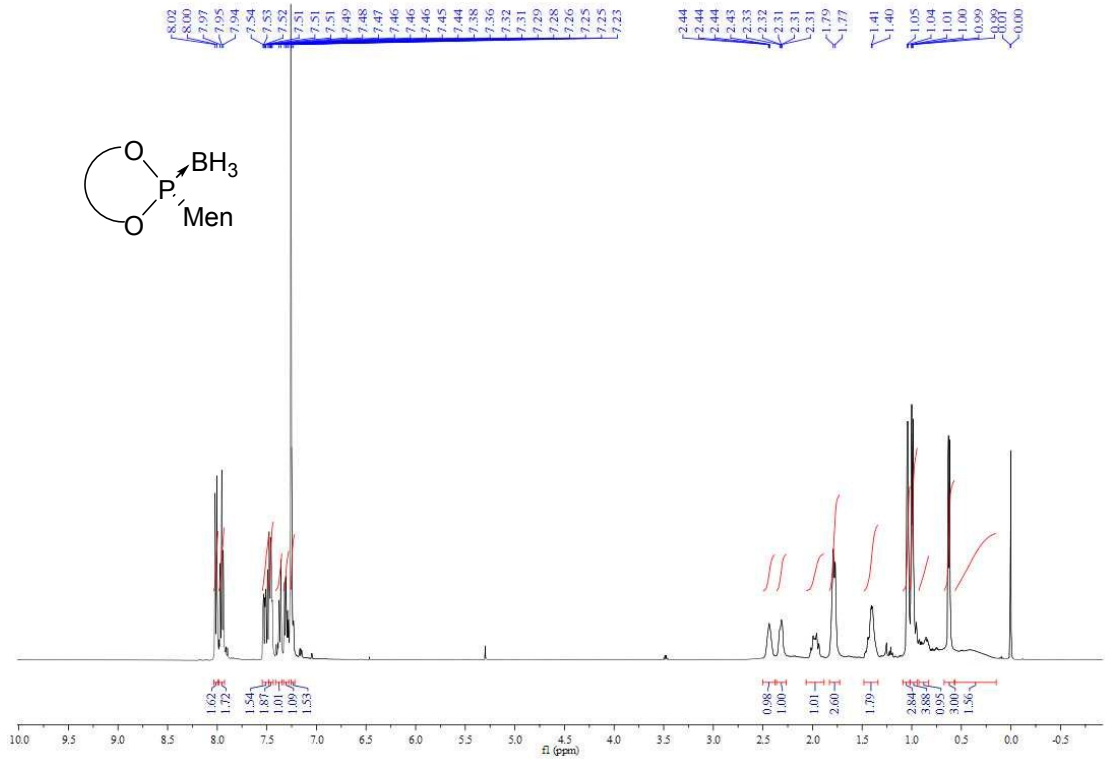


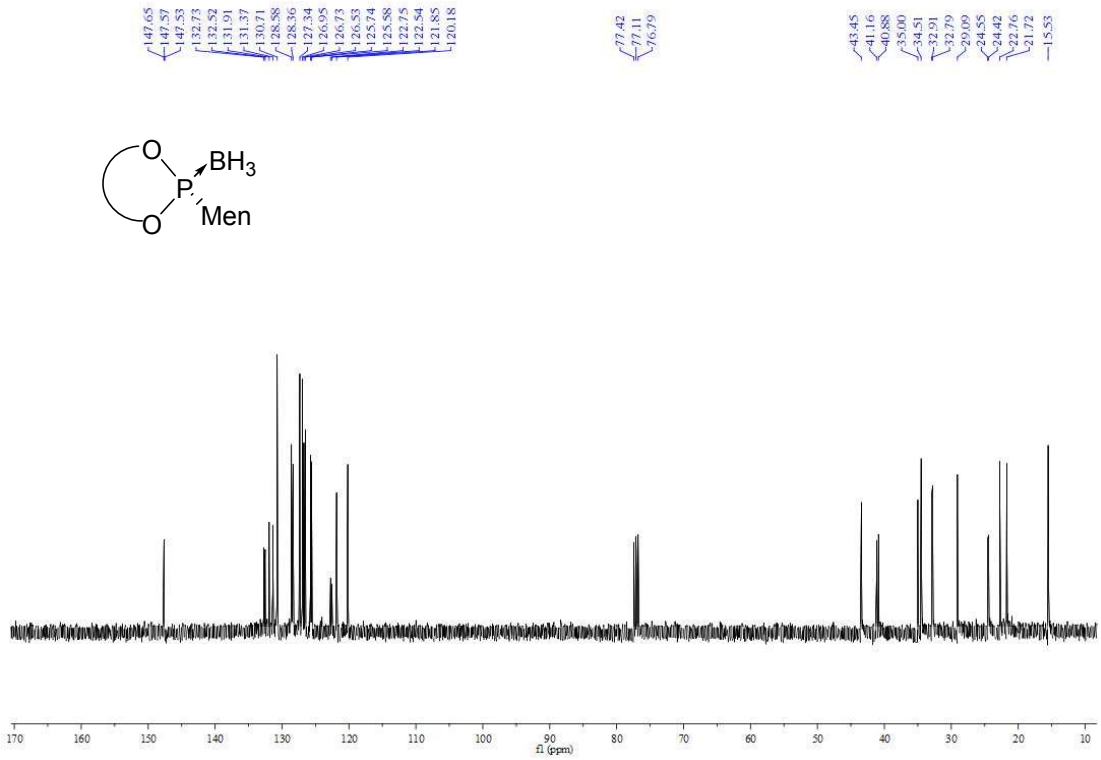

O
P
BH3
Men
O
fl (ppm)


O
P
BH3
Men
O
fl (ppm)

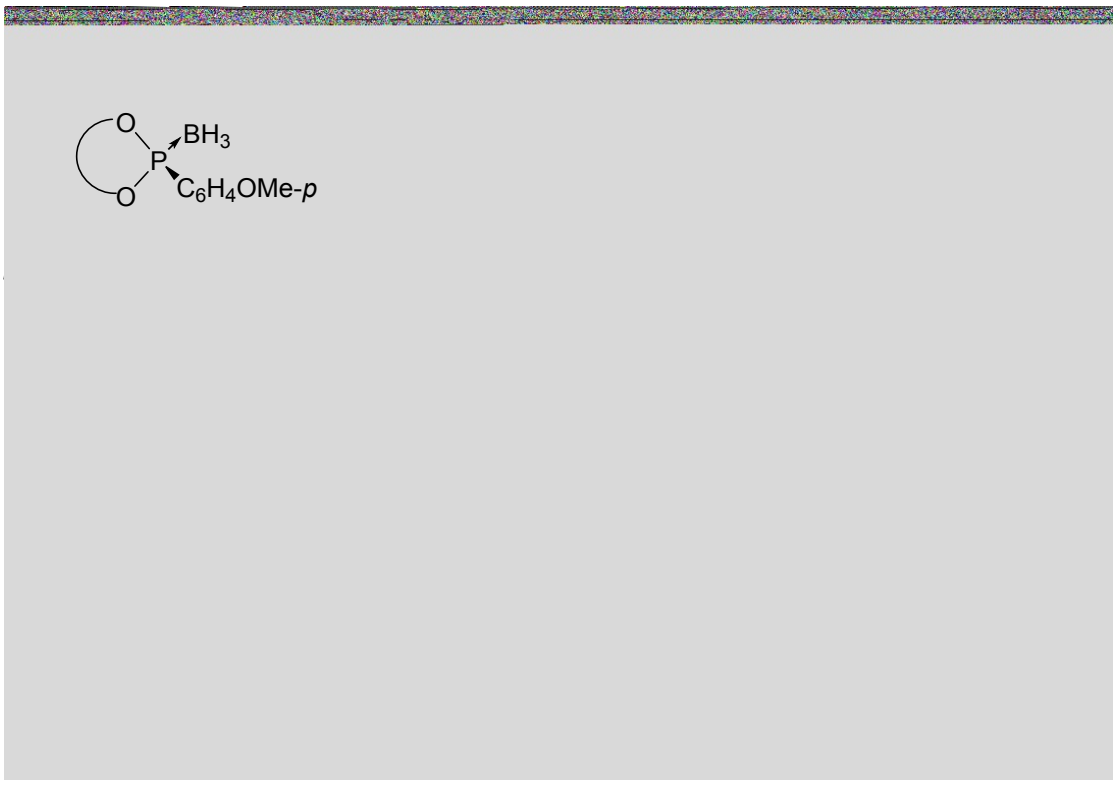
***S*-(-)-menthylbinaphthoxy phosphonites borane, 10a'**

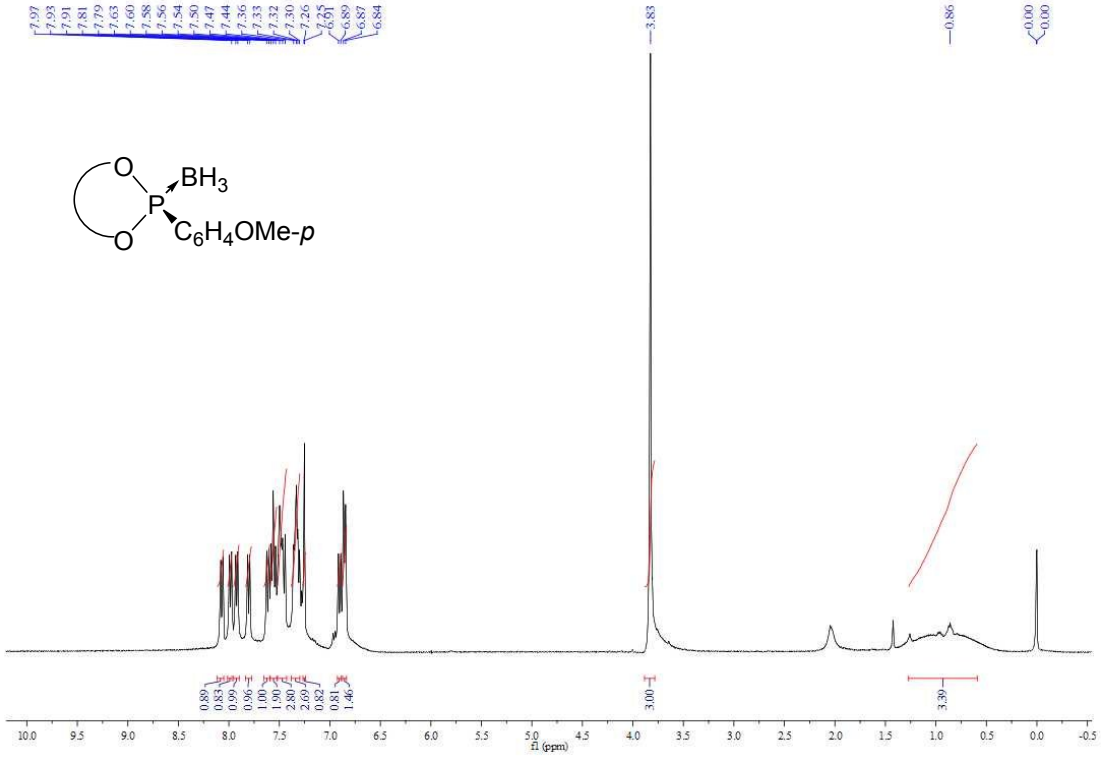


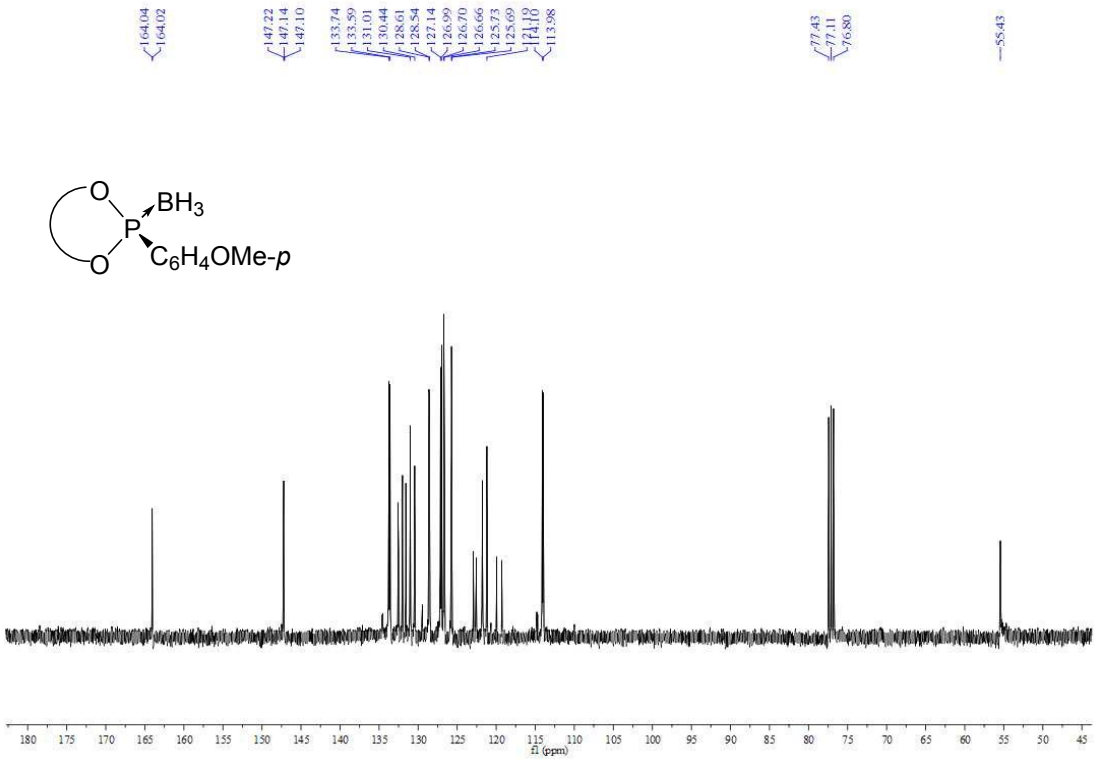




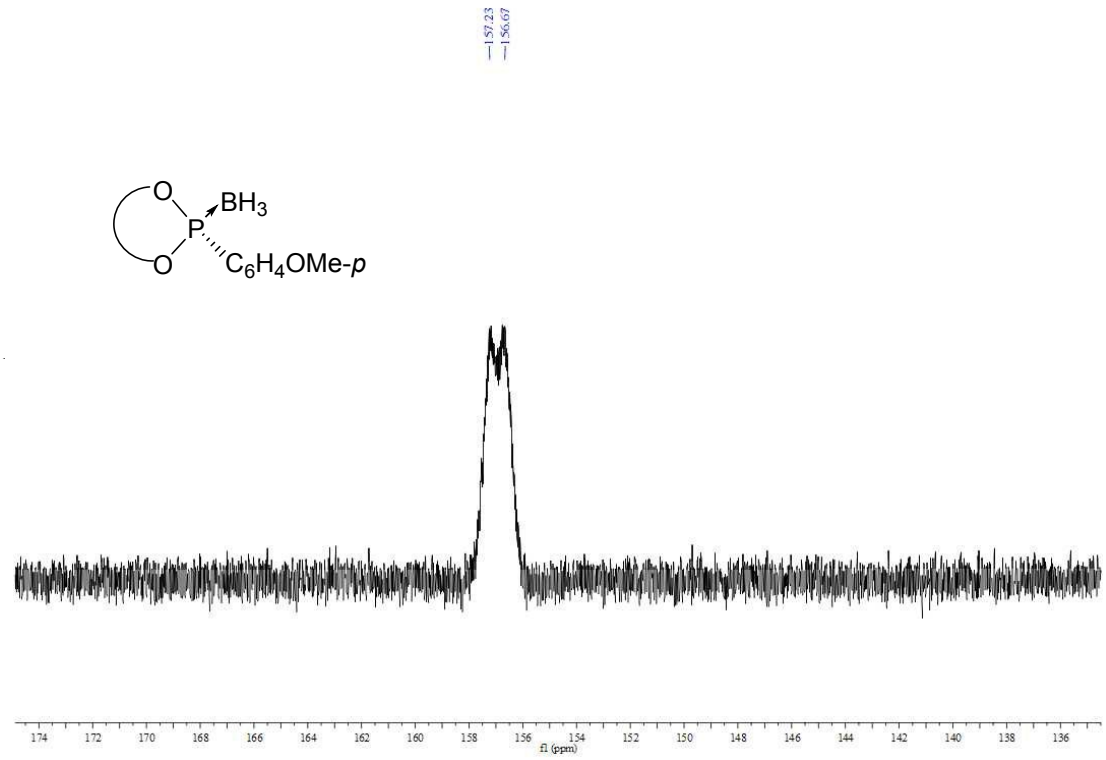
***R-p*-methyoxyphenyl binaphthoxy phosphonites borane, 10b**

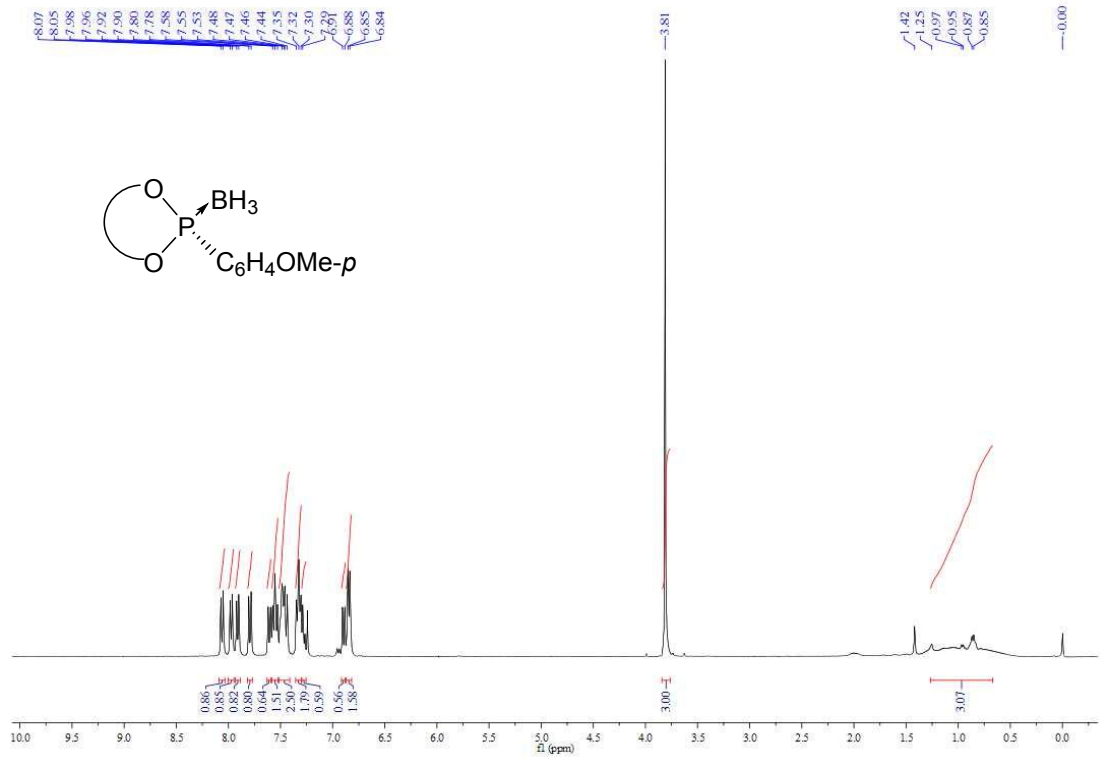


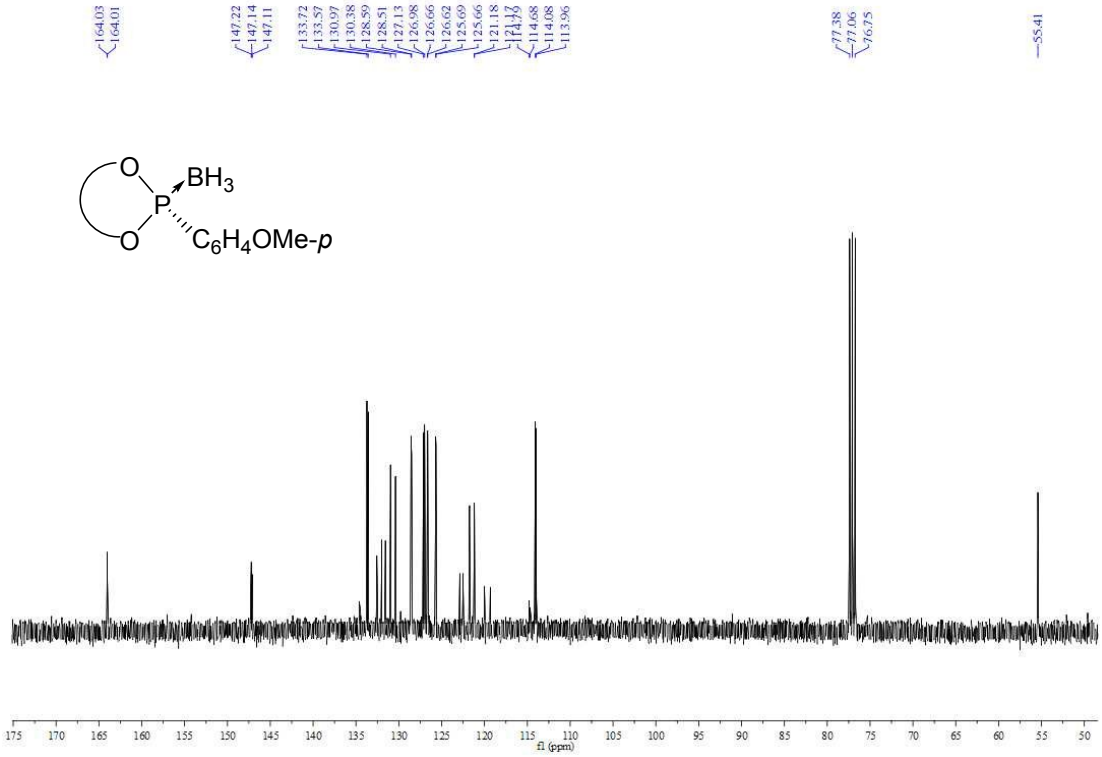

7.97
7.93
7.91
7.81
7.79
7.63
7.60
7.58
7.56
7.54
7.50
7.47
7.44
7.36
7.33
7.32
7.30
7.26
6.89
6.87
6.84
3.83
0.86
0.00
0.00
O
P
O
BH3
C6H4OMe-p
0.89
0.83
0.99
0.96
1.00
1.90
2.80
2.69
0.82
0.81
1.46
3.00
3.39
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


164.04
164.02
147.22
147.14
147.10
133.74
133.59
131.01
130.44
128.61
128.54
127.14
126.99
126.70
126.66
125.73
125.69
114.10
113.98
77.43
77.11
76.80
55.43
O
P
O
BH3
C6H4OMe-p
180
175
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
f1 (ppm)

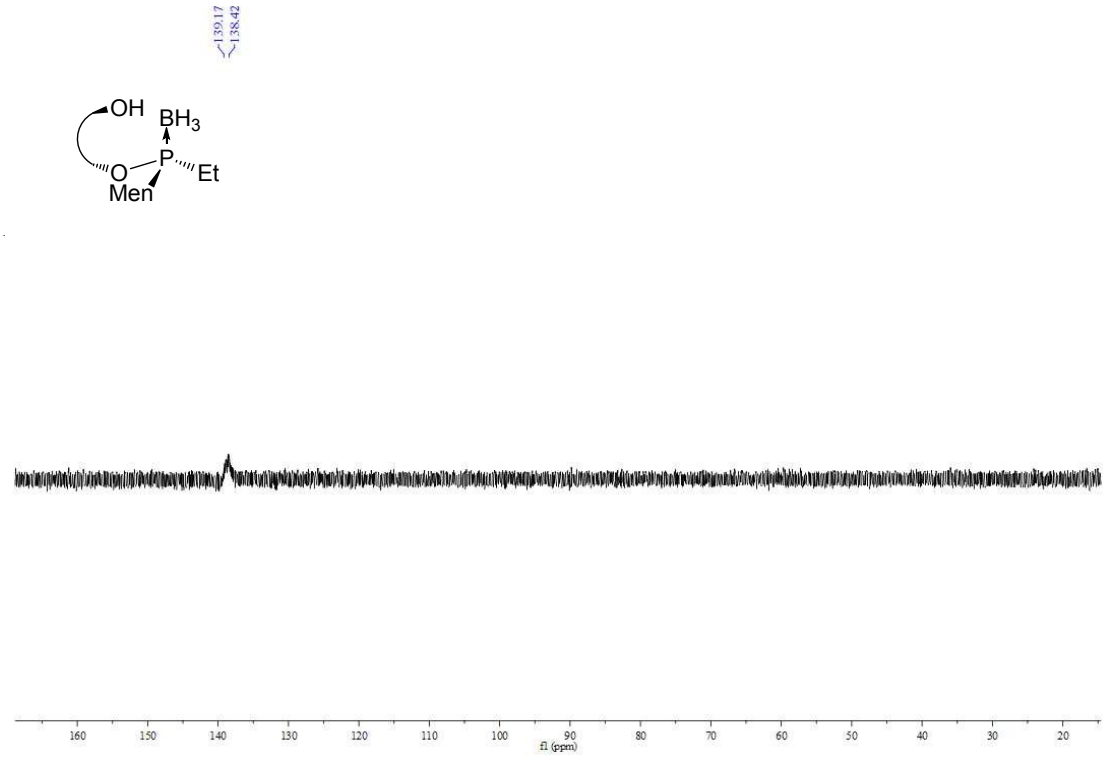
***S-p*-methyoxyphenyl binaphthoxy phosphonites borane, 10b'**

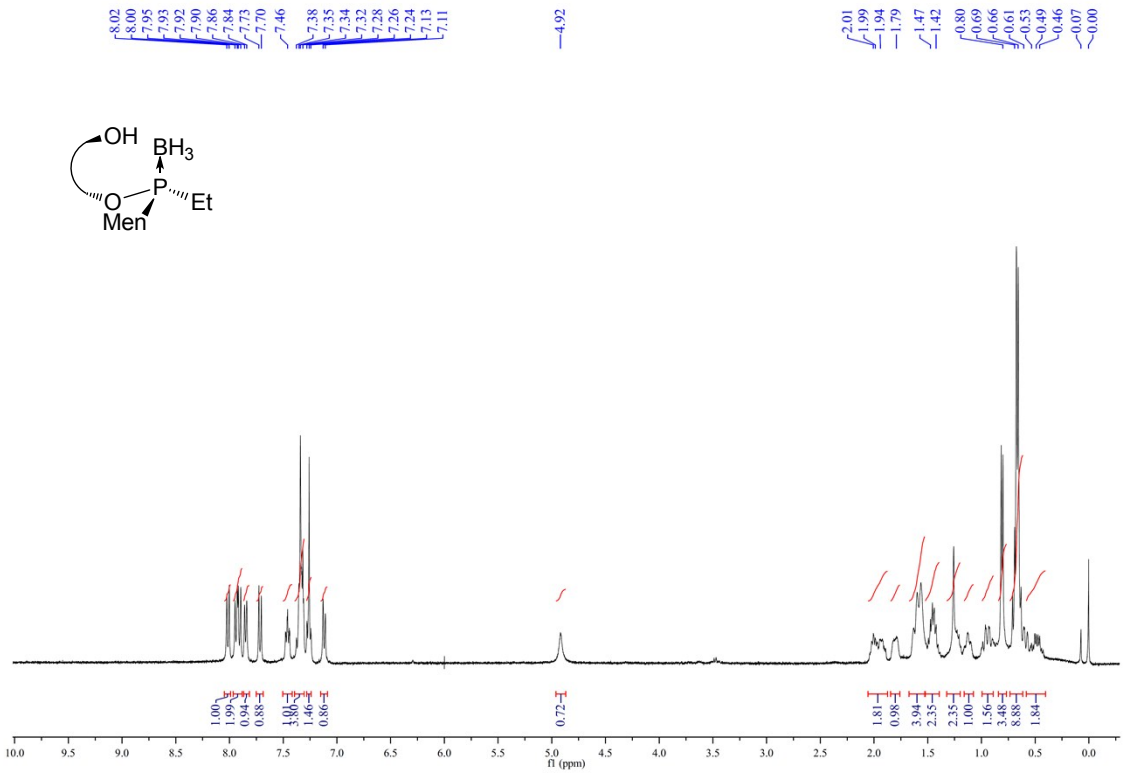


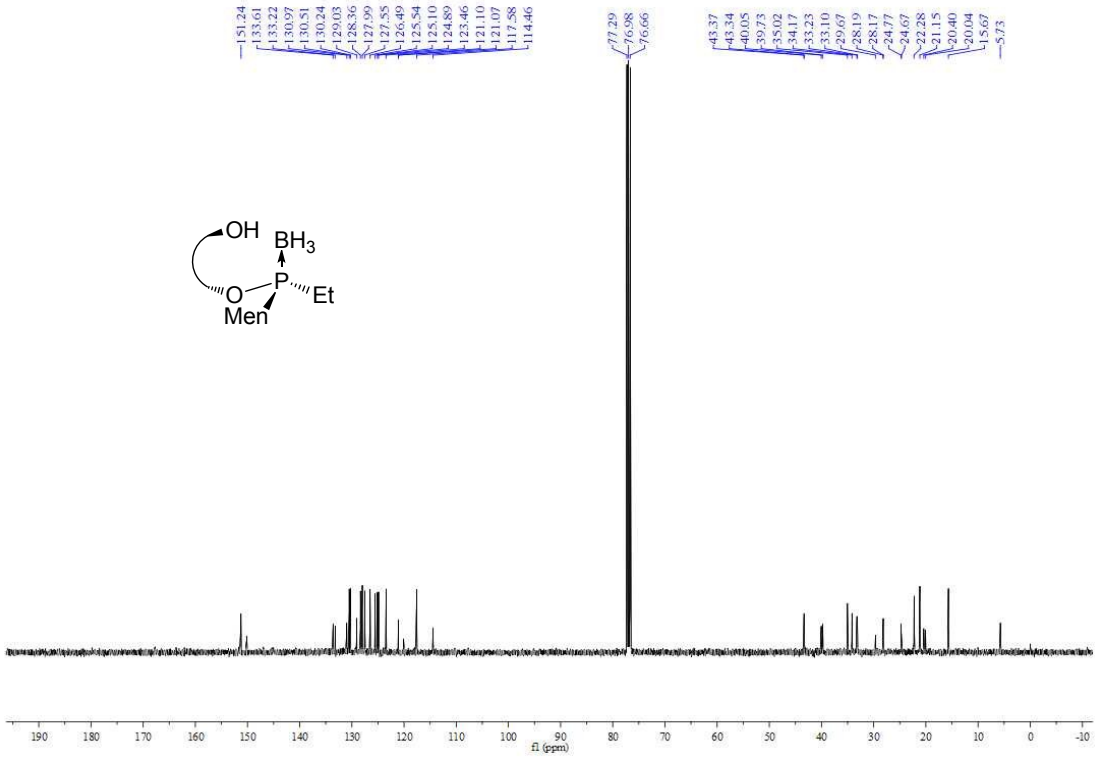




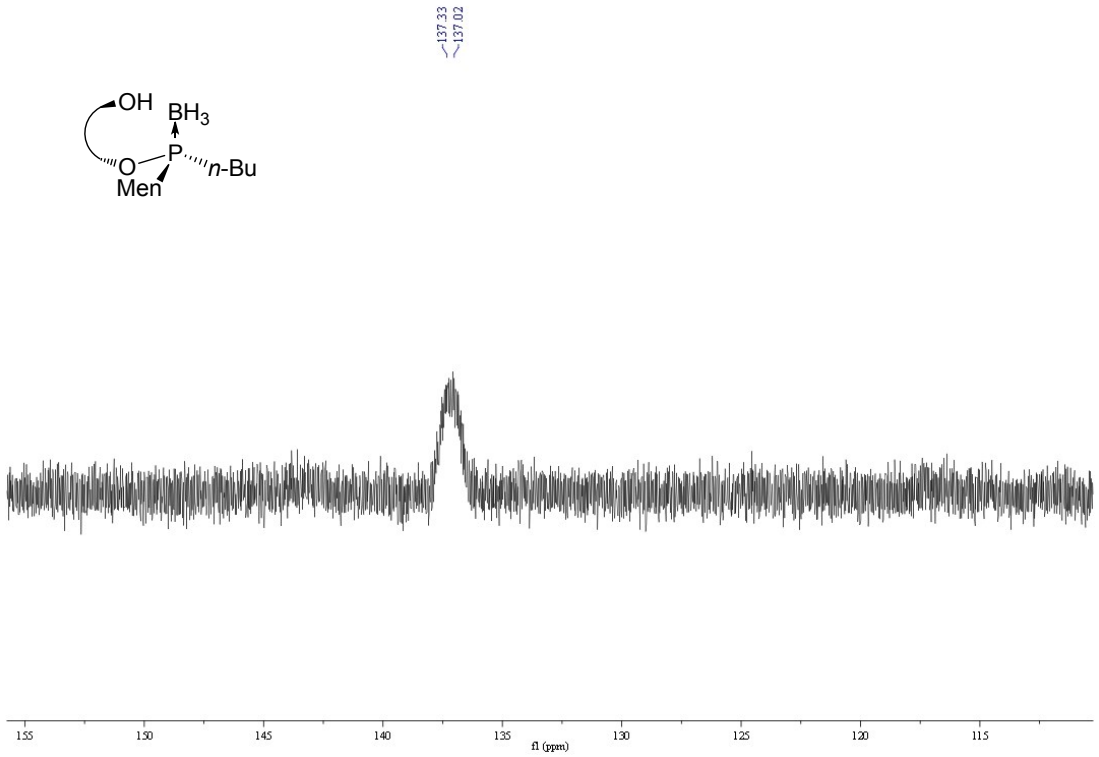
R_AR_P- (-)-menthyl ethyl (2'-hydroxyl-1,1'-binaphthalen-2-yloxy) phosphine borane, 9a

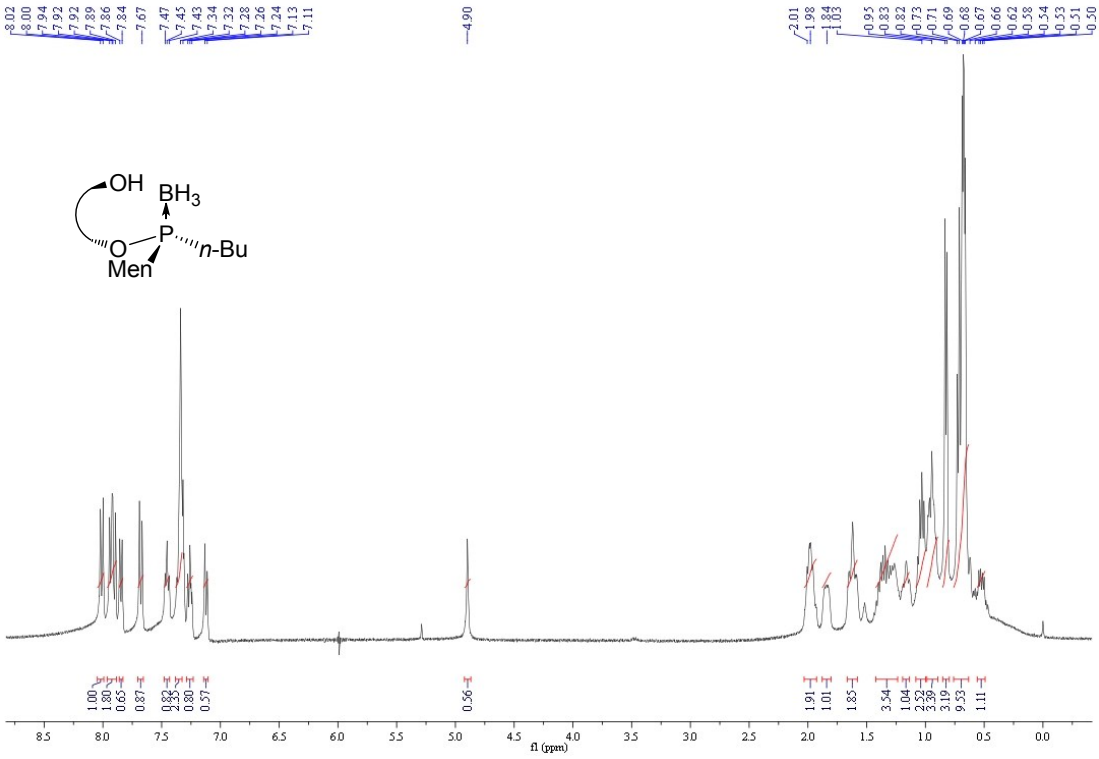


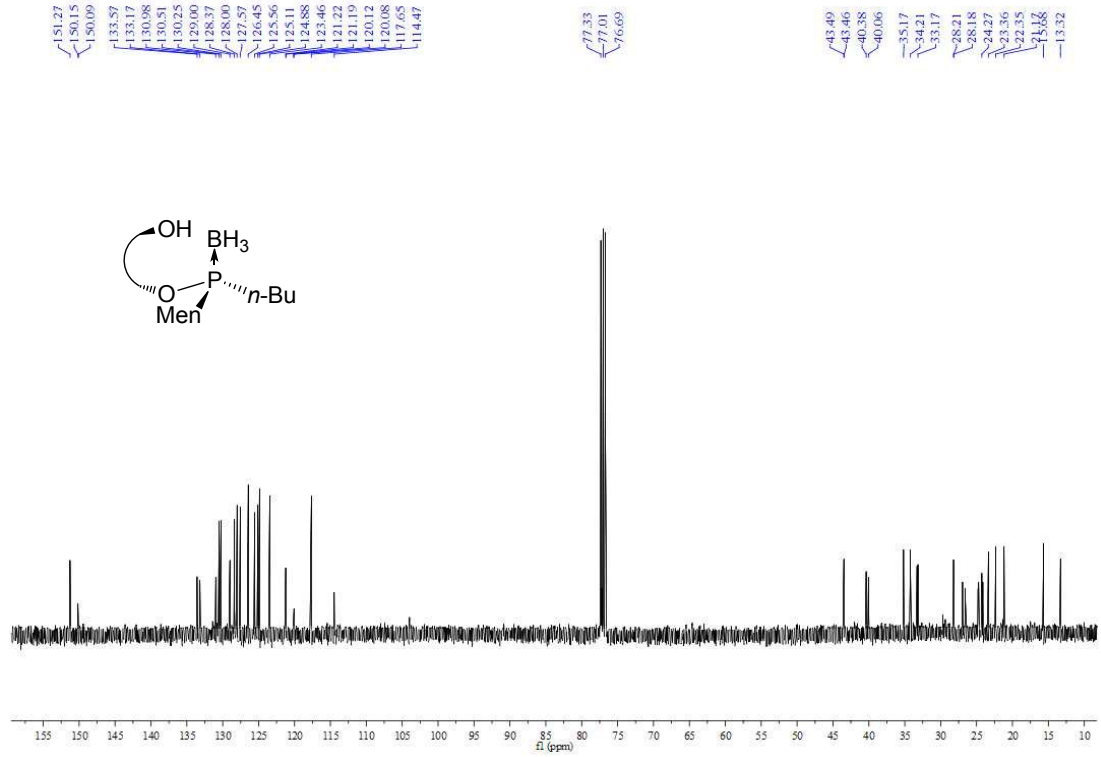

8.02
8.00
7.95
7.93
7.92
7.90
7.86
7.84
7.73
7.70
7.46
7.38
7.35
7.34
7.32
7.28
7.26
7.24
7.13
7.11
4.92
2.01
1.99
1.94
1.79
1.47
1.42
0.80
0.69
0.66
0.61
0.53
0.49
0.46
0.07
0.00
OH
BH3
P
Et
O
Men
f1 (ppm)


151.24
133.61
133.22
130.97
130.51
130.24
129.03
128.36
127.99
127.55
126.49
125.54
125.10
124.89
123.46
121.10
121.07
117.58
114.46
77.29
76.98
76.66
43.37
43.34
40.05
39.73
35.02
34.17
33.23
33.10
29.67
28.19
28.17
24.77
24.67
22.28
21.15
20.40
20.04
15.67
5.73
OH
BH3
P
Et
O
Men
f1 (ppm)

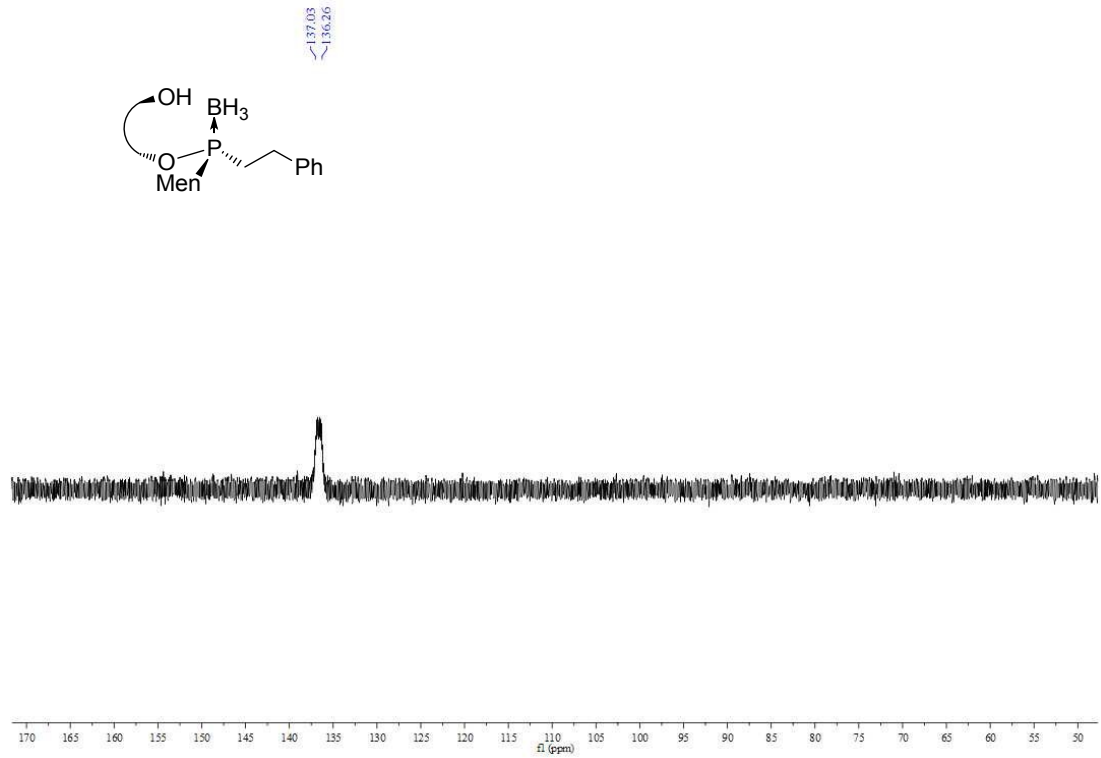
R_AR_P- (-)-menthyl butyl (2'-hydroxyl-1,1'-binaphthalen-2-yloxy)phosphine borane, 9b

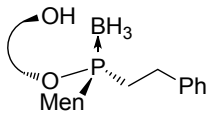


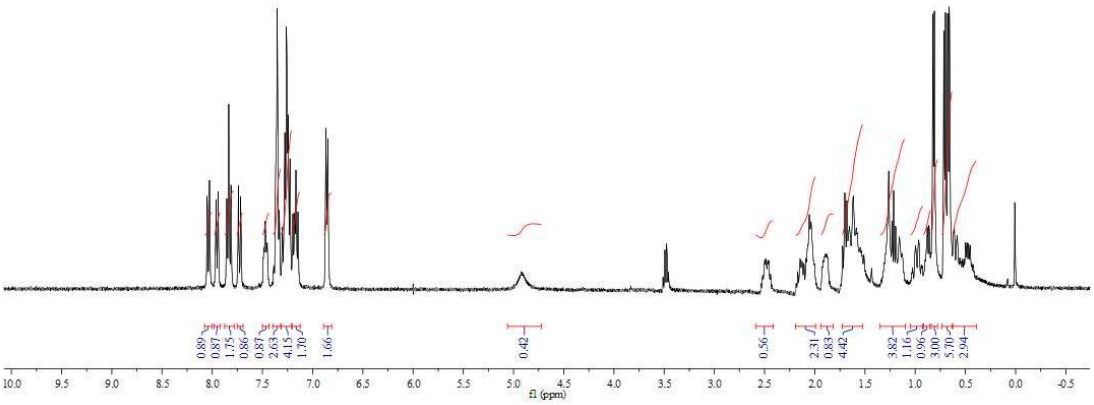


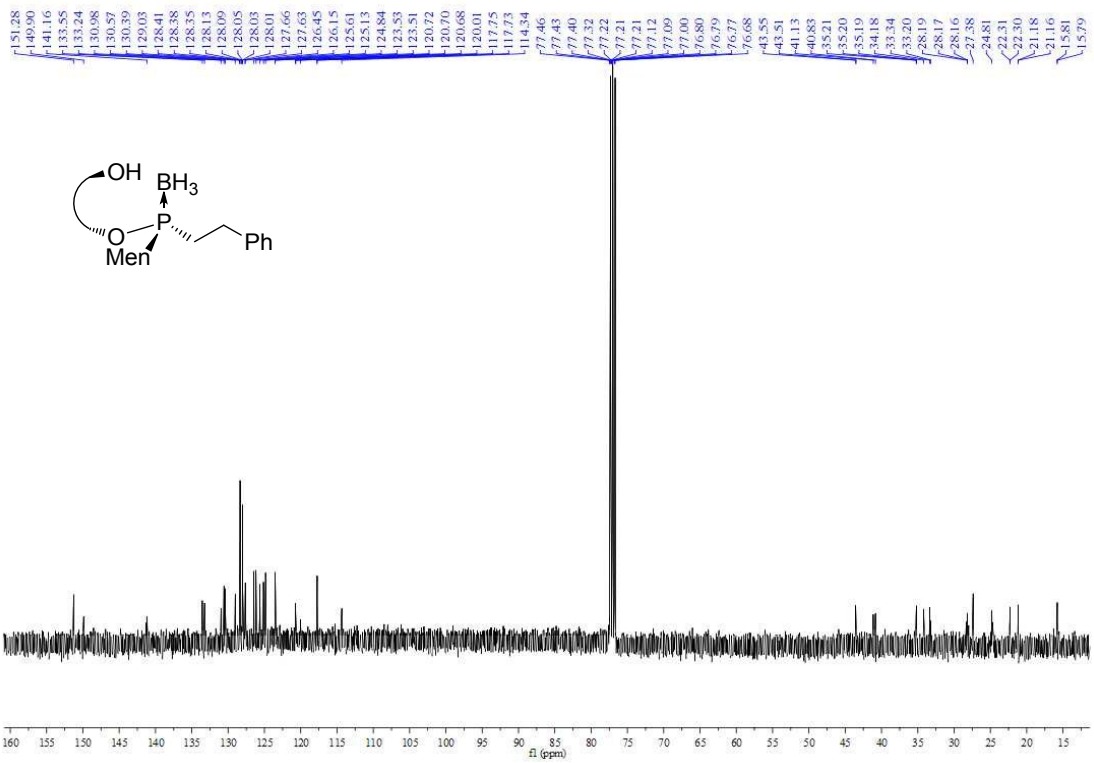


***R*$_A$*R*$_P$- (-)-menthyl b-phenylethyl (2'-hydroxyl-1,1'-binaphthalen-2-yloxy)phosphine borane, 9c**



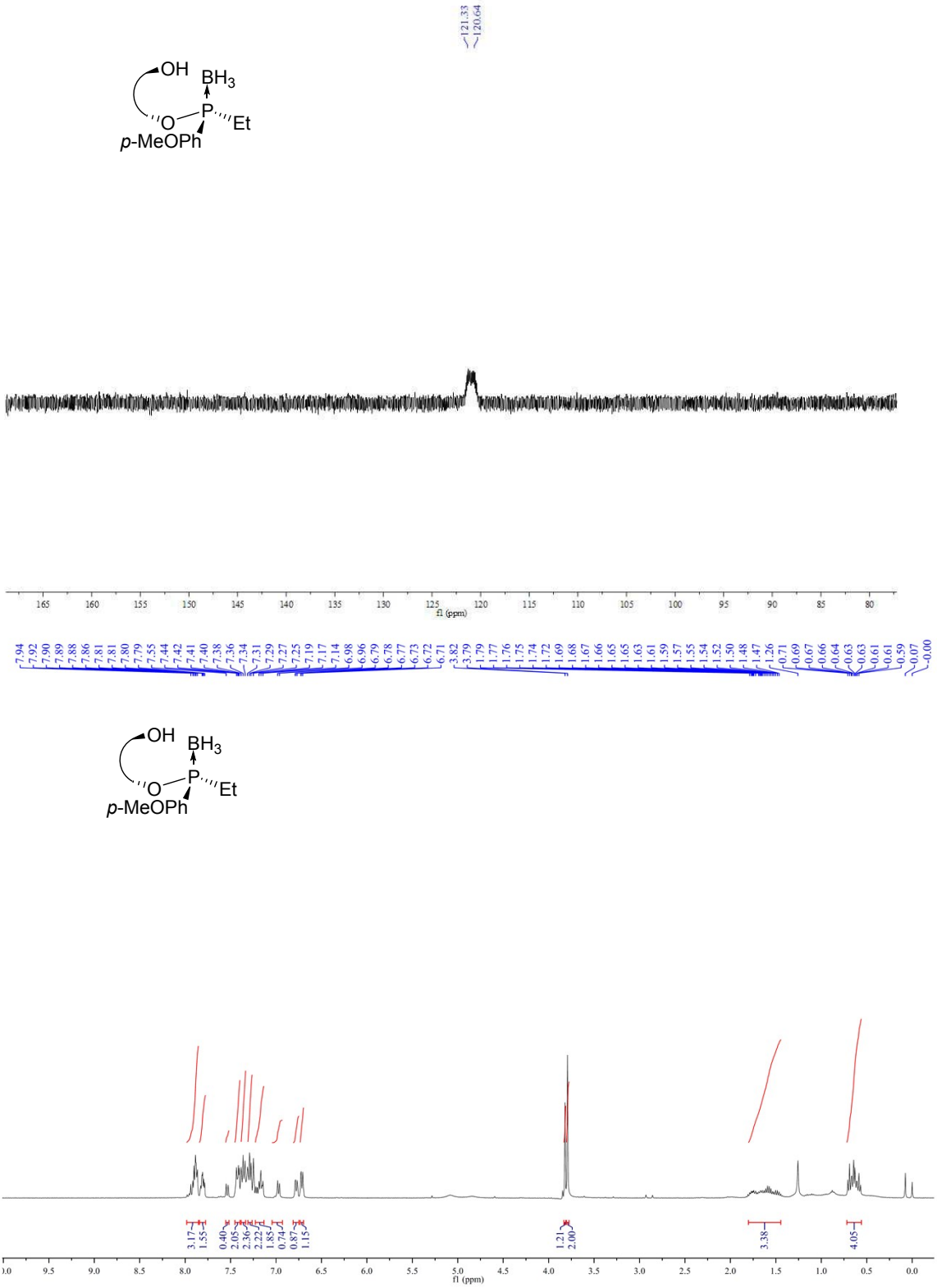

OH
BH3
P
O
Men
Ph

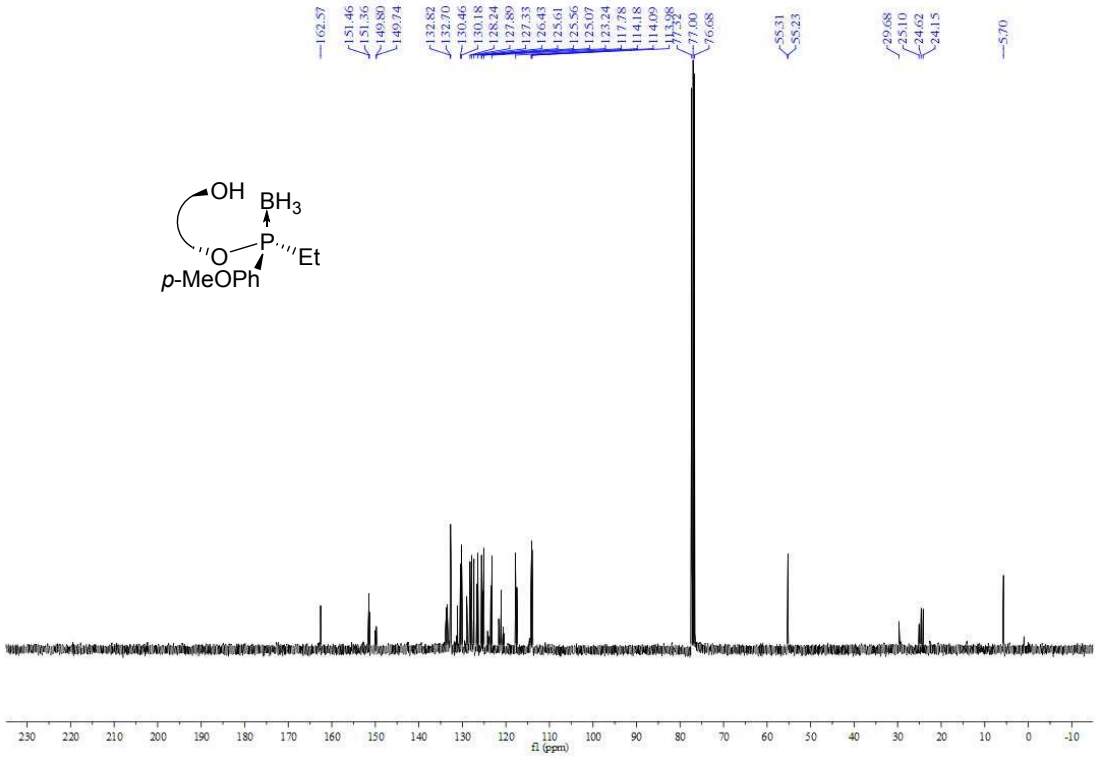




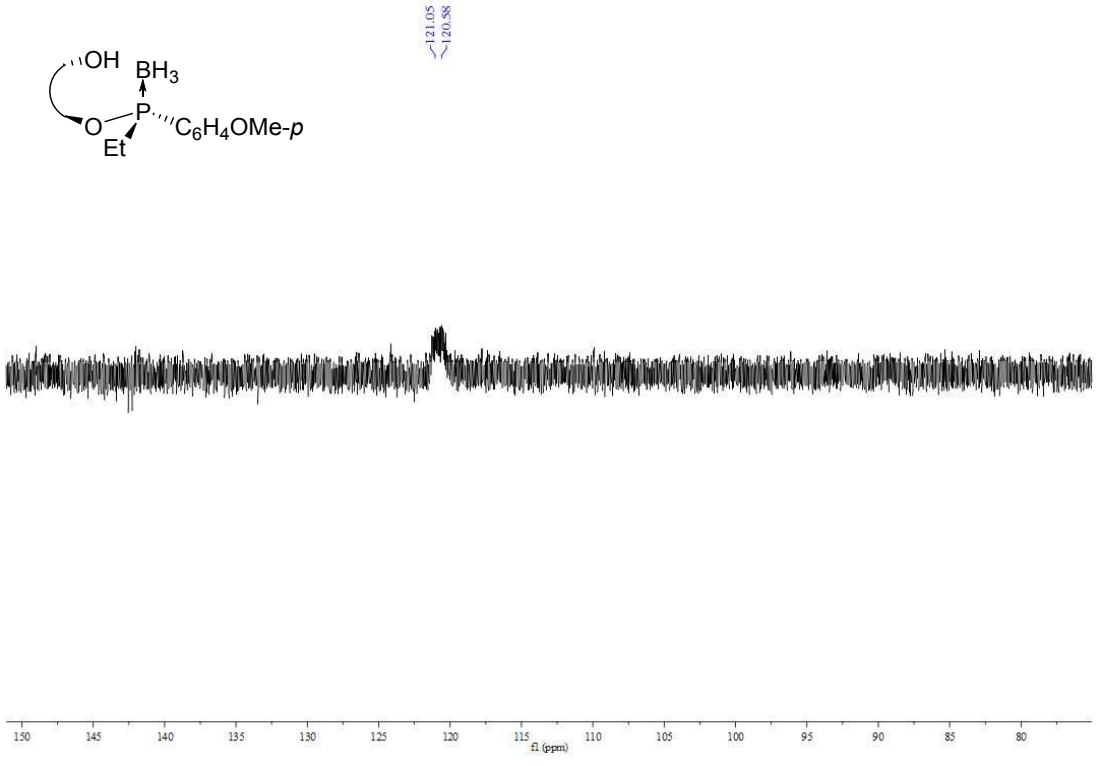
OH
BH3
P
O
Men
Ph

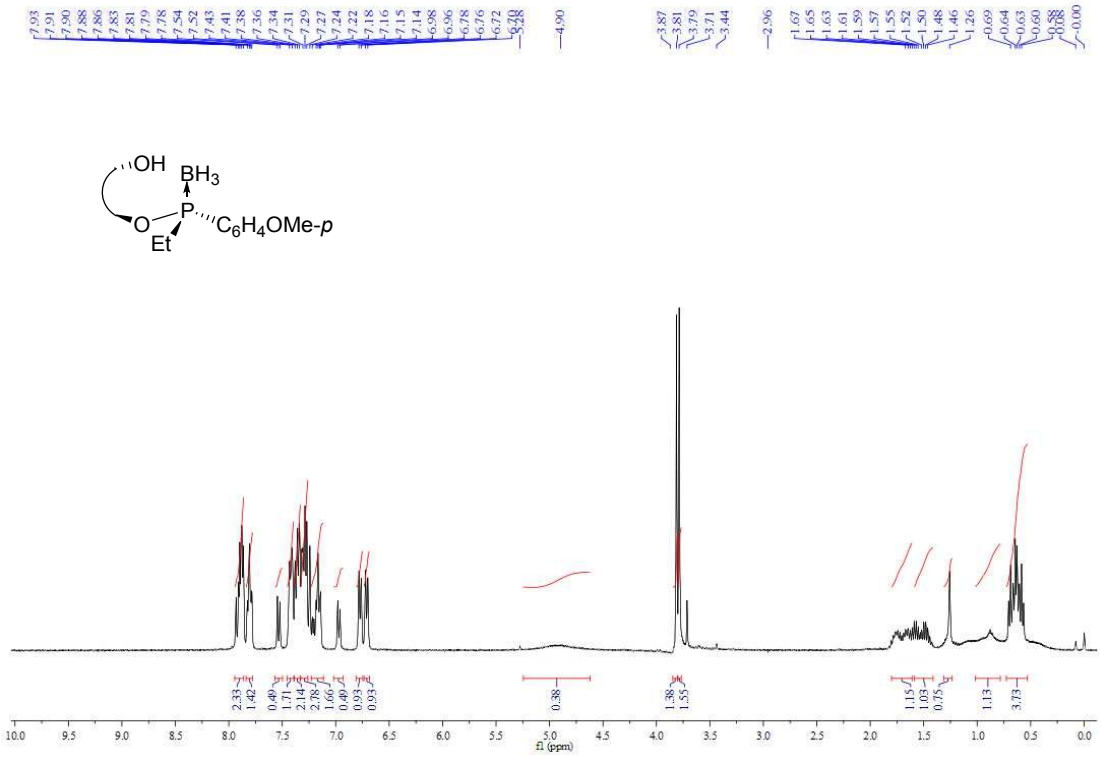
R_A-(-)- *p*-methyoxyphenyl ethyl (2'-hydroxyl-1,1'-binaphthalen-2-yloxy) phosphine borane, 9f/9f'



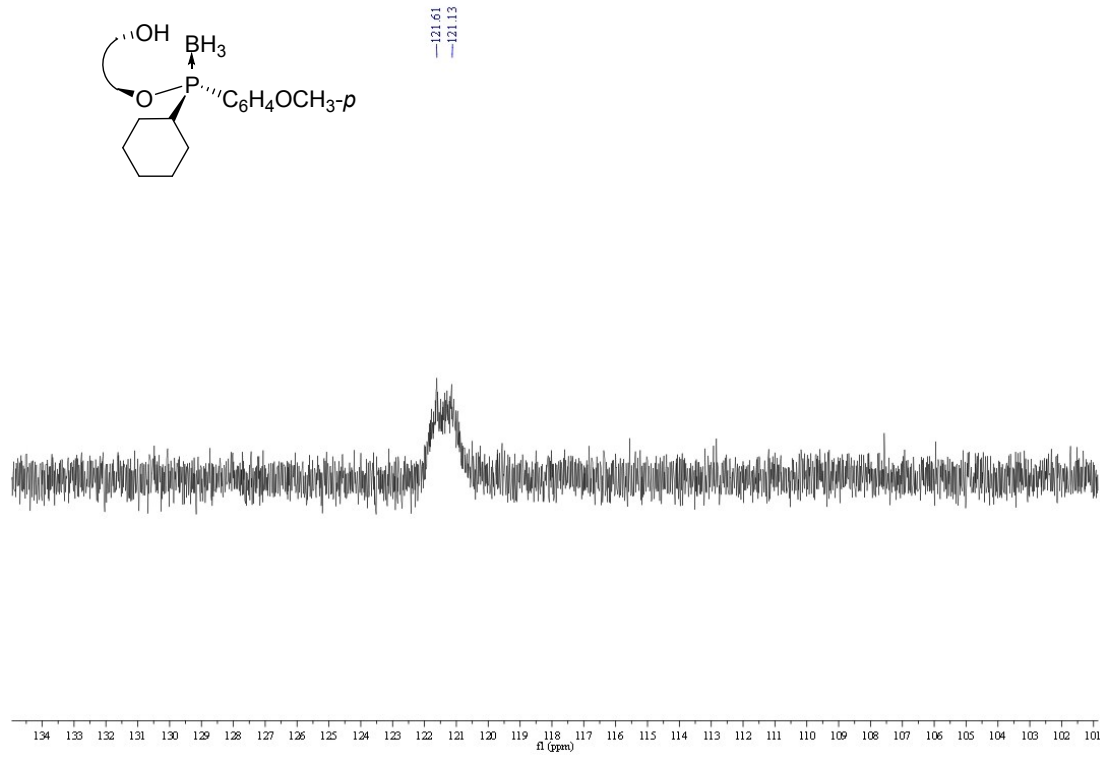


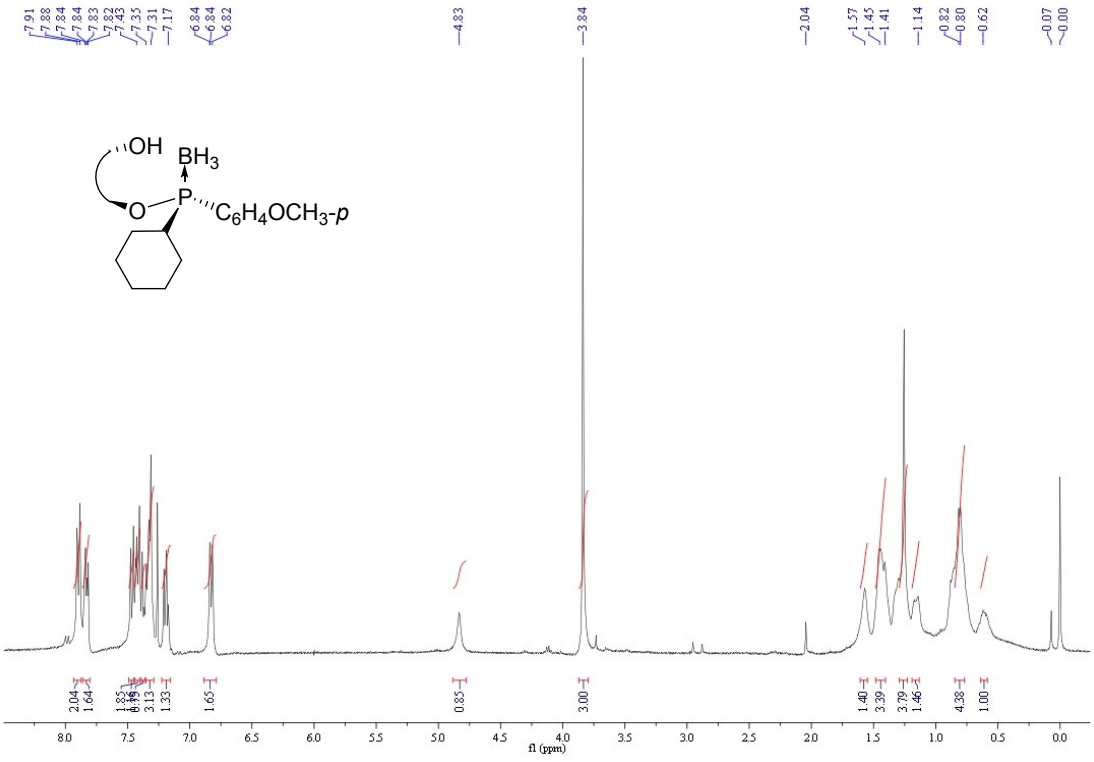
(R_P/S_P)-(-)- *p*-methyoxyphenyl ethyl (2'-hydroxyl-1,1'-binaphthalen-2-yloxy)phosphine borane, 9g/9g'

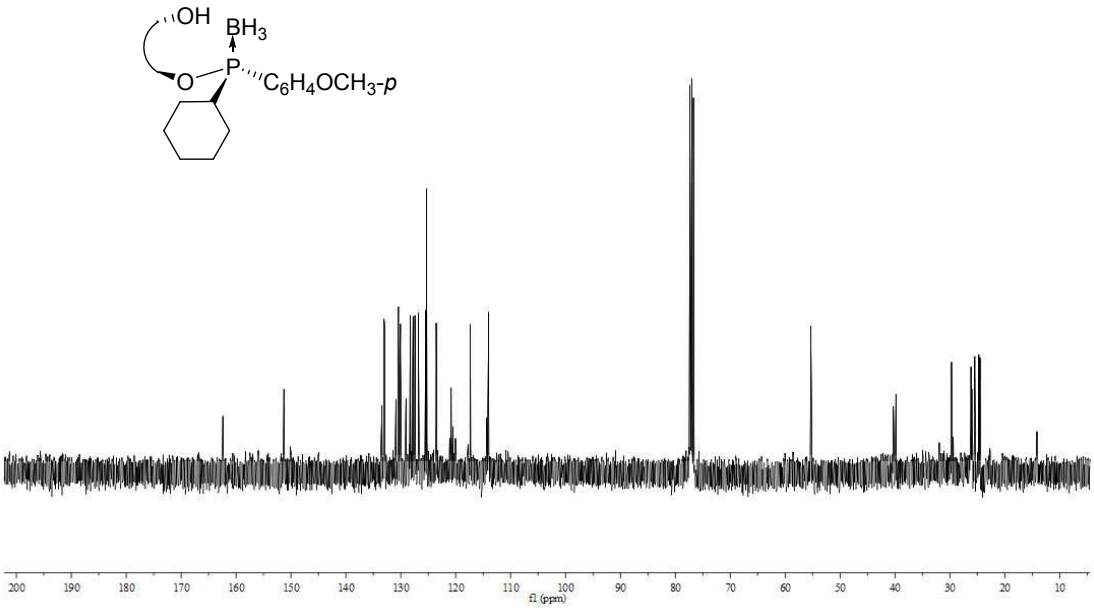




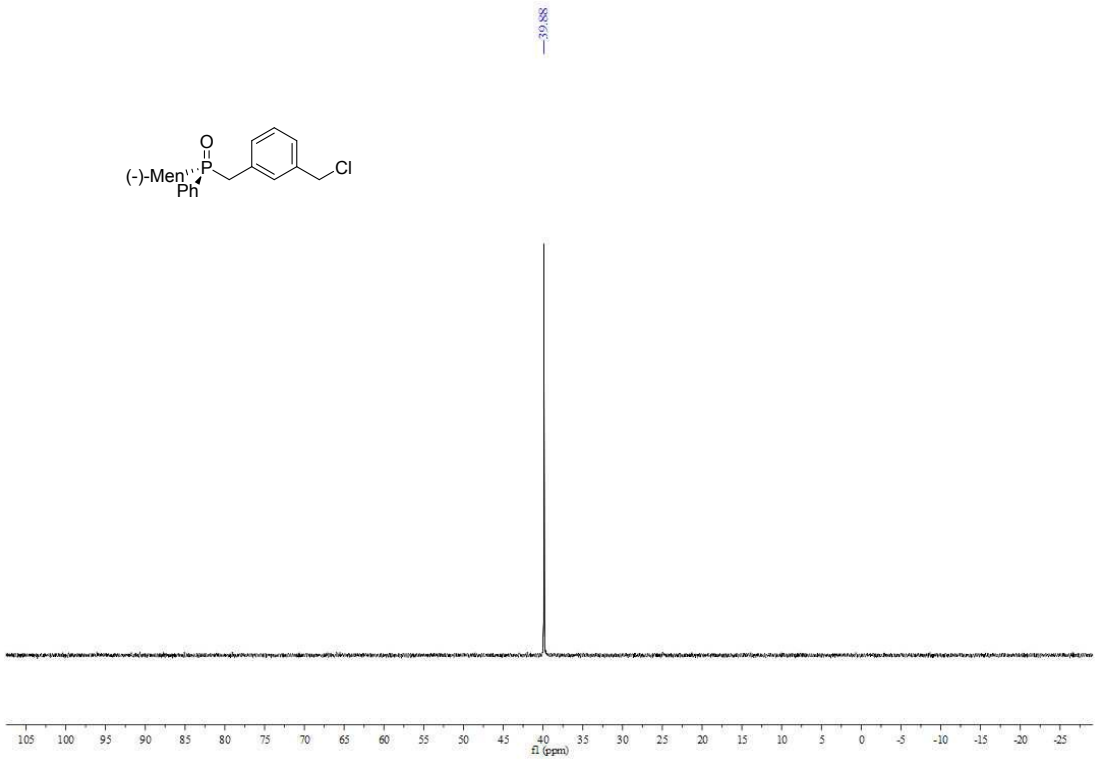
S_A-(-)-*p*-methyoxyphenyl cyclohexyl (2'-hydroxyl-1,1'-binaphthalen-2-yloxy)phosphine borane, 9i

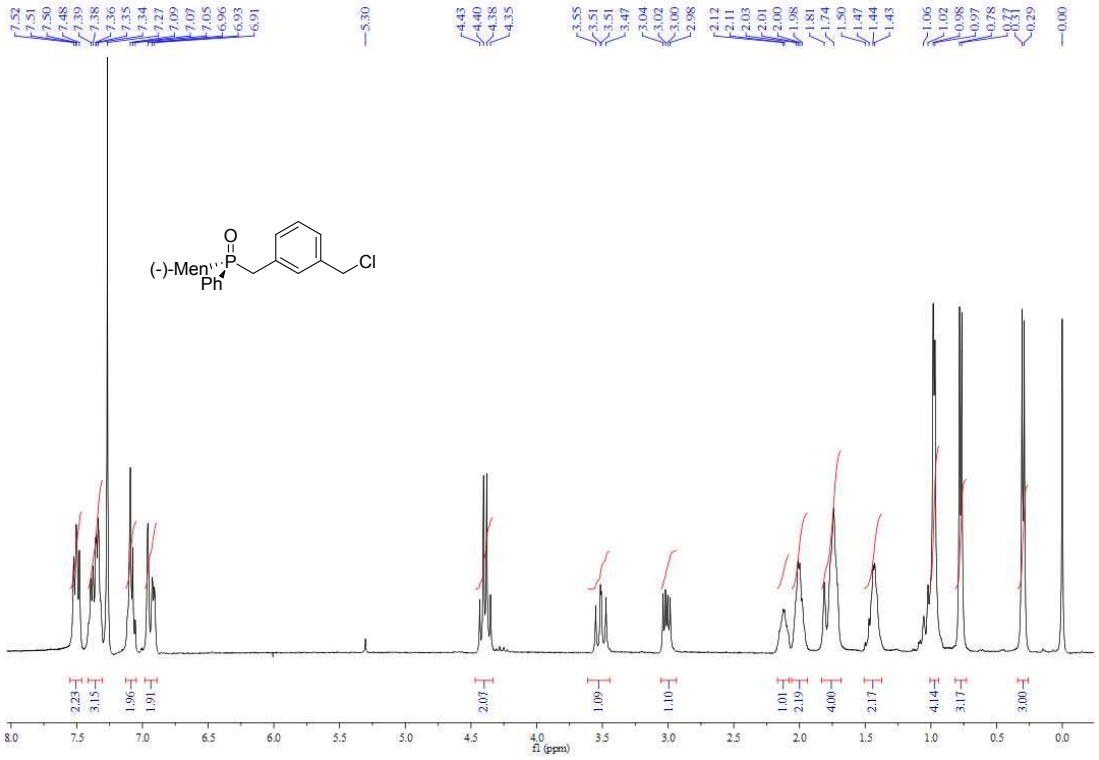


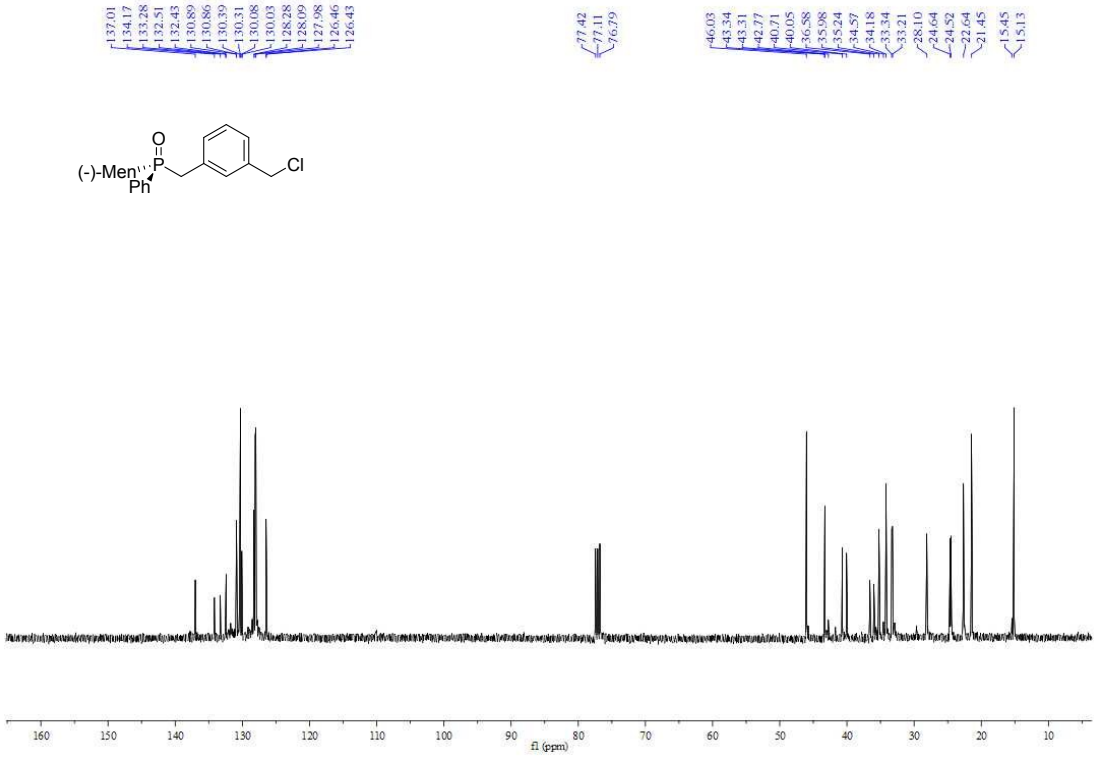

OH
BH3
O
P
C6H4OCH3-p
f1 (ppm)


OH
BH3
O
P
C6H4OCH3-p
f1 (ppm)

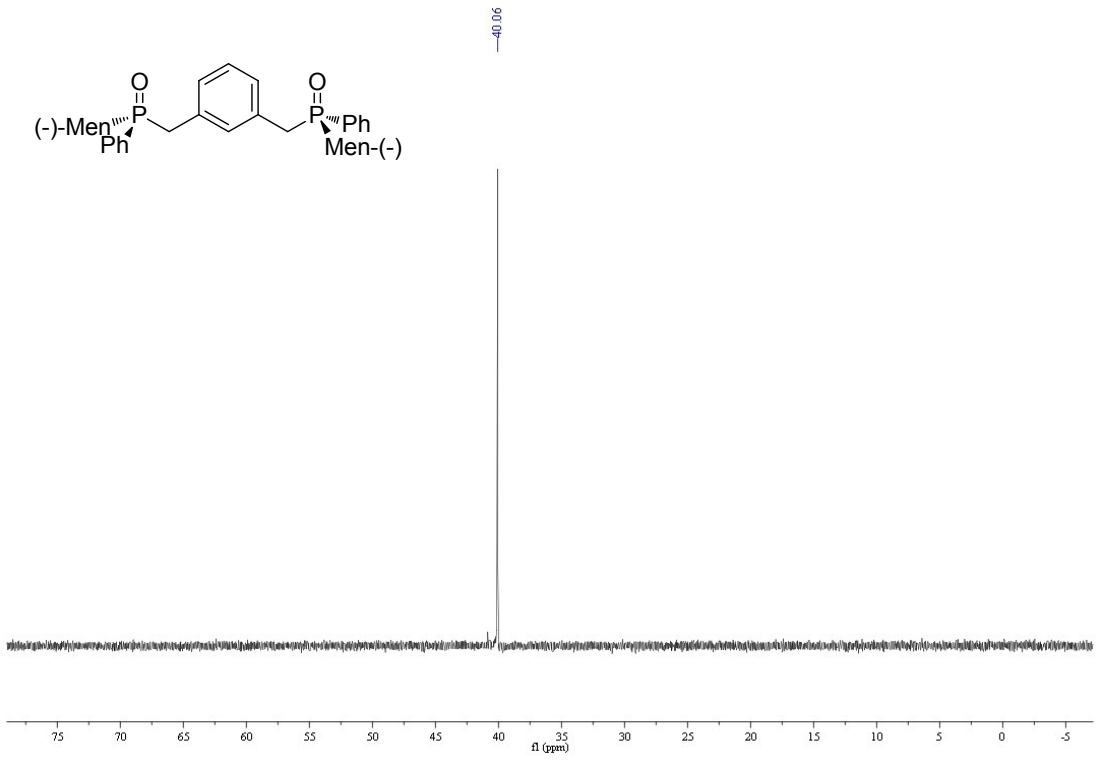
R_P-(-)-Menthyl phenyl (3-(chloromethyl)benzyl)phosphine oxide, 11a

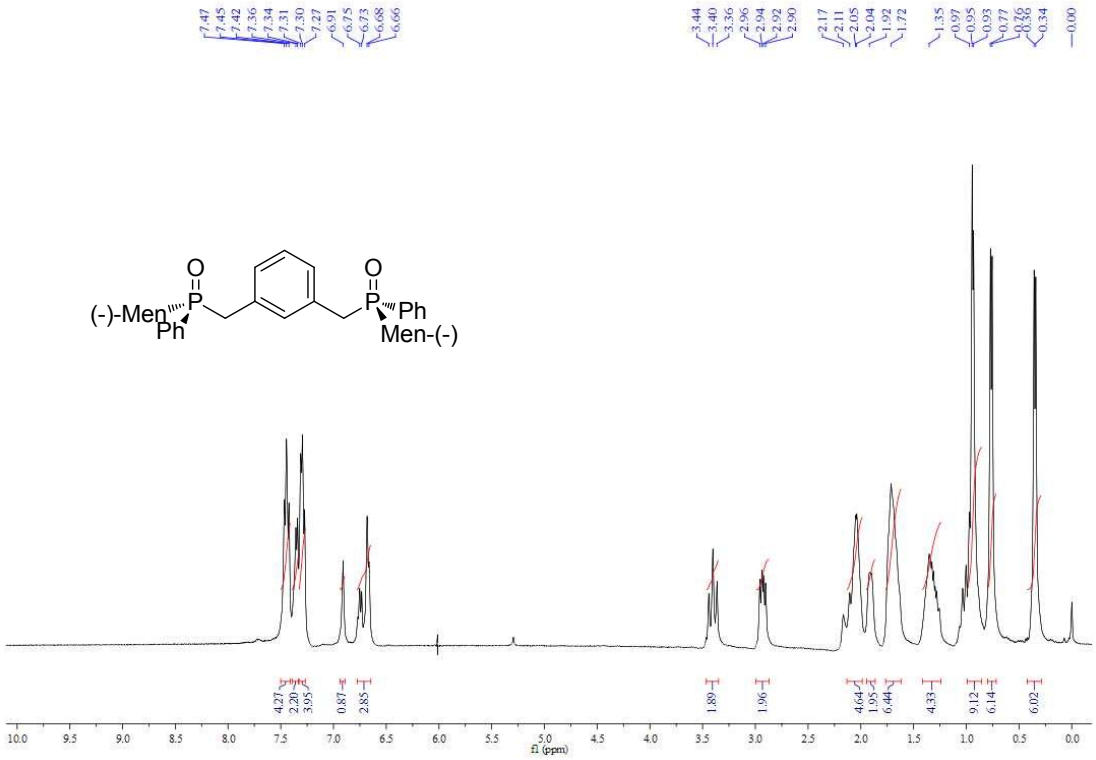


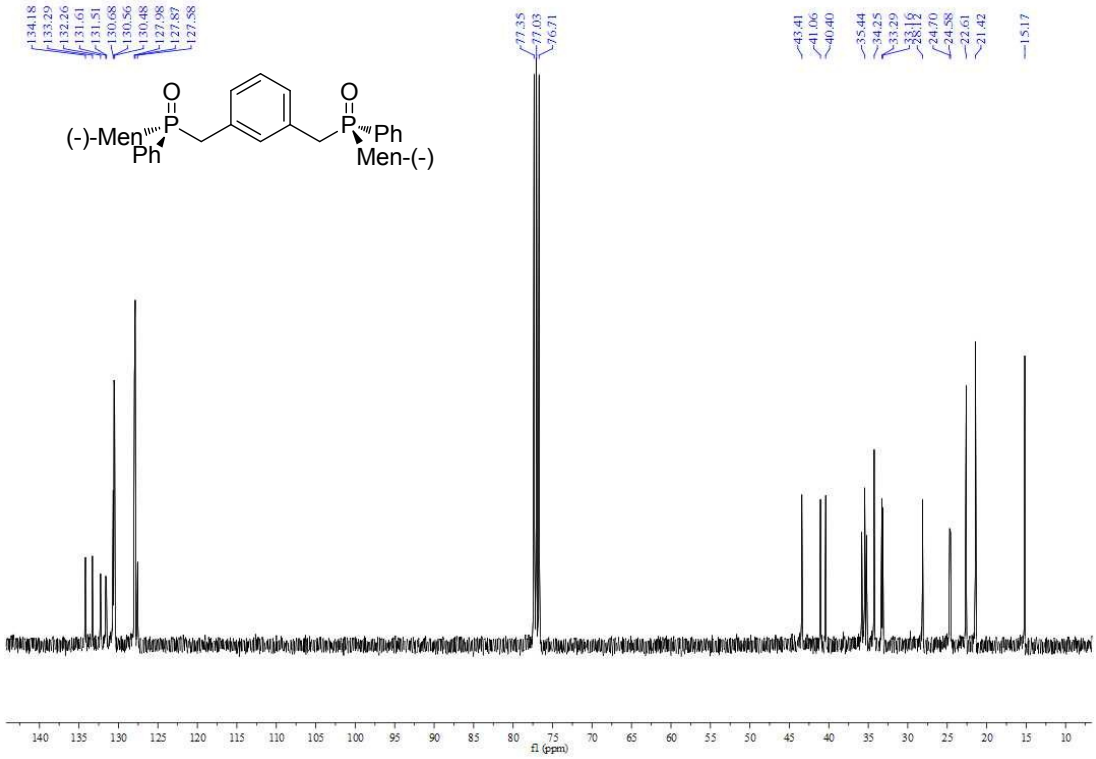




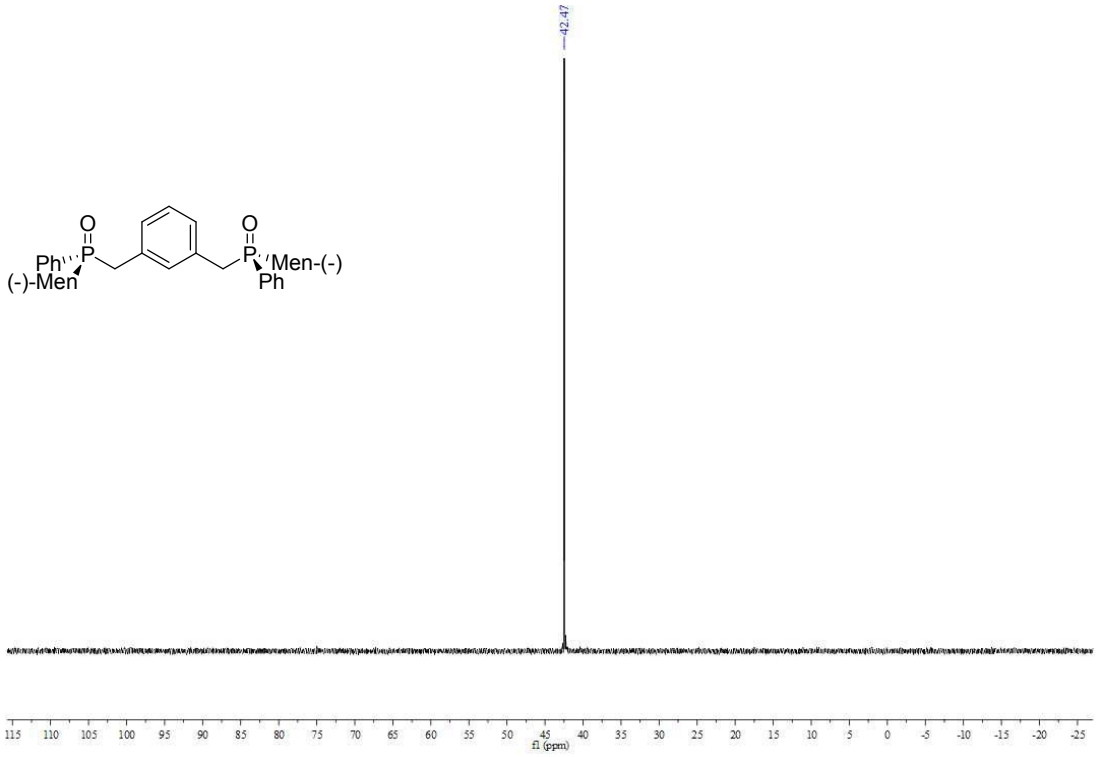
(R_P,R_P)-(1,3-Phenylenebis(methylene)) bis((−)-menthylphenylphosphine oxide), 12a

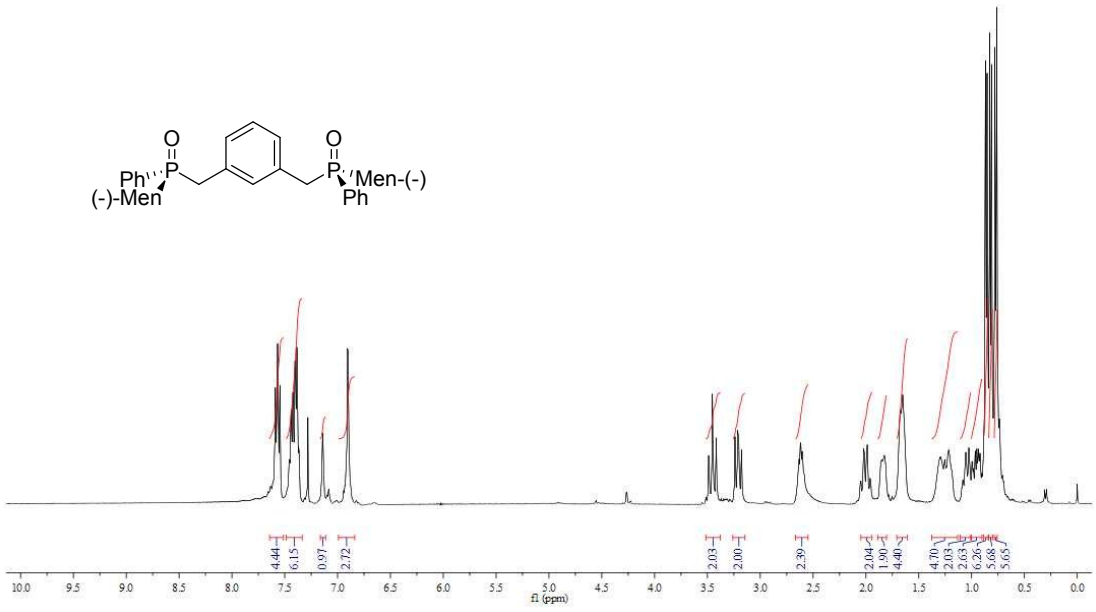


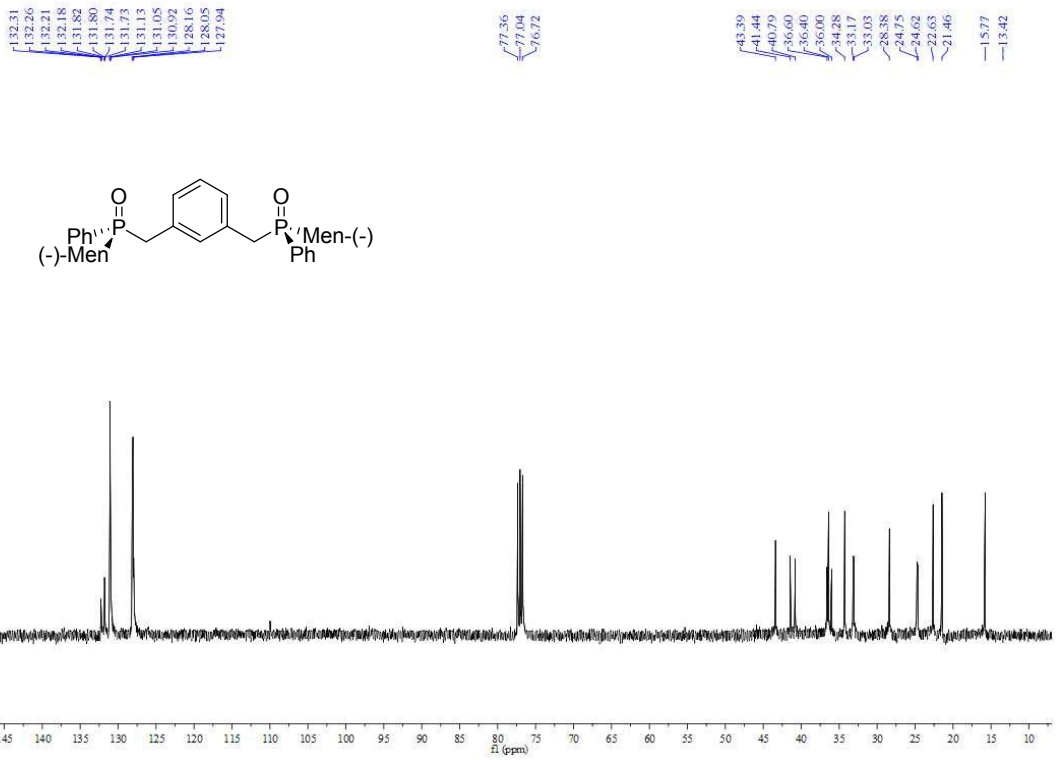

(-)-Men
Ph
O
P
Ph
Men-(-)
fl (ppm)


(-)-Men
Ph
O
P
Ph
Men-(-)
fl (ppm)

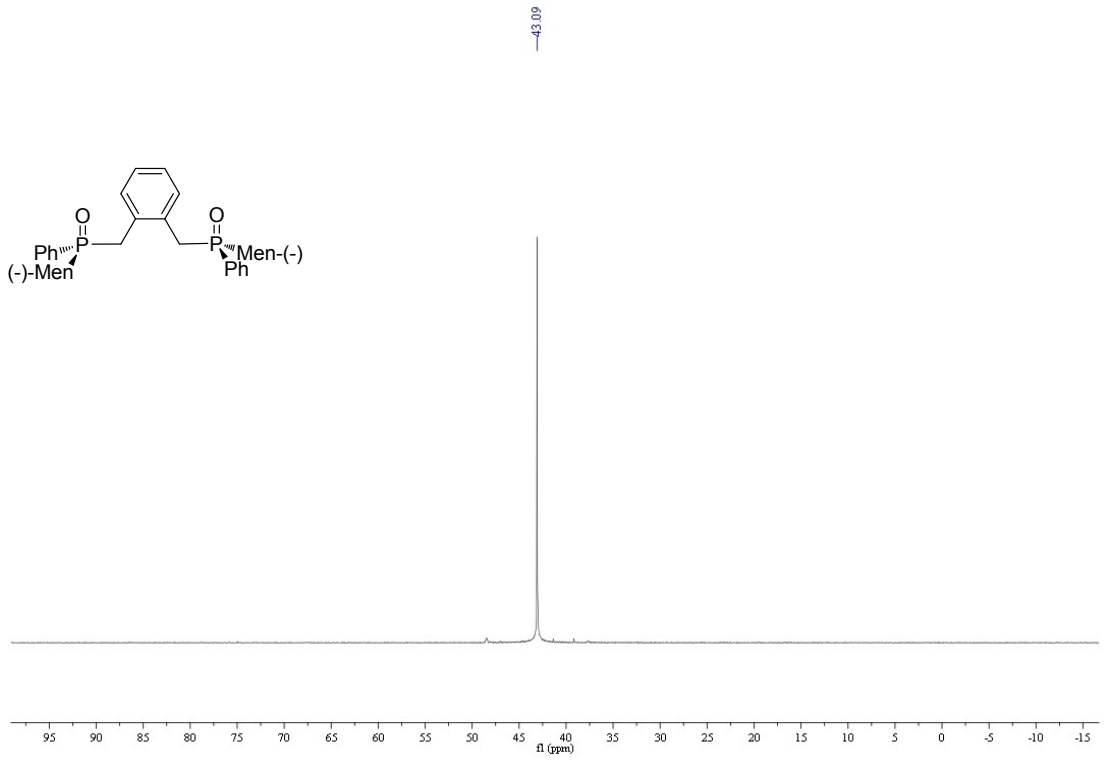
(S_P,S_P)-(1,3-Phenylenebis(methylene)) bis((−)-menthylphenylphosphine oxide), 12b

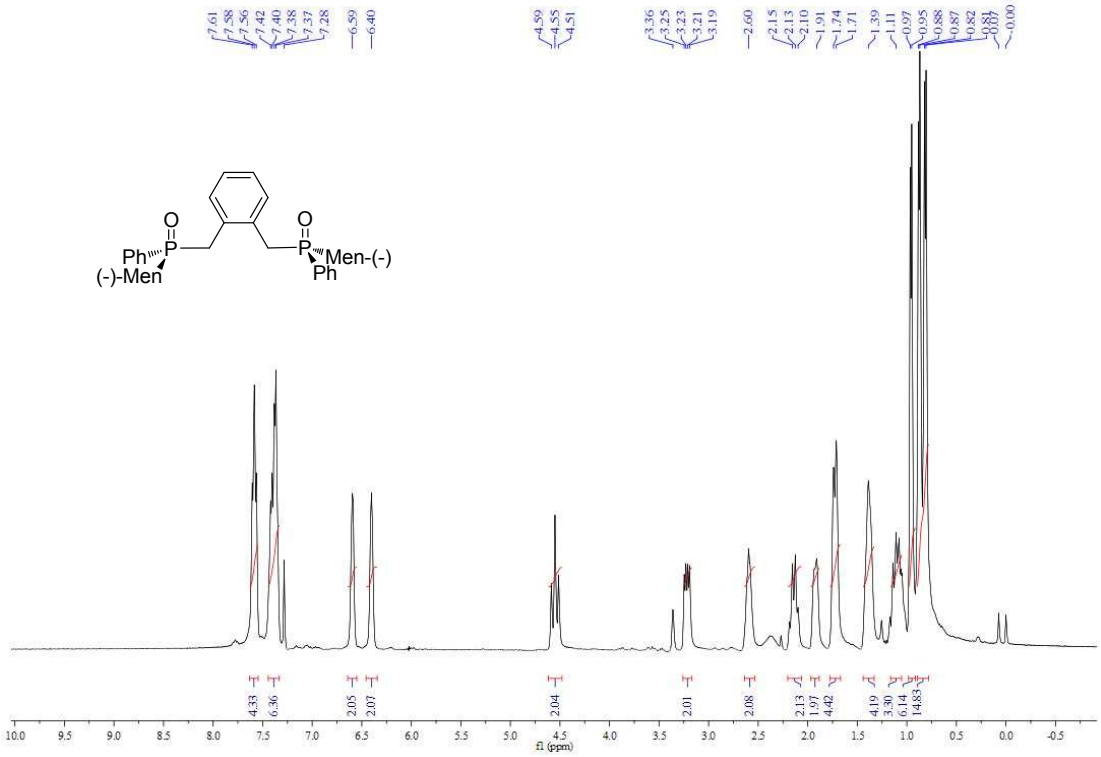


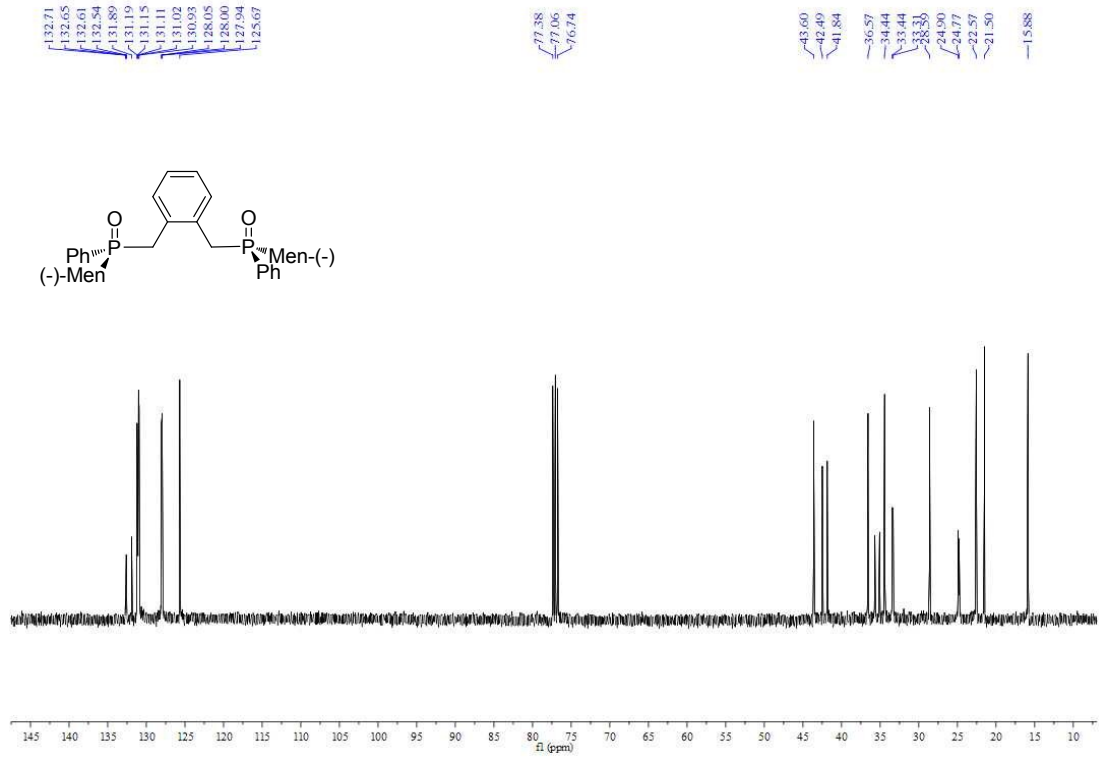




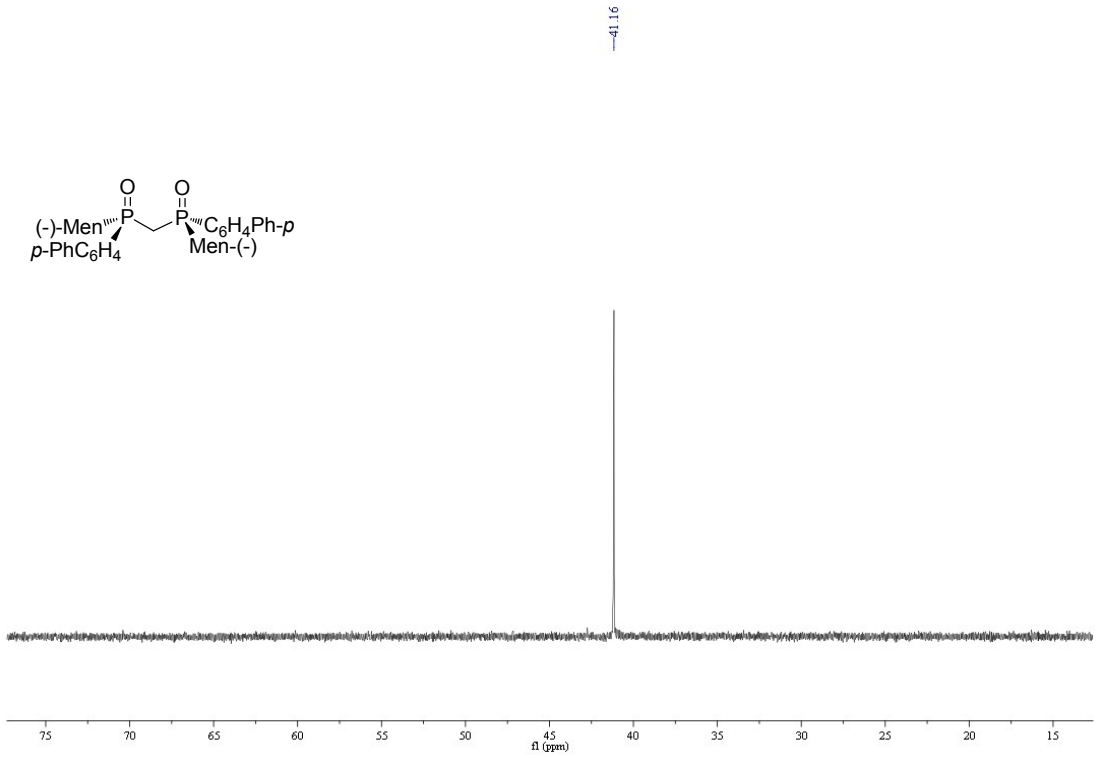
(S_P,S_P)-(1,2-Phenylenebis(methylene)) bis((−)-menthyl phenyl phosphine oxide), 12c

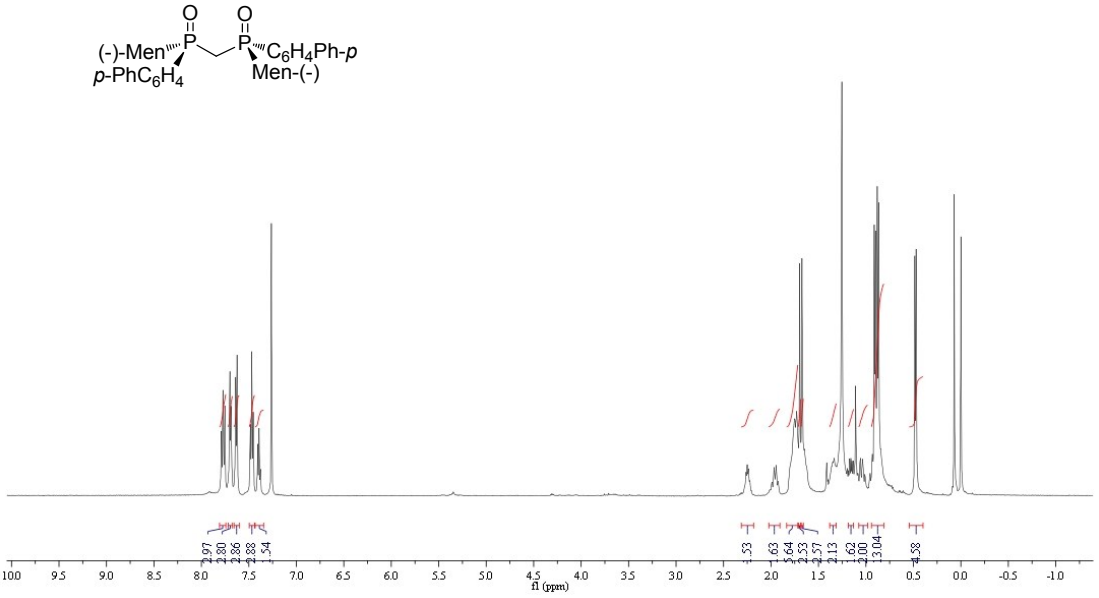


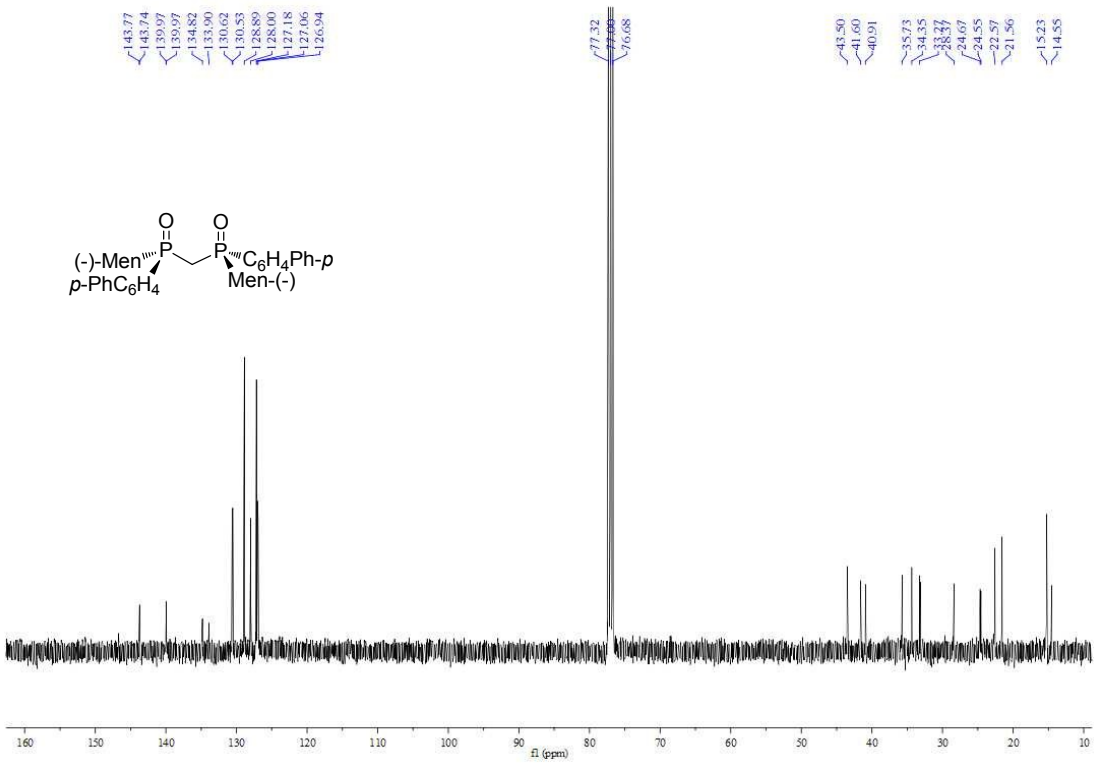

7.61
7.58
7.56
7.42
7.40
7.38
7.37
7.28
6.59
6.40
4.59
4.55
4.51
3.36
3.25
3.23
3.21
3.19
2.60
2.15
2.13
2.10
1.91
1.74
1.71
1.39
1.11
0.97
0.95
0.88
0.87
0.82
0.81
0.07
0.00
Ph
O
P
(-)-Men
O
P
Men-(-)
Ph
4.33
6.36
2.05
2.07
2.04
2.01
2.08
2.13
1.97
4.42
4.19
3.30
6.14
14.83
f1 (ppm)


132.71
132.65
132.61
132.54
131.89
131.19
131.15
131.11
131.02
130.93
128.05
128.00
127.94
125.67
77.38
77.06
76.74
43.60
42.49
41.84
36.57
34.44
33.44
33.31
28.39
24.90
24.77
22.57
21.50
15.88
Ph
O
P
(-)-Men
O
P
Men-(-)
Ph
f1 (ppm)

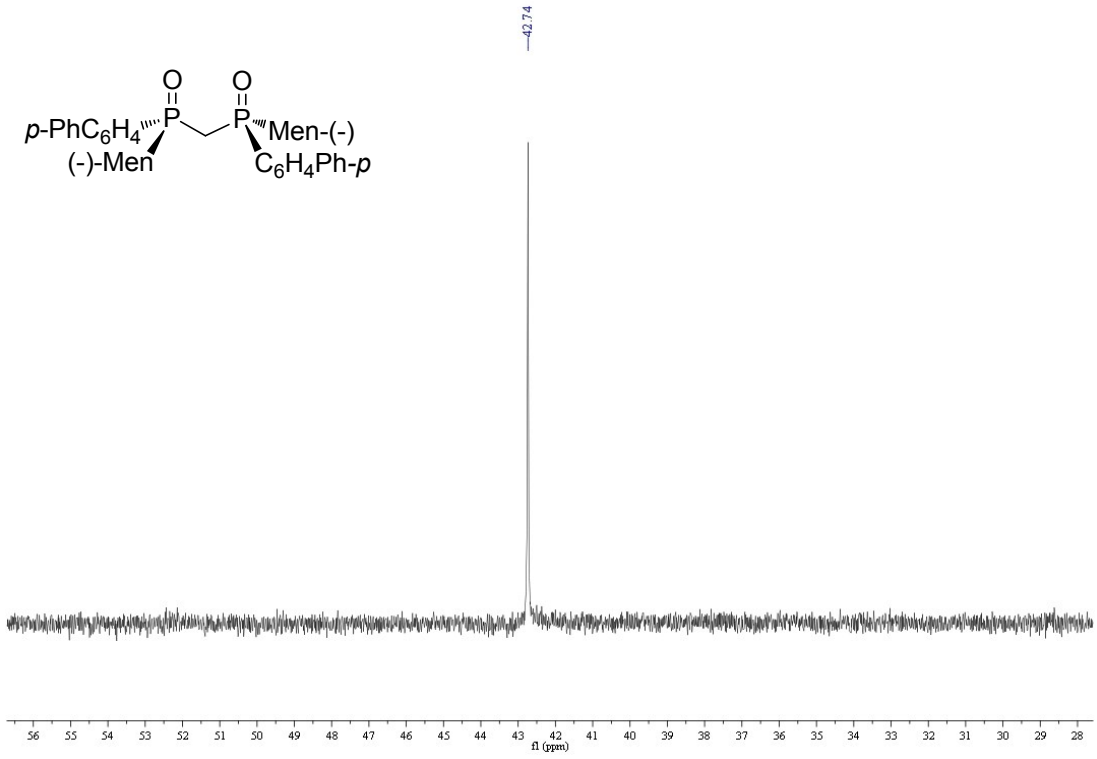
(R_P,R_P)-(−)-Methylene-bis(((−)-menthyl)(biphenyl) phosphine oxide), 12d

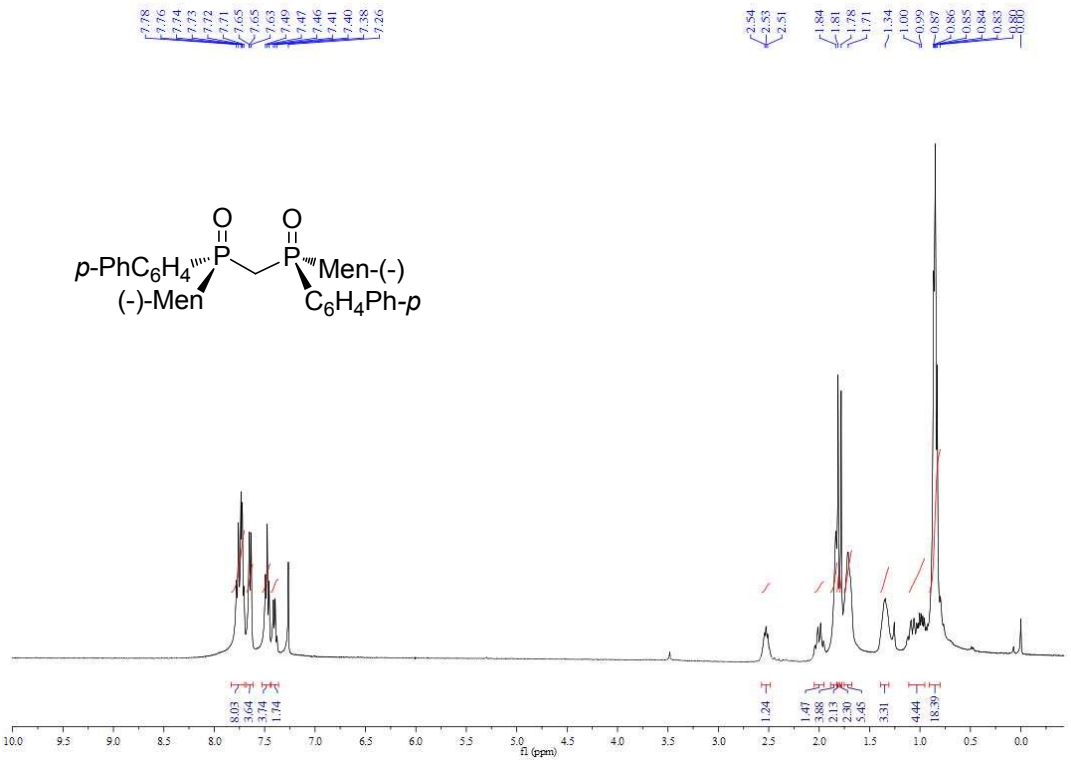


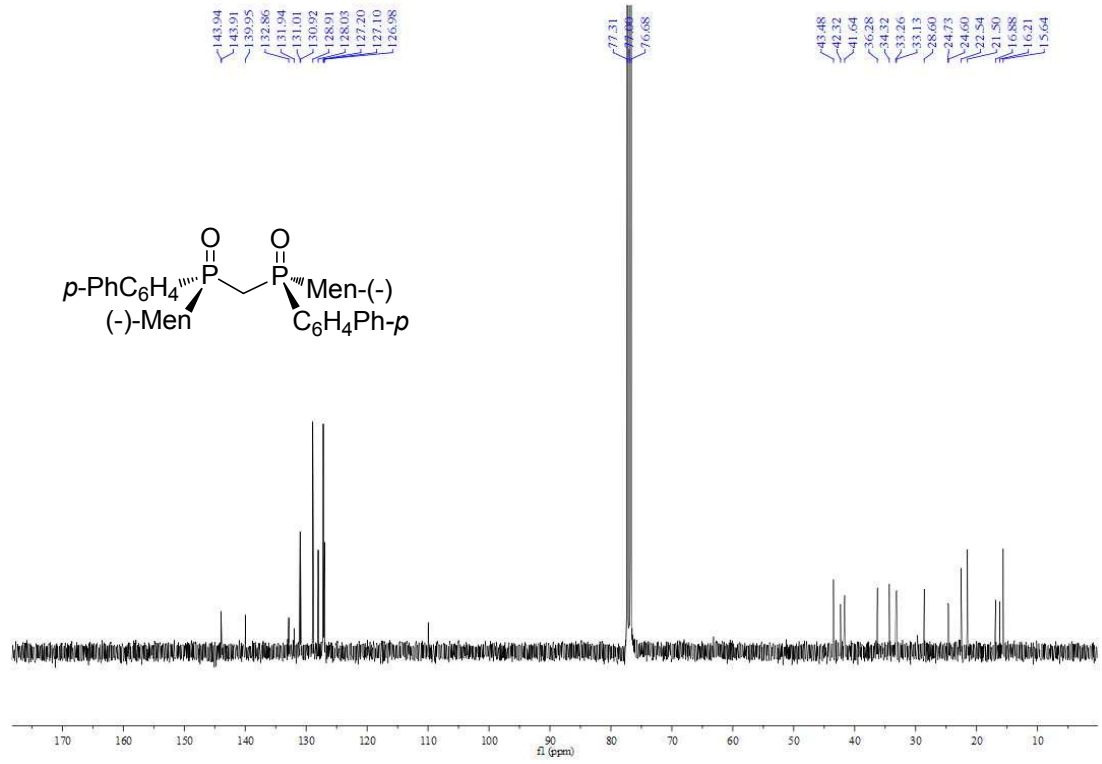




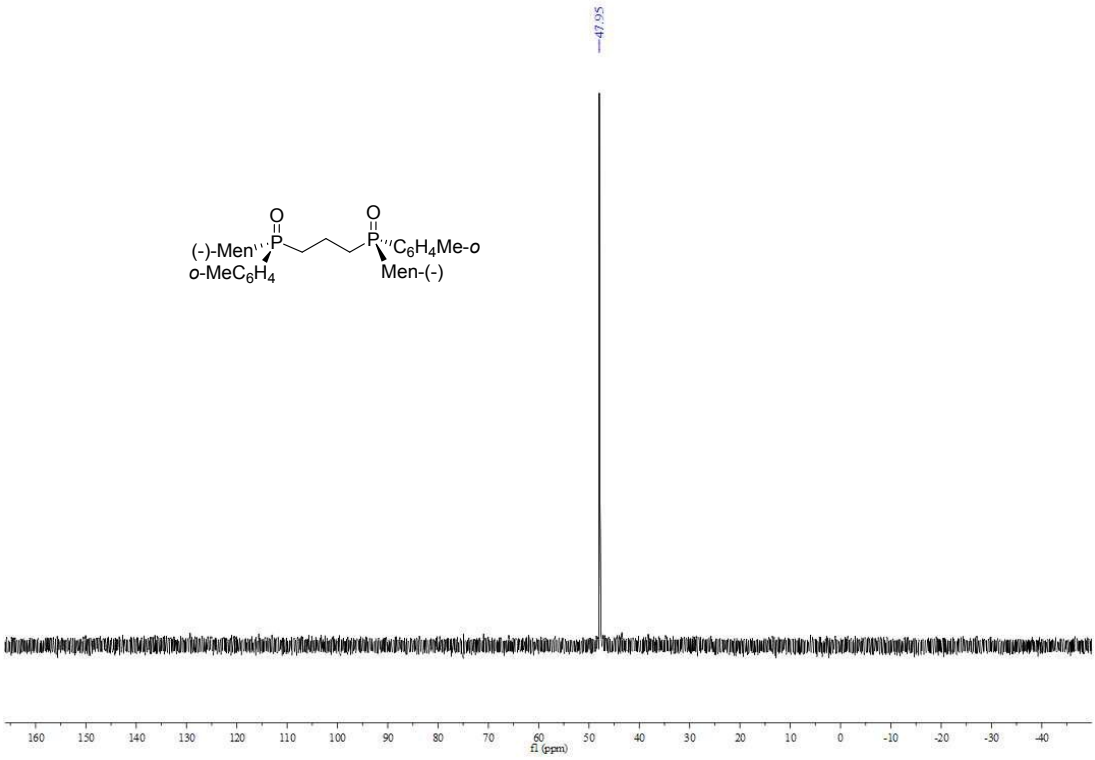
(S_P,S_P)-(−)-Methylene-bis(((−)-menthyl)(biphenyl) phosphine oxide), 12e

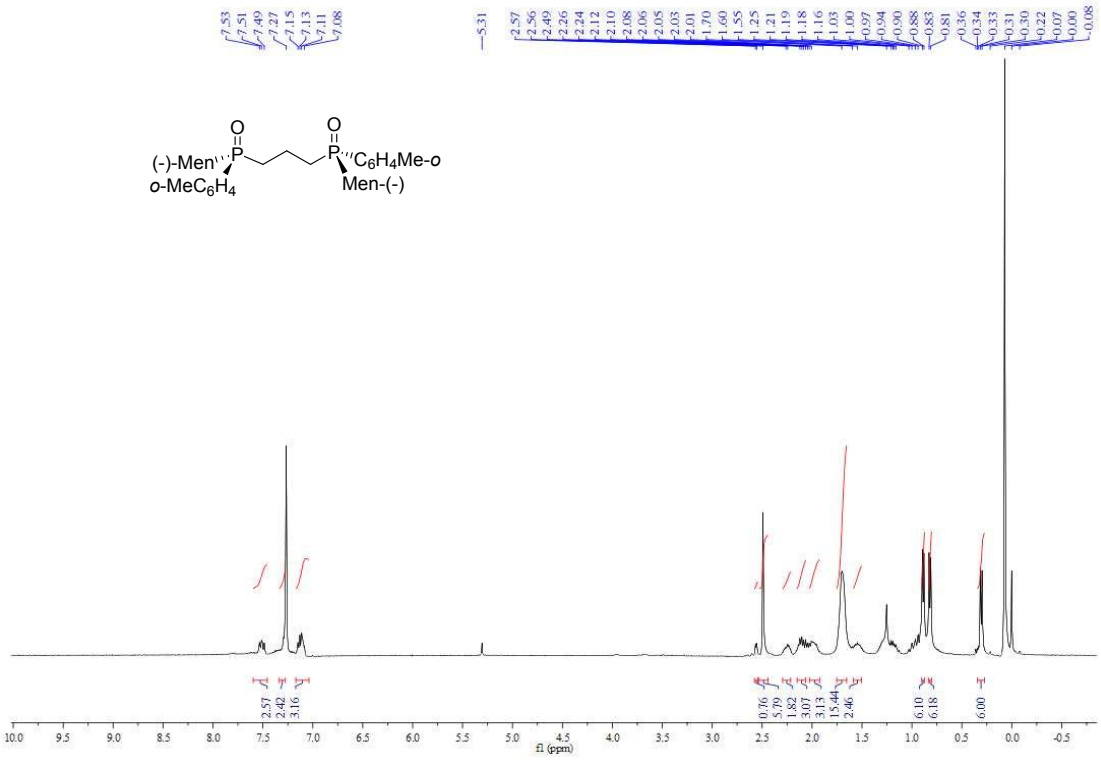


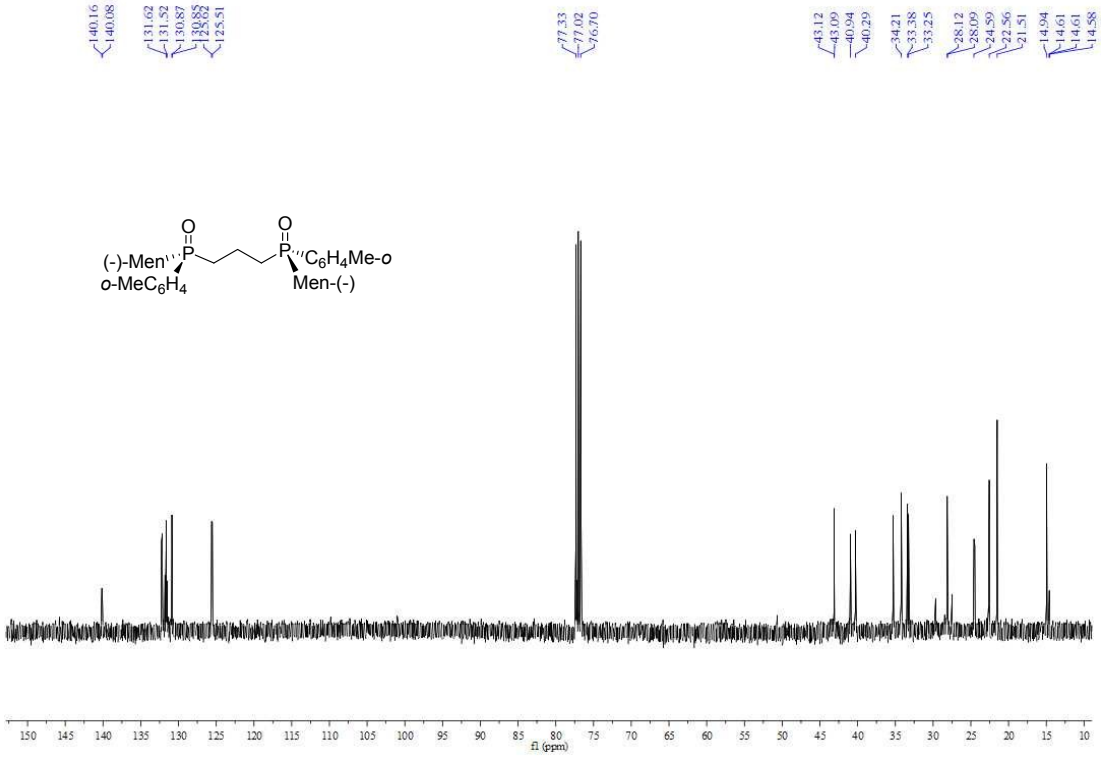

p-PhC6H4
(-)-Men
Men-(-)
C6H4Ph-p
f1 (ppm)


p-PhC6H4
(-)-Men
Men-(-)
C6H4Ph-p
f1 (ppm)

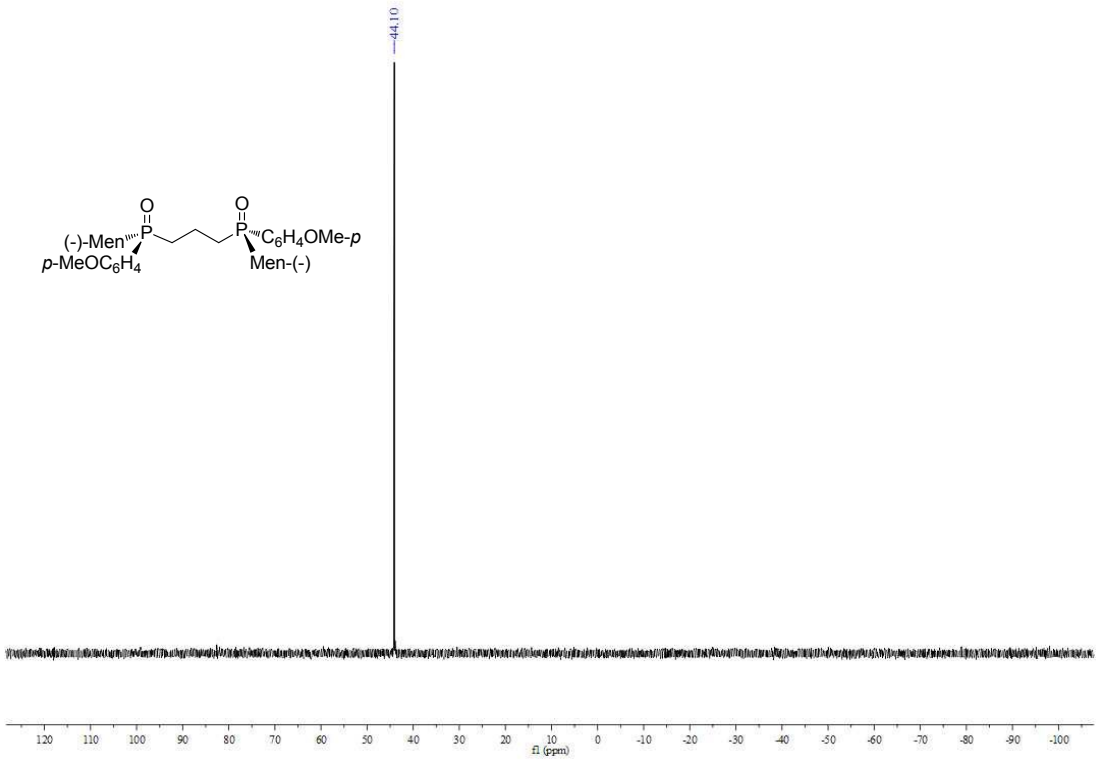
(R_P,R_P)-Propane-1,3-diylbis((−)-menthy 2-methylphenylphosphine oxide), 12f

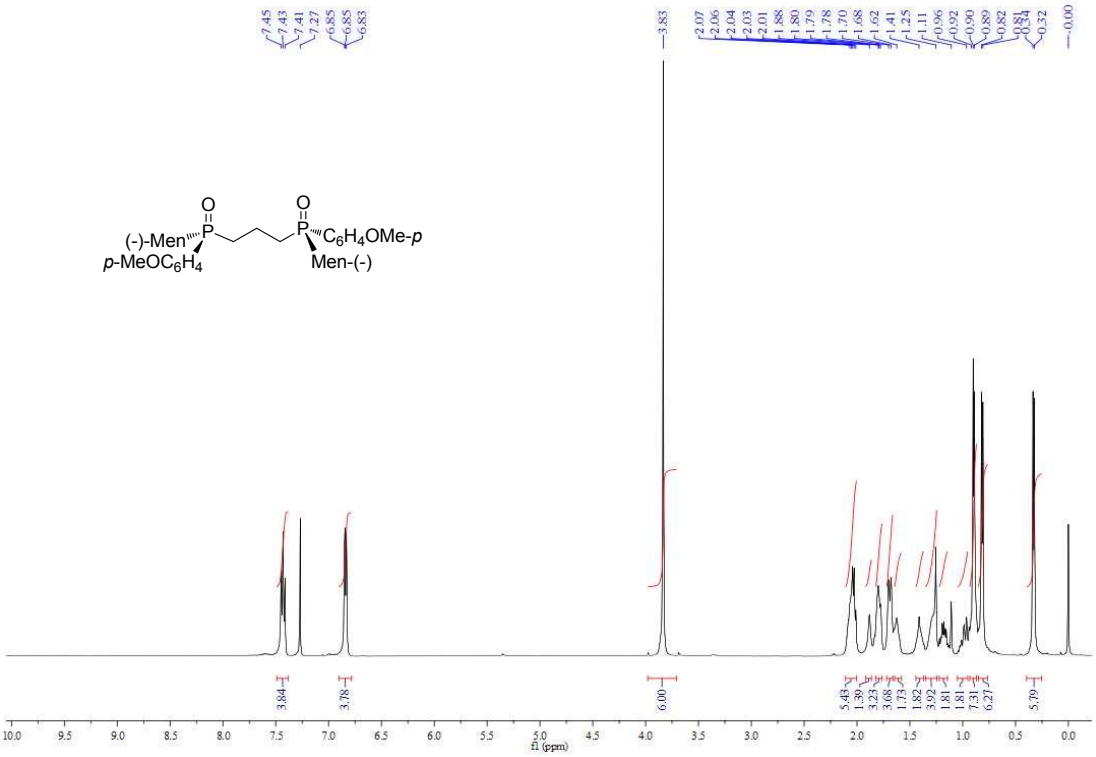


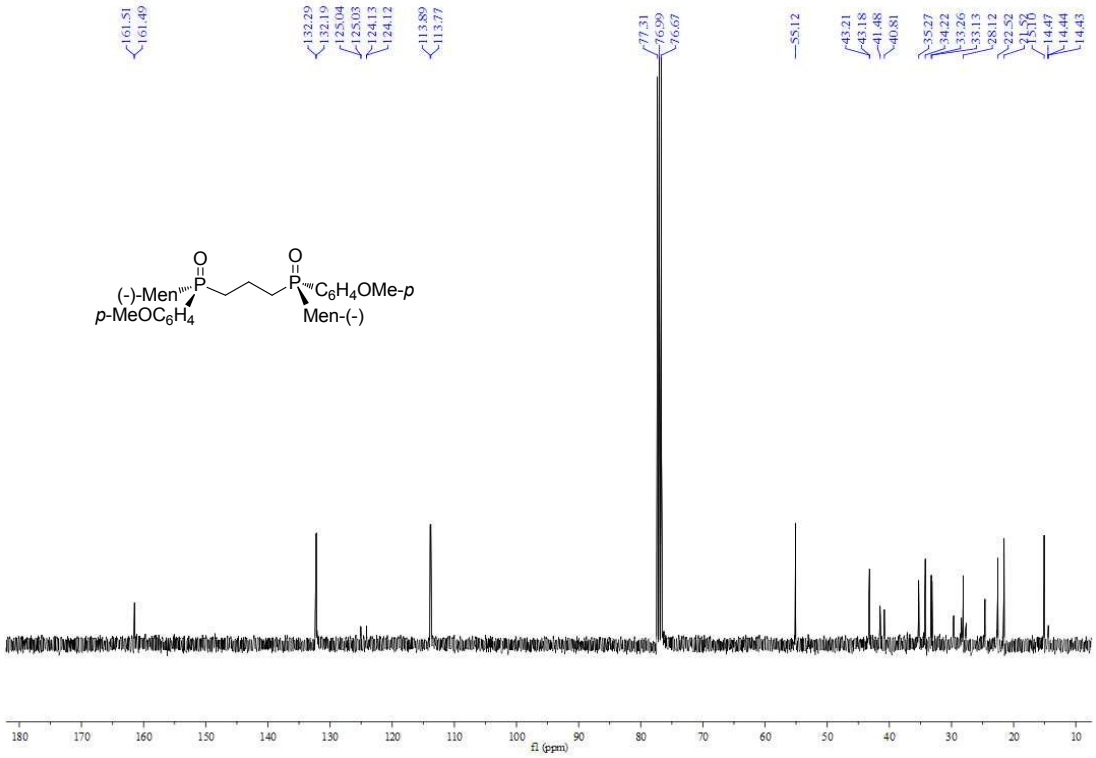




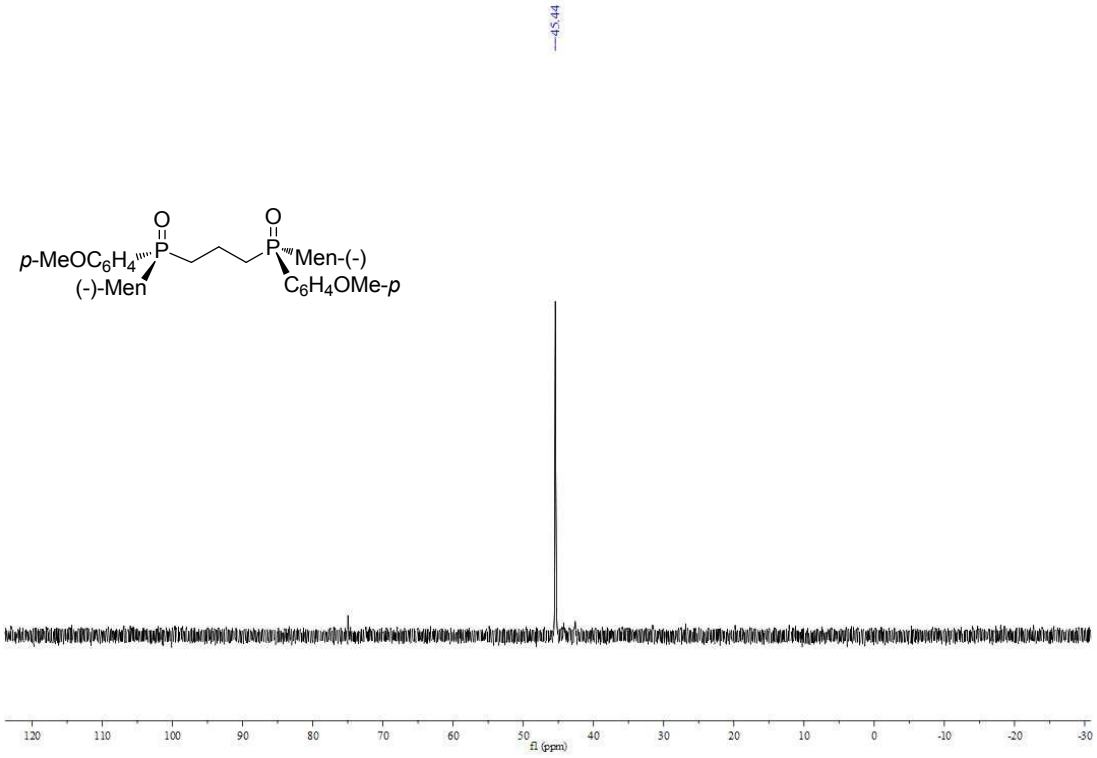
(R_P,R_P)-Propane -1,4-diylbis((−)-menthyl *p*-methoxyphenylphosphine oxide),12g

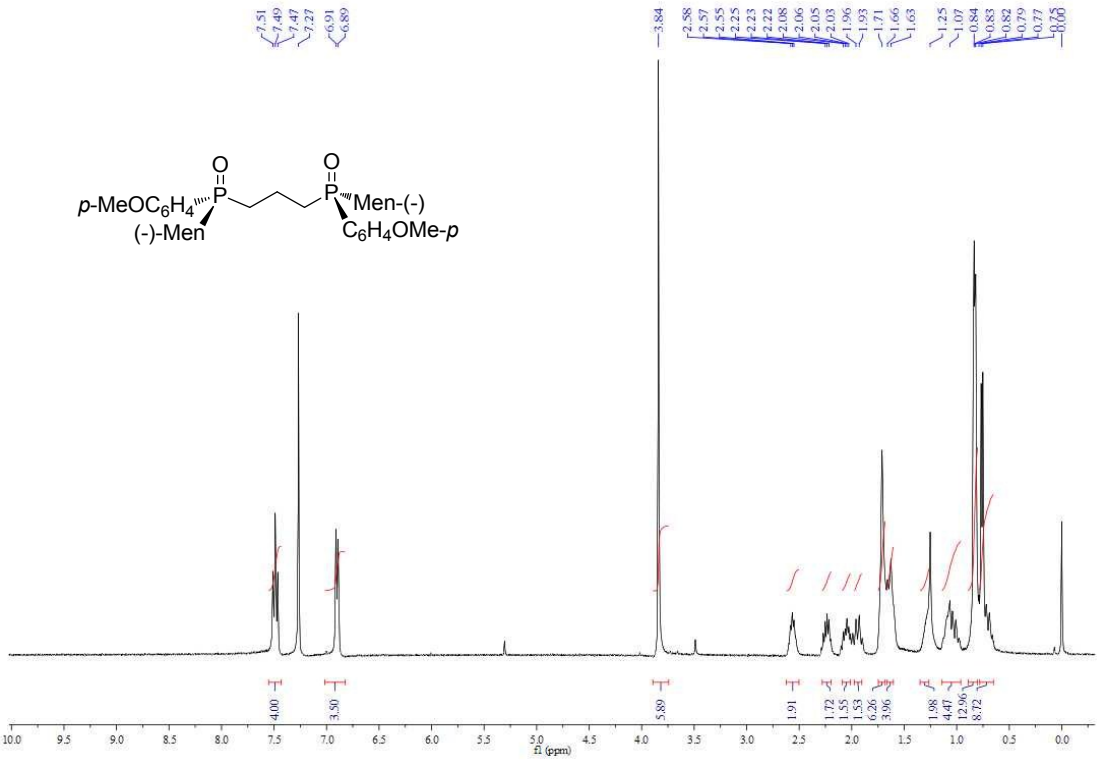


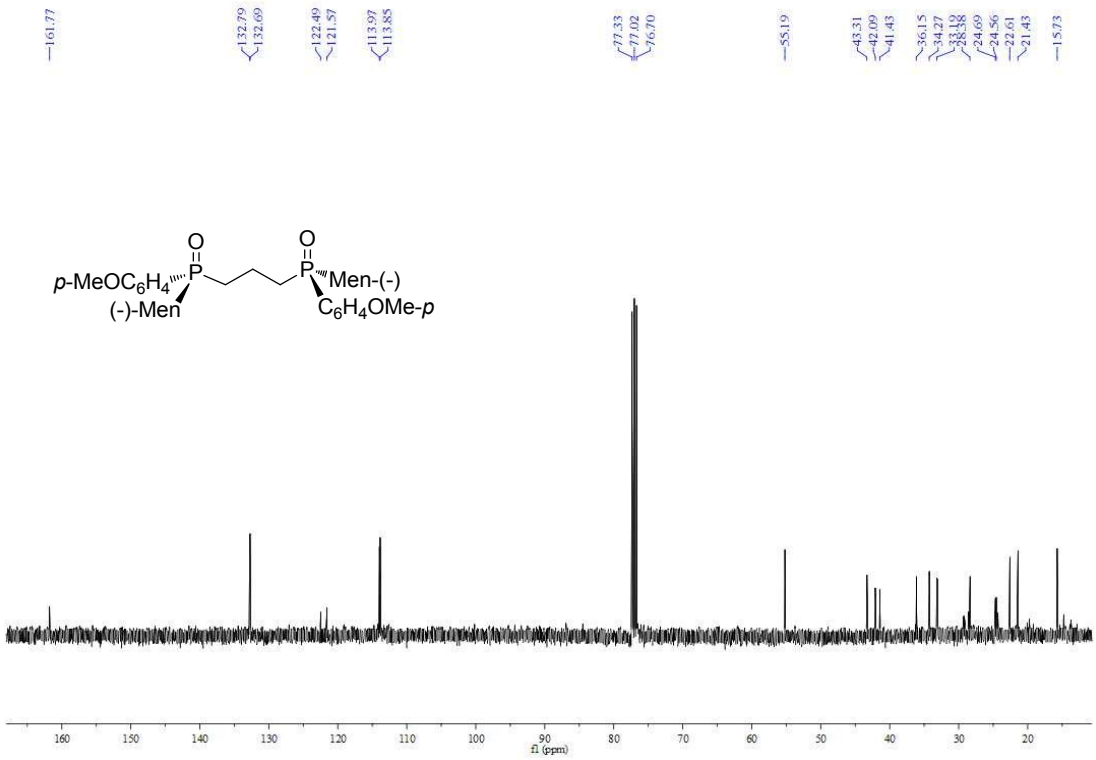

(-)-Men
p-MeOC6H4
C6H4OMe-p
Men-(-)
fl (ppm)


(-)-Men
p-MeOC6H4
C6H4OMe-p
Men-(-)
fl (ppm)

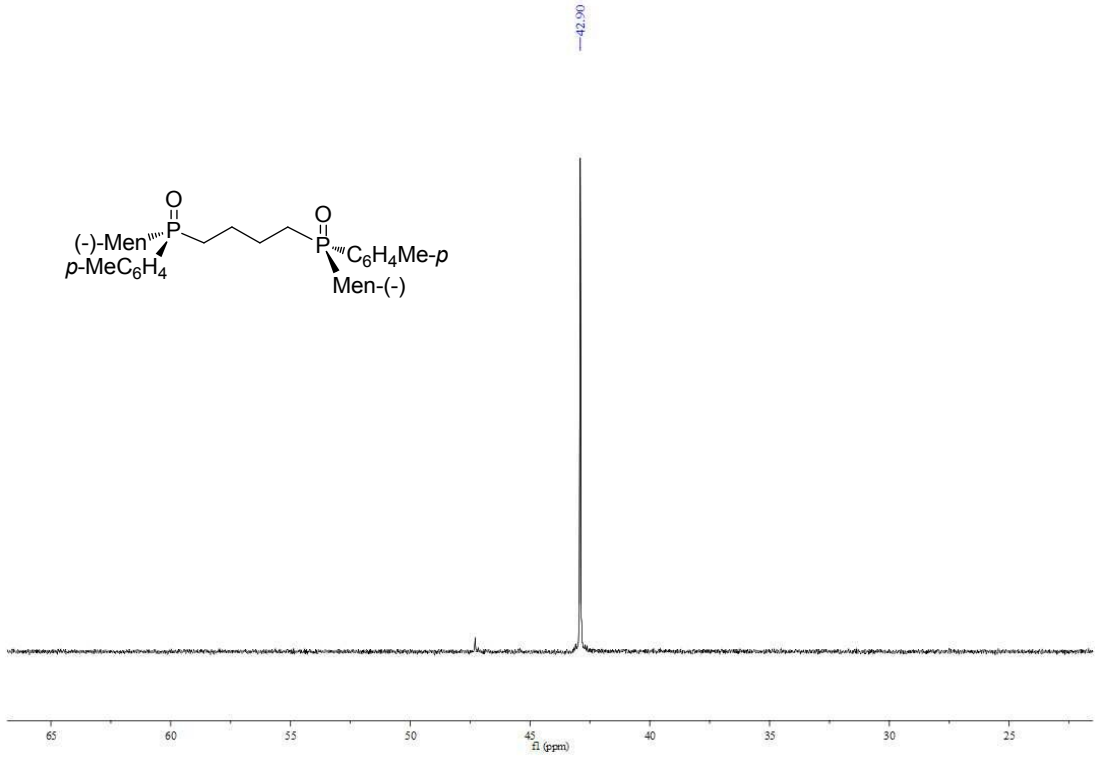
(S_P,S_P)-Propane -1,4-diylbis((−)-menthyl *p*-methoxyphenylphosphine oxide),12h

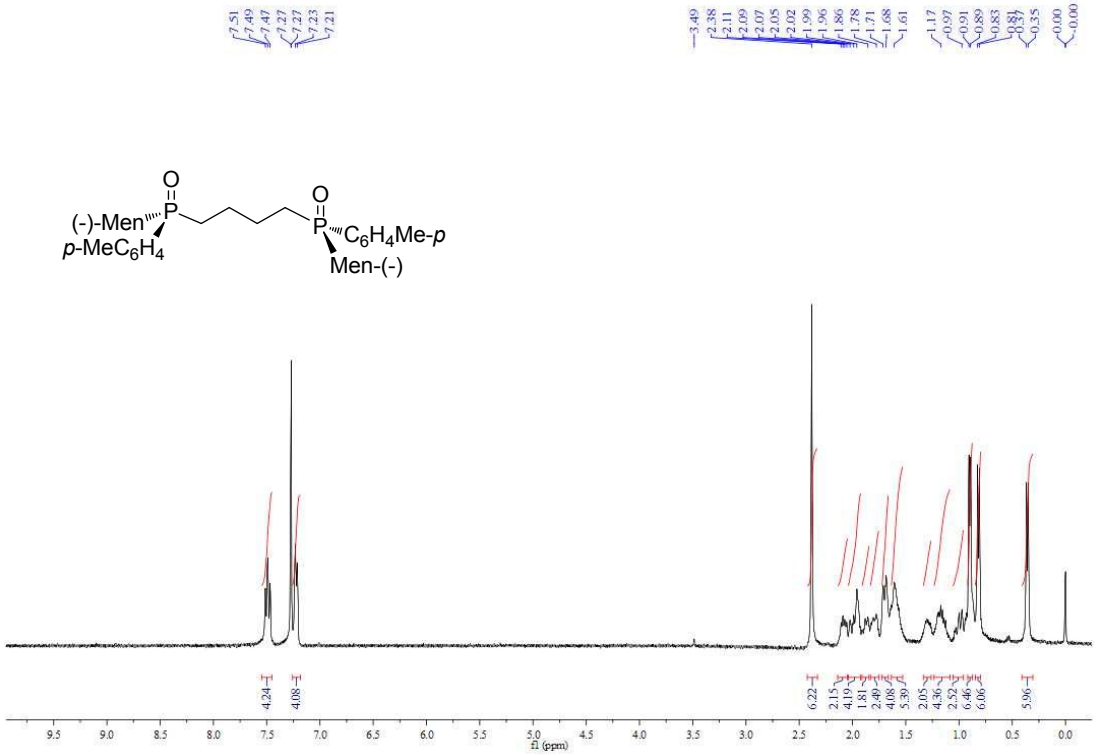


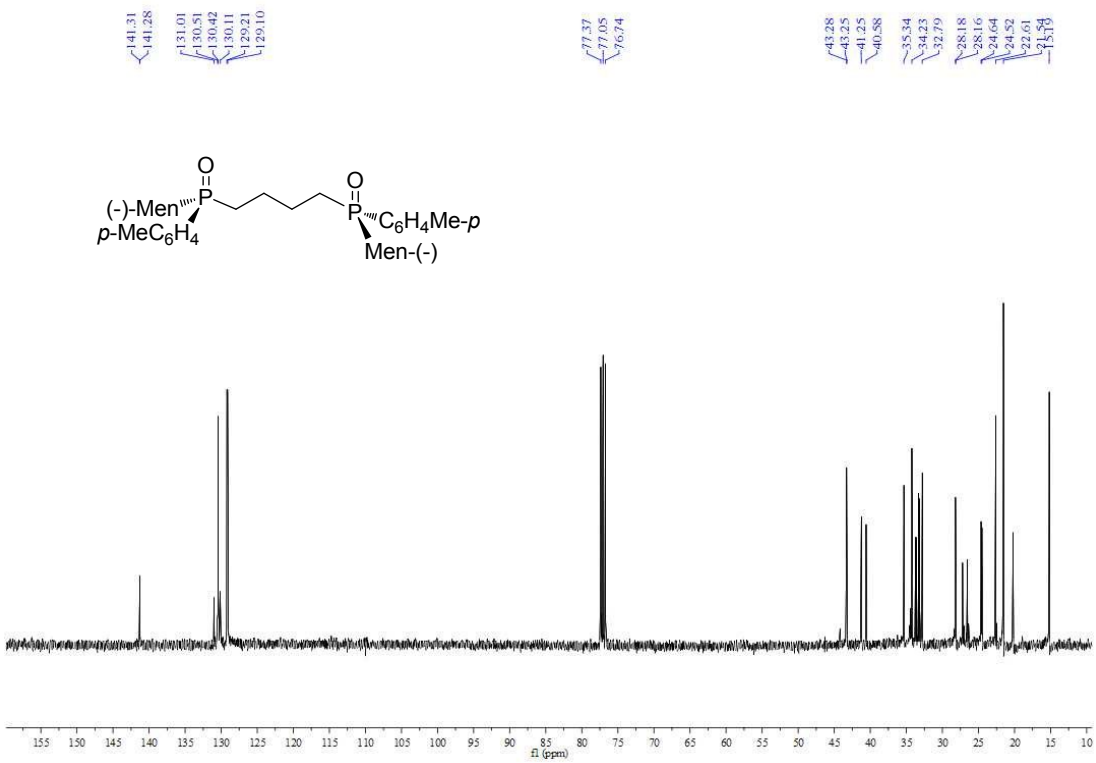




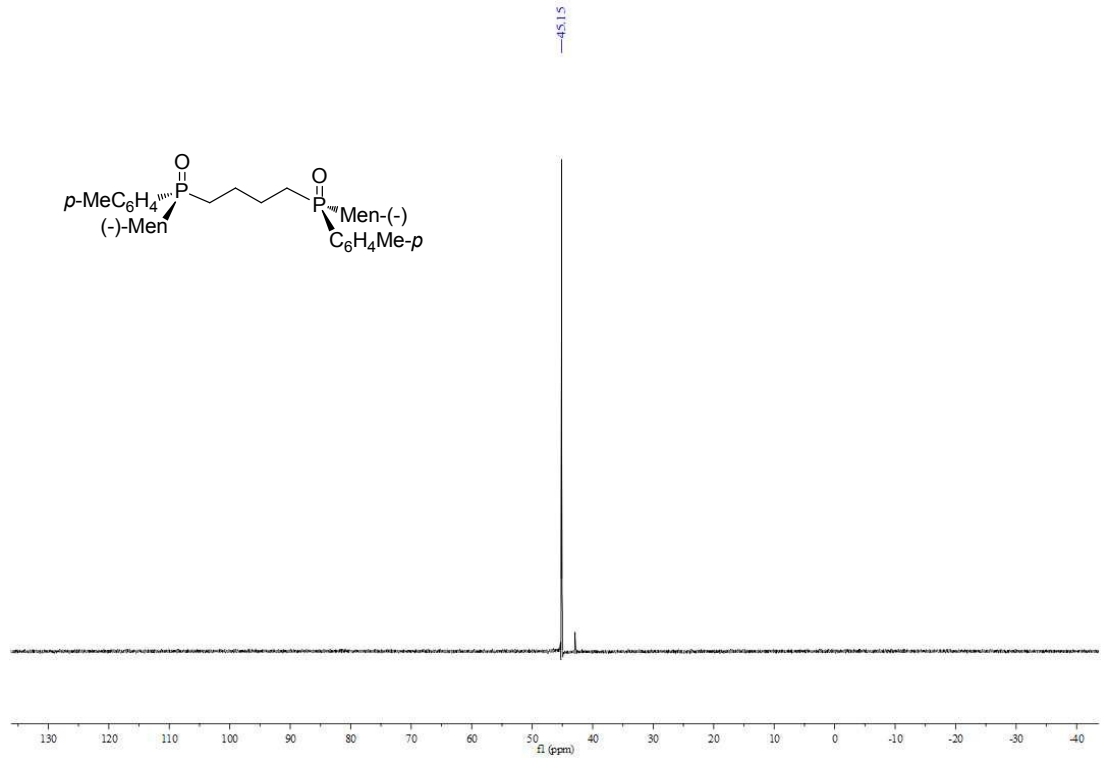
(R_P,R_P)-Butane-1,4-diylbis ((−)-menthyl *p*-tolylphosphine oxide),12i

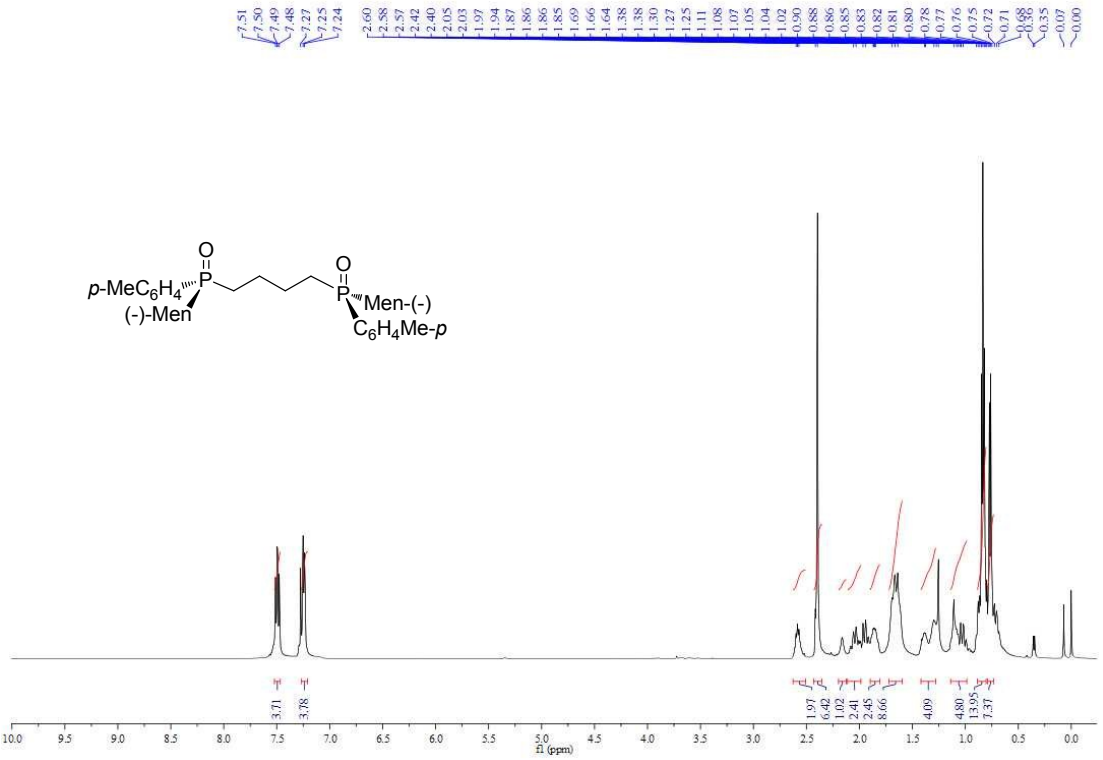


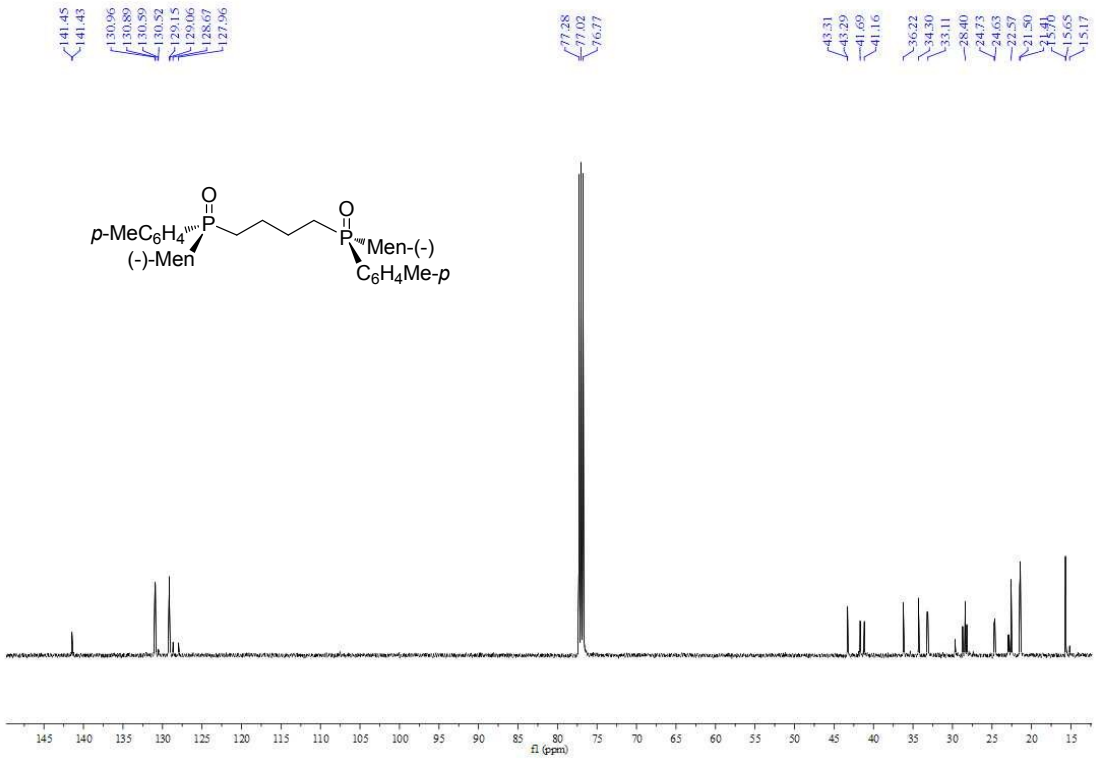

(-)-Men
p-MeC6H4
C6H4Me-p
Men-(-)
f1 (ppm)


(-)-Men
p-MeC6H4
C6H4Me-p
Men-(-)
f1 (ppm)

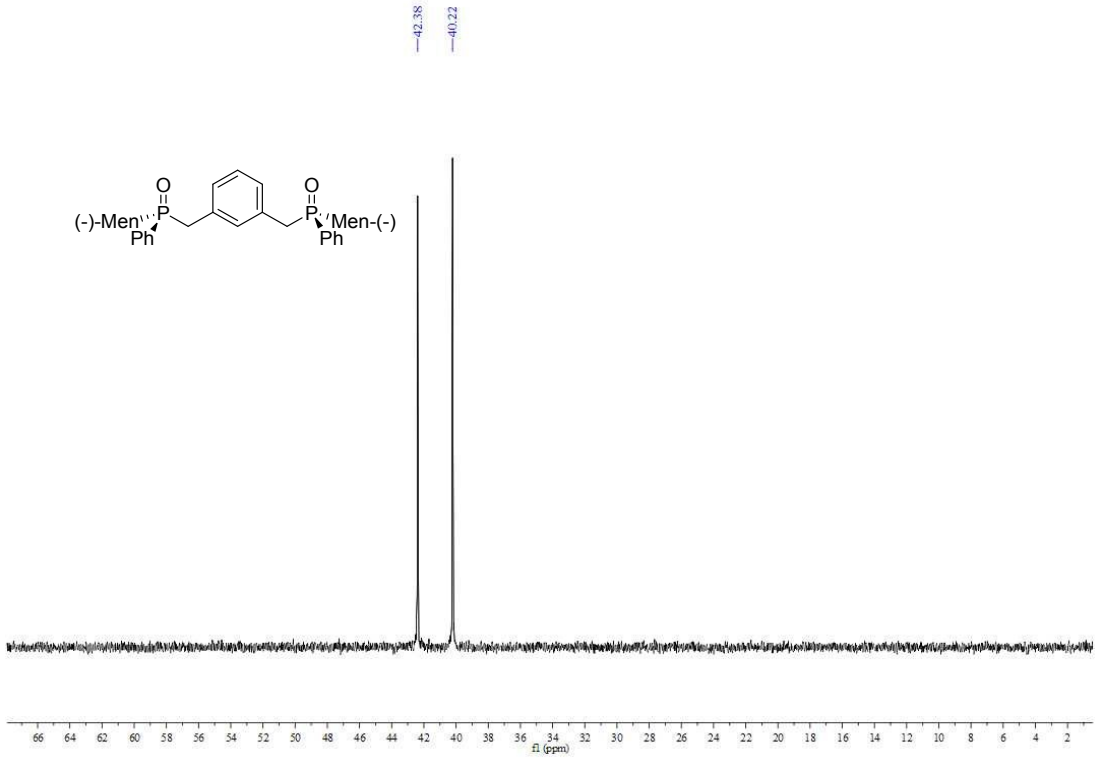
(S_P,S_P)-Butane-1,4-diylbis ((−)-menthyl *p*-tolylphosphine oxide),12j

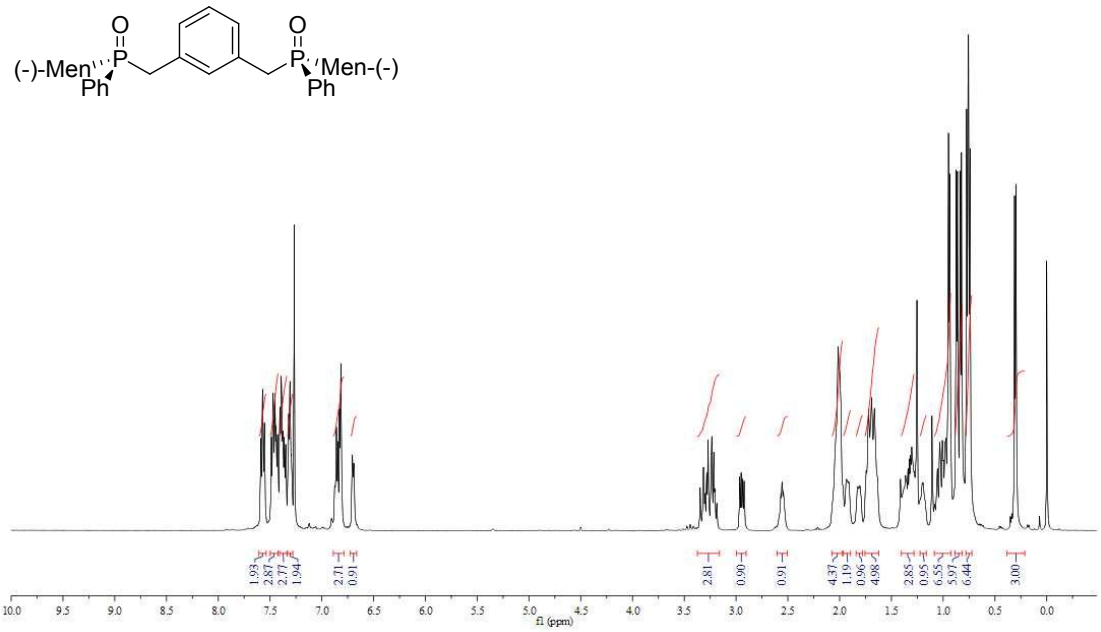


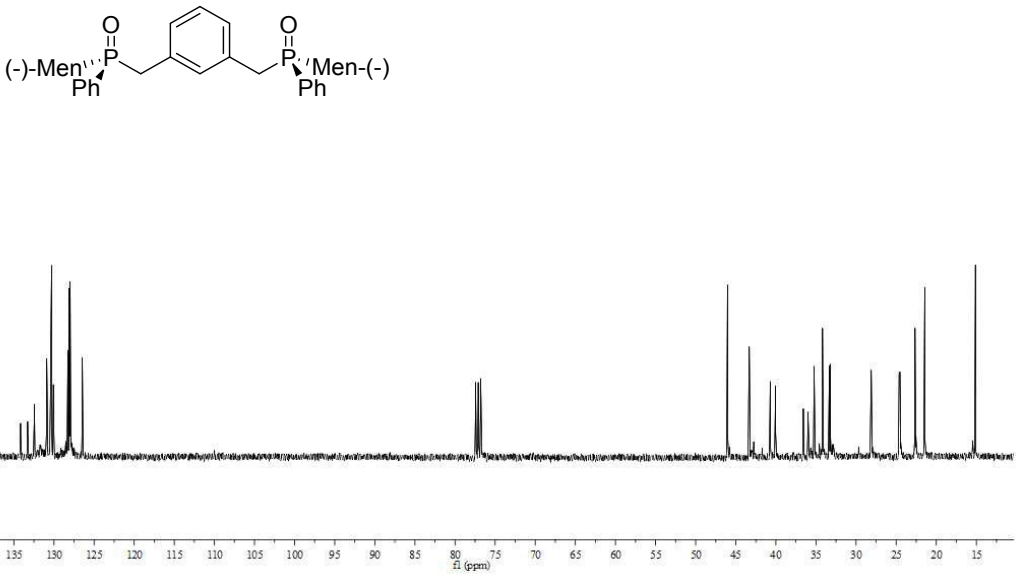




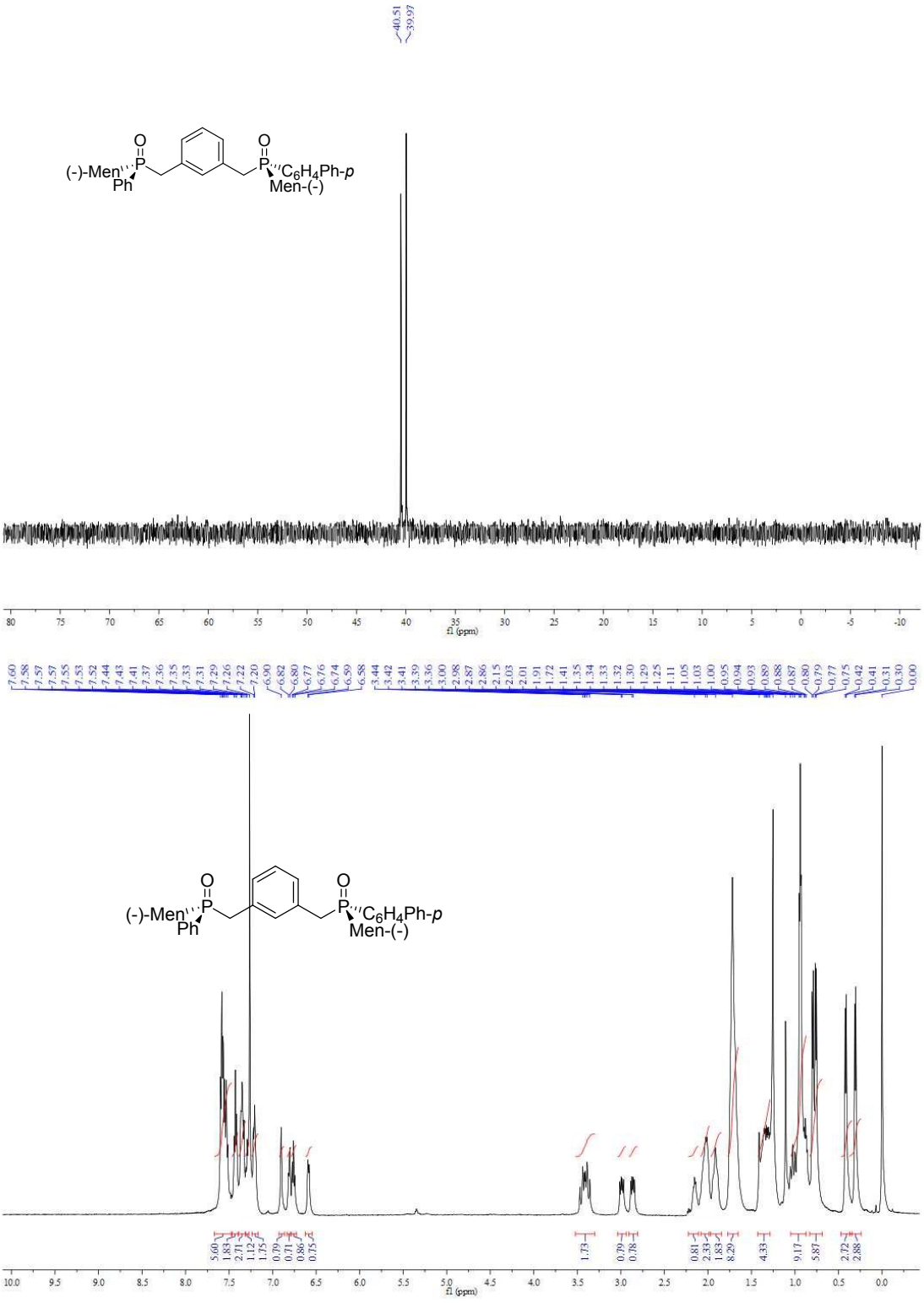
(R_P,S_P)-(1,3-Phenylenebis (methylene)) bis[(−)-menthylphenylphosphine oxide],12k




(-)-Men
Ph
O
P
O
P
Men-(-)
Ph


(-)-Men
Ph
O
P
O
P
Men-(-)
Ph

(R_P,R_P)-1,3-Di(menthyl phenyl phosphinylmenthyl)benzene, 12l




143.23
139.95
134.19
133.25
132.66
132.34
132.29
132.25
131.63
131.61
131.60
131.58
131.58
131.57
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131.52
131.51
131.50
131.20
131.11
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130.43
130.35
128.85
127.90
127.09
126.66
120.84
77.40
77.08
76.76
43.48
43.45
43.42
43.38
41.27
40.90
40.61
36.02
36.01
35.69
35.51
35.36
34.24
33.27
33.15
29.68
28.20
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24.67
24.62
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24.32
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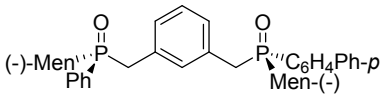
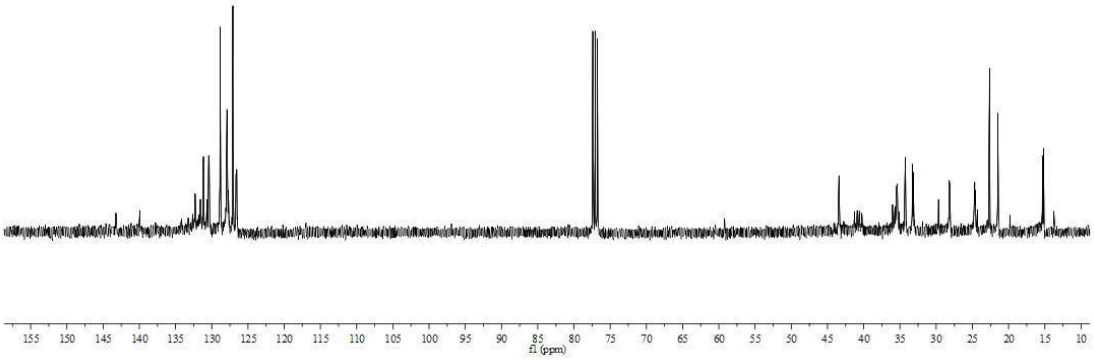
21.48
21.45
15.32
15.18
13.76


O
O
(-)-Men
P
P
C6H4Ph-p
Ph
Men-(-)


155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)