The Stereoselective Conversion of Epimerized Alkoxyl Phosphine-Borane to *P, C, axial*-Stereogenic Tertiary Phosphine via Cleavage of P-O Bond

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General Chemistry:

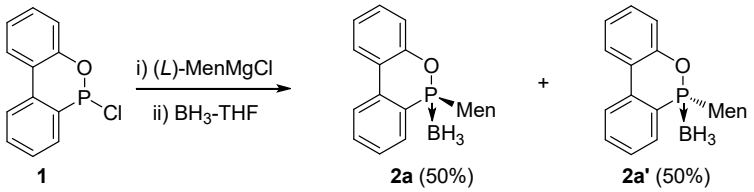
^{1}H NMR spectrum were recorded on a 500 MHz spectrometer. Chemical shift for ^{1}H NMR spectrum (in parts per million) relative to internal tetramethylsilane (Me_4Si, δ = 0.00 ppm) with $CDCl_3$. ^{13}C NMR spectrum were recorded at 126 MHz. Chemical shifts for ^{13}C NMR spectrum are reported (in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

Reagent and solvents:

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

Part 1. Examination of the stereoselective cleavage of P-O bond.

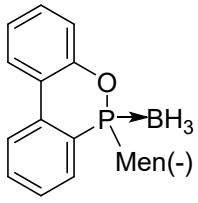
Preparation of 2a/2a'



1 **2a** (50%) **2a'** (50%)

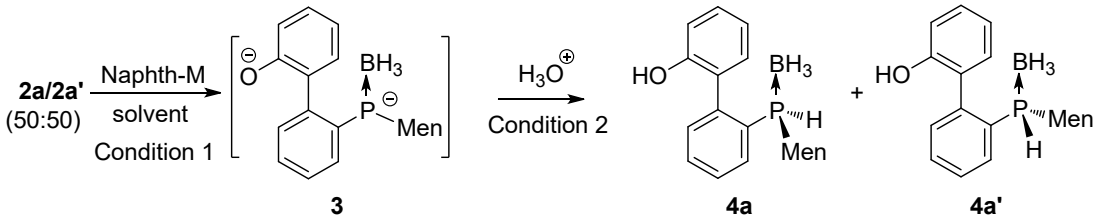
To the ice-cooled solution of **1** (5.00 g, 21.31 mmol) in THF (10 mL), was added dropwise the solution of (-)-menthyl magnesium chloride (prepared according standard procedure, 0.8 M solution in THF, 40 mL, 32 mmol). The mixture was stirred at room temperature for 8 hours, and the solution of borane (4.0 mL, 1.0 mol/L in THF) was added dropwise. After stirring for 2 hours, the reaction was quenched with diluted hydrochloric acid (8%, 3 mL). Most of solvent was removed in vacuo, and the residue was extracted with dichloromethane (3×30 mL), washed with water (3×30 mL), dried over magnesium sulfate. After removing solvent, the residue was purified with recrystallization from dichloromethane-petroleum ether (60-90 °C) to afford **2a/2a'** (4.48 g, 59%, 50:50 dr).

***R*P/*S*P-6-(-)-Menthyl-6*H*-dibenzo[*c*,*e*][1,2]oxaphosphinine-borane complex (2a/2a')**



The compound **2a/2a'** was obtained as white solid, m.p. 123.4 – 124.8 °C. **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 112.28 (s, 50%), 109.47 (s, 50%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.91 (ddd, *J*=17.4, 14.9, 8.2, 2H), 7.85 – 7.71 (m, 1H), 7.63 (dd, *J*=14.5, 7.5, 1H), 7.47 (td, *J*=7.2, 3.8, 1H), 7.42 – 7.31 (m, 1H), 7.30 – 7.21 (m, 1H), 7.16 (dd, *J*=15.1, 8.1, 1H), 2.64 (dt, *J*=13.3, 6.5,0.5H), 2.19 – 1.88 (m, 1.5H), 1.88 – 1.53 (m, 4H), 1.33 (ddd, *J*=25.0, 12.4, 6.0, 1H), 1.16 – 0.94 (m, 4H), 0.94 – 0.78 (m, 6H), 0.72 (d, *J*=6.2, 2H), 0.65 (d, *J*=6.8, 1.6H), 0.06 (d, *J*=6.8, 1.4H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 149.27 (dd, *J*=12.2, 8.8), 134.16 (s), 133.56 (s), 132.58 (d, *J*=17.1), 131.88 (d, *J*=18.3), 130.60 (s), 130.27 (s), 128.14 (dd, *J*=27.5, 12.3), 126.30 (s), 125.79 (s), 125.16 (d, *J*=10.8), 124.60 (s), 124.13 (dd, *J*=11.3, 5.7), 123.79 (s), 123.31 (d, *J*=9.9), 121.18 (d, *J*=4.3), 120.62 (d, *J*=4.3), 43.61 (d, *J*=4.1), 43.06 (d, *J*=2.7), 38.21 (s), 37.96 (s), 35.94 (s), 35.69 (s), 35.44 – 34.92 (m), 34.13 (d, *J*=19.0), 32.84 (dd, *J*=11.7, 7.4), 28.98 (d, *J*=3.5), 24.47 (dd, *J*=12.3, 4.9), 22.43 (d, *J*=12.3), 21.46 (s), 21.21 (s), 16.64 (s), 14.24 (s). HRMS (ESI^+) Calcd for $C_{22}H_{28}OP$ [M-BH_3+H^+]: 339.1878, Found: 339.3457.

The cleavage of P-O bond of 2a/2a' and stereoselective formation of 4/4'.



Typical procedure (entry 4 of Table 1):

To the solution of **2a**/**2a'** (50 mg, 0.14 mmol) in toluene (1 mL) was added lithium-naphthalene (0.5 mL, 0.50 mmol, 1M solution in THF) slowly, and the solution was stirred at room temperature for 1 hours. The reaction was quenched with dilute hydrochloric acid (8%) and the solvent was removed in vacuo. The mixture was extracted with dichloromethane (3×3 mL), washed with water (3×3 mL), and dried with anhydrous magnesium sulfate. After removing the solvents, the residue was analyzed with NMR spectrum. The peaks at -15.7/-16.5 (bm, 86%) and -2.3 ppm (bm, 14%) were observed on ^{31}P NMR spectrum, which were used to estimate the ratio of **4a**/ **4a'** as 86:14.

Entry 1 of Table 1: Similar to entry 4, THF (1 mL) was used and the mixture was stirred at room temperature for 10 hours. Two peaks at -15.7 / -16.5 (bm, 80%) and -2.3 (bm, 20%) ppm were observed.

Entry 2 of Table 1: Similar to entry 4, THF (1 mL) was used, lithium naphthalene (0.5 mL) was added at -30^{o}C and stirred for 14 h at the same temperature. Two peaks at -15.7 / -16.5 (bm, 80%) and -2.3 (bm, 20%) ppm were observed.

Entry 3 of Table 1: Similar to entry 4, THF (1 mL) was used, lithium naphthalene (0.5 mL) was added at 0 ^{o}C and the reaction was quenched after 3min. Two peaks at -15.7 / -16.5 (bm, 72%) and -2.3 (bm, 28%) ppm were observed.

Entry 5 of Table 1: Similar to entry 4, after being stirred at room temperature for 1 hour, the mixture was stirred at -45 ^{o}C for 10 mins, then quenched with tert-butyl alcohol (1 mL). Two peaks at -15.7 / -16.5 (bm, 86%) and -2.3 (bm, 14%) ppm were observed.

Entry 6 of Table 1: Similar to entry 4, after being stirred at room temperature for 3 hours, the mixture was stirred at -80 ^{o}C for 10 hs, then quenched with acetic acid/toluene (25%, 0.5 mL) at the same temperature. After quenching, the solution was warmed slowly to room temperature. Two peaks located at -15.7 /-16.5 (bm, 85%) and -2.3 (bm, 15%) ppm were observed.

Entry 7 of Table 1: Similar to entry 4, lithium naphthalene (0.5 mL) was added at -20 °C and quenched by acetic acid/toluene (25%, 0.5 mL) immediately after stirring for 1 min. Two peaks located at -15.7 / -16.5 (bm, 50%) and -2.3 (bm, 50%) ppm were observed.

Entry 8 of Table 1: Similar to entry 4, lithium naphthalene (0.5 mL) was added at -20 °C, and quenched by acetic acid/toluene (25%, 0.5 mL) after stirring at the same temperature for 30 mins at the same temperature. Two peaks located at -15.7 / -16.5 (bm, 70%) and -2.3 (bm, 30%) ppm were observed.

Entry 9 of Table 1: Similar to entry 4, lithium naphthalene (0.5 mL) was added at -20°C, and quenched by acetic acid/toluene (25%, 0.5 mL) after stirring at the same temperature for 2 hs. Two peaks located at -15.7 /-16.5 (bm, 81%) and -2.3 (bm, 19%) ppm were observed.

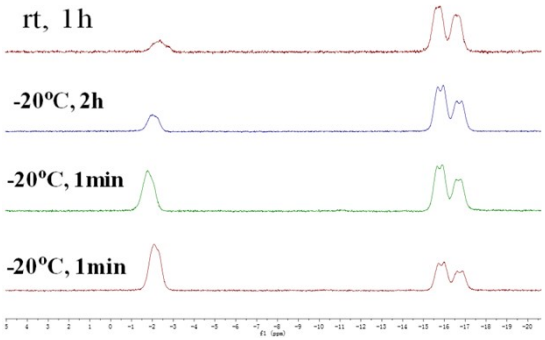


Fig. S1. The comparison of NMR spectrum of entries 4, 7, 8 and 9.

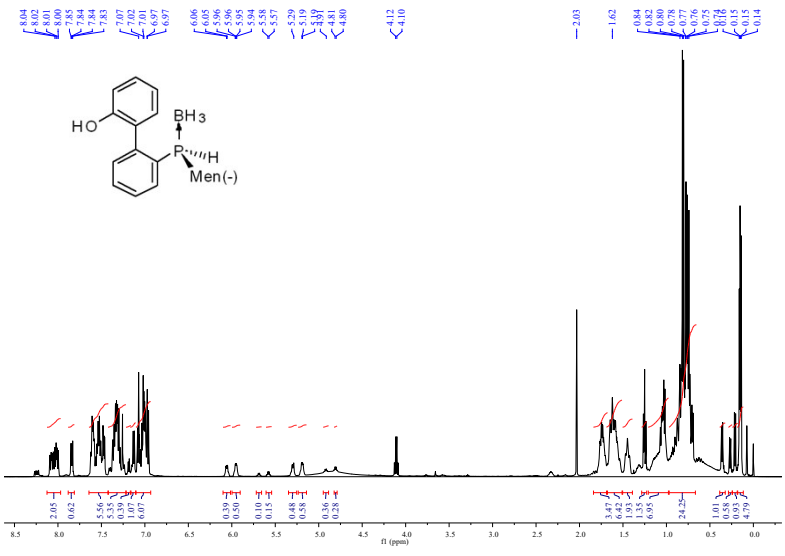
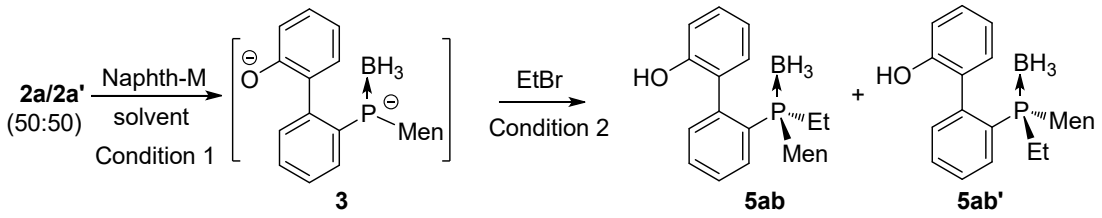


Fig. S2. The ^{1}H-NMR spectrum of entries 4a/4a'.

The cleavage of P-O bond of 2a/2a' and stereoselective formation of 5ab/5ab'.



Typical procedure (entry 1 of Table 2):

To the solution of **2a**/**2a'** (50 mg, 0.14 mmol) in toluene (1 mL) was added lithium naphthalene reagent (0.5 mL, 0.50 mmol, 1M solution in THF) slowly. The solution was stirred at room temperature for 1 hour, ethyl bromide (42 μL, 0.56 mmol) was added and the stirring was continued for 4 hours at the same temperature. After quenched with dilute hydrochloric acid (8%), the mixture was extracted with dichloromethane (3×5 mL), washed with water (3×5 mL), dried over magnesium sulfate. After removing the solvents, the sample was analyzed with NMR spectrum. The peaks at 35.7 (bm, 94%) and 28.4 / 27.3 (bm, 6%) ppm were observed on ^{31}P NMR spectrum, which were used to estimate the ratio of **5ab**/ **5ab'** as 94:6.

Entry 2 of Table 2: Similar to entry 1, petroleum ether (1 mL) was used. After addition of naphthalene lithium, the mixture was stirred at room temperature for 10 hours. After addition of ethyl bromide, the mixture was stirred at room temperature for other 10 hours. Two peaks at 35.7 (bm, 94%) and 28.4 / 27.3 (bm, 6%) ppm were observed.

Entry 3 of Table 2: Similar to entry 1, ethyl bromide was added at 0 °C. After the addition, the mixture was stirred for 10 hours at the same temperature. Two peaks at 35.7 (bm, 96%) and 28.4 / 27.3 (bm, 4%) ppm were observed.

Entry 4 of Table 2: Similar to entry 1, petroleum ether (1 mL) was used. After addition of ethyl bromide at 0 °C, the mixture was stirred at the same temperature for 4 hours. Two peaks at 35.7 (bm, 96%) and 28.4 / 27.3 (bm, 4%) ppm were observed.

Entry 5 of Table 2: Similar to entry 1, after adding lithium naphthalene (0.5 mL) at room temperature for 1 minute, ethyl bromide was added, and the reaction was quenched after stirring for 2 hours at the same temperature. Two peaks at 35.7 (bm, 93%) and 28.4 / 27.3 (bm, 7%) ppm were observed.

Entry 6 of Table 2: Similar to entry 1, petroleum ether (1 mL) was used, lithium naphthalene (0.25 mL, 3M solution in THF) was added at room temperature, Two peaks at 35.7 (bm, 91%) and

28.4 / 27.3 (bm, 9%) ppm were observed.

Entry 7 of Table 2: Similar to entry 1, petroleum ether (1 mL) was used, lithium naphthalene (0.25 mL, 3M solution in THF) was added and the mixture was stirred for 1 hour at room temperature, then ethyl bromide was added at 0 °C. Two peaks at 35.7 (bm, 94%) and 28.4 / 27.3 (bm, 6%) ppm were observed.

Entry 8 of Table 2: Similar to entry 1, lithium naphthalene (0.25 mL, 3M solution in THF) was added and the mixture was stirred for 1 hour at room temperature, then ethyl bromide added at 0 °C. Two peaks at 35.7 (bm, 94%) and 28.4 / 27.3 (bm, 6%) ppm were observed.

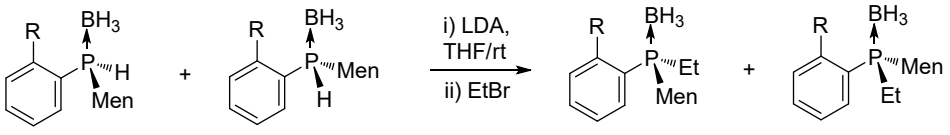
Entry 9 of Table 2: Similar to entry 1, toluene (3 mL) was used, lithium naphthalene (0.25 mL, 3M solution in THF) was added and the mixture was stirred for 10 hour at room temperature, then ethyl bromide was added at room temperature. Two peaks at 35.7 (bm, 87%) and 28.4 /27.3 (bm, 13%) ppm were observed.

Entry 10 of Table 2: Similar to entry 1, 0.5 M solution Nap-Li (0.25 mL) was used. Two peaks at 35.7 (bm, 94%) and 28.4 / 27.3 (bm, 6%) ppm were observed.

Entry 11 of Table 2: Similar to entry 1, petroleum ether (1 mL) and 0.5 M solution Nap-Li (0.25 mL) were used. Two peaks at 35.7 (bm, 95%) and 28.4 / 27.3 (bm, 5%) ppm were observed.

Entry 12 of Table 2: Similar to entry 1, Nap-Li was prepared in the presence of of TMEDA (v/v=1:1 to THF). Two peaks at 35.7 (bm, 94%) and 28.4 / 27.3 (bm, 6%) ppm were observed.

Stereoselective alkylation of aryl menthyl phosphine-boran in the presence of LDA



R = *o*-OHPh, **4a** (50)	:	**4a'** (50)		**5ab** (93)	:	**5ab'** (7)
R = H, **4b** (31)	:	**4b'** (69)		**5bb** (69)	:	**5bb'** (31)

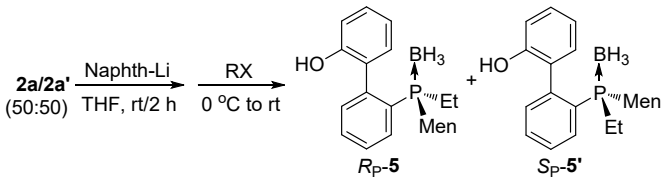
Typical procedure (entry 1 of Scheme 3):

To the solution of **4a/4a'** (43:57, 80 mg, 0.23 mmol) in THF (1 mL), LDA (345 μL, 0.69 mmol, 2 mol/L in heptane/THF/ethylbenzene) was added at -30 °C. The mixture was warmed slowly to room temperature, then ethyl bromide (67 μL, 0.90 mmol) was added and the mixture was stirred at room temperature for 10 h. The reaction was quenched with dilute hydrochloric acid (8%) and the solvent was removed. The mixture was extracted with dichloromethane (3×10 mL), washed

with water (3×10 mL), and dried over anhydrous magnesium sulfate. After removing the solvents, the sample was analyzed with ^{31}P-NMR spectrum, two single peaks at 35.8 (bm, 97%), and 28.5 (bd, 3%) ppm were observed.

Entry 2 of Scheme 3: Similar to the above, phenyl menthyl phosphine-borane (31:69) was used. After removing the solvents, the sample was analyzed with ^{31}P NMR spectrum. Two peaks of 25.1 (bm, 69%) and 22.3 ppm (bm, 31%) were observed.

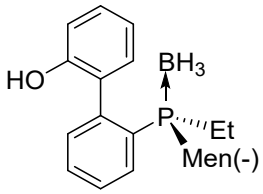
Part 2. Cleavage of P-O bond and *P*-Alkylation of 2a/2a' (Formation of 5)



Typical procedure, the preparation of 5ab:

To the solution of **2a/2a'** (80 mg, 0.23 mmol) in toluene (1.5 mL), was added lithium-naphthalene (0.8 mL, 0.81 mmol, 1M solution in THF) slowly, and the mixture was stirred at room temperature for 2 hours, then cooled with the ice-both. Ethyl bromide (68 μL, 0.92 mmol) was added, and the stirring was continued for 4 hours at the same temperature. After the reaction was completed, as monitored with TLC, the reaction was quenched with dilute hydrochloric acid (8%) and the solvent was removed in vacuo. The mixture was extracted with dichloromethane (3×10 mL), washed with water (3×10 mL), and dried with anhydrous magnesium sulfate. After removing solvent, the residue was purified by preparative TLC (silica gel, petroleum ether/ethyl acetate = 4/1 as eluent) to afford **5ab**. R_P-**5ab** was obtained by recrystallization from dichloromethane and petroleum ether (3/1).

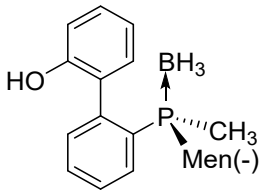
(R_P)-(–)-Menthyl ethyl (2'-hydroxy-1,1'-biphenyl-2-yl)phosphine borane (R_P-5ab)



The crude **5ab** was formed in a ratio of 95:5 (estimated by ^{31}P-NMR spectrum), the pure ***R*$_P$-5ab** was obtained as a white solid (56.2 mg, 71%, >99:1 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 5:1 as eluent); m.p. 153.9-156.2 °C; **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 35.7 (bm); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.21 – 8.13 (m, 1H), 7.59 – 7.54 (m, 1H), 7.51 (d, *J*=1.5, 1H), 7.38 – 7.33 (m, 1H), 7.29 (ddd, *J*=7.4, 3.6, 1.8, 1H), 7.15 (dd, *J*=7.5, 1.5, 0.5H), 7.01 (dd, *J*=8.4, 5.4, 2.5H), 4.69 (d, *J*=14.2, 1H), 2.08 – 1.96 (m, 1H), 1.94 – 1.82 (m, 1.5H), 1.73 – 1.66 (m, 1H), 1.66 – 1.53 (m, 4H), 1.48 (ddd, *J*=16.5, 12.6, 2.3, 0.5H), 1.34 – 1.21 (m, 1H), 1.21 – 1.10 (m, 1H), 1.11 – 0.99 (m, 2H), 0.93 (dd, *J*=12.9, 5.3, 1H), 0.88 (dd, *J*=12.3, 5.5, 5H), 0.83 (d, *J*=6.8, 2H), 0.78 (d, *J*=6.4, 2H), 0.71 (d, *J*=6.3, 2H), 0.43 (d, *J*=6.9, 2H), 0.38 (d, *J*=6.9, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 153.20 (d, *J*=3.0), 139.56 (s), 139.27 (s), 138.79 (dd, *J*=35.5, 16.2), 131.94 (dd, *J*=15.8, 6.1), 131.18 (d, *J*=2.0), 130.34 (d, *J*=10.3), 130.12 (s), 129.81 (s), 128.48 (dd, *J*=12.0, 4.7), 127.27 (s), 44.16 (d, *J*=29.4), 37.52 – 37.20 (m), 37.11 (s), 35.85 (d, *J*=29.5), 34.20

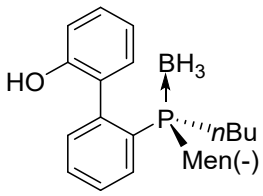
(s), 33.11 (dd, *J*=30.7, 11.7), 28.69 (d, *J*=14.7), 24.90 (dd, *J*=11.7, 5.1), 22.40 (d, *J*=18.8), 21.54 – 21.07 (m), 20.95 (s), 18.35 (d, *J*=33.7), 15.04 (d, *J*=15.8), 8.99 (s), 8.77 (s). HRMS (ESI+): The compound was reported, as seen in Y. Zhang; S.-Z. Nie, J.-J. Ye, J.-P. Wang, M.-M. Zhou, C.-Q. Zhao and Q. Li, *J. Org. Chem.*, **2019**, 84, 8423-8439.

(R_P/S_P)-(–)-Menthyl methyl (2'-hydroxy-1,1'-biphenyl-2-yl)phosphine borane (R_P-5aa /S_P-5aa')



The crude **5aa/5aa'** was formed in a ratio of 86:14 (estimated by ^{31}P-NMR spectrum). After isolation with preparative TLC (silica gel, petroleum ether/ethyl acetate = 5:1 as eluent), the compound was obtained as a white foamy solid (61.1 mg, 81%, 86:14 dr) m.p. 62.0-64.6 °C; **^{31}P NMR (202 MHz, CDCl3)** δ = 21.40 (bm, 86%), 18.4 / 17.5 (bm, 14%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.13 (dd, J=13.2, 7.8, 1H), 7.54 (dd, J=14.9, 7.5, 1H), 7.47 (dd, J=15.0, 7.6, 1H), 7.39 – 7.31 (m, 1H), 7.26 (d, J=8.0, 1H), 7.18 (d, J=7.5, 0.5H), 7.06 – 6.97 (m, 2.5H), 4.98 (s, 1H), 2.22 – 2.06 (m, 1H), 2.02 – 1.85 (m, 2H), 1.86 – 1.74 (m, 1H), 1.69 (d, J=10.5, 2.5H), 1.61 – 1.50 (m, 1H), 1.41 (d, J=10.0, 1.5H), 1.21 (d, J=10.1, 3H), 1.13 (s, 1H), 0.89 (d, J=15.9, 3H), 0.87 – 0.83 (m, 2H), 0.83 – 0.78 (m, 3H), 0.74 (s, 1H), 0.46 – 0.39 (m, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 153.27 (d, *J*=16.8), 139.40 (s), 137.03 (d, *J*=17.2), 132.03 (d, *J*=6.1), 131.68 (s), 131.59 – 131.12 (m), 130.92 (d, *J*=4.2), 130.47 (s), 130.02 (s), 128.34 (d, *J*=12.1), 127.55 (d, *J*=12.6), 119.91 (s), 115.99 (s), 44.32 (d, *J*=37.4), 37.86 (d, *J*=30.2), 36.99 (s), 34.27 (s), 33.34 (d, *J*=12.1), 28.50 (d, *J*=2.3), 24.83 (d, *J*=11.5), 22.50 (s), 21.29 (d, *J*=19.9), 15.07 (d, *J*=11.8), 11.90 (d, *J*=36.8). HRMS (ESI+): The compound was reported, as seen in Y. Zhang; S.-Z. Nie, J.-J. Ye, J.-P. Wang, M.-M. Zhou, C.-Q. Zhao and Q. Li, *J. Org. Chem.*, **2019**, 84, 8423-8439.

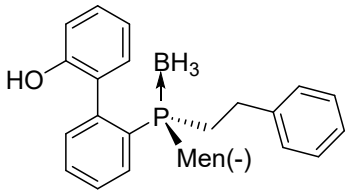
(R_P)-(–)-Menthyl butyl (2'-hydroxy-1,1'-biphenyl-2-yl)phosphine borane (R_P-5ac)



The crude **5ac** was formed in a ratio of 96:4 (estimated by ^{31}P-NMR spectrum), the pure ***R_P*-5ac** was obtained as a white solid (54.6 mg, 69%, >99:1 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 6:1 as eluent); m.p. 142.9-144.5 °C; **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 32.2 (bm); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.14 – 8.05 (m, 1H), 7.49 (td, *J*=7.4, 1.3, 1H), 7.43 (t, *J*=7.5, 1H), 7.31 – 7.25 (m, 1H), 7.22 (td, *J*=5.6, 2.0, 1H), 7.04 (dd, *J*=7.5, 1.4, 0.5H), 6.97 – 6.89 (m, 2.5H), 4.68 (d, *J*=17.9, 1H), 2.03 – 1.93 (m, 0.5H), 1.90 – 1.79 (m, 1.5H), 1.77 – 1.68 (m,

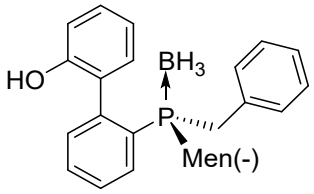
0.5H), 1.67 – 1.51 (m, 3H), 1.51 – 1.36 (m, 3H), 1.31 – 1.17 (m, 2H), 1.18 – 1.02 (m, 3H), 1.01 – 0.90 (m, 1.5H), 0.87 – 0.80 (m, 4H), 0.77 (d, *J*=7.2, 3H), 0.69 (dd, *J*=8.7, 6.9, 5H), 0.63 (d, *J*=6.3, 1H), 0.39 (d, *J*=6.9, 2H), 0.32 (d, *J*=6.8, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 153.16 (d, *J*=14.6), 139.74 – 138.15 (m), 132.19 – 131.72 (m), 131.14 (dd, *J*=8.7, 2.0), 130.34 (d, *J*=13.8), 129.93 (d, *J*=4.1), 129.14 (s), 128.81 (d, *J*=10.6), 128.49 (dd, *J*=12.0, 8.6), 127.22 (d, *J*=1.8), 119.96 (d, *J*=19.5), 115.99 (d, *J*=18.8), 44.50 – 43.79 (m), 37.55 (d, *J*=28.8), 37.19 (s), 35.90 (d, *J*=29.4), 34.19 (s), 33.29 (d, *J*=11.1), 32.98 (d, *J*=12.0), 28.86 – 28.49 (m), 27.66 (d, *J*=32.0), 26.88 – 26.26 (m), 25.22 – 24.69 (m), 24.32 (dd, *J*=14.7, 6.7), 22.41 (d, *J*=18.4), 21.27 (d, *J*=26.9), 15.09 (d, *J*=9.2), 13.62 (s). HRMS (ESI+): The compound was reported, as seen in Y. Zhang; S.-Z. Nie, J.-J. Ye, J.-P. Wang, M.-M. Zhou, C.-Q. Zhao and Q. Li, *J. Org. Chem.*, **2019**, 84, 8423-8439.

(R_P)-(–)-Menthyl phenylethyl (2'-hydroxy-1,1'-biphenyl-2-yl)phosphine borane (R_P-5ad)



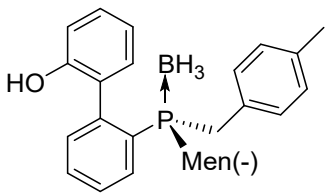
The crude **5ad** was formed in a ratio of 96:4 (estimated by ^{31}P-NMR spectrum), the pure compound ***R*$_P$-5ad** was obtained as white solid (58.6 mg, 74%, >99:1 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 4:1 as eluent); m.p. 185.4-186.2 °C; **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 32.2 (bm); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.23 (dd, *J*=12.8, 8.2, 1H), 7.62 – 7.50 (m, 2H), 7.36 – 7.25 (m, 3H), 7.25 – 7.17 (m, 2H), 7.15 (d, *J*=7.3, 0.5H), 7.11 (d, *J*=7.3, 0.5H), 7.05 (d, *J*=7.4, 1H), 7.01 (dd, *J*=7.4, 5.1, 1H), 6.96 – 6.89 (m, 1H), 4.81 (s, 0.5H), 4.73 (s, 0.5H), 2.97 – 2.83 (m, 1H), 2.41 – 2.28 (m, 1H), 2.26 – 2.11 (m, 1H), 2.10 – 2.01 (m, 0.5H), 2.01 – 1.75 (m, 2.5H), 1.75 – 1.51 (m, 4H), 1.35 – 1.12 (m, 2H), 1.11 – 1.00 (m, 1.5H), 0.88 (t, *J*=7.0, 3.5H), 0.82 (d, *J*=6.8, 2H), 0.78 (d, *J*=6.4, 2H), 0.72 (d, *J*=6.3, 2H), 0.43 (d, *J*=6.9, 2H), 0.37 (d, *J*=6.8, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 152.96 (s), 141.80 (d, *J*=15.7), 141.38 (d, *J*=14.7), 139.71 (s), 138.70 (d, *J*=16.6), 138.41 (d, *J*=16.4), 132.26 – 131.77 (m), 131.30 (d, *J*=2.1), 130.39 (d, *J*=2.8), 130.06 (d, *J*=24.6), 128.75 – 128.19 (m), 128.16 (d, *J*=13.3), 127.92 (d, *J*=4.3), 127.34 (d, *J*=15.6), 126.13 (d, *J*=39.9), 120.13 (d, *J*=18.2), 116.14 (d, *J*=14.9), 44.15 (d, *J*=29.6), 37.46 (d, *J*=28.7), 37.16 (d, *J*=4.8), 35.99 (d, *J*=29.2), 34.17 (s), 33.29 (d, *J*=11.4), 33.03 (d, *J*=12.1), 30.67 (s), 29.85 (s), 29.35 (d, *J*=29.8), 28.74 (dd, *J*=13.0, 1.5), 26.29 (d, *J*=31.1), 24.93 (dd, *J*=11.8, 3.8), 22.41 (d, *J*=19.0), 21.28 (d, *J*=23.0), 15.12 (d, *J*=4.8). **HRMS (ESI+)** Calcd. for $C_{30}H_{40}BOP$ [M+Na^+]: 481.2808, Found: 481.2826.

(R_P)-(–)-Menthyl benzyl (2'-hydroxy-1,1'-biphenyl-2-yl)phosphine borane (R_P-5ae)



The crude **5ae** was formed in a ratio of 96:4 (estimated by ^{31}P-NMR spectrum), the pure compound ***R*$_P$-5ae** was obtained as white solid (49.1 mg, 62%, >99:1 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 5:1 as eluent); m.p. 143.1-146.2 °C; **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 34.0 (bm, 51%), 32.4 (bm, 49%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 7.97 (dd, *J*=12.9, 7.8, 0.5H), 7.73 (dd, *J*=12.8, 7.5, 0.5H), 7.54 (t, *J*=7.5, 0.5H), 7.48 (t, *J*=7.5, 0.5H), 7.45 – 7.40 (m, 1H), 7.35 (td, *J*=8.8, 1.6, 1H), 7.27 (d, *J*=1.2, 1H), 7.13 – 7.07 (m, 2H), 7.06 (s, 1H), 7.04 – 6.97 (m, 1.5H), 6.93 (d, *J*=8.2, 0.5H), 6.91 – 6.88 (m, 2H), 4.77 (s, 0.5H), 4.48 (s, 0.5H), 3.58 (t, *J*=14.5, 0.5H), 3.41 – 3.30 (m, 1H), 2.96 (dd, *J*=14.4, 8.2, 0.5H), 2.24 – 2.10 (m, 1H), 1.97 (td, *J*=13.2, 2.7, 0.5H), 1.76 – 1.63 (m, 3H), 1.63 – 1.50 (m, 2H), 1.44 – 1.30 (m, 1.5H), 1.15 – 1.01 (m, 2H), 0.90 (dd, *J*=6.7, 3.6, 4H), 0.88 – 0.83 (m, 1H), 0.78 (d, *J*=6.5, 2H), 0.74 (d, *J*=6.1, 2H), 0.59 (dd, *J*=13.1, 6.9, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 152.97 (d, *J*=37.3), 140.11 (d, *J*=75.6), 137.58 (dd, *J*=43.7, 14.7), 133.60 (d, *J*=3.6), 133.17 (d, *J*=5.3), 132.43 (d, *J*=6.5), 132.12 (d, *J*=6.4), 131.06 (s), 130.63 (s), 130.50 – 129.99 (m), 128.94 (dd, *J*=45.9, 18.3), 128.45 – 127.94 (m), 127.76 (d, *J*=2.6), 126.59 (dd, *J*=14.3, 2.8), 120.11 (d, *J*=16.5), 116.35 (d, *J*=60.6), 44.28 (d, *J*=44.7), 37.54 (d, *J*=26.7), 37.17 (d, *J*=20.2), 36.36 (dd, *J*=51.3, 26.4), 34.23 (s), 33.19 (dd, *J*=16.5, 11.7), 32.17 (s), 31.94 (s), 31.60 (s), 28.72 (d, *J*=51.7), 25.03 (dd, *J*=11.4, 4.0), 22.34 (d, *J*=28.4), 21.32 (d, *J*=28.1), 15.38 (d, *J*=11.2), 14.12(s). HRMS (ESI+): The compound was reported, as seen in Y. Zhang; S.-Z. Nie, J.-J. Ye, J.-P. Wang, M.-M. Zhou, C.-Q. Zhao and Q. Li, *J. Org. Chem.*, **2019**, 84, 8423-8439.

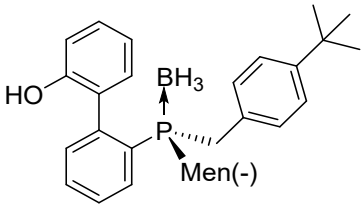
(*R*$_P$)-(–)-Menthyl *p*-methylbenzyl (2'-hydroxy-1,1'-biphenyl-2-yl)phosphine borane (*R*$_P$-5af)



The crude **5af** was formed in a ratio of 92:8 (estimated by ^{31}P-NMR spectrum), the pure compound ***R*$_P$-5af** was obtained as white solid (51.5 mg, 65%, >99:1 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 4:1 as eluent); m.p. 57.9- 60.1 °C; **^{31}P NMR (162 MHz, $CDCl_3$)** δ = 34.2 (bm, 49%), 32.3 (bm, 51%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.93 (dd, *J*=12.9, 7.9, 1H), 7.76 – 7.68 (m, 1H), 7.47 (t, *J*=7.0, 1H), 7.43 – 7.29 (m, 2H), 7.29 – 7.16 (m, 2H), 7.01 (t, *J*=7.9, 1H), 6.89 (dd, *J*=14.7, 8.6, 3H), 6.78 (dd, *J*=14.1, 7.3, 2H), 4.81 (s, 1H), 3.56 (t, *J*=14.5, 1H), 3.41 – 3.24 (m, 1H), 2.86 (dd, *J*=14.2, 9.1, 1H), 2.23 (s, 3H), 2.16 – 1.86 (m, 1H), 1.66 (s, 3H), 1.59 – 1.45 (m, 1H), 1.33 (dd, *J*=28.0, 20.4, 2H), 1.18 – 0.93 (m, 2H),

0.87 (t, *J*=15.3, 4H), 0.77 (d, *J*=6.4, 2H), 0.73 (d, *J*=5.1, 2H), 0.59 (d, *J*=6.7, 2H), 0.54 (d, *J*=6.7, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 153.08 (d, *J*=31.2), 140.59 (s), 139.94 (s), 137.62 (dd, *J*=43.7, 14.7), 136.08 (d, *J*=30.4), 132.45 (d, *J*=6.4), 132.14 (d, *J*=6.4), 130.98 (dd, *J*=4.1, 2.3), 130.66 (s), 130.46 (d, *J*=3.8), 130.07 (dd, *J*=16.3, 4.4), 128.75 (d, *J*=6.3), 128.45 (dd, *J*=4.6, 2.4), 128.25 – 127.74 (m), 127.53 (s), 120.01 (d, *J*=7.4), 116.37 (d, *J*=53.0), 53.47 (s), 44.30 (d, *J*=38.9), 37.46 (s), 37.18 (d, *J*=25.0), 36.48 (d, *J*=26.3), 35.66 (d, *J*=26.9), 34.26 (s), 33.16 (dd, *J*=15.0, 11.5), 31.52 (d, *J*=28.8), 28.90 (s), 28.48 (s), 25.04 (dd, *J*=11.4, 2.9), 22.38 (d, *J*=26.5), 21.35 (d, *J*=26.7), 21.05 (d, *J*=3.6), 15.39 (d, *J*=10.0). HRMS (ESI+): The compound was reported, as seen in Y. Zhang; S.-Z. Nie, J.-J. Ye, J.-P. Wang, M.-M. Zhou, C.-Q. Zhao and Q. Li, *J. Org. Chem.*, **2019**, 84, 8423-8439.

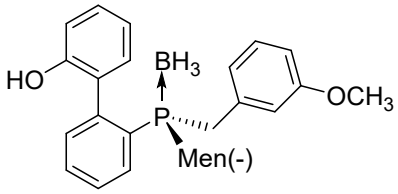
(R_P)-(–)-Menthyl *p-tert*-butylbenzyl (2'-hydroxy-1,1'-biphenyl-2-yl)phosphine borane (R_P-5ag)



The crude **5ag** was formed in a ratio of 93:7 (estimated by ^{31}P-NMR spectrum), the pure compound ***R*$_P$-5ag** was obtained as white solid (53.1 mg, 67%, >99:1 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 4:1 as eluent); m.p. 145.8-149.4 °C; **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 34.0 (bm, 51%), 32.1 (bm, 49%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 7.97 (dd, *J*=12.6, 7.8, 0.5H), 7.70 (dd, *J*=12.6, 7.9, 0.5H), 7.52 (s, 0.5H), 7.49 – 7.38 (m, 1.5H), 7.36 – 7.28 (m, 1H), 7.28 – 7.20 (m, 2H), 7.11 (d, *J*=8.2, 1H), 7.06 (d, *J*=8.2, 1H), 7.03 – 6.98 (m, 1H), 6.94 (t, *J*=7.5, 0.5H), 6.90 (d, *J*=8.1, 0.5H), 6.80 (dd, *J*=20.7, 7.7, 2H), 4.89 (s, 0.5H), 4.56 (d, *J*=7.5, 0.5H), 3.53 (t, *J*=14.4, 0.5H), 3.37 – 3.25 (m, 1H), 2.95 (td, *J*=14.8, 4.3, 0.5H), 2.23 – 2.08 (m, 1H), 1.98 (td, *J*=12.9, 2.5, 1H), 1.78 – 1.62 (m, 3H), 1.63 – 1.51 (m, 2H), 1.45 – 1.32 (m, 2H), 1.33 – 1.19 (m, 10H), 1.13 – 0.99 (m, 2H), 0.89 (t, *J*=7.3, 4H), 0.77 (d, *J*=6.5, 2H), 0.73 (d, *J*=5.8, 2H), 0.58 (dd, *J*=12.1, 6.8, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 153.07 (d, *J*=24.8), 149.49 (d, *J*=27.7), 140.66 (s), 139.85 (s), 137.66 (d, *J*=13.7), 137.03 (d, *J*=14.0), 132.47 (d, *J*=6.5), 132.08 (d, *J*=6.4), 130.94 (dd, *J*=6.8, 1.9), 130.62 (s), 130.15 (d, *J*=8.2), 129.96 (d, *J*=4.8), 129.73 (d, *J*=4.6), 129.56 – 128.34 (m), 128.18 – 127.77 (m), 127.55 (s), 124.66 (s), 120.02 (d, *J*=5.8), 116.59 (s), 116.09 (s), 44.25 (d, *J*=46.1), 37.66 (d, *J*=26.6), 37.18 (d, *J*=20.6), 36.57 (d, *J*=26.3), 35.59 (d, *J*=26.8), 34.31 (d, *J*=12.1), 33.20 (dd, *J*=20.3, 11.3), 31.74 (d, *J*=28.7), 31.32 (d, *J*=5.6), 28.92 (s), 28.49 (s), 25.05 (dd, *J*=11.4, 6.4), 22.37 (d, *J*=28.0), 21.36 (d,

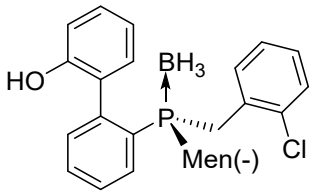
J=27.3), 15.41 (d, *J*=10.6). HRMS (ESI+): The compound was reported, as seen in Y. Zhang; S.-Z. Nie, J.-J. Ye, J.-P. Wang, M.-M. Zhou, C.-Q. Zhao and Q. Li, *J. Org. Chem.*, **2019**, 84, 8423-8439.

(R_P/S_P)-(–)-Menthyl *m*-methoxybenzyl (2'-hydroxy-1,1'-biphenyl-2-yl)phosphine borane (5ah/5ah')



The crude **5ah** was formed in a ratio of 95:5 (estimated by ^{31}P-NMR spectrum). After isolation with preparative TLC (silica gel, petroleum ether/ethyl acetate = 3:1 as eluent), the compound was obtained as white solid (59.4 mg, 75%, 96:4 dr); m.p. 99.1-102.3 °C; **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 33.5 (bm, 45%) / 32.5 (bm, 51%), 23.98 (bm, 4%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 7.94 (dd, *J*=13.0, 7.7, 0.5H), 7.76 (dd, *J*=12.8, 7.7, 0.5H), 7.49 (dt, *J*=19.3, 7.5, 1H), 7.40 (d, *J*=7.6, 1H), 7.36 – 7.32 (m, 1H), 7.31 – 7.23 (m, 1H), 7.05 – 6.96 (m, 2.5H), 6.95 (d, *J*=7.9, 0.5H), 6.91 (d, *J*=8.0, 1H), 6.68 – 6.62 (m, 1H), 6.54 – 6.46 (m, 2H), 5.11 (s, 0.5H), 4.64 (s, 0.5H), 3.62 (s, 1.5H), 3.61 – 3.51 (m, 2H), 3.39 – 3.31 (m, 1H), 2.95 (dd, *J*=14.3, 7.8, 0.5H), 2.24 – 2.08 (m, 1H), 1.95 (q, *J*=13.0, 1H), 1.69 (d, *J*=2.2, 3H), 1.57 (dd, *J*=23.7, 12.0, 1H), 1.38 (ddt, *J*=20.8, 17.7, 7.9, 1H), 1.09 (ddd, *J*=19.5, 9.7, 3.7, 2H), 0.94 – 0.87 (m, 5H), 0.78 (d, *J*=6.5, 3H), 0.73 (d, *J*=5.9, 2H), 0.59 (dd, *J*=13.8, 6.9, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 157.87 (d, *J*=15.6), 152.01 (d, *J*=30.4), 139.72 (s), 138.89 (s), 136.47 (dd, *J*=43.9, 14.7), 133.99 (s), 133.60 (s), 131.49 (d, *J*=6.4), 131.13 (d, *J*=6.4), 129.95 (d, *J*=12.1), 129.71 (s), 129.11 (d, *J*=4.4), 127.72 – 127.40 (m), 127.24 – 126.72 (m), 126.41 (d, *J*=1.4), 121.71 (dd, *J*=45.5, 5.1), 119.01 (d, *J*=9.0), 115.53 (s), 115.08 (s), 114.17 (dd, *J*=16.7, 4.7), 111.98 (d, *J*=33.3), 54.07 (d, *J*=8.9), 43.23 (d, *J*=38.7), 35.77 (ddd, *J*=84.6, 46.3, 26.7), 33.18 (s), 32.11 (t, *J*=11.5), 31.13 (d, *J*=28.3), 27.68 (dd, *J*=49.4, 1.6), 23.98 (d, *J*=12.1), 21.31 (d, *J*=26.1), 20.31 (d, *J*=25.4), 14.34 (d, *J*=12.8). **HRMS (ESI+)** Calcd. for $C_{30}H_{40}BO_2P$ [M+Na^+]: 497.2757, Found: 497.2772.

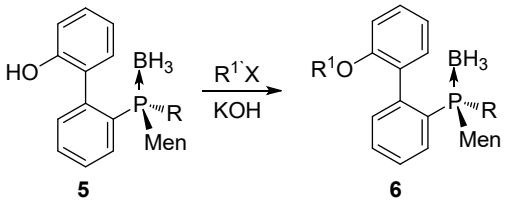
(R_P)-(–)-Menthyl *o*-chlorobenzyl (2'-hydroxy-1,1'-biphenyl-2-yl)phosphine borane (R_P-5ai)



The crude **5ai** was formed in a ratio of 95:5 (estimated by ^{31}P-NMR spectrum), the pure compound ***R_P*-5ai** was obtained as white solid (54.6 mg, 69%, >99:1 dr) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 3:1 as eluent); m.p. 146.5-149.1 °C; **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 33.54 (bm, 38%), 32.47 (bm, 62%); **^{1}H NMR (500 MHz,**

$CDCl_3$) δ = 8.10 (dd, *J*=13.5, 7.8, 0.5H), 7.93 (dd, *J*=13.1, 7.8, 0.5H), 7.54 (dt, *J*=13.7, 7.5, 1H), 7.46 (t, *J*=7.6, 0.5H), 7.40 – 7.31 (m, 1.5H), 7.30 – 7.21 (m, 2.5H), 7.09 – 6.99 (m, 3H), 6.99 – 6.94 (m, 1H), 6.90 (t, *J*=7.7, 1H), 6.78 (d, *J*=7.8, 0.5H), 4.70 (s, 1H), 3.67 (t, *J*=15.1, 0.5H), 3.55 (dd, *J*=14.9, 6.8, 0.5H), 3.34 (t, *J*=15.4, 0.5H), 3.24 (dd, *J*=15.4, 7.9, 0.5H), 2.40 – 2.22 (m, 1H), 2.02 (td, *J*=13.2, 2.2, 1H), 1.69 (dd, *J*=9.3, 3.7, 4H), 1.39 – 1.25 (m, 2H), 1.14 – 1.01 (m, 2H), 0.91 (dd, *J*=6.6, 1.5, 5H), 0.79 (d, *J*=6.3, 3H), 0.73 (d, *J*=5.9, 1H), 0.62 (t, *J*=7.5, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 151.93 (d, *J*=38.7), 139.17 (s), 136.91 (d, *J*=16.3), 133.97 (dd, *J*=6.6, 2.7), 131.65 (d, *J*=2.7), 131.42 (dd, *J*=12.8, 6.3), 130.92 (d, *J*=3.7), 130.36 (dd, *J*=13.8, 3.1), 130.20 (t, *J*=5.0), 129.82 (d, *J*=5.1), 129.35 (d, *J*=4.1), 129.18 (d, *J*=11.8), 128.27 (s), 127.83 (d, *J*=13.2), 127.31 – 127.03 (m), 126.84 (dd, *J*=24.2, 2.1), 126.34 (dd, *J*=18.6, 1.7), 125.04 (s), 52.44 (s), 43.47 (d, *J*=47.8), 36.04 (d, *J*=35.6), 35.39 (d, *J*=27.1), 33.18 (s), 32.27 (d, *J*=11.6), 30.75 (d, *J*=28.5), 27.73 (d, *J*=1.5), 27.29 (dd, *J*=16.2, 14.0), 24.02 (d, *J*=11.7), 21.35 (d, *J*=28.6), 20.22 (d, *J*=35.0), 14.28 (d, *J*=21.2). HRMS (ESI+): The compound was reported, as seen in Y. Zhang; S.-Z. Nie, J.-J. Ye, J.-P. Wang, M.-M. Zhou, C.-Q. Zhao and Q. Li, *J. Org. Chem.*, **2019**, 84, 8423-8439.

Part 3. Cleavage of P-O bond and *O,P*-alkylation of 2a/2a' (formation of 6)



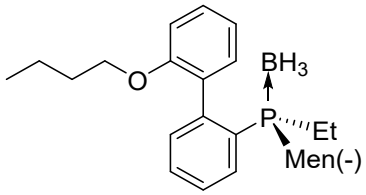
5 6

R = Et, R^1 = Et, **6a**, 98% (94:6)
Et, *n*Bu, **6b**, 97% (94:6)
*p*MeBn, Et, **6c**, 98% (95:5)
Bn, Bn, **6d**, 95% (94:6)
o-ClBn, 2-PhEt, **6e**, 96% (93:7)
*n*Bu, Bn, **6f**, 98% (94:6)
Et, 2-$PyCH_2$, **6g**, 98% (94:6)

Typical procedure A, the preparation of 6b:

To the solution of **2a/2a'** (80 mg, 0.23 mmol) in toluene (1.5 mL), was added lithium-naphthalene reagent (0.8 mL, 0.81 mmol, 1M solution in THF) slowly, and the mixture was stirred at room temperature for 2 hours. Ethyl bromide (68 μL, 0.92 mmol) was added to the ice cooled mixture, and the stirring was continued for 4 hours at the same temperature. After the reaction was completed, as monitored with TLC, the solvent was removed in vacuo. The residue was dissolved in acetonitrile (1 mL), and potassium hydroxide (15 mg, 0.23 mmol) was added. After stirring for 5 minutes, the solution was cooled with an ice bath, and *n*-butyl bromide (96 μL, 0.908 mmol) was added. After the reaction was completed, the reaction was quenched with dilute hydrochloric acid (8%). The solvent was removed in vacuo, and the mixture was extracted with dichloromethane (3×10 mL), washed with water (3×10 mL) and dried with anhydrous magnesium sulfate. After removing solvent, the residue was purified by preparative TLC (silica gel, petroleum ether/ dichloromethane = 2/1 as eluent) to afford **6b**.

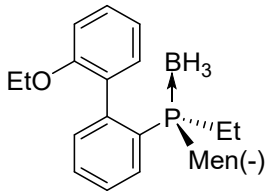
(R_P/S_P)-(–)-Menthyl ethyl (2'-butoxy-1,1-biphenyl-2-yl)phosphine borane (6b/6b')



The crude **6b/6b'** was formed in a ratio of 94:6 (estimated by ^{31}P-NMR spectrum). After isolation with preparative TLC (silica gel, petroleum ether/ dichloromethane = 2:1 as eluent), the compound was obtained as colorless oil (58.2 mg, 75%, 95:5 dr); **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 34.7 (bm, 95%), 27.5 (bm, 3%) / 26.4 (bm, 2%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.06 (dd, *J*=13.1, 8.0, 1H), 7.44 (t, *J*=7.5, 1H), 7.42 – 7.35 (m, 2H), 7.23 – 7.13 (m, 1H), 7.05 – 6.94 (m, 3H), 3.99 – 3.94 (m, 0.5H), 3.90 (t, *J*=6.5, 1H), 3.87 – 3.83 (m, 0.5H), 2.09 – 1.95 (m, 1H), 1.93 – 1.78 (m, 2H), 1.71 – 1.63 (m, 2H), 1.61 – 1.48 (m, 5H), 1.40 – 1.31 (m, 2H), 1.26 (d, *J*=7.4, 3H), 1.09 (ddd, *J*=24.5, 12.5, 5.8, 1H), 0.99 – 0.91 (m, 2H), 0.86 (dt, *J*=6.1, 3.9, 6H), 0.84 – 0.79 (m, 4H), 0.78 (d, *J*=6.4, 2H), 0.70 (d, *J*=5.7, 1H), 0.40 (dd, *J*=12.4, 6.9, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 156.74 (d, *J*=26.4), 141.94 (s), 137.59 (d,

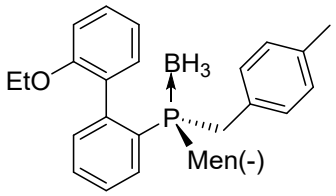
J=16.6), 132.32 (dd, *J*=16.7, 6.2), 130.09 (ddd, *J*=38.8, 28.9, 22.7), 127.05 (d, *J*=12.2), 126.35 (dd, *J*=48.8, 34.2), 119.44 (d, *J*=40.4), 112.59 (s), 111.55 (s), 68.41 (s), 67.60 (s), 43.92 (d, *J*=30.0), 37.27 (t, *J*=14.7), 36.32 (s), 35.53 (d, *J*=30.1), 34.24 (d, *J*=18.1), 33.24 (d, *J*=11.5), 32.84 (d, *J*=12.2), 31.02 (d, *J*=9.8), 28.62 (d, *J*=9.4), 25.29 – 24.57 (m), 22.45 (d, *J*=14.7), 21.30 (d, *J*=21.5), 19.03 (s), 18.55 (d, *J*=34.0), 15.10 (d, *J*=24.5), 13.69 (d, *J*=2.5), 9.05 (d, *J*=2.3), 8.43 (d, *J*=1.1). **HRMS (ESI+)** Calcd. for $C_{28}H_{44}BOP$ [M+Na^+]: 461.3121, Found: 461.3133.

(R_P/S_P)-(–)-Menthyl ethyl (2'-ethoxy-1,1-biphenyl-2-yl)phosphine borane (6a/6a')



The crude **6a/6a'** was formed in a ratio of 94:6 (estimated by ^{31}P-NMR spectrum). After isolation from preparative TLC (silica gel, petroleum ether/ethyl acetate = 30:1 as eluent), the compound was obtained as white solid (54.9 mg, 70%, 94:6 dr); m.p. 119.8-121.5 °C; **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 34.7 (bm, 94%), 27.4 (bm, 3%) / 26.5 (bm, 3%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 7.90 (dd, *J*=13.5, 7.8, 1H), 7.28 (t, *J*=7.5, 1H), 7.22 (ddd, *J*=9.0, 3.2, 1.7, 2H), 7.07 – 6.96 (m, 1.5H), 6.87 – 6.77 (m, 2.5H), 3.88 – 3.74 (m, 2H), 1.90 – 1.79 (m, 1H), 1.76 – 1.68 (m, 1H), 1.63 (td, *J*=13.5, 2.4, 1H), 1.49 (d, *J*=1.9, 2H), 1.40 (dd, *J*=13.3, 5.0, 2H), 1.24 – 1.14 (m, 1.5H), 1.03 (t, *J*=7.0, 3H), 1.00 – 0.88 (m, 1H), 0.79 (dd, *J*=12.3, 4.6, 2H), 0.76 – 0.66 (m, 6.5H), 0.64 (d, *J*=6.7, 2H), 0.61 (d, *J*=6.4, 2H), 0.54 (d, *J*=6.1, 2H), 0.23 (t, *J*=6.9, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 156.58 (d, *J*=25.5), 142.09 (d, *J*=16.1), 137.56 (d, *J*=16.6), 132.31 (dd, *J*=11.7, 6.3), 130.78 (s), 130.65 – 129.59 (m), 127.05 (d, *J*=12.2), 119.53 (d, *J*=42.2), 112.74 (s), 111.55 (s), 77.78 – 76.65 (m), 64.32 (s), 63.48 (s), 43.93 (d, *J*=30.8), 37.25 (d, *J*=6.1), 36.99 (s), 36.33 (s), 34.25 (d, *J*=19.3), 33.20 (d, *J*=11.5), 32.87 (d, *J*=12.2), 28.81 – 28.57 (m), 25.23 – 24.66 (m), 22.45 (d, *J*=15.2), 21.58 – 21.01 (m), 18.62 (d, *J*=33.9), 15.10 (d, *J*=25.3), 14.61 (d, *J*=14.2), 9.06 (d, *J*=2.2), 8.53 (s). **HRMS (ESI+)** Calcd. for $C_{26}H_{40}BOP$ [M+Na^+]: 433.2808, Found: 433.2820.

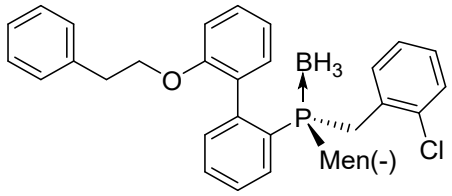
(R_P/S_P)-(–)-Menthyl *p*-methylbenzyl (2'-ethoxy-1,1-biphenyl-2-yl)phosphine borane (6c/6c')



The crude **6c/6c'** was formed in a ratio of 93:7 (estimated by ^{31}P-NMR spectrum). After isolation from preparative TLC (silica gel, petroleum ether/ dichloromethane = 2:1 as eluent), the compound was obtained as colorless oil (61.2 mg, 78%, 95:5 dr); **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 33.55 (bm, 96%), 23.86 (bm, 4%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.82 – 7.75 (m, 0.7H), 7.65 (dd, *J* = 14.1, 7.9, 0.3H), 7.51 – 7.44 (m, 1H), 7.43 – 7.35 (m, 1H),

7.29 (dq, *J* = 7.6, 5.7, 1H), 7.23 (dd, *J* = 7.6, 2.8, 1H), 6.98 (dd, *J* = 18.8, 11.4, 3H), 6.87 (d, *J* = 7.5, 2H), 6.68 (d, *J* = 7.9, 1.5H), 6.59 (dt, *J* = 8.1, 2.1, 0.5H), 3.97 (tq, *J* = 15.8, 7.2, 1.7H), 3.46 (q, *J* = 14.6, 1H), 3.33 – 3.26 (m, 0.3H), 2.82 (dd, *J* = 13.3, 7.4, 1H), 2.26 (d, *J* = 31.2, 4H), 2.14 – 2.08 (m, 1H), 1.92 – 1.76 (m, 1H), 1.75 – 1.62 (m, 3H), 1.59 – 1.40 (m, 2H), 1.34 – 1.24 (m, 1H), 1.18 (q, *J* = 8.3, 6.9, 3H), 0.89 (dd, *J* = 21.3, 7.0, 6H), 0.78 (d, *J* = 6.4, 3H), 0.70 (dd, *J* = 6.3, 1.5, 1H), 0.54 (d, *J* = 6.8, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 156.59 (s), 156.02 (s), 155.88 (s), 142.44 (s), 141.61 (d, *J*=16.7), 137.24 (dd, *J*=32.7, 16.4), 135.88 (d, *J*=29.6), 133.59 (d, *J*=17.4), 132.70 (dd, *J*=19.6, 6.4), 131.30 (s), 130.75 (dd, *J*=9.7, 6.5), 130.29 (dd, *J*=19.1, 12.8), 129.79 (d, *J*=18.5), 129.07 (s), 128.42 (s), 128.17 (d, *J*=2.6), 127.60 (s), 127.31 – 126.92 (m), 126.87 – 126.47 (m), 70.01 (s), 63.73 (s), 44.32 (s), 37.36 (s), 37.07 – 35.28 (m), 34.34 (d, *J*=14.2), 33.14 (d, *J*=11.3), 31.56 (d, *J*=28.3), 28.46 (s), 25.02 (dd, *J*=11.0, 7.4), 22.52 (s), 21.86 – 20.72 (m), 15.51 (d, *J*=4.7), 15.28 (s), 14.66 (s). **HRMS (ESI+)** Calcd. for $C_{32}H_{44}BOP$ [M+K^+]: 525.2860, Found: 525.2874.

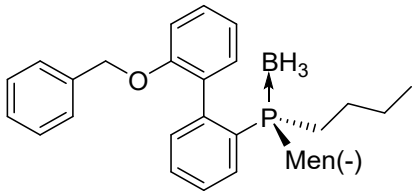
(R_P/S_P)-(–)-Menthyl *o*-chlorobenzyl (2'-phenylethoxy-1,1-biphenyl-2-yl)phosphine borane (6e/6e')



The crude **6e/6e'** was formed in a ratio of 93:7 (estimated by ^{31}P-NMR spectrum). After isolation from preparative TLC (silica gel, petroleum ether/ dichloromethane = 1:1 as eluent), the compound was obtained as colorless oil (56.8 mg, 74%, 97:3 dr); **^{31}P NMR (202 MHz, CDCl3)** δ= 33.0 (bm, 97%), 26.0 (bm, 2%) / 24.6 (bm, 1%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.04 – 7.93 (m, 1H), 7.54 (t, *J*=7.5, 1H), 7.52 – 7.36 (m, 3H), 7.33 (d, *J*=7.5, 1H), 7.31 – 7.25 (m, 1H), 7.25 – 7.22 (m, 1H), 7.18 (d, *J*=7.8, 1H), 7.16 – 7.06 (m, 3H), 7.07 – 7.00 (m, 2H), 6.97 (t, *J*=8.7, 1H), 6.94 – 6.90 (m, 0.5H), 6.81 (t, *J*=7.7, 0.5H), 6.49 (d, *J*=7.8, 0.5H), 6.33 (t, *J*=7.5, 0.5H), 5.15 – 5.03 (m, 0.5H), 4.99 (d, *J*=13.1, 1H), 4.73 (d, *J*=13.1, 0.5H), 3.66 – 3.51 (m, 0.5H), 3.32 (dd, *J*=15.1, 7.3, 1H), 3.18 (t, *J*=15.6, 0.5H), 2.69 – 2.62 (m, 0.2H), 2.53 – 2.40 (m, 0.8H), 2.28 – 2.18 (m, 0.3H), 2.01 (dd, *J*=25.2, 12.0, 1H), 1.72 (d, *J*=7.1, 3H), 1.60 – 1.50 (m, 0.7H), 1.48 – 1.29 (m, 3H), 1.18 – 1.04 (m, 1H), 1.00 – 0.83 (m, 6H), 0.78 (d, *J*=6.4, 3H), 0.61 (dd, *J*=9.4, 7.0, 4H), 0.37 (d, *J*=6.2, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 154.42 (s), 140.84 (s), 136.52 (d, *J*=16.7), 133.59 (d, *J*=6.9), 133.05 (s), 131.78 (d, *J*=6.3), 131.38 (d, *J*=2.6), 131.14 (s), 130.63 (s), 130.36 (d, *J*=4.7),

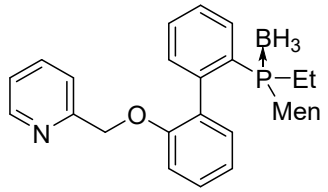
129.86 (d, *J*=5.5), 129.29 (d, *J*=24.3), 128.89 (s), 128.06 (s), 127.96 – 127.55 (m), 127.33 (s), 126.84 (s), 126.41 (dd, *J*=23.2, 10.7), 125.84 (s), 125.65 (s), 125.02 (s), 124.75 (s), 65.83 (s), 52.40 (s), 43.43 (s), 36.26 (d, *J*=28.4), 35.28 (d, *J*=25.3), 33.28 (s), 32.33 (d, *J*=11.3), 31.92 (d, *J*=12.1), 30.50 (d, *J*=29.3), 27.78 (s), 27.15 (s), 26.77 (d, *J*=29.9), 24.09 (d, *J*=11.4), 21.48 (s), 20.87 (s), 20.23 (d, *J*=33.5), 14.31 (d, *J*=34.7). **HRMS (ESI+)** Calcd. for $C_{37}H_{45}BClOP$ [M+Na^+]: 605.2887, Found: 605.2903.

(R_P/S_P)-(–)-Menthyl butyl (2'-benzyloxy-1,1-biphenyl-2-yl)phosphine borane (6f/6f')



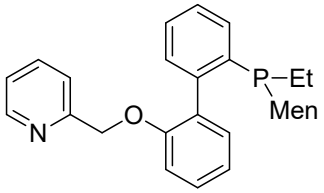
The crude **6f/6f'** was formed in a ratio of 94:6 (estimated by ^{31}P-NMR spectrum). After isolation from preparative TLC (silica gel, petroleum ether/ dichloromethane = 3:1 as eluent), the compound was obtained as colorless oil (56.4 mg, 72%, 96:4 dr); **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 31.4 (bm, 96%), 23.2 (bm, 2%) / 22.8 (bm, 2%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.05 – 7.97 (m, 1H), 7.42 (dd, *J*=16.2, 7.5, 1H), 7.39 – 7.31 (m, 2H), 7.21 – 7.13 (m, 4H), 7.10 (dd, *J*=7.5, 1.5, 0.5H), 7.05 (t, *J*=6.5, 2H), 7.02 – 6.93 (m, 2.5H), 4.96 (s, 2H), 2.03 – 1.94 (m, 0.5H), 1.83 (dd, *J*=23.8, 10.4, 1.5H), 1.66 – 1.54 (m, 2H), 1.46 – 1.31 (m, 3H), 1.30 – 1.20 (m, 3H), 1.06 – 0.97 (m, 1H), 0.96 – 0.85 (m, 3H), 0.84 – 0.75 (m, 6H), 0.72 (dd, *J*=10.2, 6.5, 4H), 0.68 – 0.60 (m, 1H), 0.42 (t, *J*=7.1, 2H), 0.38 (d, *J*=6.9, 2H), 0.32 (d, *J*=6.8, 1H), 0.26 (d, *J*=5.8, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 155.11 (d, *J*=32.7), 140.66 (d, *J*=31.9), 136.42 (dd, *J*=34.8, 16.5), 135.58 (d, *J*=11.1), 131.27 (d, *J*=6.2), 129.61 (d, *J*=26.6), 129.17 – 128.63 (m), 127.37 (d, *J*=5.0), 126.62 (d, *J*=1.5), 126.27 (d, *J*=12.1), 125.96 (d, *J*=27.6), 125.39 (d, *J*=9.9), 119.04 (d, *J*=27.2), 111.71 (d, *J*=54.4), 68.97 (d, *J*=47.1), 42.88 (d, *J*=28.2), 36.64 (d, *J*=29.3), 36.12 (s), 35.22 (s), 34.72 (d, *J*=29.8), 33.19 (d, *J*=17.9), 32.30 (d, *J*=11.2), 31.98 (d, *J*=12.2), 27.56 (dd, *J*=13.7, 1.5), 26.89 (d, *J*=32.1), 25.71 (s), 24.91 (s), 24.26 (d, *J*=33.1), 24.05 – 23.48 (m), 23.30 (d, *J*=14.5), 21.49 (s), 20.96 (s), 20.24 (d, *J*=21.8), 14.11 (d, *J*=10.9), 12.50 (d, *J*=24.6). **HRMS (ESI+)** Calcd. for $C_{33}H_{46}BOP$ [M+Na^+]: 523.3277, Found: 523.3291.

(R_P/S_P)-(–)-Menthyl ethyl (2'-pyridinylmethoxy-1,1-biphenyl-2-yl) phosphine borane (6g/6g')



The compound was obtained as colorless oil (84 mg, 79%) from preparative TLC (silica gel, petroleum ether/ dichloromethane = 1:2 as eluent); **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 35.25 (bm, 90%), -20.63 / -22.41 (bs, 1%), -25.53 / -28.32 (bs, 9%); **HRMS (ESI+)** Calcd. for $C_{30}H_{41}BNOP$ [M+K^+]: 512.2656, Found: 512.2664.

(R_P/S_P)-(–)-Menthyl ethyl (2'-pyridinylmethoxy-1,1-biphenyl-2-yl) phosphine (7/7')



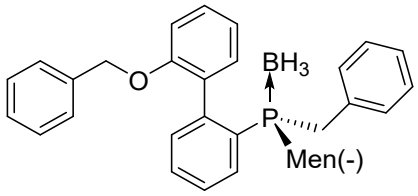
To the solution of **6a/6a'** (35 mg, 0.059 mmol) in toluene (0.5 mL), was added triethylene diamine (10mg, 0.088 mmol) slowly, and the mixture was stirred at 70 °C for 5 hours. After removing solvent, The compound was obtained as colorless oil (23.6 mg, 81%) from a silica gel short column (petroleum ether as eluent); **^{31}P NMR (202 MHz, $CDCl_3$)** δ = -20.66 (s), -22.44 (s), -25.59 (s), -28.44 (s); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.43 (dd, *J*=9.6, 4.2, 1H), 7.47 (t, *J*=7.7, 0.7H), 7.44 – 7.39 (m, 1.3H), 7.37 (d, *J*=7.4, 0.5H), 7.29 (dd, *J*=8.9, 3.8, 2.5H), 7.21 (dd, *J*=8.6, 7.7, 1H), 7.18 – 7.12 (m, 1H), 7.04 (t, *J*=7.1, 2H), 7.00 – 6.89 (m, 1.5H), 6.82 (d, *J*=8.2, 0.5H), 5.11 (d, *J*=3.4, 1.5H), 5.05 (s, 0.5H), 1.86 – 1.77 (m, 0.5H), 1.74 – 1.63 (m, 2H), 1.57 (d, *J*=4.8, 2H), 1.49 – 1.42 (m, 0.5H), 1.43 – 1.35 (m, 0.5H), 1.31 (d, *J*=9.2, 1H), 1.16 – 1.07 (m, 1H), 1.06 – 0.98 (m, 2H), 0.84 – 0.75 (m, 2H), 0.68 (d, *J*=6.4, 3H), 0.64 – 0.56 (m, 1H), 0.53 (d, *J*=6.8, 1H), 0.46 (dd, *J*=10.3, 4.2, 4H), 0.37 (d, *J*=6.5, 2H), 0.34 – 0.28 (m, 0.5H), 0.27 – 0.12 (m, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 156.82 (d, *J*=65.6), 154.32 (d, *J*=60.2), 147.70 (d, *J*=14.7), 135.53 (d, *J*=34.9), 132.01 (d, *J*=6.3), 131.57 (d, *J*=5.9), 130.82 (d, *J*=1.8), 130.29 (dd, *J*=12.0, 4.8), 129.19 (d, *J*=6.1), 127.58 (d, *J*=6.8), 127.11 (s), 126.13 (s), 125.51 (d, *J*=12.0), 121.11 (d, *J*=22.6), 119.72 (d, *J*=6.7), 119.36 (s), 111.18 (d, *J*=48.7), 69.70 (s), 68.84 (s), 43.96 (d, *J*=13.5), 43.58 (d, *J*=13.8), 38.50 (d, *J*=19.0), 37.00 (d, *J*=42.6), 33.80 (d, *J*=36.2), 32.92 (dd, *J*=20.7, 2.1), 28.68 (s), 26.50 (d, *J*=18.0), 24.19 (s), 21.05 (dd, *J*=81.1, 38.8), 16.86 (dd, *J*=15.8, 12.4), 13.97 (d, *J*=16.7), 9.78 (t, *J*=20.3).

Typical procedure B, the preparation of 6d:

The residue of crude **5ab** (as the above) was dissolved in toluene (0.5 mL), followed by the additions of tetrabutylammonium bromide (7.3 mg, 0.0227 mmol), potassium iodide (7.5 mg, 0.0454 mmol), potassium hydroxide (0.5 mL, 50% solution in water) and ethanol (0.1 mL). The

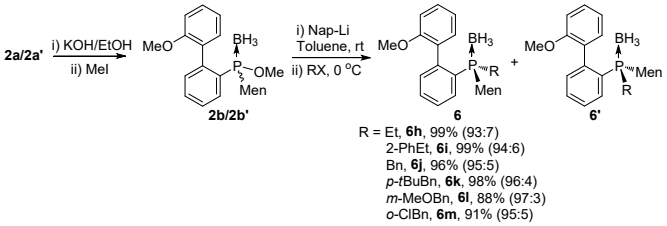
mixture was stirred for 24 hours under air atmosphere. After the reaction was completed, dilute hydrochloric acid (8%) was added, and the solvent was removed in vacuo. The residue was extracted with dichloromethane (3×10 mL), washed with water (3×10 mL), dried with anhydrous magnesium sulfate, and the solvent was removed in vacuo. The crude products were purified by preparative TLC (silica gel, petroleum ether/ethyl acetate = 5/1 as eluent) to afford **6d**.

(R_P/S_P)-(–)-Menthyl benzyl (2'- benzyloxy-1,1-biphenyl-2-yl)phosphine borane (6d/6d')



The crude **6d/6d'** was formed in a ratio of 94:6 (estimated by ^{31}P-NMR spectrum). After isolation from preparative TLC (silica gel, petroleum ether/ dichloromethane = 1:1 as eluent), the pure compound was obtained as white solid (60.8 mg, 80%, 98:2 dr); m.p. 118.6-119.5 °C; **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 33.4 (bm, 98%), 23.7 (bm, 2%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 7.81 (dd, *J*=12.8, 8.2, 0.6H), 7.70 – 7.63 (m, 0.4H), 7.55 (d, *J*=6.8, 0.3H), 7.49 (t, *J*=7.5, 0.7H), 7.46 – 7.35 (m, 1.5H), 7.33 – 7.26 (m, 2H), 7.26 – 7.16 (m, 3.5H), 7.12 (dd, *J*=7.6, 5.2, 2H), 7.10 – 6.93 (m, 5H), 6.83 (t, *J*=7.6, 1H), 6.72 (d, *J*=6.8, 1H), 5.08 – 5.01 (m, 1H), 4.93 (d, *J*=12.3, 1H), 3.62 (t, *J*=14.5, 0.3H), 3.44 (t, *J*=15.0, 0.7H), 3.38 – 3.30 (m, 0.3H), 2.92 – 2.83 (m, 0.7H), 2.27 (s, 0.7H), 2.13 (s, 0.3H), 1.92 (dd, *J*=24.3, 12.2, 1H), 1.79 – 1.58 (m, 3H), 1.58 – 1.40 (m, 2H), 1.29 (d, *J*=2.4, 1H), 1.14 (ddd, *J*=24.9, 12.3, 4.9, 1H), 0.96 – 0.83 (m, 5.5H), 0.75 (dd, *J*=6.4, 2.6, 2.5H), 0.73 – 0.66 (m, 1H), 0.59 (dd, *J*=6.7, 3.5, 2H), 0.55 (dd, *J*=6.7, 3.5, 1H), 0.46 (dd, *J*=6.1, 2.9, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 156.02 (d, *J*=44.4), 142.31 (s), 141.52 (s), 137.02 (d, *J*=15.5), 136.62 (d, *J*=15.9), 133.64 (d, *J*=3.8), 132.65 (d, *J*=6.6), 131.21 (s), 130.71 (d, *J*=31.1), 130.51 – 130.22 (m), 129.92 (d, *J*=12.6), 128.45 (d, *J*=3.4), 127.92 (s), 127.81 (s), 127.77 – 127.63 (m), 127.54 (s), 127.44 (d, *J*=2.4), 127.26 (d, *J*=12.0), 127.06 (d, *J*=13.9), 126.51 (s), 126.20 (d, *J*=3.1), 120.24 (s), 113.00 (d, *J*=76.2), 70.07 (s), 44.34 (s), 37.47 – 36.63 (m), 36.16 (d, *J*=56.5), 34.36 (d, *J*=8.2), 33.24 (d, *J*=11.4), 32.11 (d, *J*=28.0), 28.71 (d, *J*=53.4), 25.10 (d, *J*=11.1), 22.35 (d, *J*=41.4), 21.41 (d, *J*=22.6), 15.47 (d, *J*=16.9). **HRMS (ESI+)** Calcd. for $C_{36}H_{44}BOP$ [M+K^+]: 573.2860, Found: 573.2858.

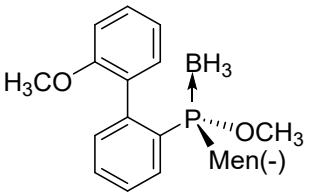
Preparation and cleavage of P-O bond of 2b/2b'



Preparation of 2b/2b':

To the solution of **2a**/**2a'** (1.0 g, 2.84 mmol) in ethanol (4 mL), was added potassium hydroxide (375 mg, 5.68 mmol). After the mixture was stirred at room temperature for 10 h, the reaction was quenched with dilute hydrochloric acid (8%) and the solvent was removed. The mixture was extracted with dichloromethane (3×30 mL), washed with water (3×30 mL) and dried over anhydrous magnesium sulfate. After the solvent was removed, the crude product was obtained as a white foamy solid. The above crude (1.04 g, 2.81 mmol) was dissolved in acetonitrile (10 mL), then potassium hydroxide (371 mg, 5.62 mmol) was added. The mixture was stirred at room temperature for 5 minutes. Methyl iodide (0.7 mL, 11.24 mmol) was added. After the reaction was completed, as monitored with NMR spectrum, dilute hydrochloric acid (8%) was added. The solvent was removed and the residue was extracted with dichloromethane (3×20 mL), washed with water (3×20 mL), dried over anhydrous magnesium sulfate. After removing solvent, the yellowish oily residue was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 8/1) to afford **2b/2b'**.

(R_P/S_P)-(–)-Menthyl methoxy (2'-methoxy-1,1-biphenyl-2-yl)phosphine borane (2b/2b')



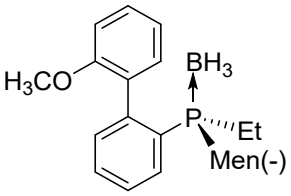
The pure compound was obtained as colorless oil (0.87 g, 87%) from column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1 as eluent); **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 131.16 (bm, 72%), 122.61 (bm, 28%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.18 – 8.11 (m, 0.4H), 8.10 – 8.03 (m, 0.3H), 8.03 – 7.88 (m, 0.3H), 7.56 – 7.47 (m, 1H), 7.44 (dd, *J*=4.8, 2.8, 1.1H), 7.40 – 7.34 (m, 1H), 7.30 – 7.27 (m, 0.5H), 7.25 – 7.20 (m, 0.9H), 7.08 (dd, *J*=7.5, 1.6, 0.2H), 7.02 – 6.89 (m, 2.3H), 3.75 – 3.69 (m, 3H), 3.53 – 3.33 (m, 3H), 2.14 – 1.99 (m, 1H), 1.92 – 1.84 (m, 0.2H), 1.62 (dd, *J*=6.4, 3.8, 2.8H), 1.50 – 1.32 (m, 1H), 1.32 – 1.08 (m, 1.5H), 1.07 – 0.95 (m, 0.9H), 0.93 – 0.85 (m, 1.6H), 0.83 (dd, *J*=6.9, 2.5, 3.3H), 0.81 – 0.75 (m, 4.2H), 0.72 (d, *J*=6.4, 1.7H), 0.37 (d, *J*=6.8, 1.3H), 0.29 (d, *J*=6.8, 1H), 0.23 (dd, *J*=10.4, 3.6, 0.5H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 156.35 (s), 155.45 (s), 140.89 (d, *J*=5.6), 135.14 (s), 131.61 (d,

J=6.3), 130.98 (s), 130.55 (d, *J*=6.4), 130.33 (d, *J*=2.2), 129.98 (d, *J*=1.7), 129.36 (s), 128.32 (t, *J*=10.2), 125.84 (d, *J*=12.9), 118.28 (d, *J*=48.4), 109.01 (d, *J*=11.9), 54.07 (d, *J*=19.7), 52.20 (d, *J*=4.2), 51.56 (d, *J*=4.3), 42.53 (d, *J*=14.6), 37.60 (d, *J*=43.6), 36.56 (d, *J*=43.1), 33.64 – 32.79 (m), 32.01 – 31.62 (m), 26.97 (s), 23.57 (t, *J*=12.4), 21.75 – 21.03 (m), 20.51 – 19.98 (m), 13.62 (d, *J*=22.2).

Typical procedure, the preparation of 6h/6h':

To the solution of **2b/2b'** (80 mg, 0.20 mmol) in toluene (1.5 mL), lithium-naphthalene reagent (1M solution in THF, 0.8 mL, 0.80 mmol) was added slowly, and the mixture was stirred at room temperature for 2 hours. Ethyl bromide (60 μL, 0.80 mmol) was added to the ice-cooled mixture, and the stirring was continued for 6 hours at the same temperature. The reaction was quenched with dilute hydrochloric acid (8%). After the solvent was removed in vacuo, the mixture was extracted with dichloromethane (3×10 mL), washed with water (3×10 mL) and dried with anhydrous magnesium sulfate. The residue was purified with preparative TLC (silica gel, petroleum ether/ethyl acetate = 4/1 as eluent) to afford **6h/6h'**.

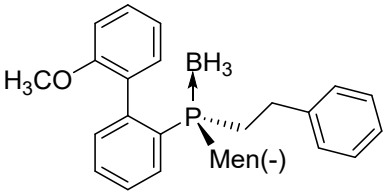
(R_P/S_P)-(–)-Menthyl ethyl (2'-methoxy-1,1-biphenyl-2-yl)phosphine borane (6h/6h')



The crude **6h/6h'** was formed in a ratio of 93:7 (estimated by ^{31}P-NMR spectrum). After isolation from preparative TLC (silica gel, petroleum ether/ ethyl acetate = 6:1 as eluent), the compound was obtained as white solid (64.9 mg, 82%, 94:6 dr); m.p. 164.7-165.3 °C; **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 34.8 (bm, 94%), 26.7 (bm, 6%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.06 (dd, *J*=13.3, 7.7, 1H), 7.50 – 7.44 (m, 1H), 7.44 – 7.37 (m, 2H), 7.21 – 7.13 (m, 1.5H), 7.00 (ddd, *J*=22.9, 12.3, 7.1, 2.5H), 3.71 (d, *J*=4.2, 3H), 2.01 (ddd, *J*=13.0, 11.2, 8.8, 1H), 1.87 (ddd, *J*=27.3, 13.3, 7.0, 1.5H), 1.79 – 1.71 (m, 1H), 1.71 – 1.54 (m, 4.5H), 1.54 – 1.43 (m, 1H), 1.34 – 1.21 (m, 2H), 1.12 – 1.03 (m, 1.5H), 0.96 (dd, *J*=10.0, 5.8, 1H), 0.93 – 0.89 (m, 2H), 0.85 (d, *J*=6.1, 3H), 0.82 (d, *J*=6.7, 2H), 0.77 (d, *J*=6.3, 2H), 0.72 (d, *J*=6.0, 1.5H), 0.40 (d, *J*=6.9, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 156.99 (s), 141.88 (s), 137.58 (d, *J*=16.3), 132.69 – 131.78 (m), 130.77 (s), 130.58 – 129.73 (m), 127.18 (dd, *J*=12.2, 7.6), 119.68 (d, *J*=14.6), 110.62 (d, *J*=53.3), 55.50 (s), 54.86 (s), 43.86 (d, *J*=32.1), 37.19 (s), 37.07 – 36.42 (m), 36.64 (d, *J*=32.7), 35.89 – 35.44 (m), 34.19 (d, *J*=21.1), 33.33 – 33.08 (m), 28.63 (d, *J*=13.7), 24.89 (d, *J*=11.8), 22.40 (d,

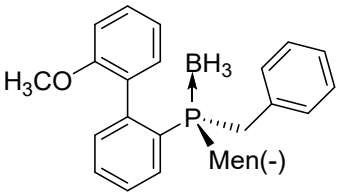
J=23.6), 21.36 (s), 21.23 (s), 18.89 (d, *J*=33.9), 15.06 (d, *J*=17.1), 8.97 (s), 8.23 (s). **HRMS (ESI+)** Calcd. for $C_{25}H_{38}BOP$ [M+Na^+]: 419.2651, Found: 419.2660.

(R_P/S_P)-(–)-Menthyl phenylethyl (2'-methoxy-1,1-biphenyl-2-yl)phosphine borane (6i/6i')



The crude **6i/6i'** was formed in a ratio of 94:6 (estimated by ^{31}P-NMR spectrum). After isolation from preparative TLC (silica gel, petroleum ether/ ethyl acetate = 7:1 as eluent), the compound was obtained as white solid (62.6 mg, 79%, 92:8 dr); m.p. 170.2 - 171.5 °C; **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 31.49 (bm, 92%), 23.46 (bm, 8%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.14 (dd, *J*=13.5, 7.6, 1H), 7.52 – 7.42 (m, 2H), 7.42 – 7.36 (m, 1H), 7.29 – 7.24 (m, 1H), 7.24 – 7.17 (m, 3H), 7.11 (dd, *J*=15.0, 7.4, 1.5H), 7.03 (dd, *J*=10.4, 4.4, 1H), 7.00 – 6.90 (m, 2H), 6.82 (d, *J*=8.3, 0.5H), 3.72 (s, 1H), 3.28 (s, 2H), 2.98 – 2.82 (m, 1H), 2.48 (ddd, *J*=15.0, 12.2, 5.2, 1H), 2.33 – 2.21 (m, 1H), 2.16 – 2.03 (m, 1H), 2.02 – 1.86 (m, 2H), 1.85 – 1.75 (m, 1H), 1.45 – 1.24 (m, 3H), 1.17 – 1.08 (m, 1H), 0.97 (dd, *J*=11.5, 5.1, 1H), 0.89 (d, *J*=6.7, 4H), 0.80 (dd, *J*=9.5, 6.6, 5H), 0.73 (d, *J*=5.9, 2H), 0.48 (d, *J*=6.9, 2H), 0.39 (d, *J*=6.8, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 156.95 (d, *J*=30.3), 142.05 (dd, *J*=25.9, 10.2), 141.64 (d, *J*=14.7), 137.62 – 136.96 (m), 132.73 – 132.17 (m), 130.80 (s), 130.34 (s), 129.96 (s), 128.53 (s), 128.21 (s), 127.96 (s), 127.57 (s), 127.34 (dd, *J*=12.3, 4.9), 126.17 (s), 125.82 (s), 119.72 (d, *J*=36.1), 110.92 (d, *J*=10.5), 55.32 (d, *J*=53.5), 43.88 (d, *J*=43.5), 37.58 (d, *J*=29.1), 37.12 (s), 36.38 (s), 35.88 (d, *J*=29.6), 34.18 (d, *J*=27.1), 33.24 (t, *J*=12.4), 30.57 (s), 29.35 (s), 28.66 (d, *J*=1.6), 25.32 (d, *J*=32.1), 24.93 (dd, *J*=11.7, 5.8), 22.43 (d, *J*=24.2), 21.29 (d, *J*=15.2), 15.17 (d, *J*=7.4). **HRMS (ESI+)** Calcd. for $C_{31}H_{42}BOP$ [M+Na^+]: 495.2964, Found: 495.2976.

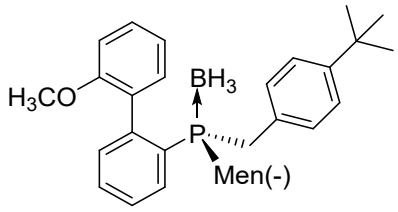
(R_P/S_P)-(–)-Menthyl benzyl (2'-methoxy-1,1-biphenyl-2-yl)phosphine borane (6j/6j')



The crude **6j/6j'** was formed in a ratio of 95:5 (estimated by ^{31}P-NMR spectrum). After isolation from preparative TLC (silica gel, petroleum ether/ dichloromethane = 2:1 as eluent), the compound was obtained as white solid (56.1 mg, 73%, 96:4 dr); m.p. 132.5 - 133.1 °C; **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 33.2 (bm, 96%), 23.5 (bm, 4%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 7.74 (dd, *J*=13.1, 7.9, 0.7H), 7.66 (dd, *J*=13.5, 7.9, 0.3H), 7.50 – 7.36 (m, 2.5H), 7.29 (t, *J*=7.6, 1H), 7.22 – 7.16 (m, 1H), 7.07 (dq, *J*=14.1, 7.0, 3 H), 7.03 – 6.93 (m, 2H), 6.88 (d, *J*=7.3, 1H), 6.84 – 6.80 (m, 1.5H), 3.67 (d, *J*=10.4, 3H), 3.64 – 3.52 (m, 0.3H), 3.43 (t, *J*=14.9, 0.7H),

3.30 (dd, *J*=13.9, 6.9, 0.3H), 2.93 (dd, *J*=13.7, 7.0, 0.7H), 2.28 – 2.18 (m, 0.7H), 2.17 – 2.08 (m, 0.3H), 1.84 – 1.60 (m, 4H), 1.60 – 1.40 (m, 2H), 1.30 – 1.19 (m, 1H), 1.13 (ddd, *J*=18.8, 11.9, 5.6, 1H), 1.05 – 0.96 (m, 1H), 0.96 – 0.84 (m, 5H), 0.78 (d, *J*=6.4, 3H), 0.72 (d, *J*=6.2, 1H), 0.55 (dd, *J*=6.4, 4.7, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 157.07 (s), 156.54 (s), 142.57 (s), 141.80 (s), 137.01 (d, *J*=16.0), 136.65 (d, *J*=14.9), 133.85 (d, *J*=4.3), 132.73 (d, *J*=6.6), 132.42 (d, *J*=6.8), 131.23 (s), 130.88 (s), 130.61 – 130.09 (m), 129.89 (t, *J*=12.5), 127.63 (dd, *J*=21.6, 3.0), 127.35 (s), 127.02 (dd, *J*=27.8, 12.0), 126.64 – 126.19 (m), 119.88 (d, *J*=33.1), 111.02 (d, *J*=74.5), 54.88 (d, *J*=2.9), 44.20 (s), 37.22 (s), 36.91 – 36.19 (m), 35.56 (d, *J*=26.8), 34.25 (d, *J*=20.9), 33.57 – 32.91 (m), 32.55 (d, *J*=27.6), 28.70 (d, *J*=43.8), 25.02 (d, *J*=11.1), 22.42 (d, *J*=13.3), 21.39 (d, *J*=15.7), 15.39 (d, *J*=24.7). **HRMS (ESI+)** Calcd. for $C_{30}H_{40}BOP$ [M+Na^+]: 481.2808, Found: 481.2812.

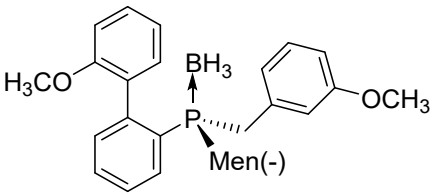
(R_P)-(–)-Menthyl *p*-tert-butylbenzyl (2'-methoxy-1,1-biphenyl-2-yl)phosphine borane (R_P-6k)



The crude **6k/6k'** was formed in a ratio of 96:4 (estimated by ^{31}P-NMR spectrum). After isolation from preparative TLC (silica gel, petroleum ether/ dichloromethane = 2:1 as eluent), the pure compound was obtained as white solid (53.9 mg, 68%, >99:1 dr); m.p. 92.1 - 93.8 °C; **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 32.66 (bm); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 7.80 – 7.68 (m, 0.7H), 7.66 (dd, *J*=13.4, 7.9, 0.3H), 7.51 – 7.42 (m, 1H), 7.40 (t, *J*=7.9, 1H), 7.32 (t, *J*=7.6, 1H), 7.19 (dt, *J*=15.7, 8.0, 1H), 7.10 (d, *J*=8.1, 2H), 7.03 (dd, *J*=15.4, 7.9, 1H), 6.94 (dd, *J*=11.8, 6.4, 1.5H), 6.88 (d, *J*=7.2, 0.5H), 6.75 (d, *J*=6.9, 2H), 3.69 (d, *J*=12.9, 3H), 3.54 (t, *J*=14.5, 0.3H), 3.42 – 3.32 (m, 0.7H), 3.27 (dd, *J*=14.0, 6.9, 0.3H), 2.96 (dd, *J*=13.7, 6.8, 0.7H), 2.30 – 2.20 (m, 0.8H), 2.16 – 2.08 (m, 0.2H), 1.83 (dd, *J*=23.0, 11.0, 1H), 1.78 – 1.62 (m, 3H), 1.62 – 1.44 (m, 3H), 1.36 – 1.20 (m, 12H), 1.20 – 1.11 (m, 1H), 0.92 (d, *J*=6.7, 3H), 0.89 (d, *J*=6.4, 1H), 0.80 (d, *J*=6.4, 3H), 0.73 (d, *J*=6.0, 1H), 0.59 (d, *J*=6.8, 2H), 0.55 (d, *J*=6.8, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 155.80 (d, *J*=47.8), 148.08 (d, *J*=3.1), 141.85 (s), 140.68 (s), 135.91 (d, *J*=15.6), 135.03 (d, *J*=13.4), 131.25 (d, *J*=7.0), 130.11 (s), 129.90 (s), 129.51 (d, *J*=4.4), 129.30 (t, *J*=6.4), 129.12 (d, *J*=2.2), 128.97 (d, *J*=4.7), 128.79 (d, *J*=4.3), 128.67 (d, *J*=5.9), 127.01 (s), 126.63 (s), 125.99 (d, *J*=11.3), 125.76 (d, *J*=12.0), 123.46 (d, *J*=19.2), 118.75 (d, *J*=10.0), 109.87 (d, *J*=87.4), 54.13 (d, *J*=73.6), 43.08 (d, *J*=3.3), 36.18 (s), 35.85 (d, *J*=26.4), 35.30 (s), 33.21 (d, *J*=22.4), 32.03 (dd, *J*=15.7, 11.7), 31.50 (d, *J*=27.9), 30.32 (d, *J*=6.8), 27.61

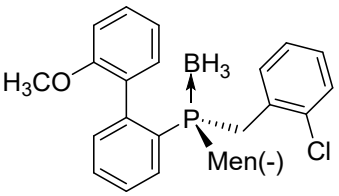
(dd, *J*=41.3, 1.5), 24.01 (d, *J*=11.0), 21.37 (d, *J*=14.6), 20.34 (d, *J*=15.0), 14.37 (d, *J*=20.6). **HRMS (ESI+)** Calcd. for $C_{34}H_{48}BOP$ [M+Na^+]: 537.3434, Found: 537.3436.

(R_P/S_P)-(–)-Menthyl *m*-methoxybenzyl (2'-methoxy-1,1-biphenyl-2-yl)phosphine borane (6l/6l')



The crude **6l/6l'** was formed in a ratio of 95:5 (estimated by ^{31}P-NMR spectrum). After isolation from preparative TLC (silica gel, petroleum ether/ dichloromethane = 1:1 as eluent), the pure compound was obtained as white solid (53.5 mg, 76%, 96:4 dr); m.p. 98.7 - 101.8 °C; **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 33.4 (bm, 96%), 23.4% (bm, 4%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 7.73 (ddd, *J*=20.8, 14.2, 7.6, 1H), 7.50 – 7.37 (m, 2.5H), 7.31 (dd, *J*=9.0, 7.7, 1H), 7.23 – 7.17 (m, 1H), 7.06 – 6.94 (m, 3H), 6.89 (d, *J*=7.2, 1H), 6.69 – 6.63 (m, 1H), 6.56 – 6.51 (m, 0.5H), 6.48 (d, *J*=7.5, 0.5H), 6.35 (s, 0.5H), 3.69 (d, *J*=8.4, 3H), 3.61 (s, 1H), 3.53 (s, 2H), 3.39 (dd, *J*=15.8, 14.0, 1H), 3.29 (dd, *J*=14.0, 6.8, 0.3H), 2.93 (dd, *J*=13.6, 6.8, 0.7H), 2.26 – 2.17 (m, 0.7H), 2.14 – 2.06 (m, 0.3H), 1.83 – 1.42 (m, 7H), 1.20 – 1.10 (m, 1H), 1.05 – 0.96 (m, 1H), 0.90 (dd, *J*=14.9, 6.7, 5H), 0.79 (d, *J*=6.4, 3H), 0.72 (d, *J*=6.2, 1H), 0.55 (d, *J*=6.9, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 158.83 (d, *J*=2.7), 156.47 (s), 142.16 (d, *J*=94.8), 136.85 (dd, *J*=44.0, 15.0), 135.06 (dd, *J*=20.4, 4.6), 132.56 (dd, *J*=35.1, 6.6), 131.22 (s), 130.81 (s), 130.40 (d, *J*=2.2), 129.85 (s), 128.35 (d, *J*=2.5), 127.77 (s), 127.39 (s), 127.03 (dd, *J*=25.8, 12.0), 123.06 (d, *J*=5.0), 119.99 (s), 114.97 (dd, *J*=13.1, 4.6), 112.98 (dd, *J*=14.8, 2.9), 111.22 (s), 110.66 (s), 55.47 (s), 55.07 (s), 54.90 (d, *J*=4.7), 44.12 (d, *J*=8.6), 37.19 (s), 36.54 (d, *J*=26.5), 34.29 (s), 33.06 (d, *J*=11.5), 28.52 (d, *J*=1.9), 24.99 (d, *J*=11.3), 22.40 (d, *J*=13.4), 21.38 (d, *J*=14.8), 15.36 (d, *J*=26.2). **HRMS (ESI+)** Calcd. for $C_{31}H_{42}BO_2P$ [M+Na^+]: 511.2913, Found: 511.2921.

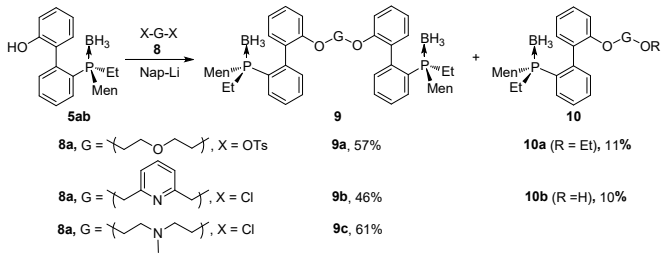
(R_P)-(–)-Menthyl *o*-chloride benzyl (2'-methoxy-1,1-biphenyl-2-yl)phosphine borane (R_P-6m)



The crude **6m/6m'** was formed in a ratio of 95:5 (estimated by ^{31}P-NMR spectrum). After isolation from preparative TLC (silica gel, petroleum ether/ dichloromethane = 3:2 as eluent), the pure compound was obtained as white solid (54.6 mg, 75%, 97:3 dr); m.p. 89.1 - 90.4 °C; **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 33.89 (bm, 77%), 31.6 (bm, 23%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 7.93 (dd, *J*=29.5, 15.9, 1H), 7.55 (dd, *J*=42.0, 35.9, 1H), 7.48 –

7.42 (m, 1H), 7.41 – 7.32 (m, 1H), 7.28 (d, *J*=8.0, 1H), 7.23 (ddd, *J*=7.6, 2.5, 1.3, 0.7H), 7.17 (ddd, *J*=7.6, 2.7, 1.2, 0.3H), 7.09 – 7.01 (m, 3H), 6.96 (tt, *J*=15.0, 7.6, 1.5H), 6.87 (t, *J*=7.5, 1H), 6.62 (d, *J*=7.8, 0.5H), 3.71 (s, 1H), 3.53 (s, 2H), 3.50 – 3.44 (m, 0.4H), 3.37 (dd, *J*=14.6, 7.4, 0.8H), 3.28 (t, *J*=15.4, 0.8H), 2.50 – 2.42 (m, 0.8H), 2.29 – 2.20 (m, 0.2H), 1.91 – 1.79 (m, 1H), 1.75 – 1.53 (m, 4.5H), 1.48 – 1.36 (m, 1H), 1.36 – 1.28 (m, 1H), 1.13 – 1.02 (m, 1.5H), 0.90 (dd, *J*=9.3, 6.7, 5.5H), 0.79 (d, *J*=6.5, 2.5H), 0.74 (d, *J*=6.1, 1H), 0.60 (d, *J*=6.9, 1H), 0.57 (d, *J*=6.9, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 156.51 (s), 142.13 (s), 137.41 (d, *J*=16.4), 135.04 (s), 132.76 (d, *J*=3.3), 132.55 (d, *J*=6.5), 131.22 (d, *J*=5.0), 130.79 (dd, *J*=33.1, 3.1), 130.38 (s), 130.08 (s), 129.91 – 129.76 (m), 129.14 (d, *J*=1.9), 127.73 (s), 127.57 (d, *J*=2.7), 127.31 (d, *J*=12.1), 125.94 (d, *J*=2.3), 120.01 (d, *J*=13.3), 110.89 (d, *J*=23.3), 55.21 (d, *J*=94.2), 44.47 (d, *J*=1.4), 37.11 (s), 36.60 (d, *J*=27.2), 36.44 – 36.06 (m), 34.30 (s), 33.23 (d, *J*=11.6), 30.97 (d, *J*=29.9), 28.77 (s), 27.92 (dd, *J*=46.9, 15.7), 25.05 (d, *J*=11.4), 22.45 (d, *J*=16.2), 21.27 (d, *J*=25.0), 15.30 (d, *J*=31.4). **HRMS (ESI+)** Calcd. for $C_{30}H_{39}BClOP$ $[M+K^+]$: 531.2157, Found: 531.2167.

Part 4. Formation of bis-phosphine-borane via *O*-alkylation.



The preparation of 5ab in gram scale

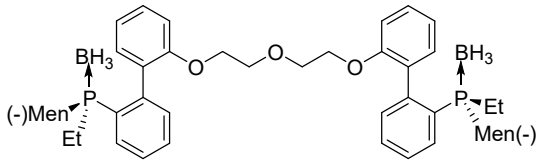
To the solution of **2a/2a'** (1 g, 2.84 mmol) in toluene (20 mL), was added lithium-naphthalene reagent (10 mL, 9.94 mmol, 1 M solution in THF) slowly. The mixture was stirred at room temperature for 2 hours, then cooled with the ice-both. Ethyl bromide (0.85 mL, 11.36 mmol) was added, and the stirring was continued for 4 hours at the same temperature. After the reaction was completed, as monitored with TLC, the reaction was quenched with dilute hydrochloric acid (8%) and the solvent was removed in vacuo. The mixture was extracted with dichloromethane (3×20 mL), washed with water (3×20 mL), and dried with anhydrous magnesium sulfate. After removing solvent, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1 as eluent) to afford **5ab** (0.91 g, 84%, 95:5 dr). R_P-**5ab** was obtained (0.68 g, 63%, >99:1 dr) by recrystallization from dichloromethane and petroleum ether (3/1).

The preparation of 9a

To the solution of R_P-**5ab** (100 mg, 0.26 mmol) in ethanol (1 mL), potassium hydroxide (22 mg, 0.31 mol) was added. The mixture was warmed to 50 °C with stirring, then diethylene glycol di(*p*-toluenesulfonate) (54 mg, 0.13 mmol) was added (in two portions by an interval of 12 hours). After the reaction was completed, as monitored by TLC, the mixture was quenched with saturated sodium bicarbonate, and the solvent was removed in vacuo. The residue was extracted with dichloromethane (3×10 mL), washed with water (3×10 mL), dried over anhydrous magnesium sulfate. After removing solvent, the residue was purified with preparative TLC (silica gel, petroleum ether/ dichloromethane = 1/3 as eluent) to afford **9a** and **10a.**

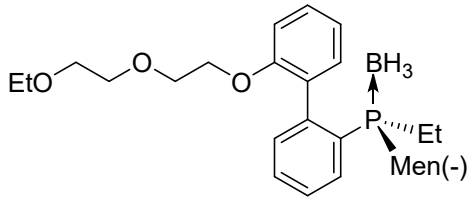
R_P,R_P-Diethylene glycol di[2-(-)-menthyl ethylphosphino-1,1'-biphenyl-2'-yl)]ether diborane (9a)

The compound was obtained as a white foamy solid (60.4 mg, 57%) from preparative TLC (silica



gel, petroleum ether/ dichloromethane = 1:3 as eluent, Rf = 0.7); m.p. 89.1 - 90.4 °C; **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 34.65 (bm); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.10 – 8.00 (m, 2H), 7.43 – 7.37 (m, 2H), 7.37 – 7.31 (m, 4H), 7.18 – 7.12 (m, 2.6H), 7.02 (dd, *J*=3.5, 2.1, 3.4H), 6.92 (dd, *J*=8.2, 5.8, 2H), 4.02 – 3.81 (m, 4H), 3.55 – 3.31 (m, 4H), 2.07 – 1.96 (m, 2H), 1.95 – 1.78 (m, 3H), 1.73 – 1.64 (m, 3H), 1.56 – 1.40 (m, 7H), 1.38 – 1.22 (m, 5H), 1.05 (dddd, *J*=15.0, 12.3, 7.5, 4.9, 2H), 0.98 – 0.91 (m, 2H), 0.91 – 0.84 (m, 10H), 0.82 (dd, *J*=6.1, 4.5, 4H), 0.80 – 0.76 (m, 6H), 0.65 (t, *J*=7.0, 4H), 0.40 (dt, *J*=8.8, 5.6, 6H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 156.19 (d, *J*=2.2), 141.67 (d, *J*=2.0), 137.64 (d, *J*=16.5), 132.21 (d, *J*=5.9), 130.72 (d, *J*=4.6), 130.46 – 130.16 (m), 129.89 (d, *J*=8.2), 127.12 (d, *J*=12.1), 126.83 (d, *J*=9.3), 126.51 (dd, *J*=17.4, 6.7), 126.20 (d, *J*=4.5), 120.15 (s), 119.86 (s), 112.75 (s), 111.76 (d, *J*=12.1), 69.58 (d, *J*=12.6), 69.46 (s), 68.31 (s), 67.78 (s), 44.01 (s), 37.26 (s), 36.33 (s), 35.57 (dd, *J*=30.0, 6.9), 34.21 (d, *J*=13.8), 33.07 (d, *J*=62.2), 28.59 (s), 24.90 (d, *J*=11.7), 22.50 (s), 22.40 (d, *J*=4.3), 21.29 (d, *J*=24.0), 18.41 (dd, *J*=34.0, 2.6), 15.11 (d, *J*=24.1), 9.05 (d, *J*=2.5), 8.44(s). **HRMS (ESI+)** Calcd. for $C_{52}H_{78}B_2OP_2$ [M+Na^+]: 857.5510, Found: 857.5533.

***R*$_P$-(-)-Menthyl 2'-ethoxyethoxyethoxy-1,1'-biphenyl-2-yl ethylphosphine borane (10a)**



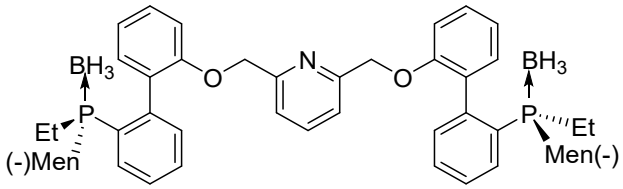
The pure compound was obtained as colorless oil (12 mg, 11%) from preparative TLC (silica gel, petroleum ether/ dichloromethane = 1:3 as eluent, Rf = 0.5); **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 34.64 (bm); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.05 (dd, *J*=13.6, 6.8, 1H), 7.56 (dt, *J*=3.1, 1.7, 0.5H), 7.43 (tt, *J*=7.5, 1.5, 1H), 7.41 – 7.35 (m, 2.5H), 7.32 (dd, *J*=7.5, 1.7, 0.4H), 7.31 – 7.27 (m, 0.6H), 7.22 – 7.19 (m, 0.7H), 7.15 (dd, *J*=7.4, 1.7, 0.3H), 7.05 – 6.95 (m, 3H), 4.14 – 4.07 (m, 1.5H), 4.06 (t, *J*=4.7, 0.3H), 4.04 – 3.99 (m, 0.7H), 3.77 (t, 0.5H), 3.70 – 3.64 (m, 1H), 3.62 (dd, *J*=6.5, 4.3, 0.6H), 3.59 (dd, *J*=6.2, 3.7, 1H), 3.54 – 3.36 (m, 7H), 2.06 – 1.95 (m, 1H), 1.94 – 1.76 (m, 1.5H), 1.58 – 1.42 (m, 2.5H), 1.18 (dd, *J*=13.2, 7.0, 4H), 1.12 – 1.03 (m, 1H), 0.96 – 0.90 (m, 2H), 0.90 – 0.82 (m, 6H), 0.81 (s, 1H), 0.77 (d, *J*=6.3, 2.5H), 0.71 (s, 1H), 0.39 (dd, *J*=12.5, 6.9, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 156.41 (d, *J*=27.6), 141.79 (d, *J*=18.5), 137.66 (d, *J*=16.5), 132.39 (dd, *J*=25.3, 6.2), 131.28 – 129.49 (m), 128.56 (s), 127.82 (s), 127.13 (d, *J*=12.1), 126.77 (s), 121.22 (s), 119.89 (d, *J*=38.2), 112.85 (d, *J*=27.5), 111.68 (s), 71.00 (s), 69.82 (s), 69.25 (s), 68.41 (d, *J*=15.0), 67.87 (s), 66.64 (s), 44.01 (d, *J*=1.4),

37.23 (d, *J*=7.4), 35.56 (d, *J*=29.8), 34.27 (s), 33.26 (d, *J*=11.6), 28.58 (d, *J*=1.5), 24.94 (s), 22.46 (d, *J*=10.2), 21.19 (s), 18.48 (d, *J*=34.0), 15.12 (dd, *J*=12.3, 10.6), 9.06 (d, *J*=2.4), 8.47 (d, *J*=1.3). **HRMS (ESI+)** Calcd. for $C_{30}H_{48}BO_3P$ [M+K^+]: 537.3071, Found: 537.3087.

The preparation of 9b:

Potassium hydroxide (43 mg, 0.65mol) was dissolved in *tert*-butanol (2 mL) with stirring and heating at 70 °C. After removing *tert*-butanol in vacuo, R_P-**5ab** (100 mg, 0.26 mmol) and fresh *tert*-butanol (1 mL) were added and the mixture was stirred at room temperature for 10 mins, then 2,6-dichloromethylpyridine (23 mg, 0.13 mmol) was added (in two portions by an interval of 12 hours). The mixture was heated at 50 °C with stirring. After the reaction was completed, as monitored by TLC, the mixture was quenched with saturated sodium bicarbonate, extracted with dichloromethane (3×10 mL), washed with water (3×10 mL), and dried over anhydrous magnesium sulfate. After removing solvent, the residue was purified with preparative TLC (silica gel, petroleum ether/ dichloromethane = 1/2 as eluent) to afford **9b** and **10b.**

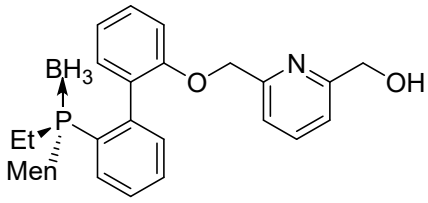
R_P,R_P-2,6-Di[2-(-)-menthyl ethylphosphino-1,1'-biphenyl-2'-oxymethyl]pyridine diborane (9b)



The pure compound **9b** was obtained as a colorless oil (52 mg, 46%) from preparative TLC (silica gel, petroleum ether/dichloromethane = 1:2 as eluent, Rf = 0.6); **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 34.99 (bm); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.14 – 8.04 (m, 1.8H), 7.54 – 7.38 (m, 7.2H), 7.30 (d, *J*=9.4, 1.6H), 7.26 – 7.22 (m, 1.2H), 7.12 – 6.97 (m, 5.4H), 6.81 (dt, *J*=13.1, 6.0, 1.8H), 5.18 – 4.97 (m, 4H), 2.07 – 1.96 (m, 2H), 1.95 – 1.78 (m, 3.2H), 1.68 (d, *J*=6.7, 2H), 1.58 – 1.40 (m, 6H), 1.30 (s, 2.8H), 1.15 – 1.03 (m, 1.6H), 1.00 – 0.89 (m, 4.8H), 0.90 – 0.84 (m, 6.2H), 0.83 – 0.76 (m, 8H), 0.76 – 0.65 (m, 6.4H), 0.45 – 0.39 (m, 4H), 0.36 (d, *J*=6.8, 2.6H), 0.25 (dd, *J*=9.5, 6.3, 1.4H), 0.19 (d, *J*=6.2, 1H). **HRMS (ESI+)** Calcd. for $C_{55}H_{77}B_2NO_2P_2$ [M+Na^+]: 890.5513, Found: 890.5534.

R_P-2-[2-(-)-Menthyl ethyl phosphino-1,1'-biphenyl-2'-oxymethyl] 6-hydroxymetnylpyridine borane (10b)

The pure compound **10b** was obtained as white foamy solid (11 mg, 10%) from preparative TLC

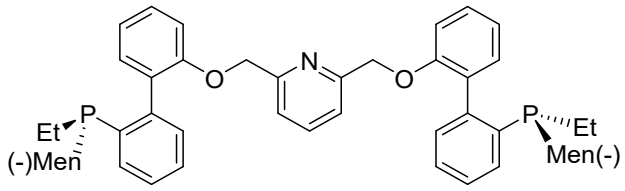


(silica gel, petroleum ether/ dichloromethane = 1:2 as eluent, Rf = 0.1); **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 35.09 (bm); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.16 – 8.08 (m, 0.8H), 7.67 – 7.48 (m, 2.3H), 7.49 – 7.39 (m, 1.9H), 7.38 – 7.27 (m, 2.2H), 7.24 (d, *J*=6.8, 0.4H), 7.12 – 6.99 (m, 2.6H), 6.86 (dd, *J*=14.8, 7.8, 0.8H), 5.23 – 5.01 (m, 2H), 4.72 (dd, *J*=15.1, 5.0, 2H), 2.08 – 1.95 (m, 1H), 1.86 (s, 1.3H), 1.73 – 1.60 (m, 3.2H), 1.52 (ddd, *J*=28.6, 13.2, 5.9, 3H), 1.31 (d, *J*=15.4, 3H), 1.09 (ddd, *J*=25.0, 12.5, 6.0, 1H), 0.95 (dt, *J*=19.6, 5.7, 1.8H), 0.86 (d, *J*=6.6, 3H), 0.83 – 0.77 (m, 3.2H), 0.77 – 0.63 (m, 3H), 0.44 – 0.40 (m, 1.5H), 0.37 (t, *J*=6.3, 1H), 0.29 – 0.24 (m, 1H). **HRMS (ESI+)** Calcd. for $C_{31}H_{43}BNO_2P$ [M+Na$^+$]: 526.3022, Found: 526.3042.

The preparation of 12b:

To the solution of **9b** (20 mg, 0.023 mmol) in toluene (0.5 mL), was added triethylene diamine (6.5 mg, 0.058 mmol) in one portion, and the mixture was stirred at 70 °C for 5 hours. After the solvent was removed, petroleum ether was added and the mixture was filtered through a silica gel short column, to afford **12b** as colorless oil (18 mg, 92%).

***R*$_P$,*R*$_P$-2,6-Di[2-(-)-menthyl ethylphosphino-1,1'-biphenyl-2'-oxymethyl]pyridine (12b)**



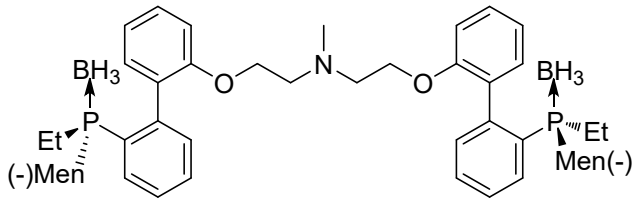
The pure compound **9b** was obtained as a colorless oil (18 mg, 92%); **^{31}P NMR (202 MHz, $CDCl_3$)** δ = -21.61 (m, 7%), -25.92 (d, 43%), -28.72 (d, 50%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 9.56 (d, *J*=7.1, 0.2H), 9.44 (d, *J*=7.3, 1.8H), 9.42 – 9.37 (m, 1.6H), 9.37 – 9.28 (m, 6.2H), 9.28 – 9.24 (m, 1.5H), 9.21 – 9.17 (m, 1H), 9.08 (d, *J*=7.3, 1.1H), 9.04 – 8.87 (m, 5H), 8.81 (dd, *J*=14.4, 8.2, 0.8H), 7.15 – 7.08 (m, 3H), 7.07 – 6.99 (m, 1H), 3.91 – 3.80 (m, 1H), 3.76 – 3.65 (m, 3H), 3.58 (dd, *J*=29.7, 11.8, 5H), 3.17 – 2.99 (m, 9.8H), 2.88 – 2.76 (m, 8H), 2.76 – 2.66 (m, 6H), 2.55 (dd, *J*=6.7, 3.5, 3H), 2.53 – 2.46 (m, 8H), 2.39 (dd, *J*=9.0, 6.6, 2H), 2.26 – 2.13 (m, 2H).

The preparation of 9c:

Potassium hydroxide (43 mg, 0.65mol) was dissolved in *tert*-butanol (2 mL) with stirring and

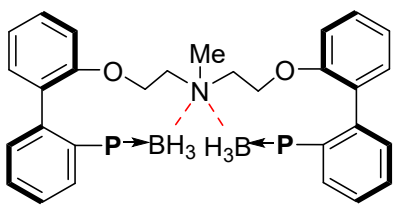
heating at 70 °C. After removing *tert*-butanol in vacuo, R_P-**5ab** (100 mg, 0.26 mmol) and fresh *tert*-butanol (1 mL) were added and the mixture was stirred at room temperature for 10 mins. Then *N*-methyldi(chloroethyl)amine hydrochloride salt (20.41 mg, 0.13 mmol) was added (in two portions by an interval of 12 hours), and the mixture was heated in a 70 °C. After the reaction was completed, as monitored by TLC, the mixture was quenched with saturated sodium bicarbonate, extracted with dichloromethane (3×10 mL), washed with water (3×10 mL), and dried over anhydrous magnesium sulfate. After removing solvent, the residue was purified with preparative TLC (silica gel, petroleum ether/ ethyl acetate = 4/1 as eluent) to afford **9c** and **9c/12c**.

***R*$_P$,*R*$_P$-Di[2-(-)-menthyl ethylphosphino-1,1'-biphenyl-2'-oxyethyl] methylamine diborane (9c)**



The pure **9c** was obtained as colorless oil (14 mg, 12%) from preparative TLC (silica gel, petroleum ether/ dichloromethane = 1:2 as eluent, Rf = 0.2); **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 34.69 (bm); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.10 – 8.01 (m, 1H), 7.44 – 7.32 (m, 3H), 7.19 – 7.11 (m, 1.3H), 7.06 – 6.97 (m, 1.7H), 6.88 (t, *J*=7.9, 1H), 3.99 – 3.76 (m, 2H), 2.60 – 2.43 (m, 2H), 2.10 (s, 0.8H), 2.05 (s, 0.7H), 2.04 – 1.95 (m, 1H), 1.94 – 1.74 (m, 1.6H), 1.72 – 1.50 (m, 5H), 1.47 – 1.38 (m, 1H), 1.12 – 1.02 (m, 0.9H), 0.99 – 0.91 (m, 1.8H), 0.87 (dt, *J*=13.7, 10.9, 5.7H), 0.82 (s, 2.5H), 0.78 (d, *J*=6.3, 2H), 0.67 (dd, *J*=10.2, 5.9, 1.5H), 0.45 – 0.36 (m, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 155.22 (s), 140.68 (s), 136.58 (s), 131.20 (s), 129.66 (s), 129.32 (s), 128.86 (t, *J*=4.1), 126.13 (d, *J*=12.4), 125.79 (s), 118.76 (d, *J*=30.4), 111.27 (s), 110.43 (s), 65.82 (s), 55.14 (d, *J*=8.6), 52.40 (s), 42.89 (d, *J*=23.4), 36.27 (t, *J*=14.6), 33.23 (s), 32.25 (d, *J*=11.5), 31.83 (d, *J*=12.3), 27.59 (d, *J*=7.7), 23.88 (d, *J*=11.4), 21.47 (s), 20.26 (d, *J*=25.8), 17.38 (dd, *J*=34.0, 4.3), 14.07 (d, *J*=23.8), 7.53 (d, *J*=3.3).

***R*$_P$,*R*$_P$-Di[2-(-)-menthyl ethylphosphino-1,1'-biphenyl-2'-oxyethyl] methylamine diborane (9c) / *R*$_P$,*R*$_P$-Di[2-(-)-menthyl ethylphosphino-1,1'-biphenyl-2'-oxyethyl] methylamine (12c)**

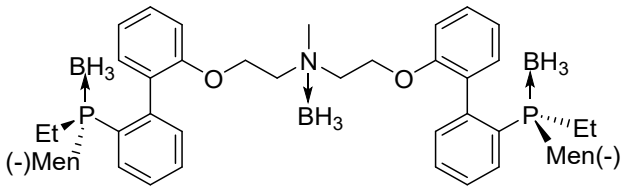


The compounds were obtained as colorless oil (54 mg, 49%) from preparative TLC (silica gel, petroleum ether/ dichloromethane = 1:2 as eluent, Rf = 0.5); **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 35.0 (bm, 90%), -18.2 - -28.9 (10%, complicated).

The preparation of 11c:

To the solution of **9c** (30 mg, 0.035 mmol) in THF (0.5 mL), the solution of borane (35 μL, 1.0 mol/L in THF) was added. After the mixture was stirred for 10 mins, most of solvent was removed in vacuo. The residue was extracted with dichloromethane (3×3 mL), washed with water (3×3 mL), dried over magnesium sulfate. After removing solvent, **11c** was obtained.

R_P,R_P-Di[2-(-)-menthyl ethylphosphino-1,1'-biphenyl-2'-oxyethyl] methylamine triborane (11c)



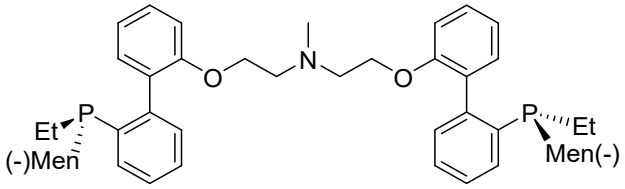
The pure compound **11c** was obtained as white foamy solid (28 mg, 92%); **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 34.84 (bm); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.21 – 7.99 (m, 2H), 7.55 – 7.31 (m, 6.6H), 7.18 – 7.12 (m, 1H), 7.12 – 7.00 (m, 4.8H), 6.94 (t, *J*=8.6, 0.7H), 6.88 (d, *J*=8.3, 0.5H), 6.82 (d, *J*=8.3, 0.2H), 6.75 (d, *J*=8.4, 0.2H), 4.60 – 3.55 (m, 4H), 3.06 – 2.60 (m, 4H), 2.20 (d, *J*=13.6, 3H), 2.09 – 1.97 (m, 2H), 1.95 – 1.78 (m, 3.6H), 1.75 – 1.65 (m, 4H), 1.65 – 1.58 (m, 4H), 1.48 – 1.32 (m, 5H), 1.17 – 0.99 (m, 4H), 0.97 – 0.84 (m, 14H), 0.84 – 0.79 (m, 4H), 0.77 (d, *J*=6.6, 5.2H), 0.73 – 0.67 (m, 3H), 0.66 – 0.62 (m, 1.4H), 0.47 – 0.35 (m, 6.8H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 155.44 (d, *J*=3.4), 141.44 (d, *J*=28.9), 137.85 (d, *J*=1.2), 132.02 (d, *J*=13.5), 131.06 – 130.47 (m), 130.31 (s), 130.18 (s), 129.92 (s), 127.45 (d, *J*=3.5), 120.50 (t, *J*=16.4), 116.24 – 115.60 (m), 112.05 (s), 111.65 (s), 111.48 (s), 63.90 – 63.51 (m), 63.33 (s), 62.21 (s), 60.60 (s), 59.12 (s), 53.11 (s), 52.11 (s), 44.34 – 43.47 (m), 37.53 (s), 37.27 (d, *J*=7.1), 36.73 – 36.27 (m), 36.12 – 35.56 (m), 34.20 (s), 33.61 – 33.19 (m), 33.06 – 32.74 (m), 29.71 (s), 28.60 (d, *J*=5.4), 24.89 (dd, *J*=11.8, 4.3), 22.66 (s), 22.49 (s), 21.40 (d, *J*=3.7), 21.17 (s), 18.25 (d, *J*=13.9), 18.04 (s), 15.19 (s), 15.01 (dd, *J*=6.3, 2.6). **HRMS (ESI+)** Calcd. for $C_{53}H_{84}B_3NO_2P_2$ [M+K^+]: 900.5894, Found: 900.5891.

The preparation of 12c:

To the solution of **9c** (30 mg, 0.035 mmol) in toluene (0.5 mL), was added triethylene diamine (8.7 mg, 0.077 mmol) in one portion, and the mixture was stirred at 70 °C for 5 hours. After the solvent was removed, petroleum ether was added and the mixture was filtered through a silica gel

short column, to afford **12c** as colorless oil (23 mg, 80%).

***R*P,*R*P-Di[2-(-)-menthyl ethylphosphino-1,1'-biphenyl-2'-oxyethyl] methylamine (12c)**

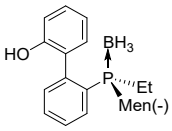


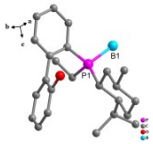
The pure compound was obtained as colorless oil (23 mg, 80%); **^{31}P NMR (202 MHz, CDCl3)** δ = -20.92 (d, 8%), -22.60 (d, 10%), -25.59 (d, 44%), -28.57 (d, 38%); **^{1}H NMR (500 MHz, CDCl3)** δ = 7.49 – 7.32 (m, 3H), 7.33 – 7.24 (m, 5H), 7.22 (s, 3H), 7.07 – 6.92 (m, 3H), 6.82 (d, J=8.2, 2H), 4.04 – 3.75 (m, 4H), 2.72 – 2.39 (m, 4H), 2.08 (dd, J=54.1, 17.6, 3H), 1.91 – 1.73 (m, 3H), 1.72 – 1.41 (m, 10.5H), 1.13 – 1.04 (m, 4H), 1.04 – 0.92 (m, 4H), 0.93 – 0.72 (m, 9H), 0.72 – 0.59 (m, 7.5H), 0.58 – 0.48 (m, 7.5H), 0.45 – 0.26 (m, 1.5H), 0.18 – 0.10 (m, 1H).

Part 5. Crystallographic information

Crystallography data of R_P-5ab

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

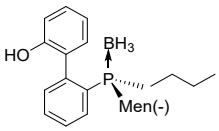


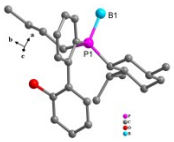


Empirical formula	C24 H36 B O P
Crystal system	Monoclinic
space group	P21
Formula weight	379.28
a, Å	9.6028(9)
b, Å	14.6741(13)
c, Å	16.2270(15)
α, deg	90
β, deg	95.398(2)
γ, deg	90
V, Å3	2276.4(4)
Z	4
T, K	298(2)
λ, Å	0.71073
ρ, Mg m-3	1.107
Rint	0.0467
R1 [I N 2σ(I)]	0.0608
R1 (all data)	0.1054
wR2 [I N 2σ(I)]	0.1396
wR2 (all data)	0.1599
Flack	0.07(11)
CCDC	2111497

Crystallography data of R_P-5ac

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

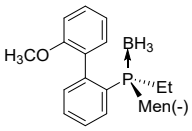


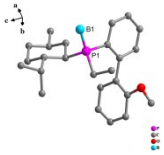


Empirical formula	C26 H40 B O P
Crystal system	Orthorhombic
space group	P212121
Formula weight	407.33
a, Å	12.84(5)
b, Å	13.69(5)
c, Å	14.68(5)
α, deg	90
β, deg	90
γ, deg	90
V, Å3	2580(16)
Z	4
T, K	298.15
λ, Å	0.71073
ρ, Mg m-3	1.048
Rint	0.1116
R1 [I N 2σ(I)]	0.1183
R1 (all data)	0.2276
wR2 [I N 2σ(I)]	0.2873
wR2 (all data)	0.3500
Flack	0.10(12)
CCDC	2111499

Crystallography data of R_P-6h

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

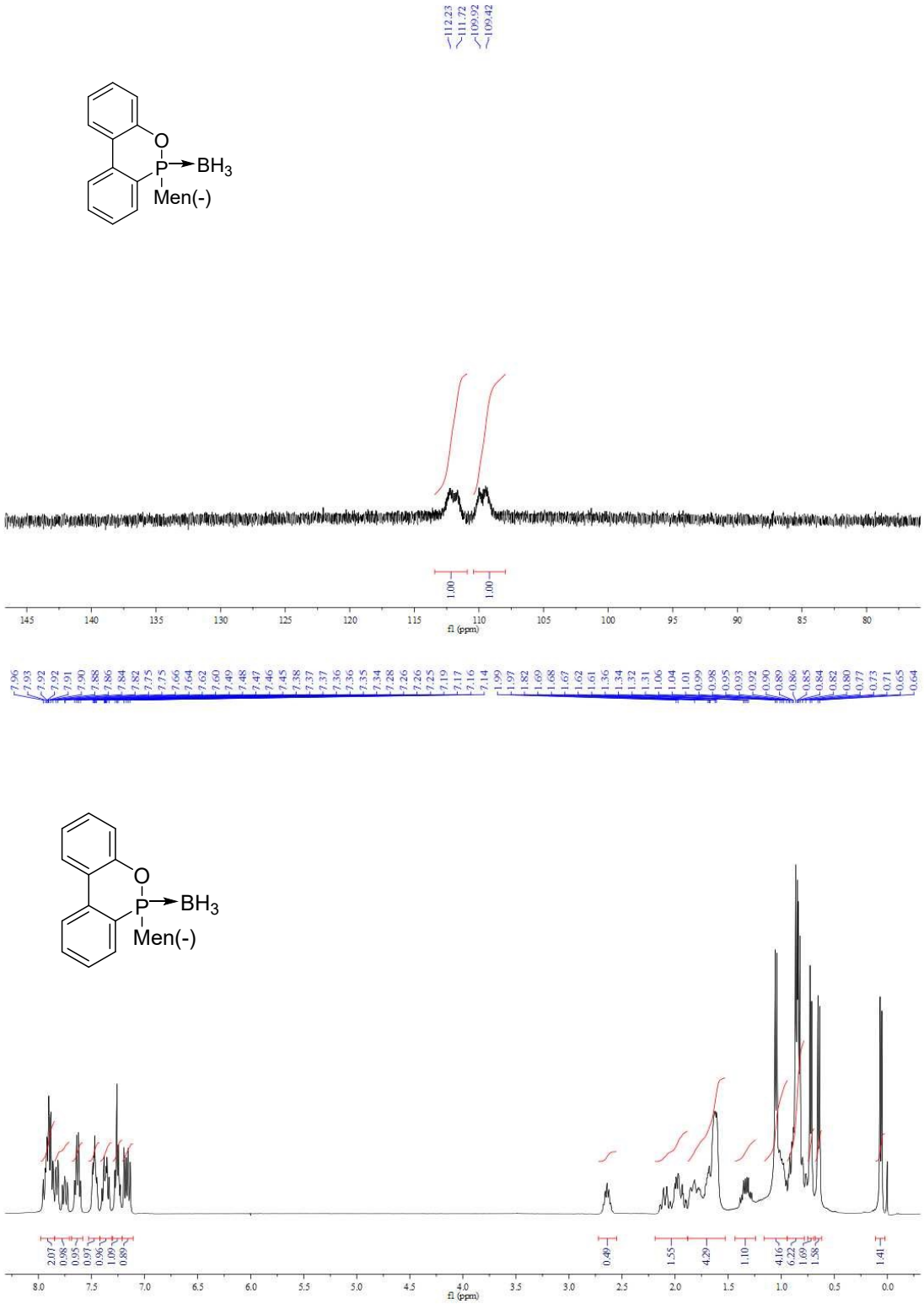


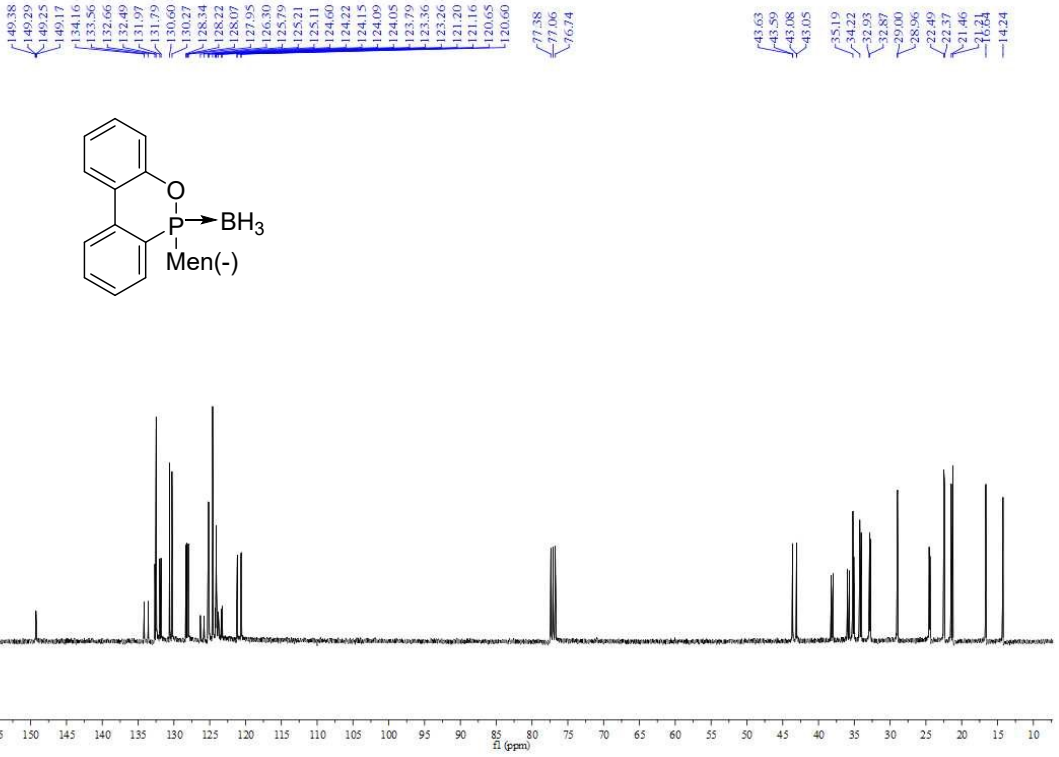


Empirical formula	C25 H38 B O P
Crystal system	Orthorhombic
space group	P -1
Formula weight	393.31
a, Å	9.1696(8)
b, Å	10.0689(9)
c, Å	25.845(2)
α, deg	90
β, deg	90
γ, deg	90
V, Å3	2386.2(4)
Z	4
T, K	293(2)
λ, Å	0.71073
ρ, Mg m-3	1.095
Rint	0.1006
R1 [I N 2σ(I)]	0.1046
R1 (all data)	0.1715
wR2 [I N 2σ(I)]	0.2575
wR2 (all data)	0.2980
Flack	-0.02(13)
CCDC	2111303

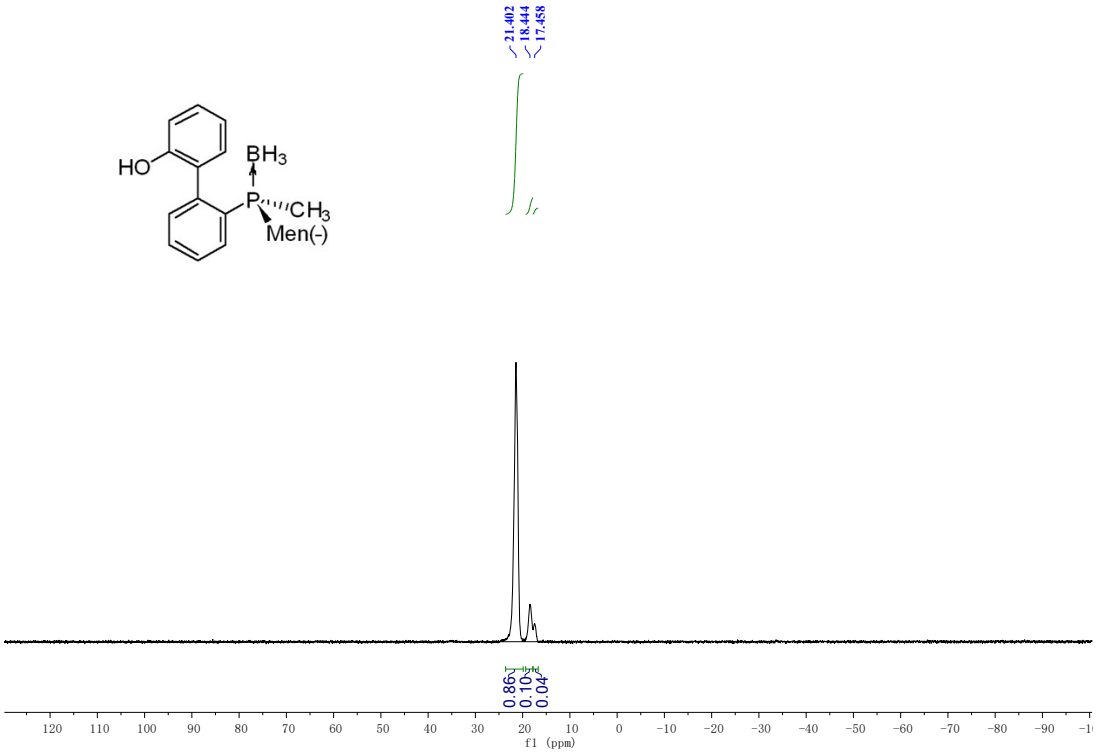
Part 6. Selected photocopies of ^{1}H, ^{31}P and ^{13}C NMR spectrum

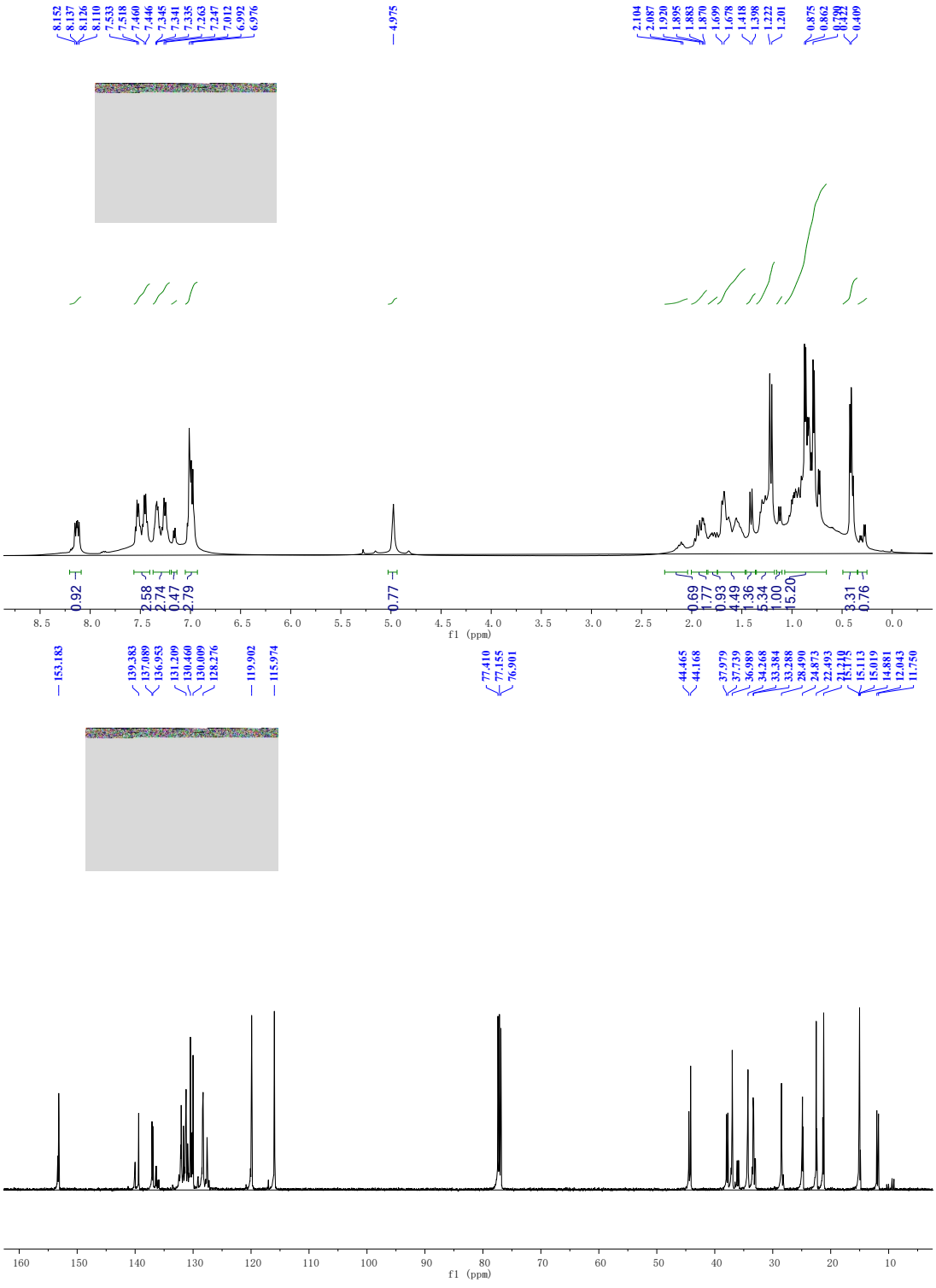
***R*$_P$/*S*$_P$-6-(-)-Menthyl-6*H*-dibenzo[*c*,*e*][1,2]oxaphosphinine-borane complex (2a/2a')**



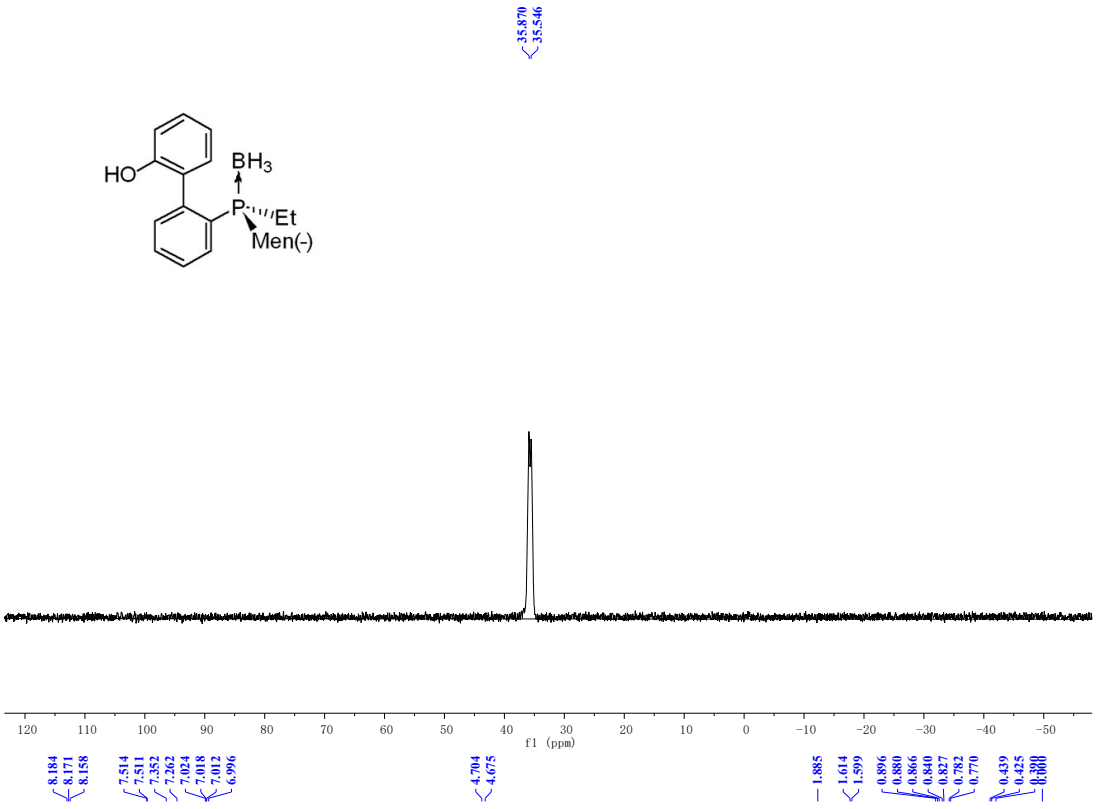


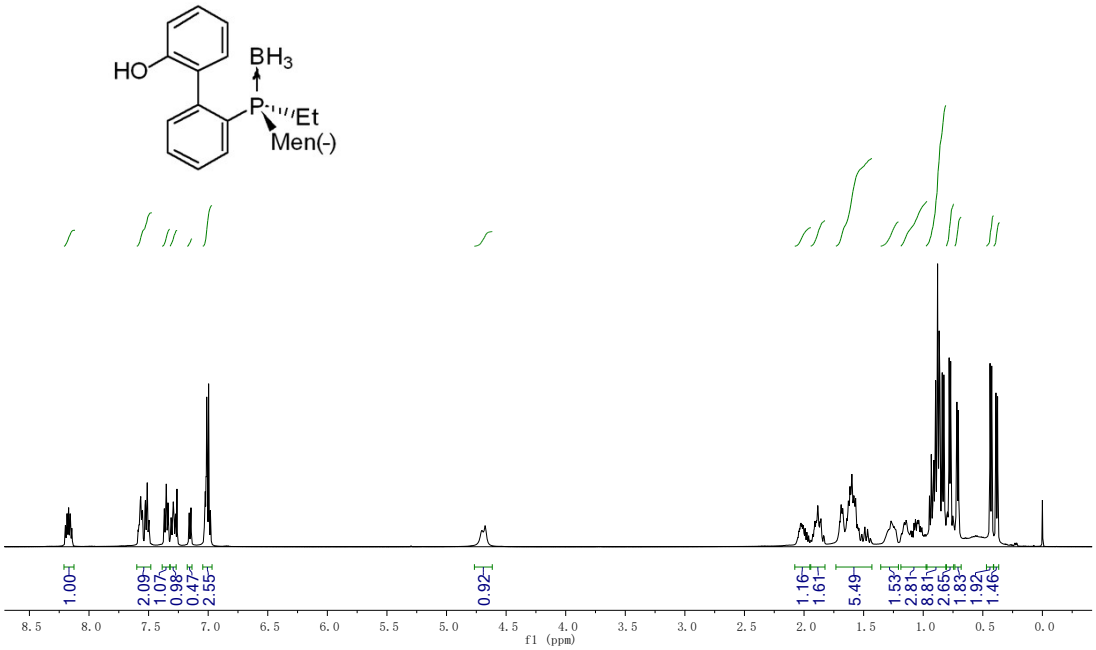
(R_P/S_P)-(–)-Menthyl methyl (2'-hydroxy-1,1'-biphenyl-2-yl)phosphine borane (5aa/5aa')

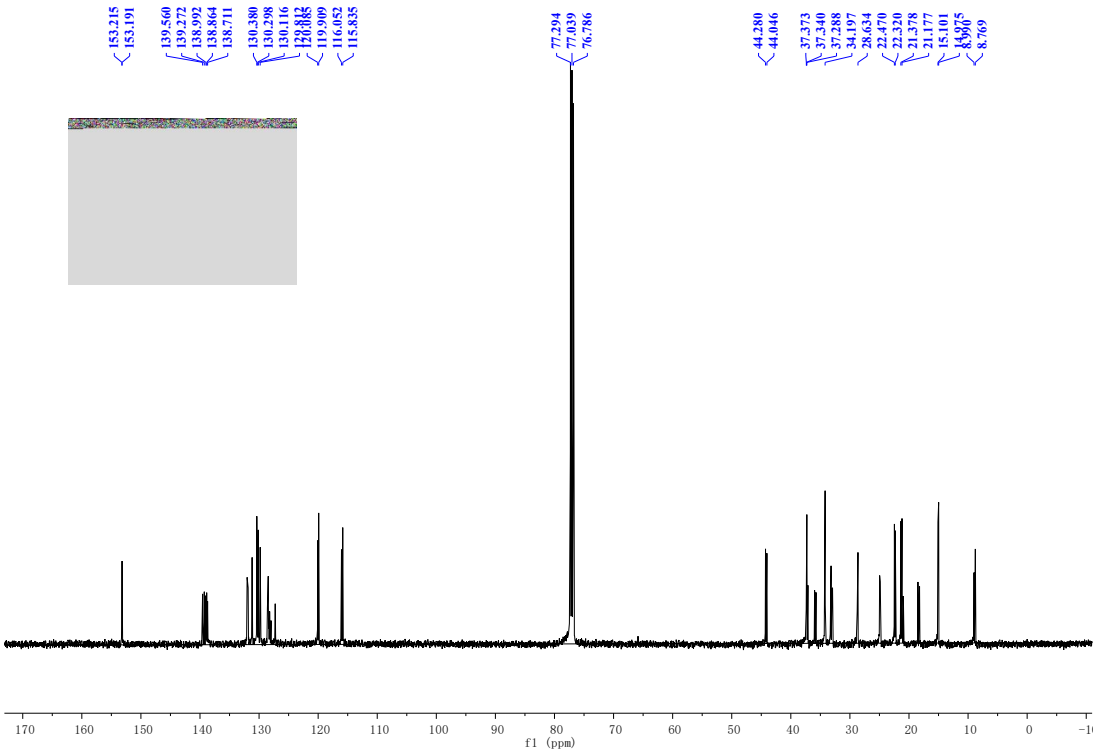




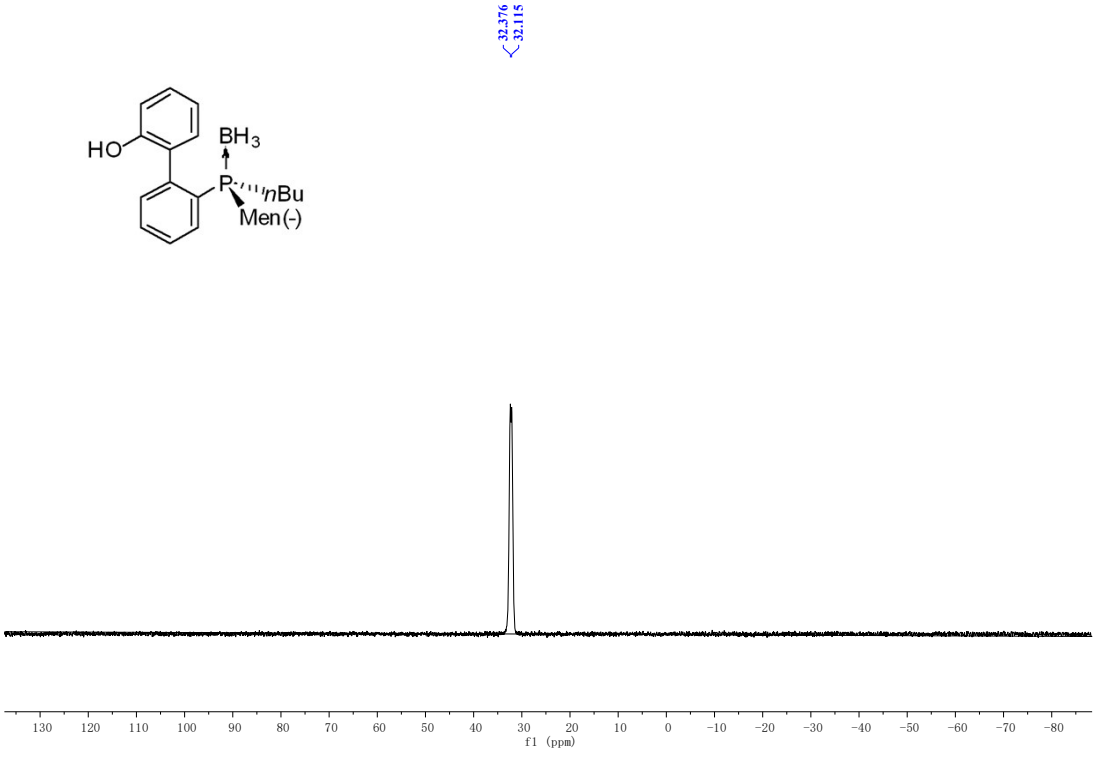
(R_P)-(–)-Menthyl ethyl (2'-hydroxy-1,1'-biphenyl-2-yl)phosphine borane (R_P-5ab)

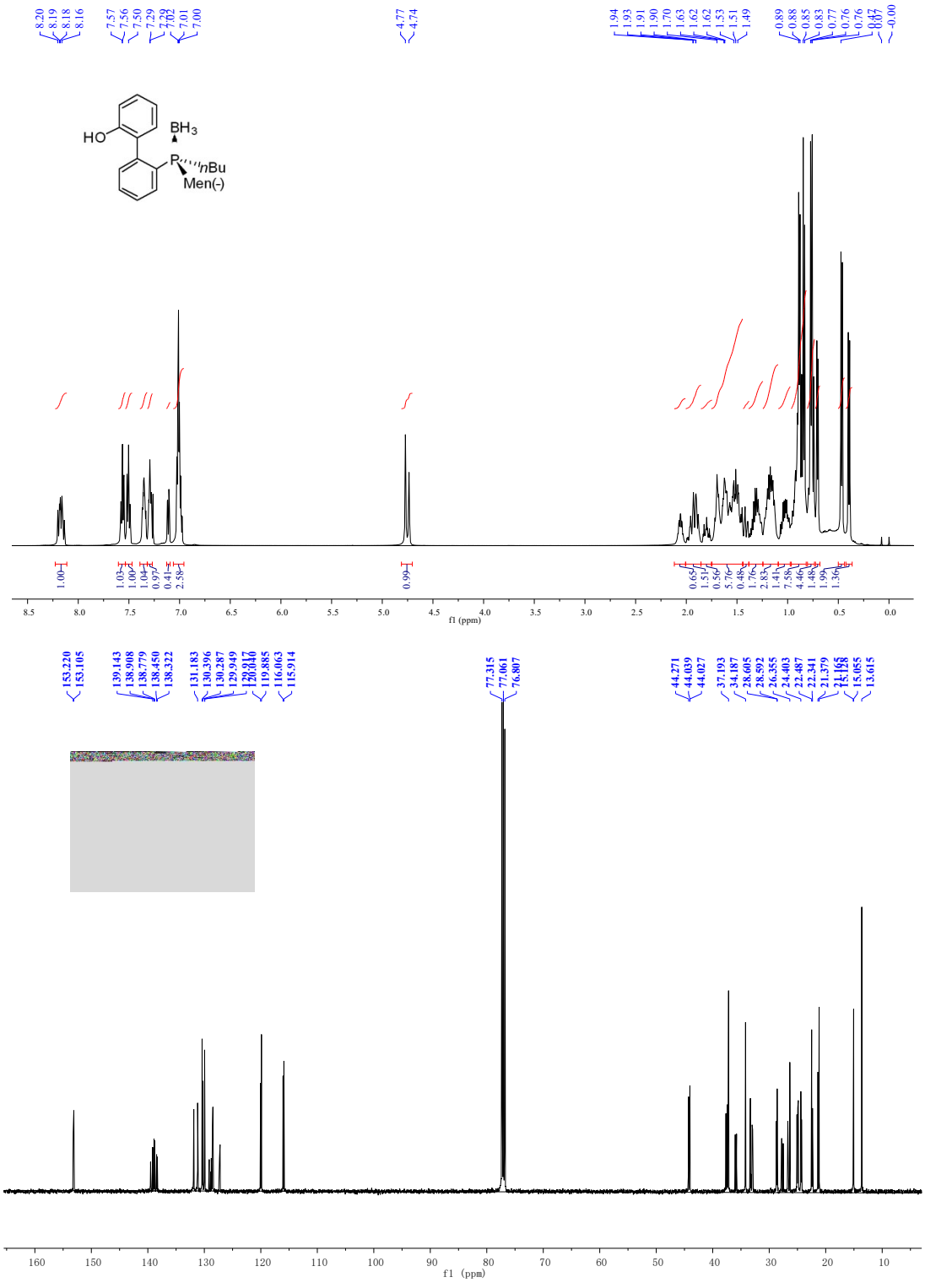

35.870
35.546
HO
BH3
P
Et
Men(-)
120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50
f1 (ppm)
8.184
8.171
8.158
7.514
7.511
7.352
7.262
7.024
7.018
7.012
6.996
4.704
4.675
1.885
1.614
1.599
0.896
0.880
0.866
0.840
0.827
0.782
0.770
0.439
0.425
0.390
0.000


HO
BH3
P
Et
Men(-)
1.00
2.09
1.07
0.98
0.47
2.55
0.92
1.16
1.61
5.49
1.53
2.81
8.81
2.65
1.83
1.92
1.46
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
f1 (ppm)

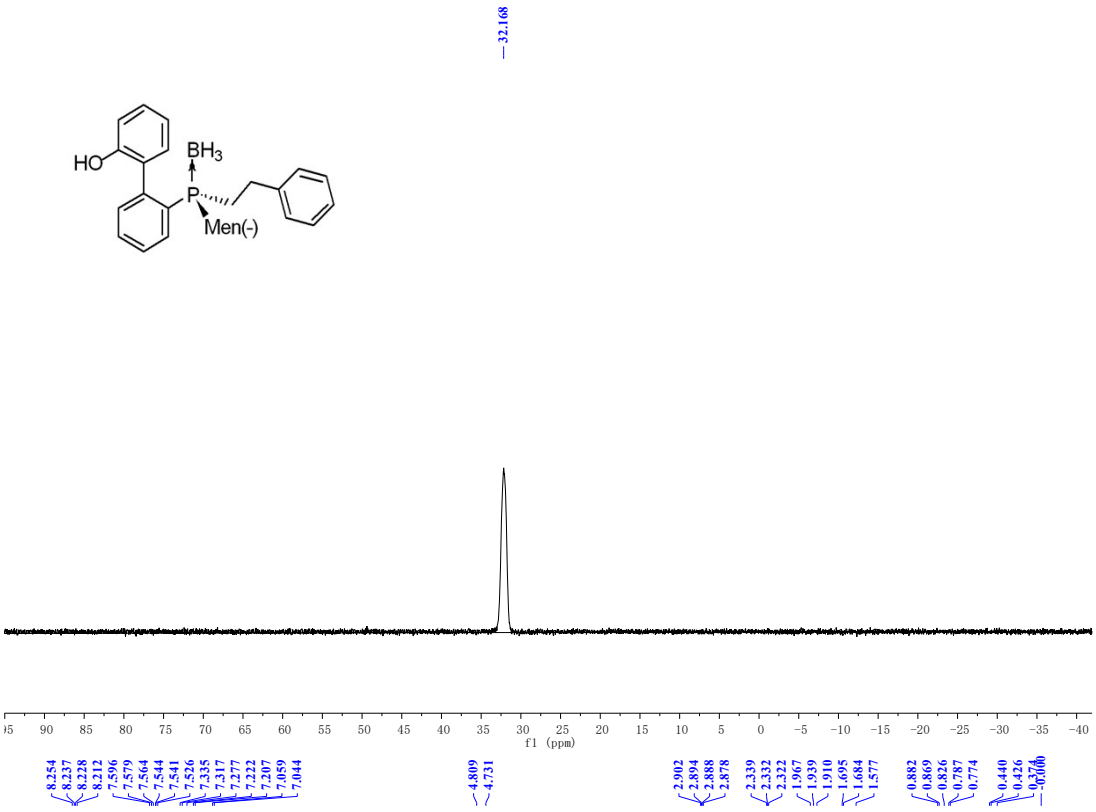


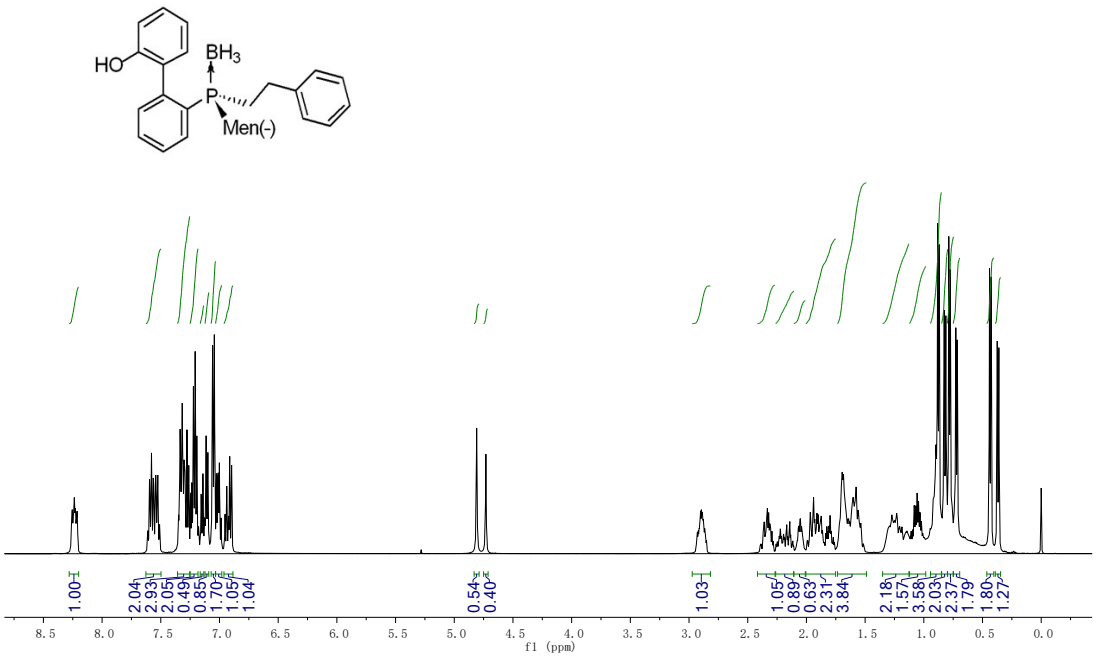
(R_P)-(–)-Menthyl butyl (2'-hydroxy-1,1'-biphenyl-2-yl)phosphine borane (R_P-5ac)

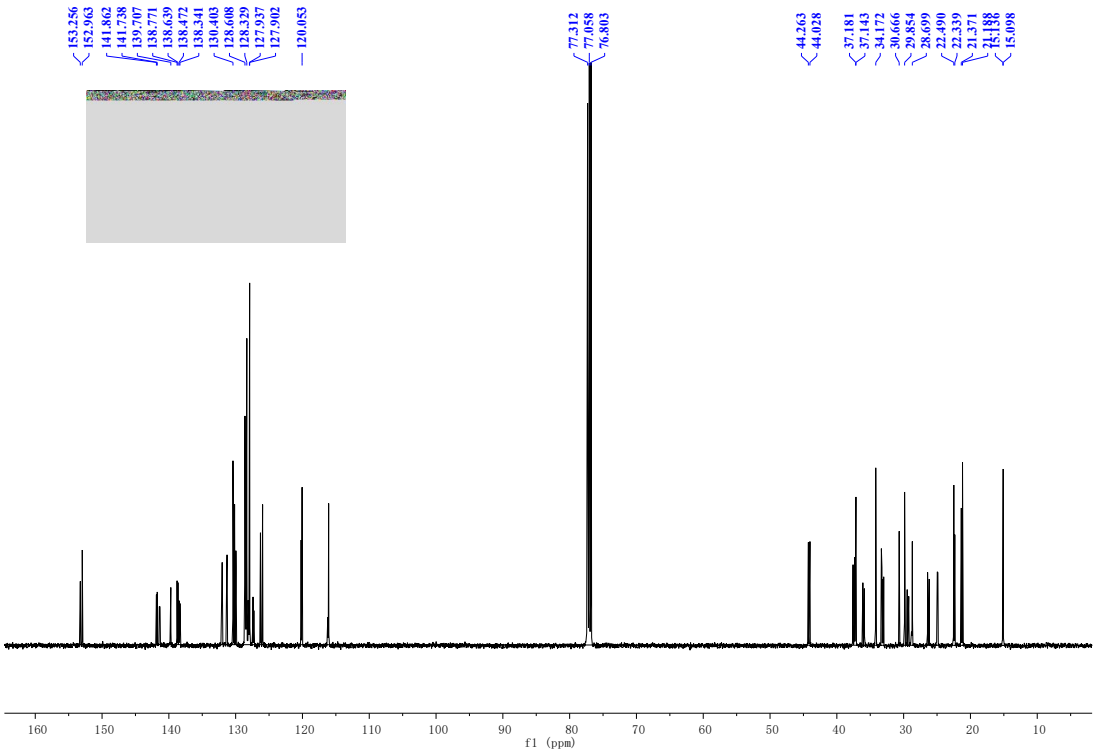




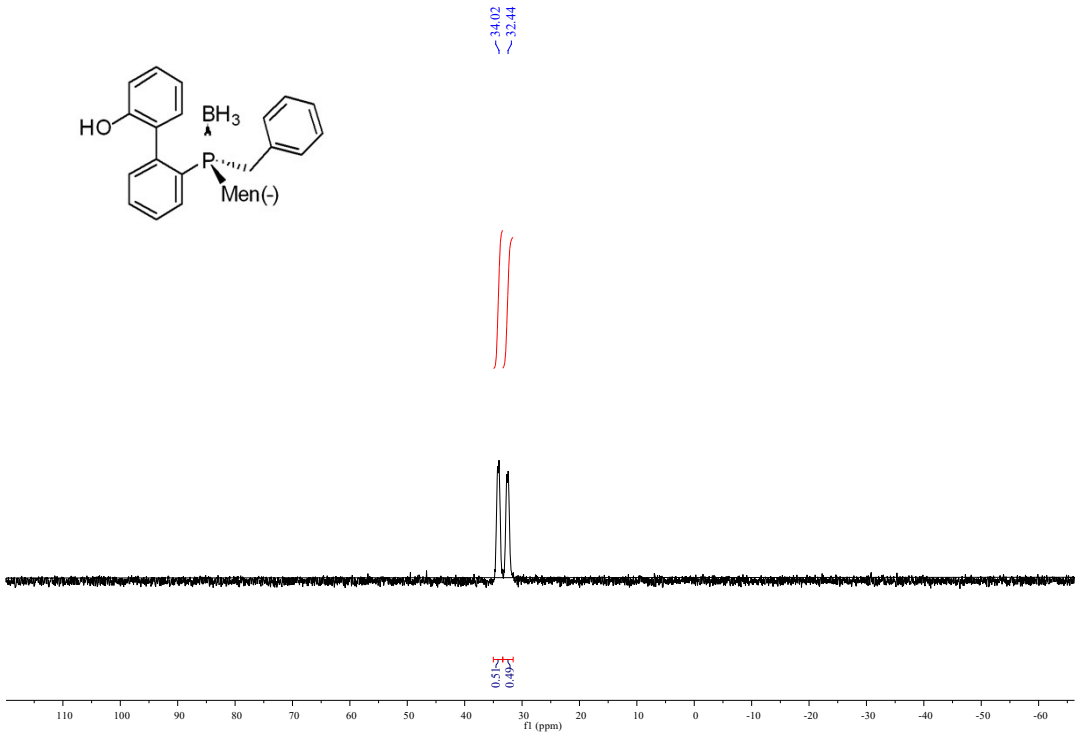
(R_P)-(–)-Menthyl phenylethyl (2'-hydroxy-1,1'-biphenyl-2-yl)phosphine borane (R_P-5ad)

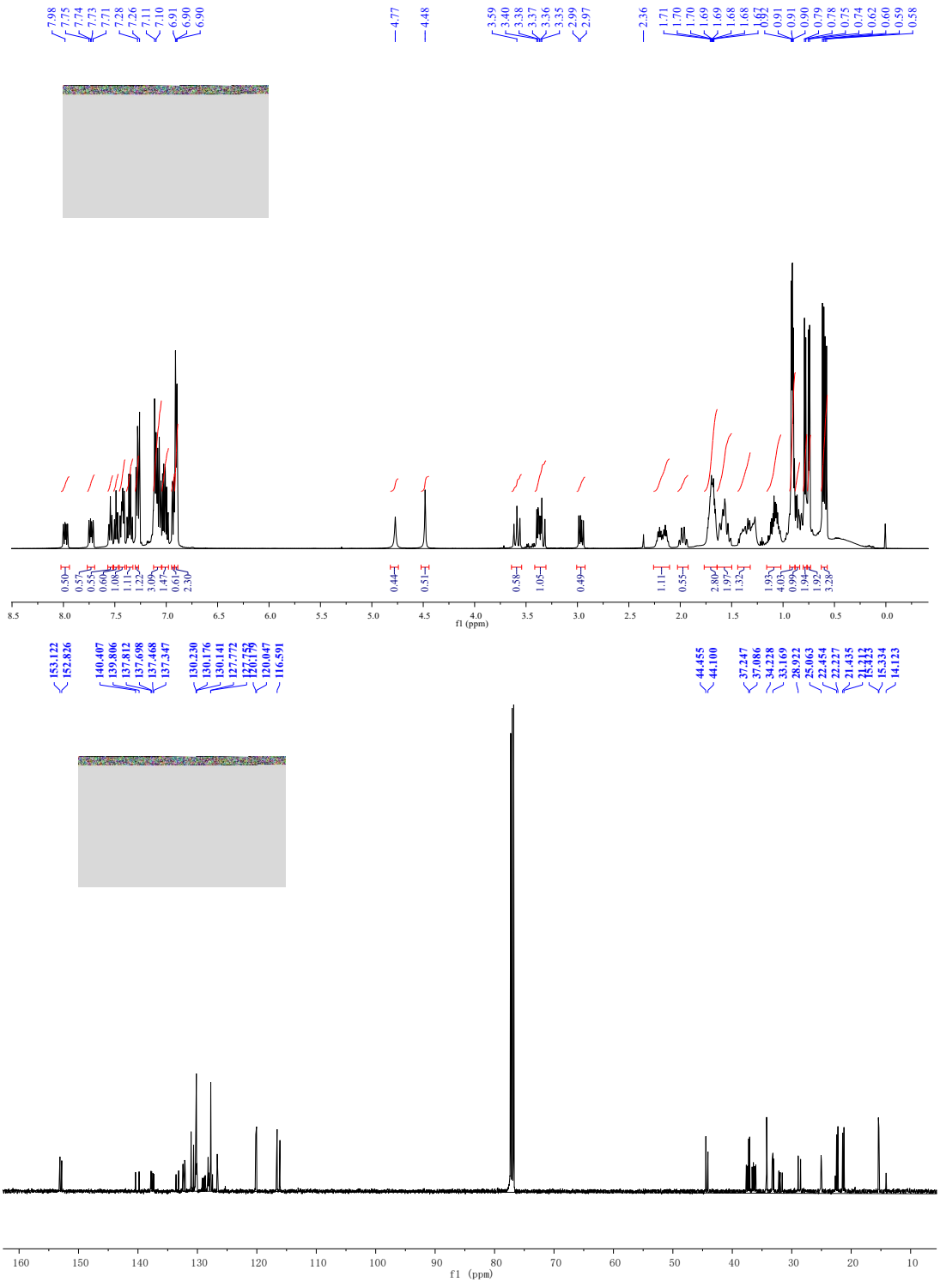

32.168
HO
BH3
P
Men(-)
f1 (ppm)


HO
BH3
P
Men(-)
f1 (ppm)

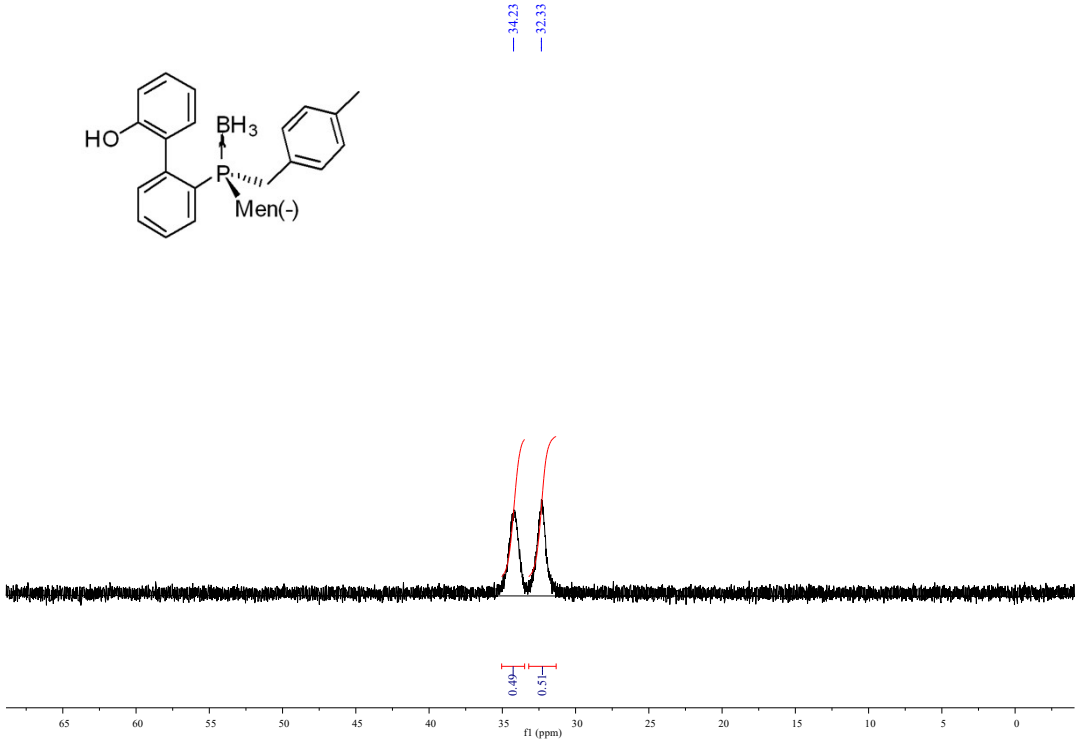


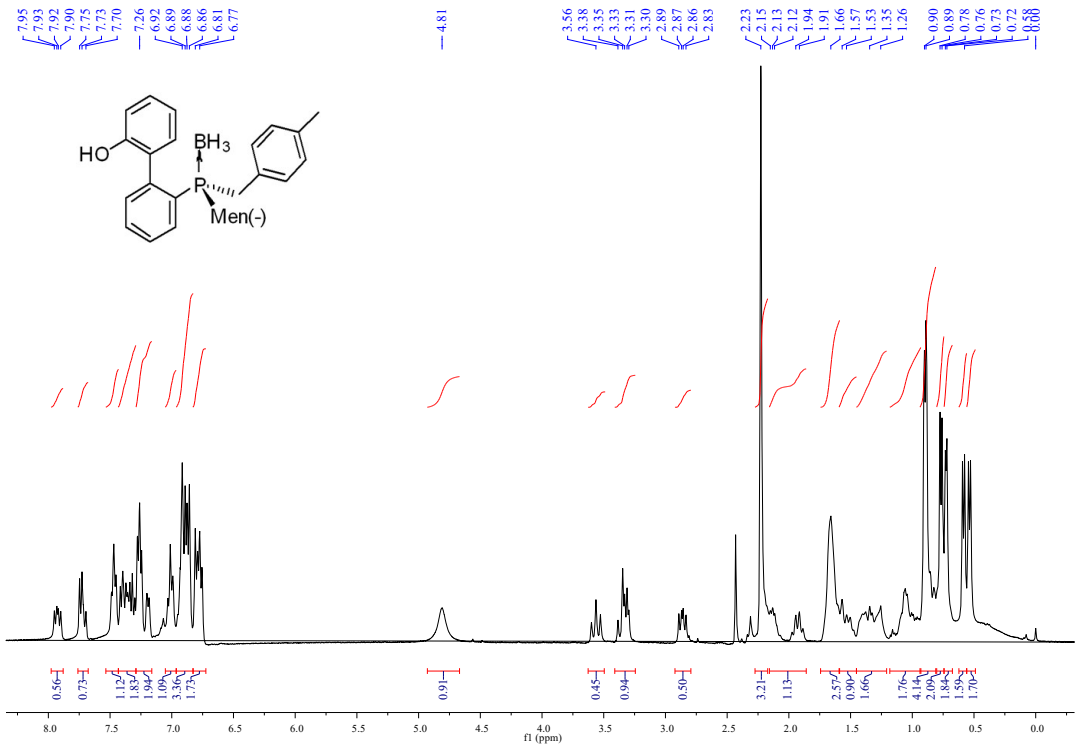
(R_P)-(–)-Menthyl benzyl (2'-hydroxy-1,1'-biphenyl-2-yl)phosphine borane (R_P-5ae)

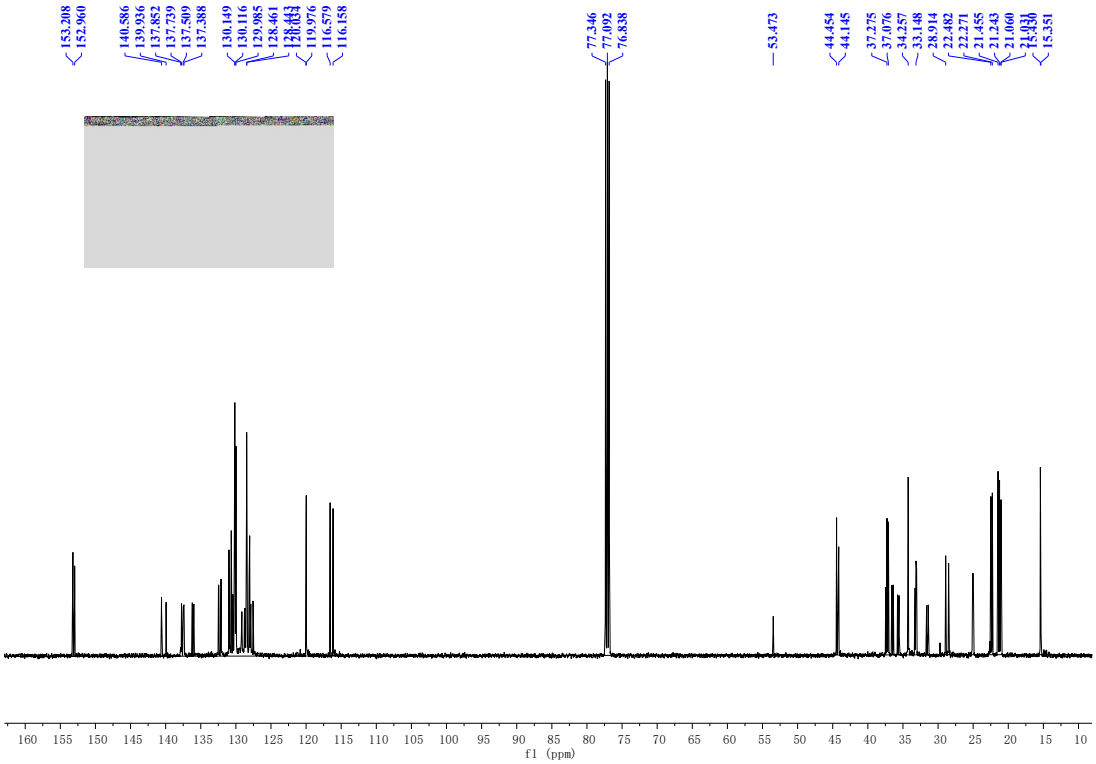




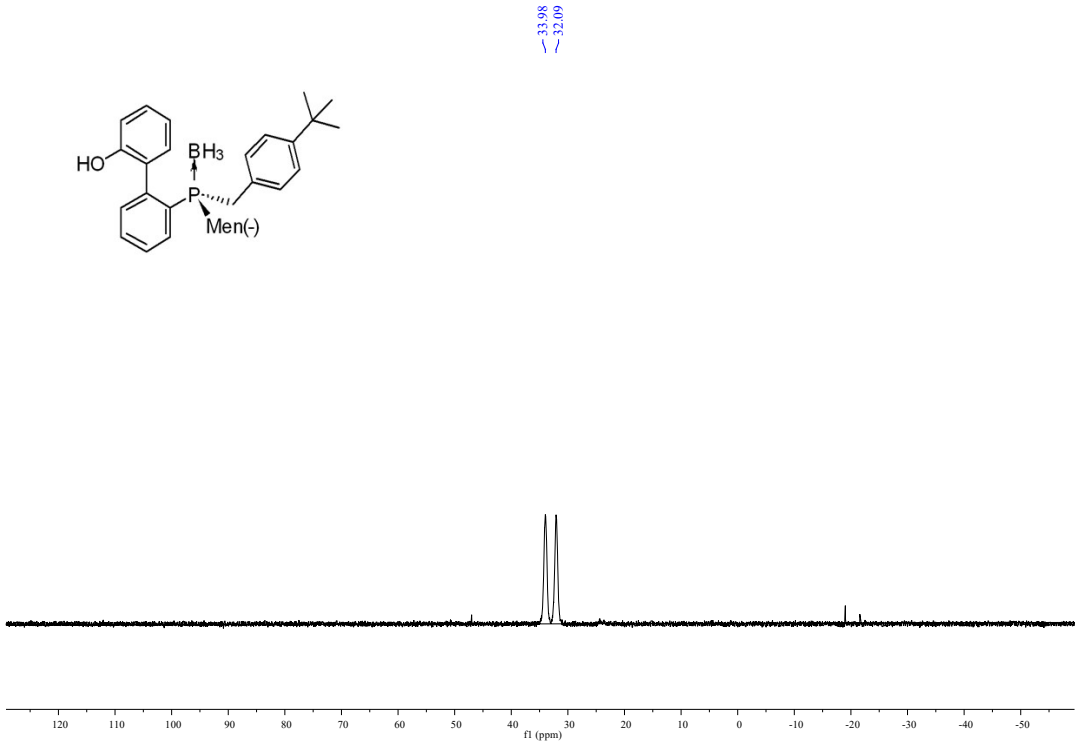
(R_P)-(–)-Menthyl *p*-methylbenzyl (2'-hydroxy-1,1'-biphenyl-2-yl)phosphine borane (R_P-5af)

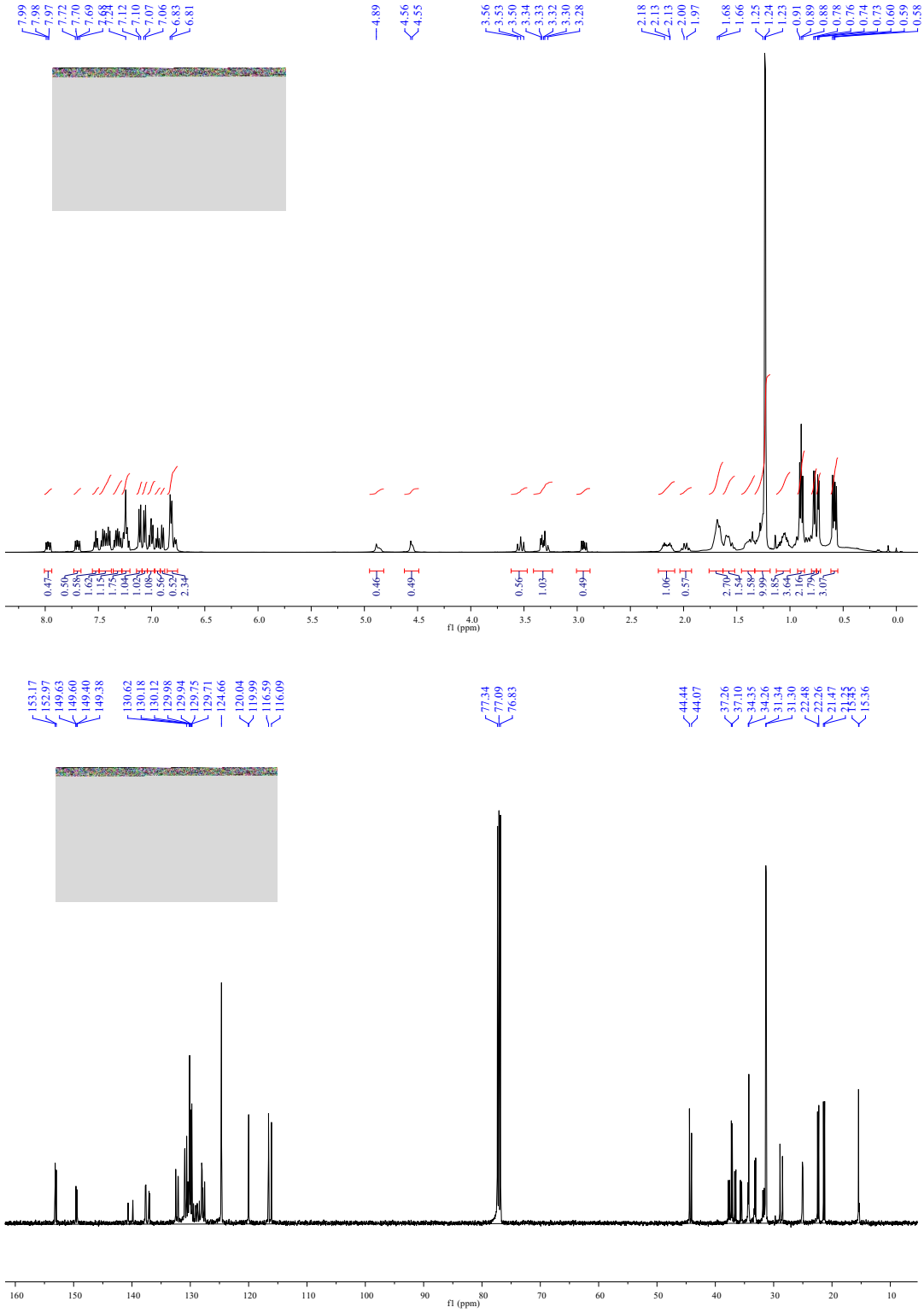

34.23
32.33
HO
BH3
P
Men(-)
0.40
0.51
f1 (ppm)


7.95
7.93
7.92
7.90
7.75
7.73
7.70
7.26
6.92
6.89
6.88
6.86
6.81
6.77
4.81
3.56
3.38
3.35
3.33
3.31
3.30
2.89
2.87
2.86
2.83
2.23
2.15
2.13
2.12
1.94
1.91
1.66
1.57
1.53
1.35
1.26
0.90
0.89
0.78
0.76
0.73
0.72
0.58
0.00
HO
BH3
P
Men(-)
0.56
0.73
1.12
1.83
1.94
1.09
3.36
1.73
0.91
0.45
0.94
0.50
3.21
1.13
2.57
0.90
1.66
1.76
4.14
2.09
1.84
1.59
1.70
f1 (ppm)

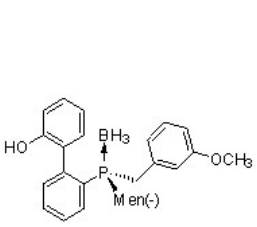


(R_P)-(–)-Menthyl *p*-tert-butylbenzyl (2'-hydroxy-1,1'-biphenyl-2-yl)phosphine borane (R_P-5ag)

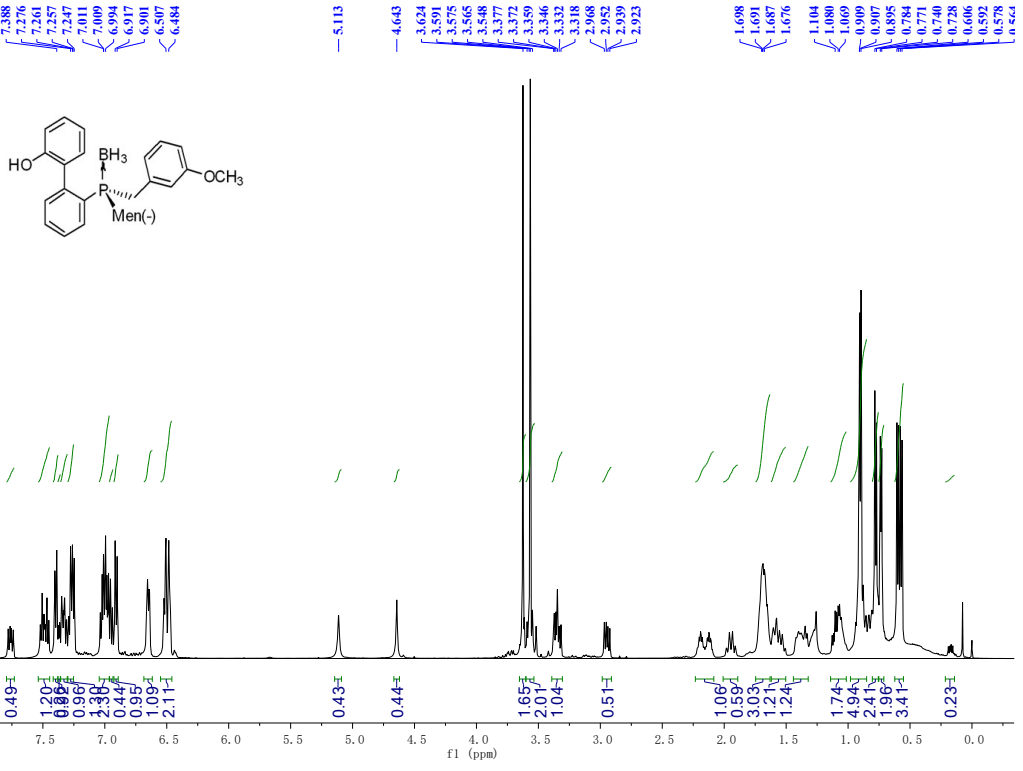


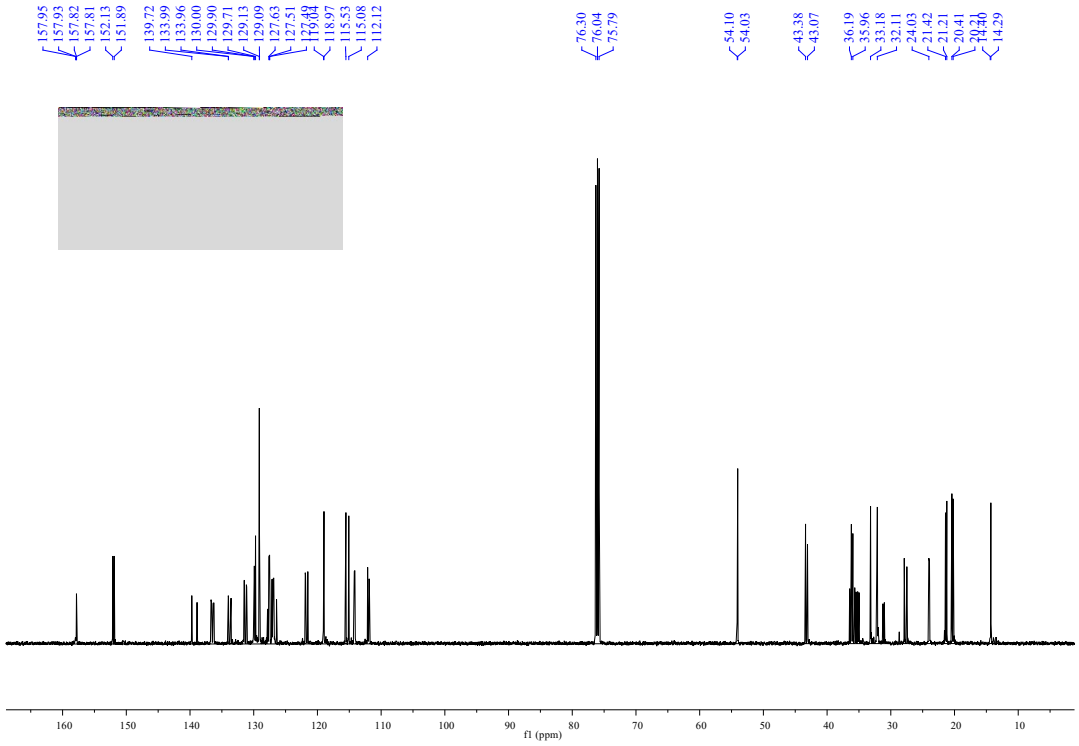


(R_P/S_P)-(–)-Menthyl *m*-methoxybenzyl (2'-hydroxy-1,1'-biphenyl-2-yl)phosphine borane (5ah/5ah')

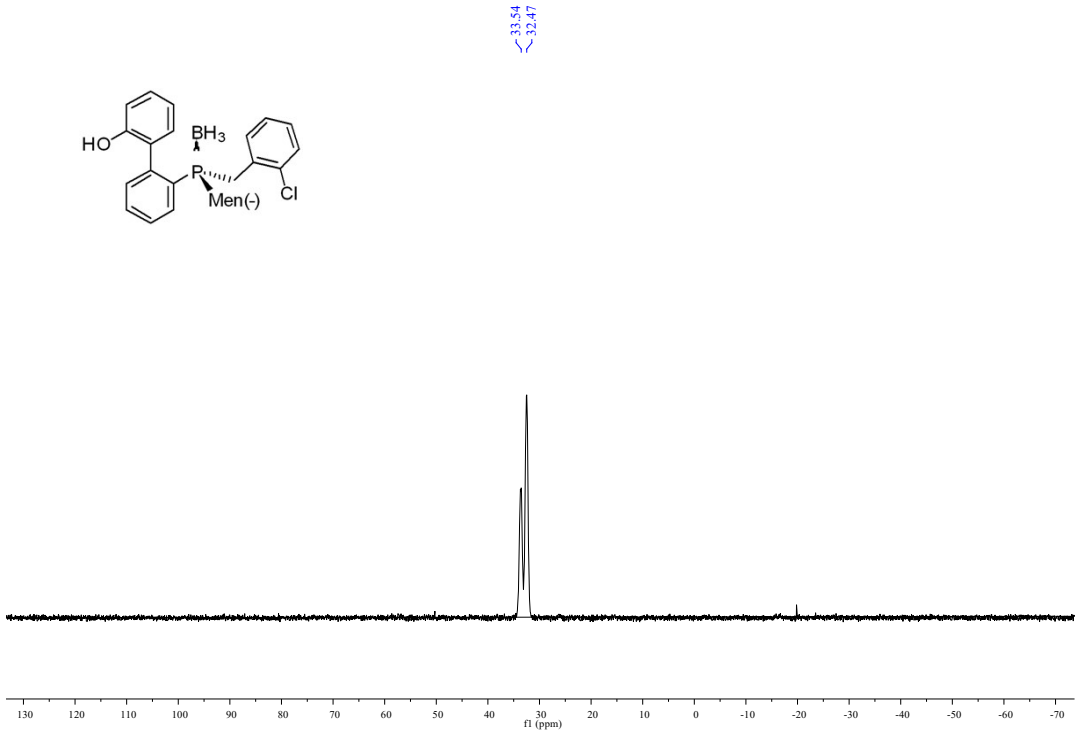

HO
BH3
P
OCH3
Men(-)

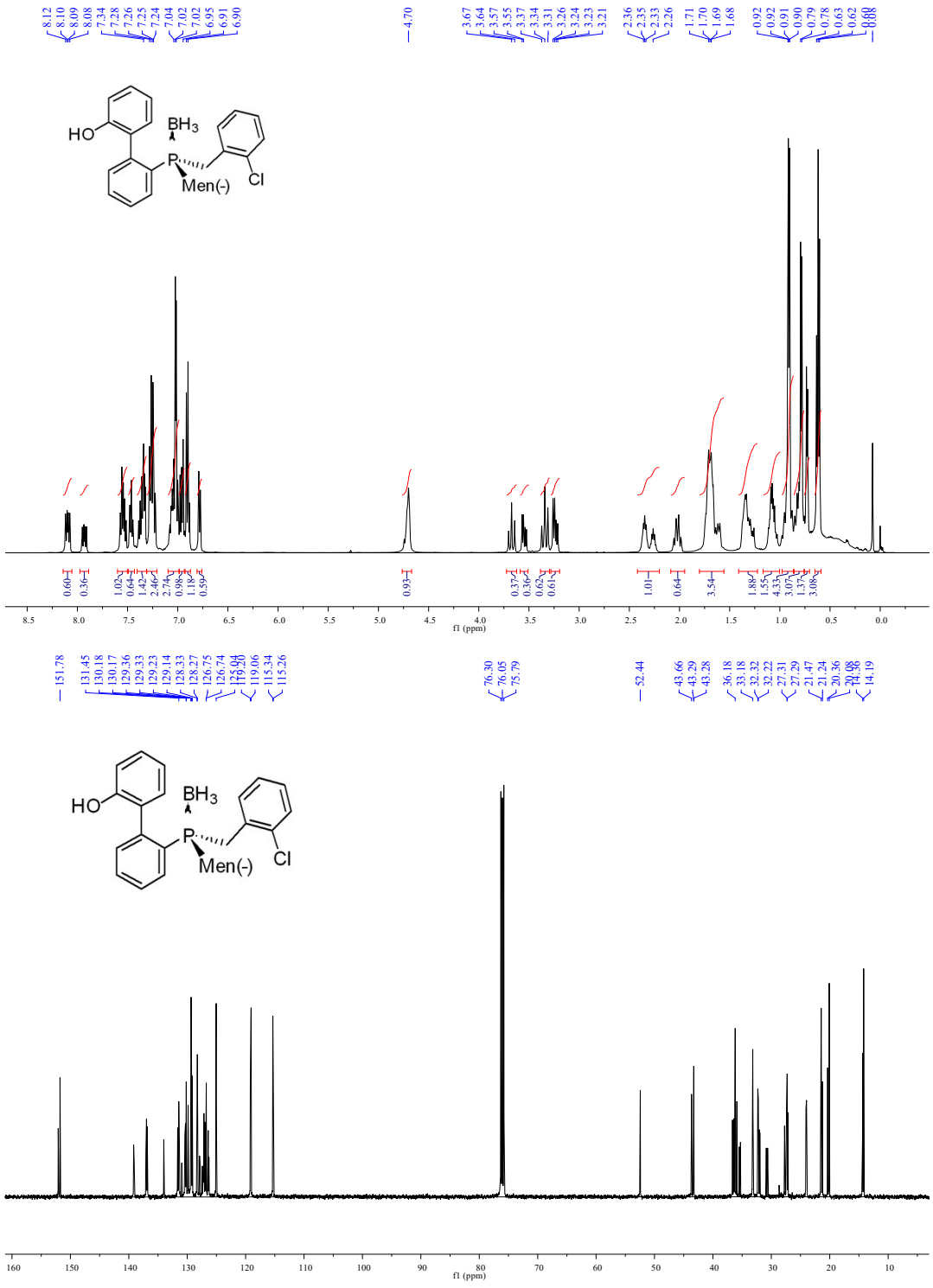
33.49
32.45
24.14
24.10
24.05
24.01
23.99
0.45
0.51
0.04
f1 (ppm)


7.388
7.276
7.261
7.257
7.247
7.011
7.009
6.994
6.917
6.901
6.507
6.484
5.113
4.643
3.624
3.591
3.575
3.565
3.548
3.377
3.372
3.359
3.346
3.332
3.318
2.968
2.952
2.939
2.923
1.698
1.691
1.687
1.676
1.104
1.080
1.069
0.909
0.907
0.895
0.784
0.771
0.740
0.728
0.606
0.592
0.578
HO
BH3
P
OCH3
Men(-)
0.53
0.49
1.20
0.96
2.30
0.44
0.95
1.09
2.11
0.43
0.44
1.65
2.01
1.04
0.51
1.06
0.59
3.03
1.21
1.24
1.74
4.94
2.41
1.96
3.41
0.23
f1 (ppm)

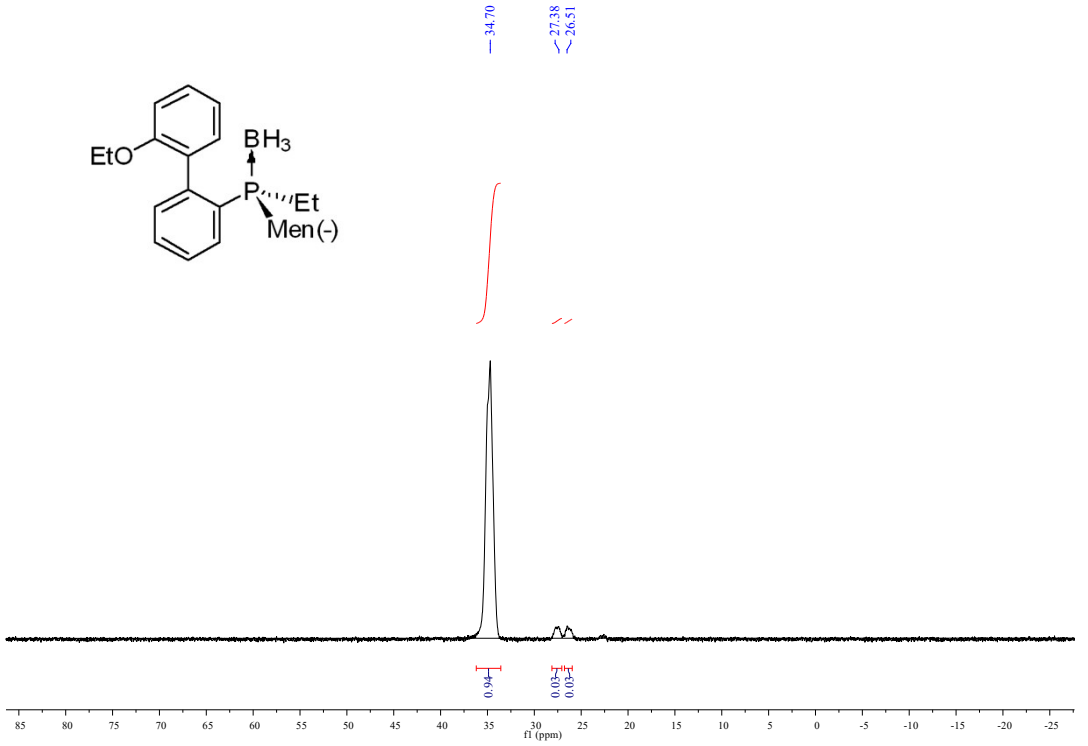


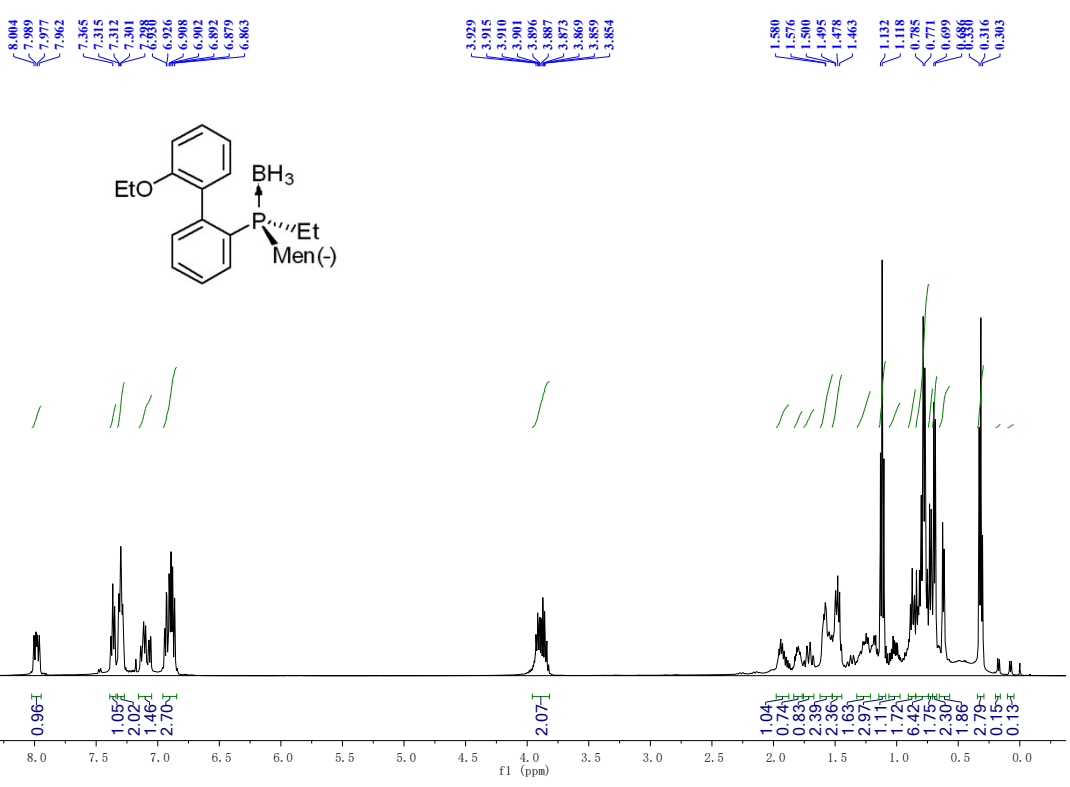
(R_P)-(–)-Menthyl *o*-chlorobenzyl (2'-hydroxy-1,1'-biphenyl-2-yl)phosphine borane (R_P-5ai)

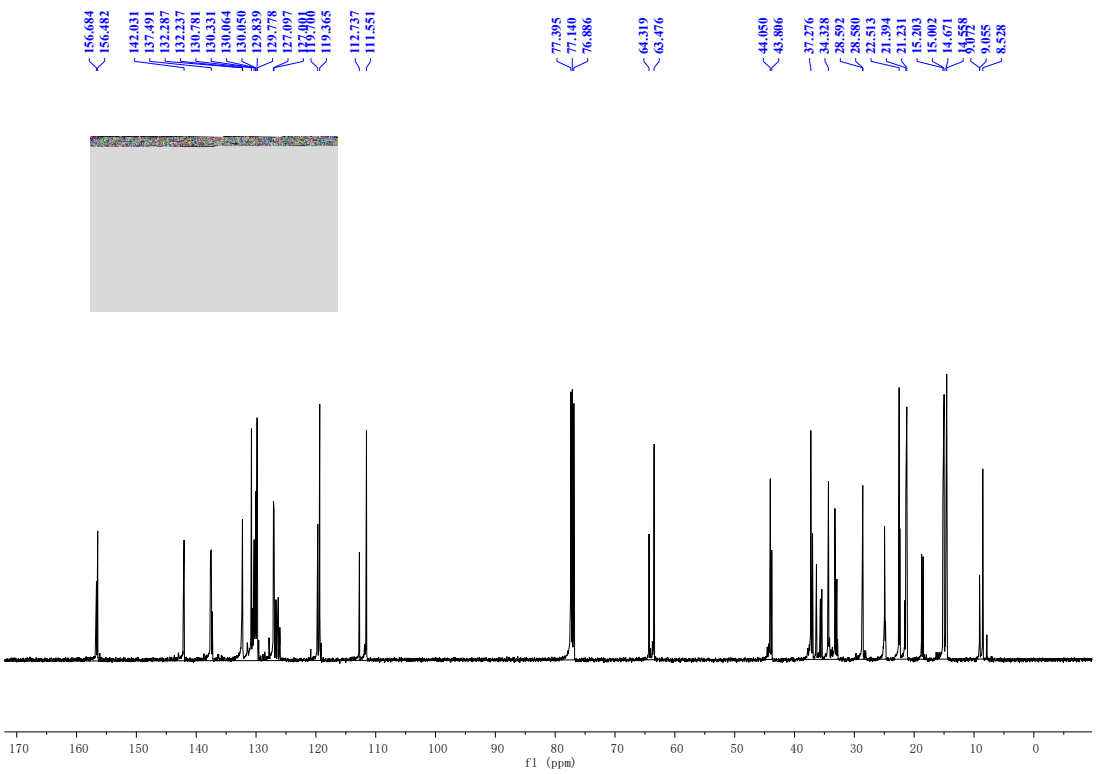




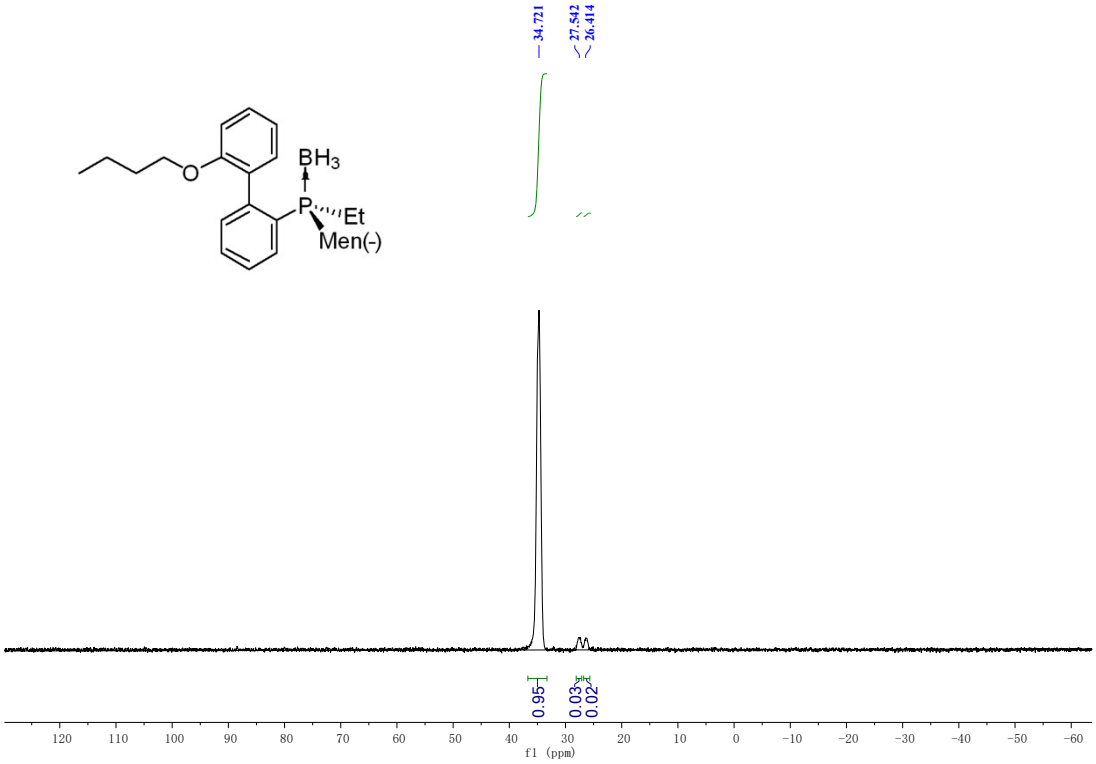
(R_P/S_P)-(–)-Menthyl ethyl (2'-ethoxy-1,1-biphenyl-2-yl) phosphine borane (6a/6a')

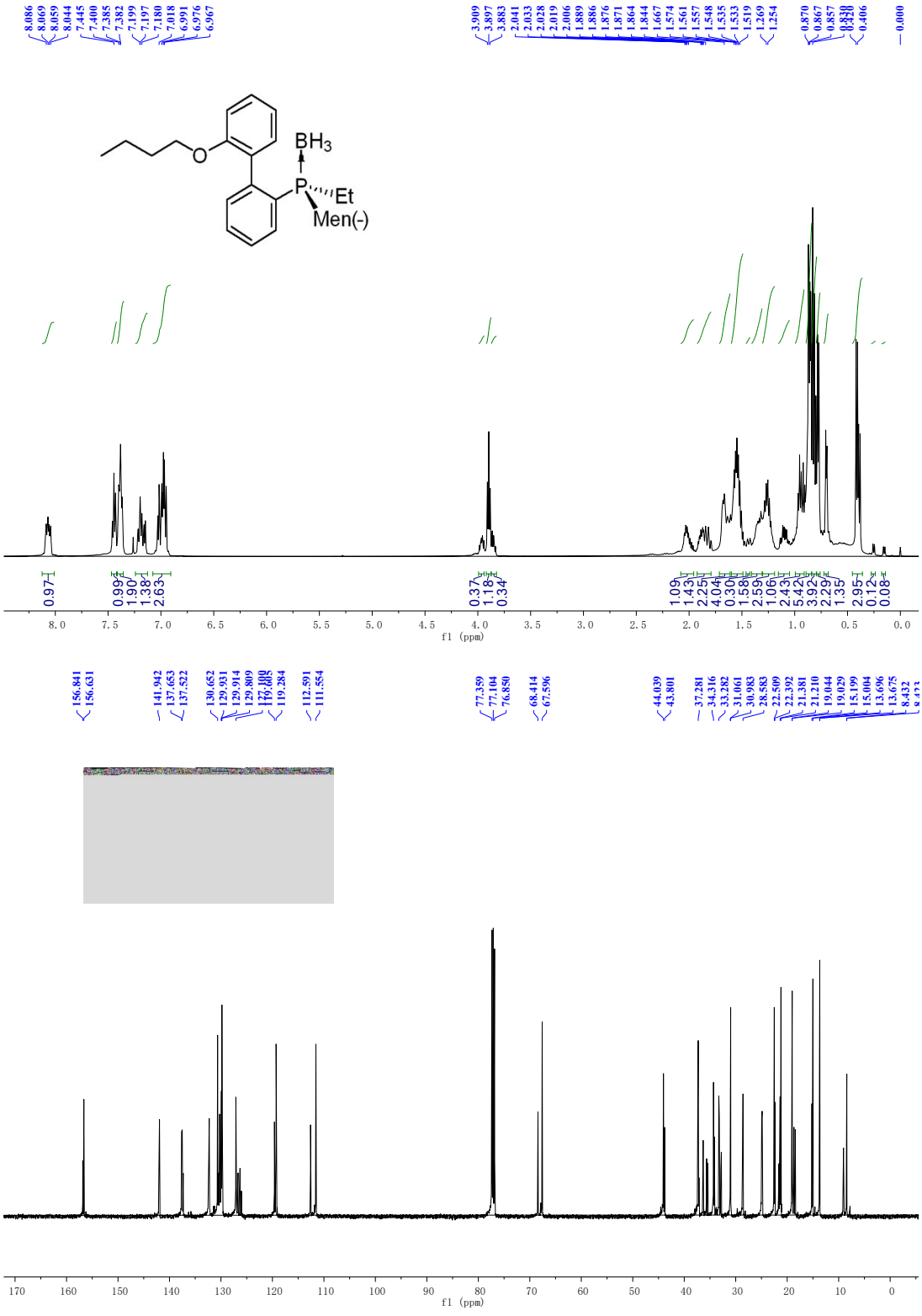

34.70
27.38
26.51
EtO
BH3
P
Et
Men(-)
0.94
0.03
0.03
f1 (ppm)


8.004
7.989
7.977
7.962
7.365
7.315
7.312
7.301
6.926
6.908
6.902
6.892
6.879
6.863
3.929
3.915
3.910
3.901
3.896
3.887
3.873
3.869
3.859
3.854
1.580
1.576
1.500
1.495
1.478
1.463
1.132
1.118
0.785
0.771
0.699
0.316
0.303
EtO
BH3
P
Et
Men(-)
0.96
1.05
2.02
1.46
2.70
2.07
1.04
0.74
0.83
2.39
2.36
1.63
2.97
1.11
1.72
6.42
1.75
2.30
1.86
2.79
0.15
0.13
f1 (ppm)

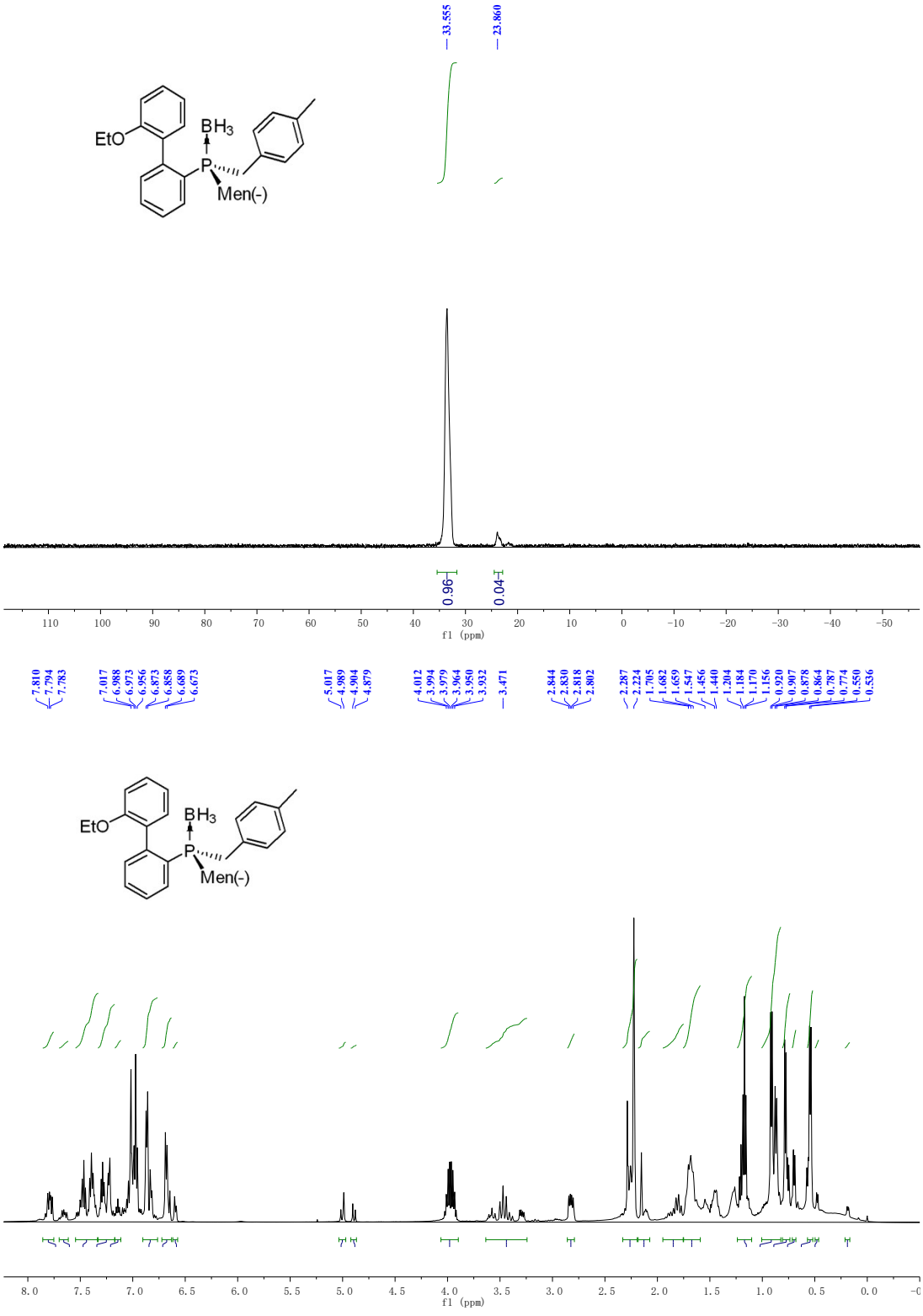


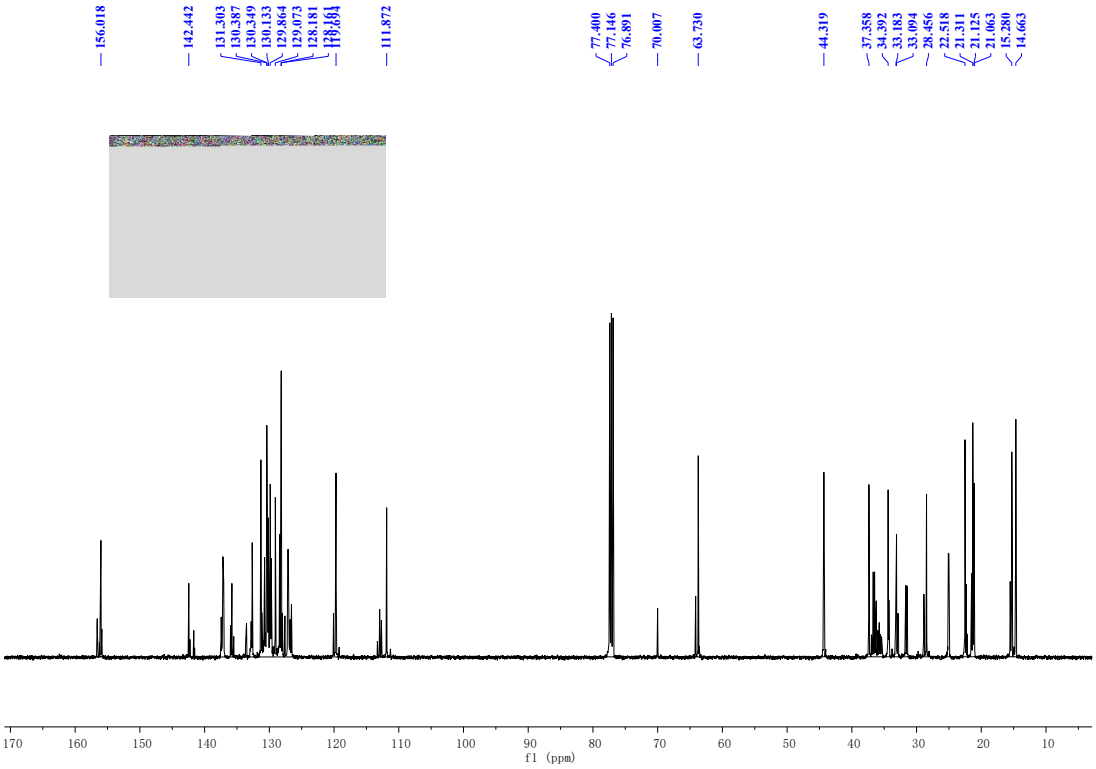
(R_P/S_P)-(–)-Menthyl ethyl (2'-butoxy-1,1-biphenyl-2-yl) phosphine borane (6b/6b')



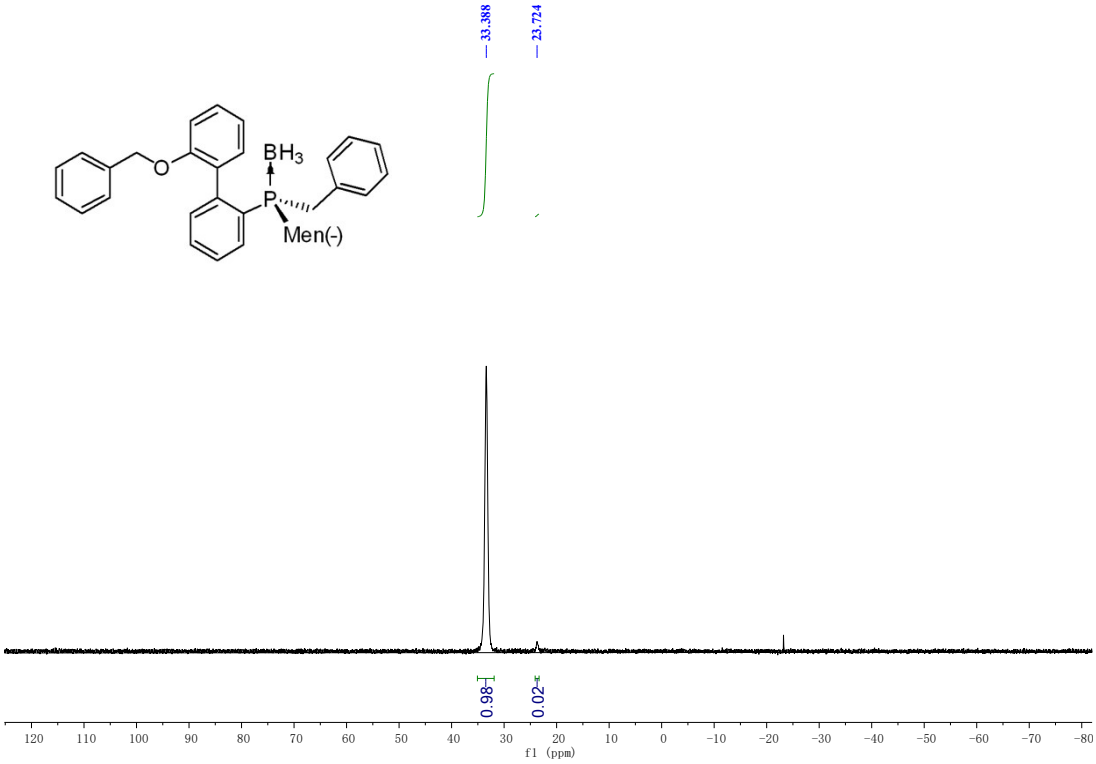


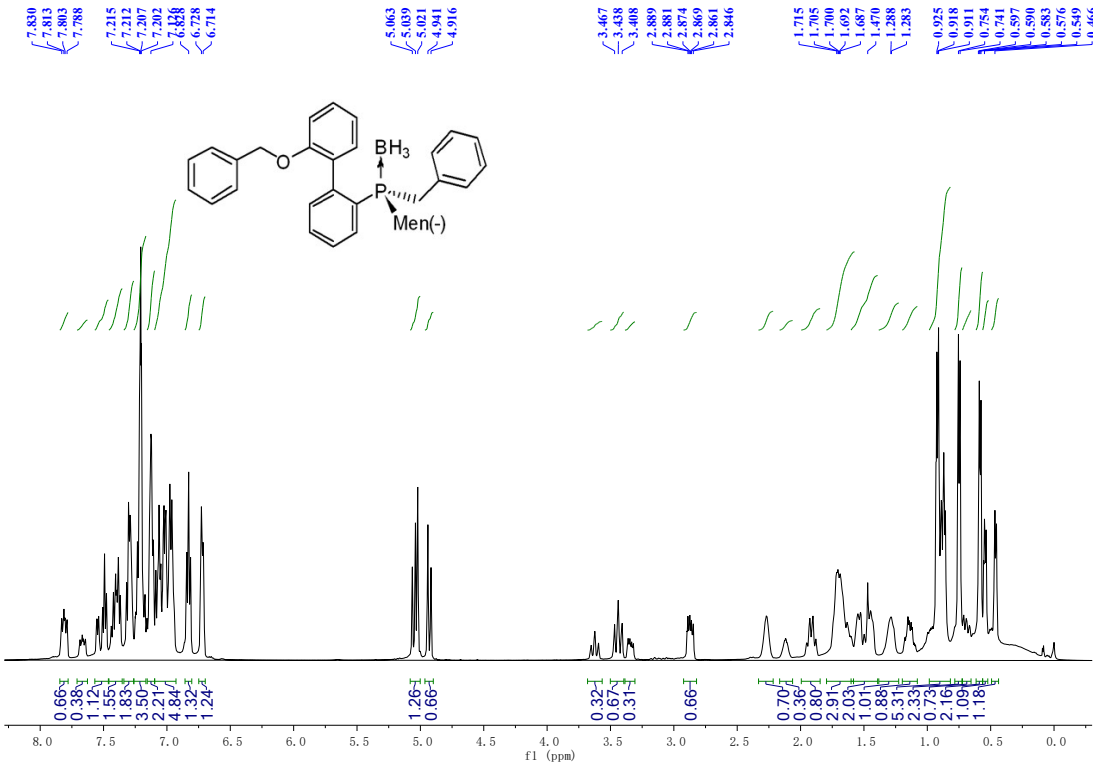
(R_P/S_P)-(–)-Menthyl *p*-methylbenzyl (2'-ethoxy-1,1-biphenyl-2-yl) phosphine borane (6c/6c')

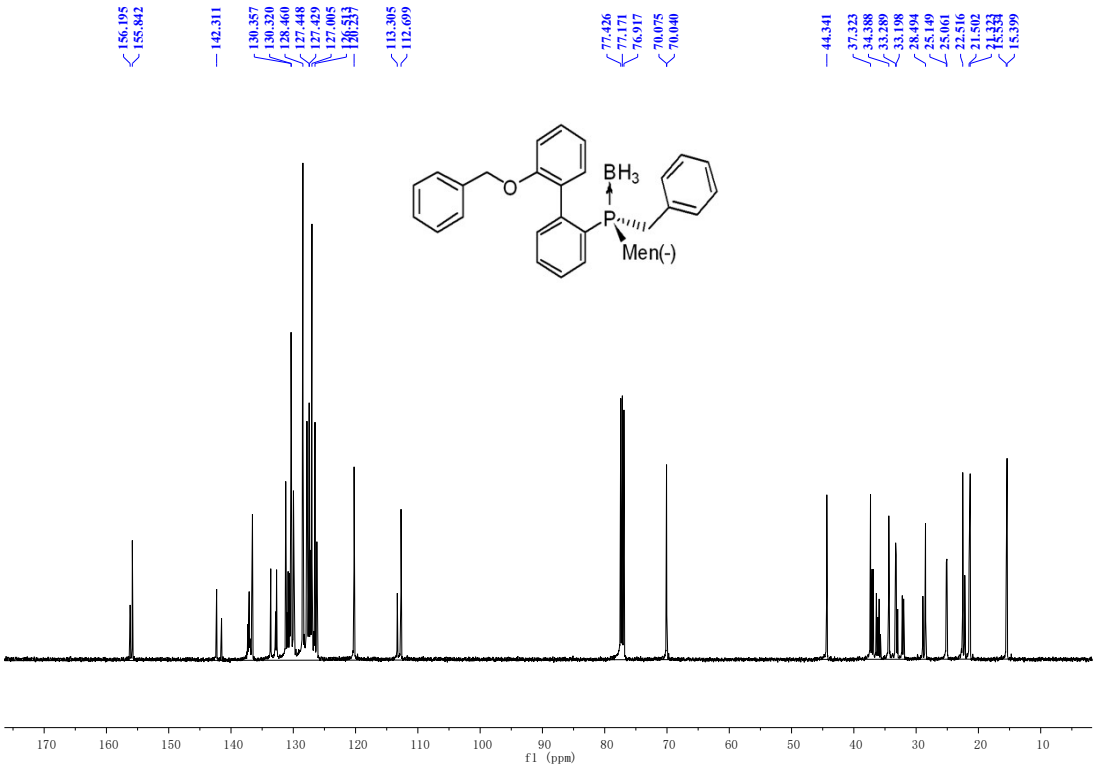

EtO
BH3
P
Men(-)
33.555
23.860
0.96
0.04
f1 (ppm)
7.810
7.794
7.783
7.017
6.988
6.973
6.956
6.873
6.858
6.689
6.673
5.017
4.989
4.904
4.879
4.012
3.994
3.979
3.964
3.950
3.932
3.471
2.844
2.830
2.818
2.802
2.287
2.224
1.705
1.682
1.659
1.547
1.456
1.440
1.204
1.184
1.170
1.156
0.920
0.907
0.878
0.864
0.787
0.774
0.550
0.536
EtO
BH3
P
Men(-)
f1 (ppm)



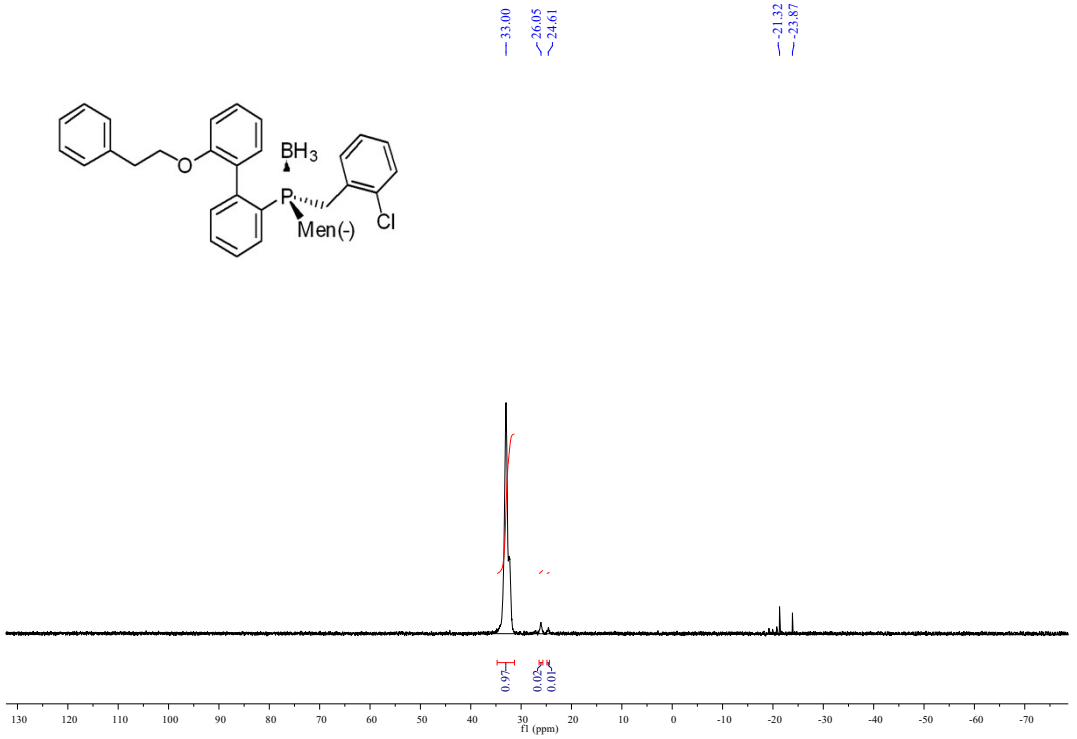
(R_P/S_P)-(–)-Menthyl benzyl (2'- benzyloxy -1,1-biphenyl-2-yl) phosphine borane (6d/6d')

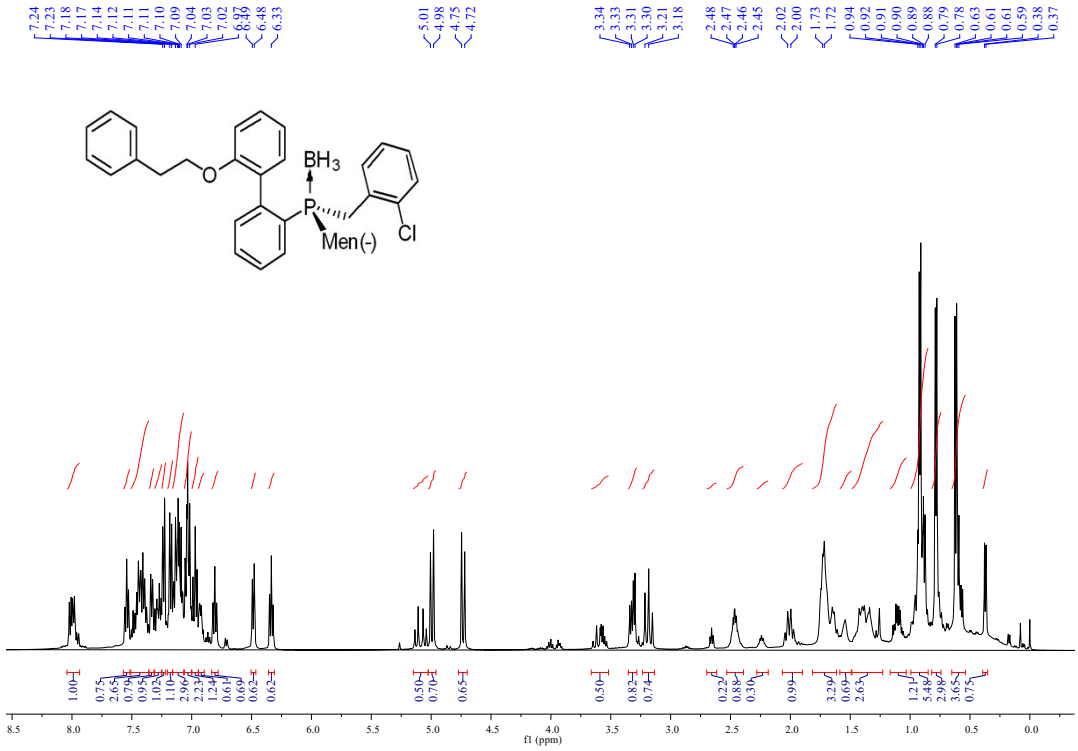


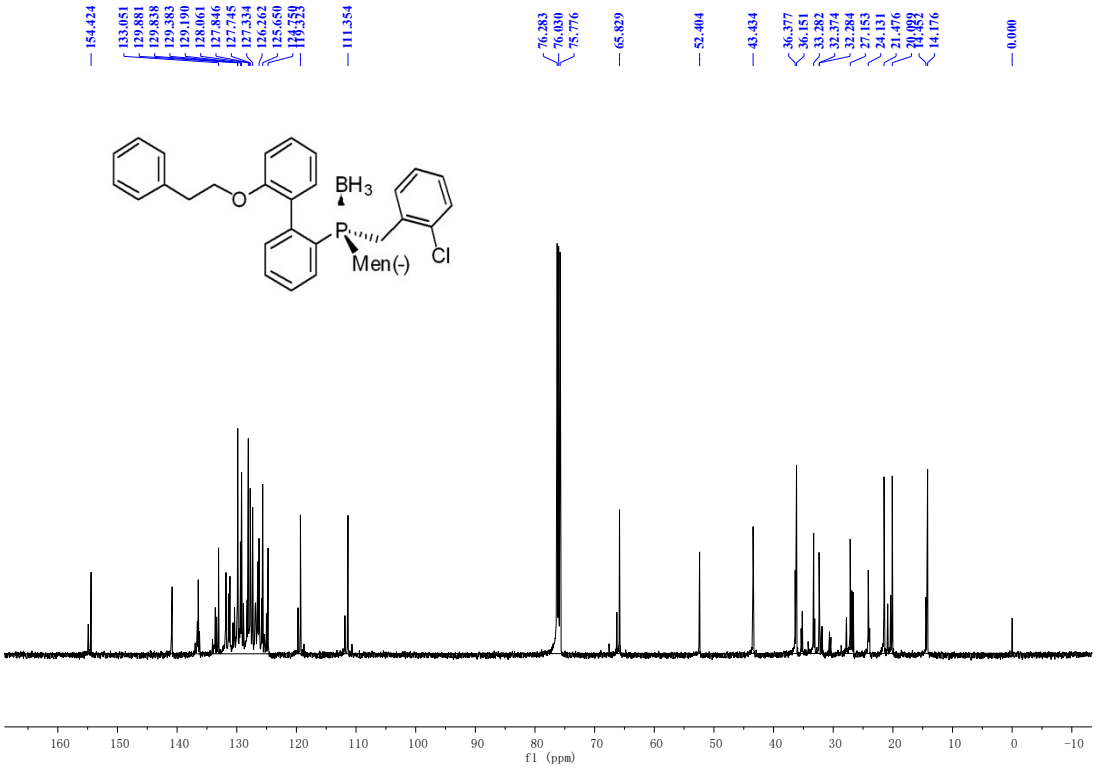




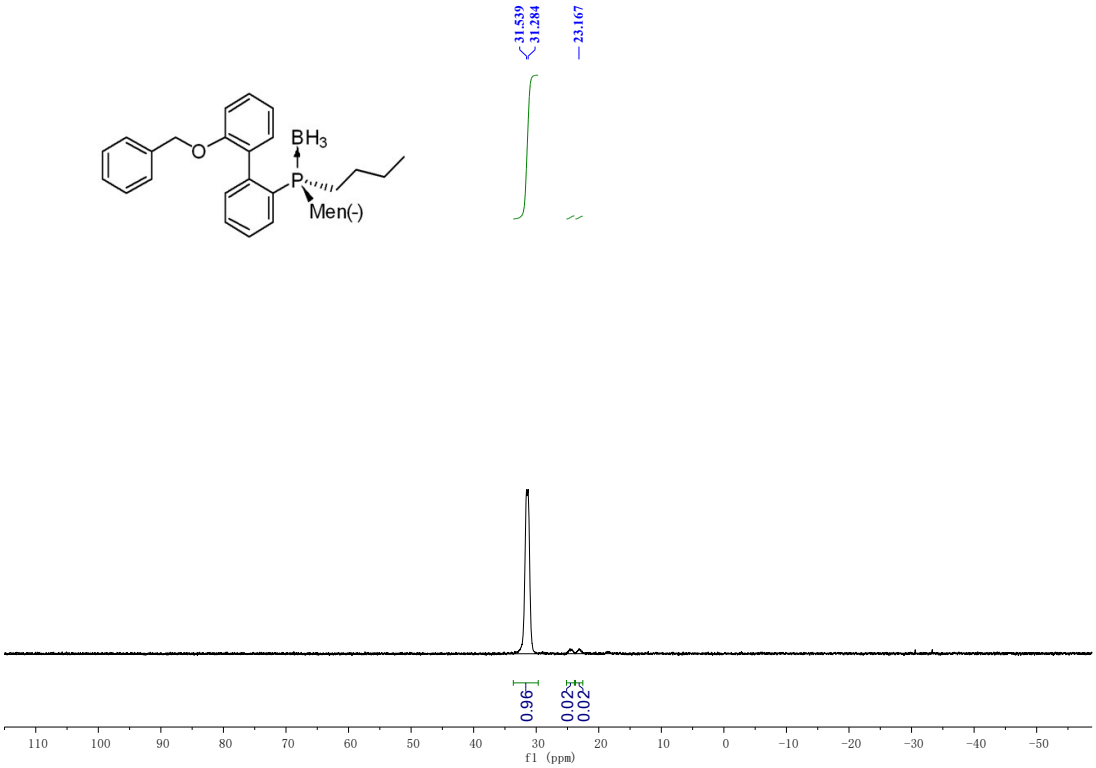
(R_P/S_P)-(–)-Menthyl *o*-chlorobenzyl (2'- ethylbenzeneoxy -1,1-biphenyl-2-yl) phosphine borane (6e/6e')

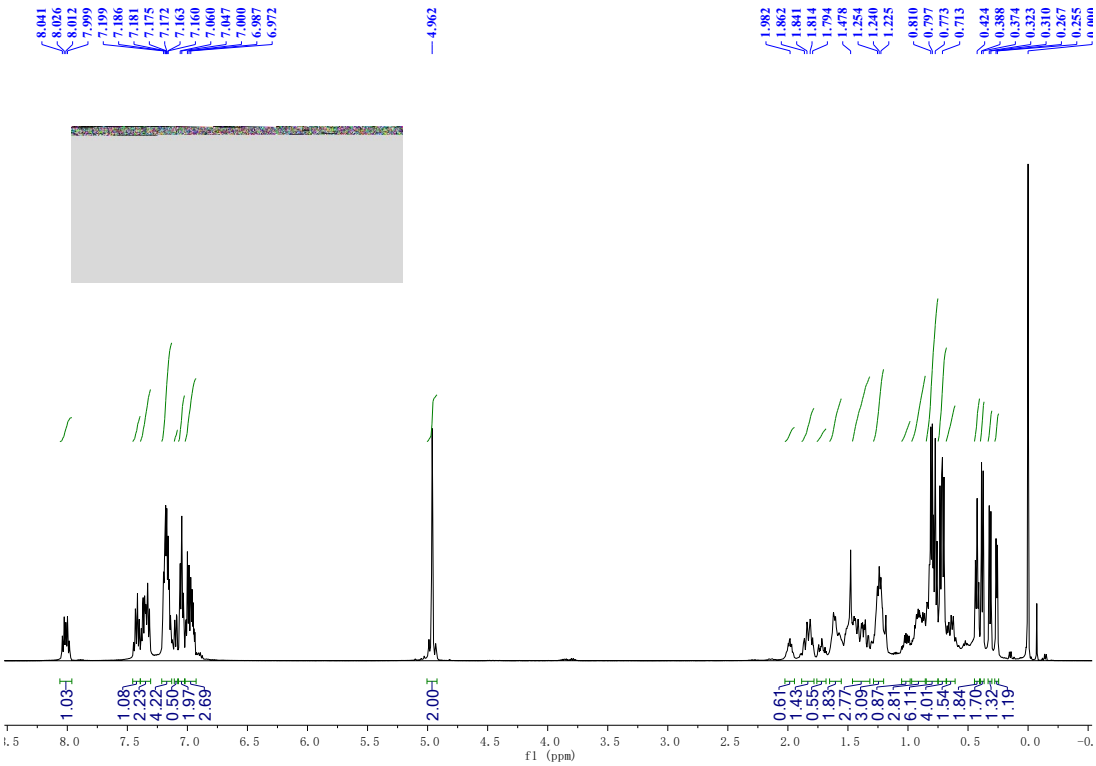

33.00
26.05
24.61
-21.32
-23.87
BH3
P
Men(-)
Cl
0.97
0.02
0.01
f1 (ppm)

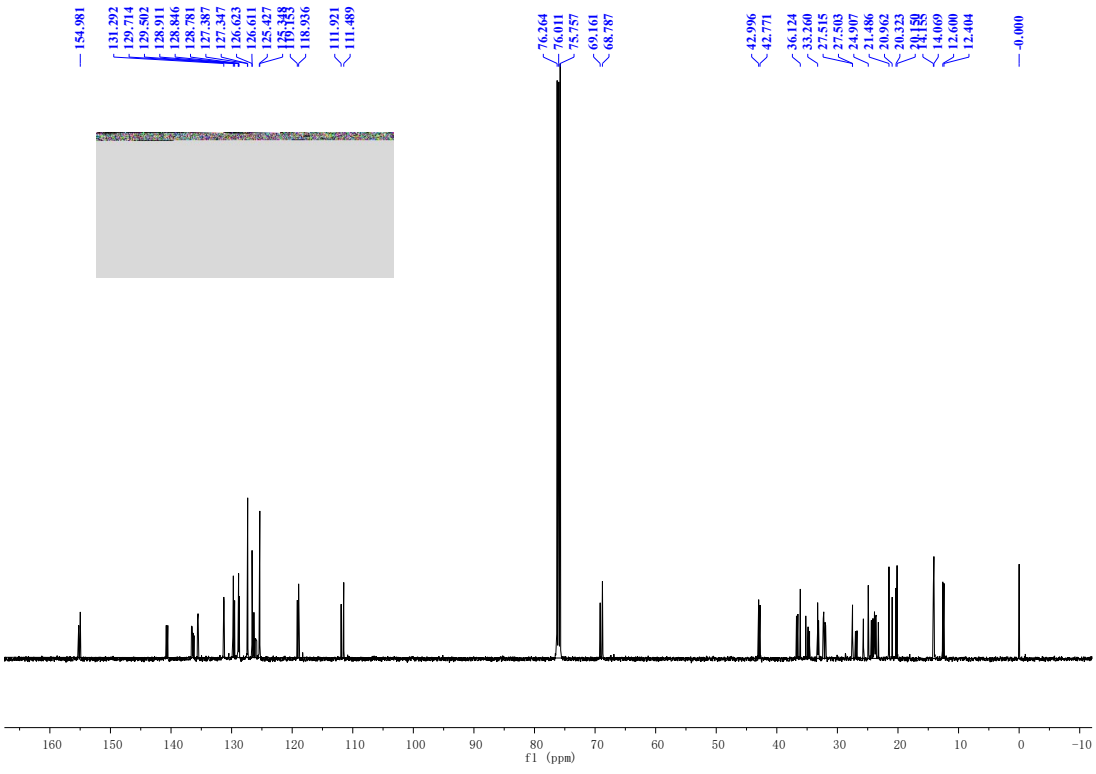

7.24
7.23
7.18
7.17
7.14
7.12
7.11
7.11
7.10
7.09
7.04
7.03
7.02
6.49
6.48
6.33
5.01
4.98
4.75
4.72
3.34
3.33
3.31
3.30
3.21
3.18
2.48
2.47
2.46
2.45
2.02
2.00
1.73
1.72
0.94
0.92
0.91
0.90
0.89
0.88
0.79
0.78
0.63
0.61
0.61
0.59
0.38
0.37
BH3
P
Men(-)
Cl
f1 (ppm)



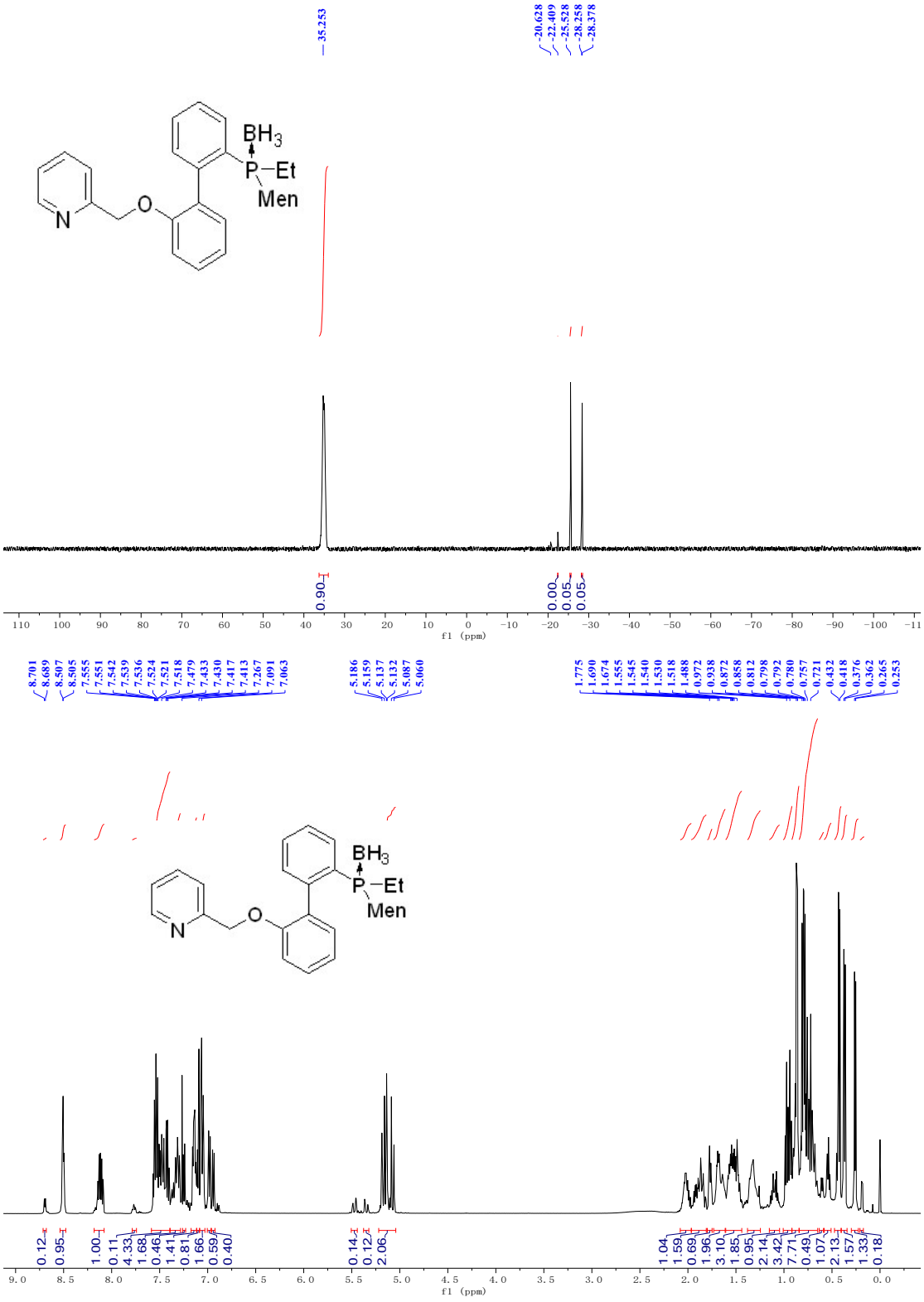
(R_P/S_P)-(–)-Menthyl butyl (2'- benzyloxy -1,1-biphenyl-2-yl) phosphine borane (6f/6f')



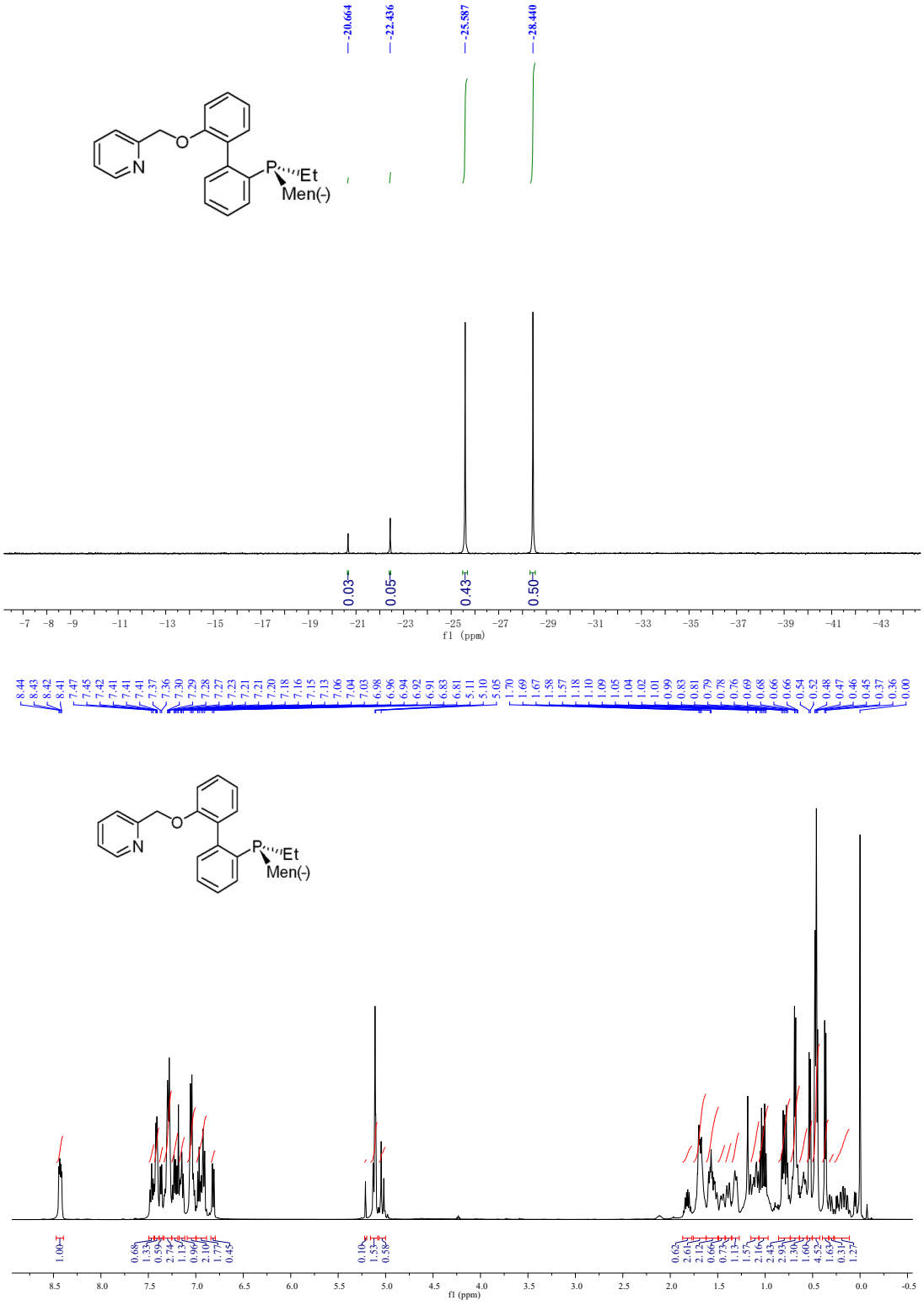


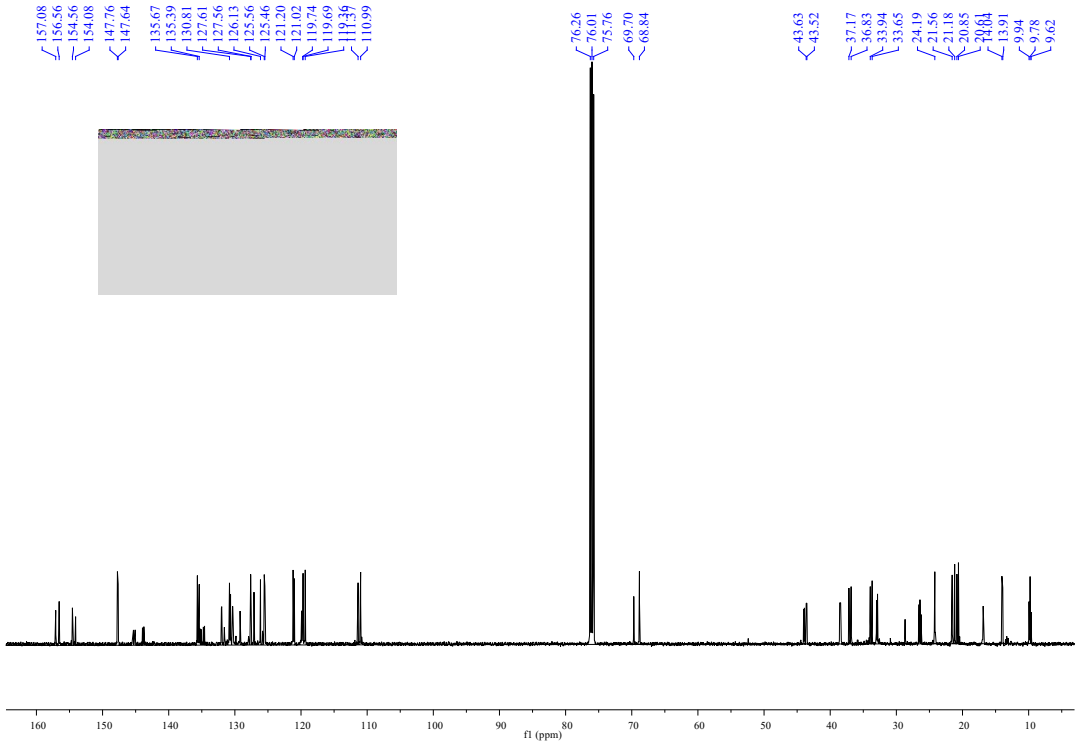


(R_P/S_P)-(–)-Menthyl ethyl (2'-pyridinyl|methoxy-1,1-biphenyl-2-yl) phosphine borane (6g/6g')

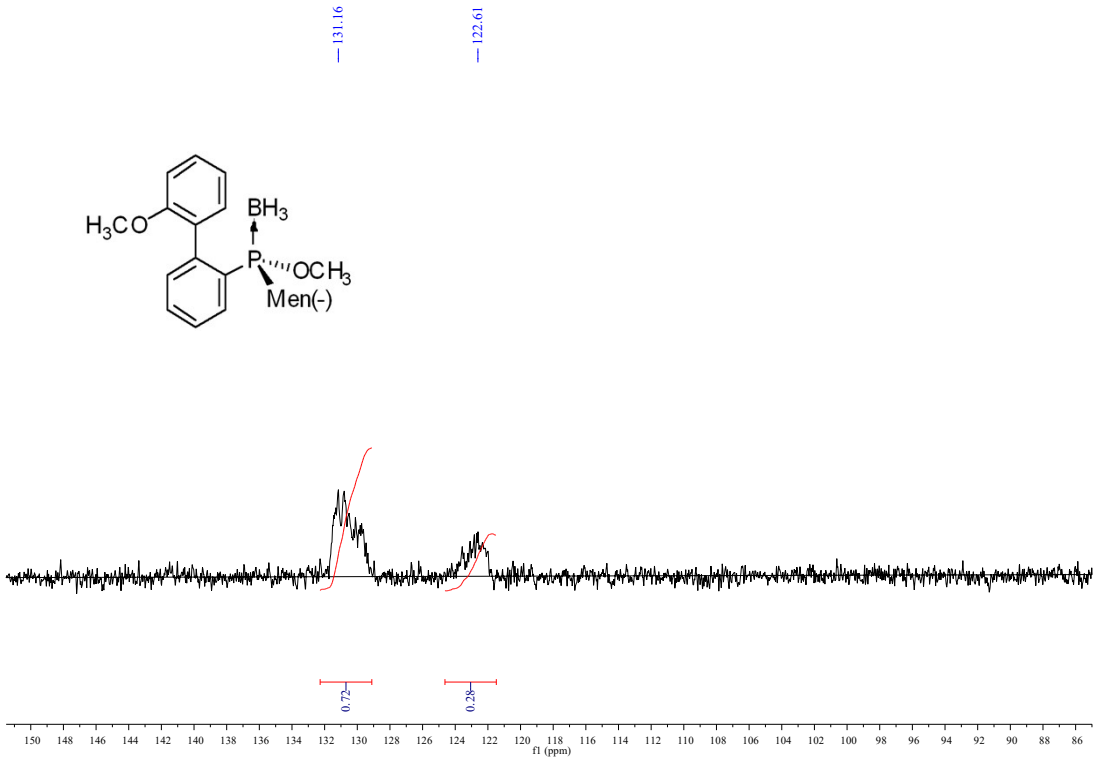


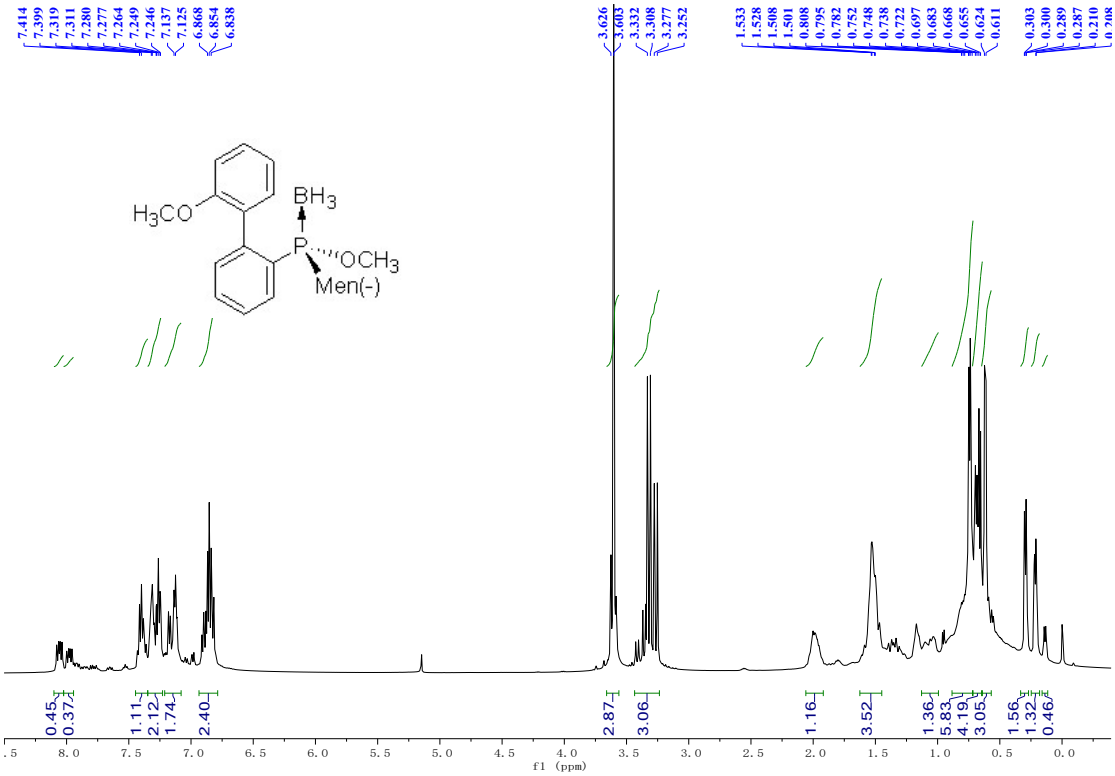
(R_P/S_P)-(–)-Menthyl ethyl (2'-pyridinylmethoxy-1,1-biphenyl-2-yl) phosphine (7/7')

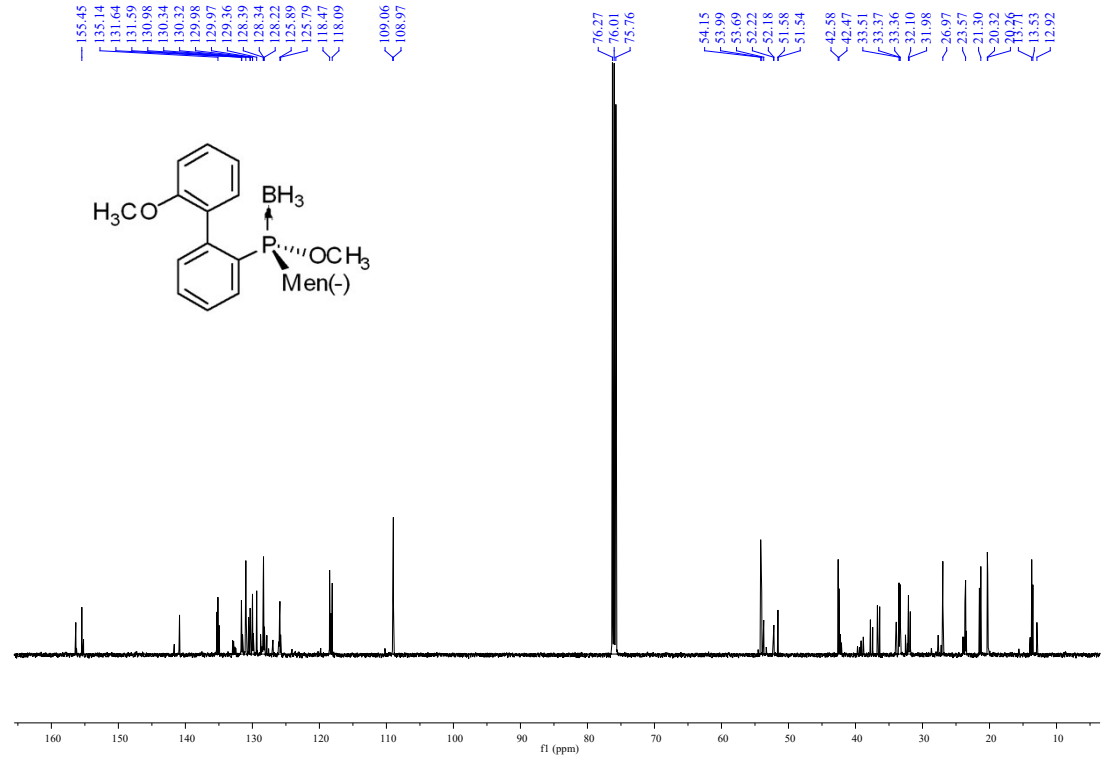

-20.664
-22.436
-25.587
-28.440
O
N
P
Et
Men(-)
0.03
0.05
0.43
0.50
f1 (ppm)
8.44
8.43
8.42
8.41
7.47
7.45
7.42
7.41
7.41
7.41
7.37
7.36
7.30
7.29
7.28
7.27
7.23
7.21
7.20
7.18
7.16
7.15
7.13
7.06
7.04
7.03
6.98
6.96
6.94
6.92
6.91
6.83
6.81
5.11
5.10
5.05
1.70
1.69
1.67
1.58
1.57
1.18
1.10
1.09
1.05
1.04
1.02
1.01
0.99
0.83
0.81
0.79
0.78
0.76
0.69
0.68
0.66
0.66
0.54
0.52
0.48
0.47
0.46
0.45
0.37
0.36
0.00
O
N
P
Et
Men(-)
1.00
0.68
1.33
0.59
2.74
1.13
0.96
2.10
1.77
0.45
0.10
1.53
0.58
0.62
2.61
2.12
0.66
0.73
1.13
1.57
2.16
2.43
2.93
1.30
1.60
4.52
1.65
0.31
1.29
f1 (ppm)



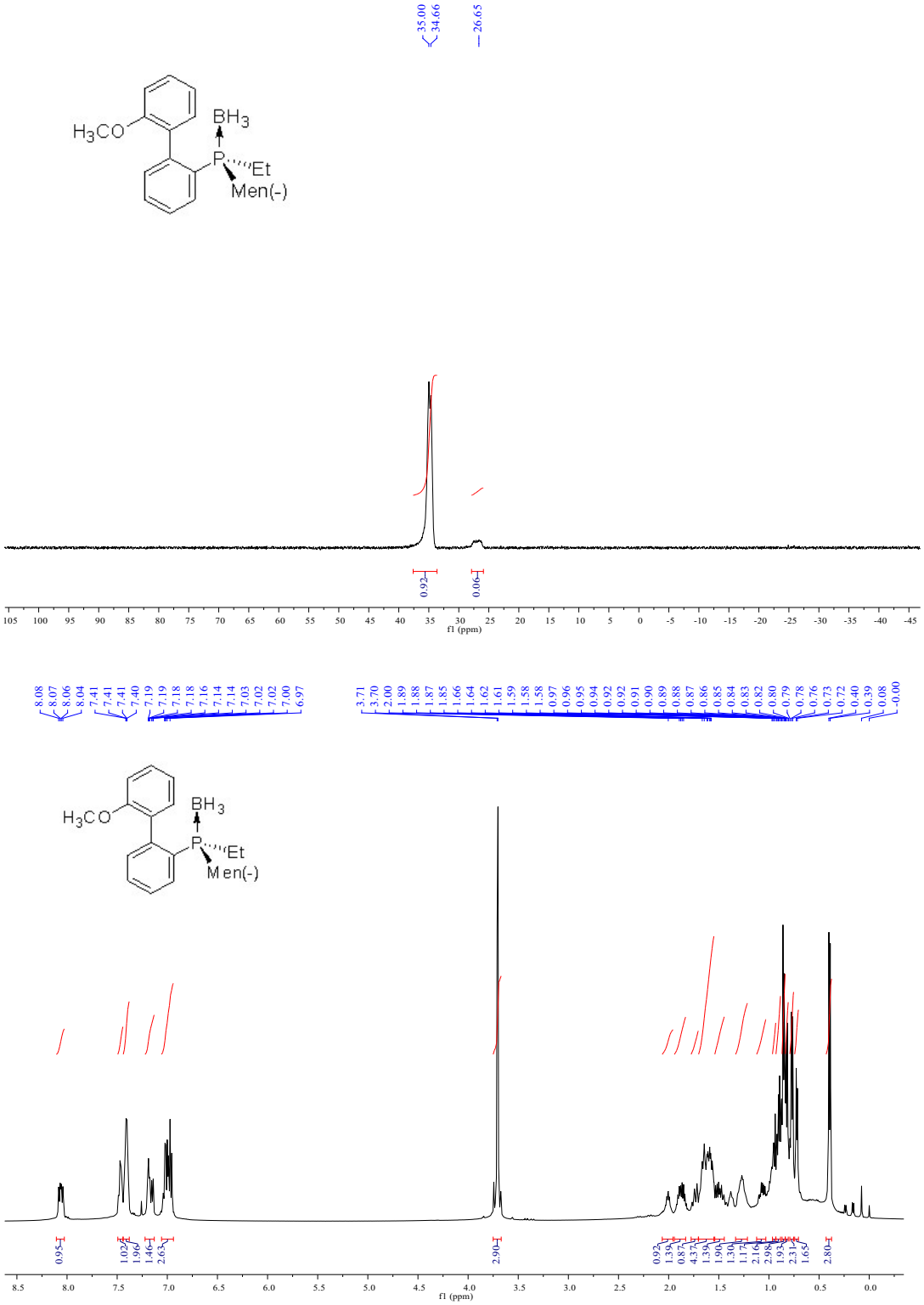
(R_P/S_P)-(–)-Menthyl methoxy (2'-methoxy-1,1-biphenyl-2-yl)phosphine borane (2b/2b')

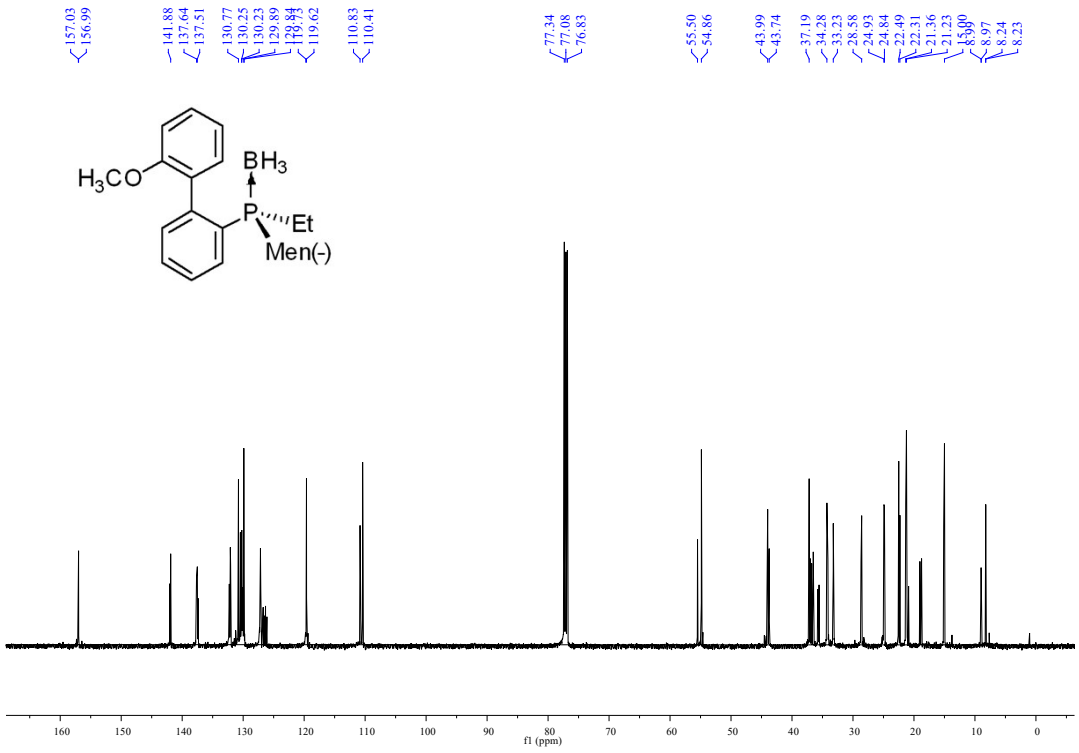



7.414
7.399
7.319
7.311
7.280
7.277
7.264
7.249
7.246
7.137
7.125
6.868
6.854
6.838
3.626
3.603
3.332
3.308
3.277
3.252
1.533
1.528
1.508
1.501
0.808
0.795
0.782
0.752
0.748
0.738
0.722
0.697
0.683
0.668
0.655
0.624
0.611
0.303
0.300
0.289
0.287
0.210
0.198
H3CO
BH3
P
OCH3
Men(-)
0.45
0.37
1.11
2.12
1.74
2.40
2.87
3.06
1.16
3.52
1.36
5.83
4.19
3.05
1.56
1.32
0.46
f1 (ppm)

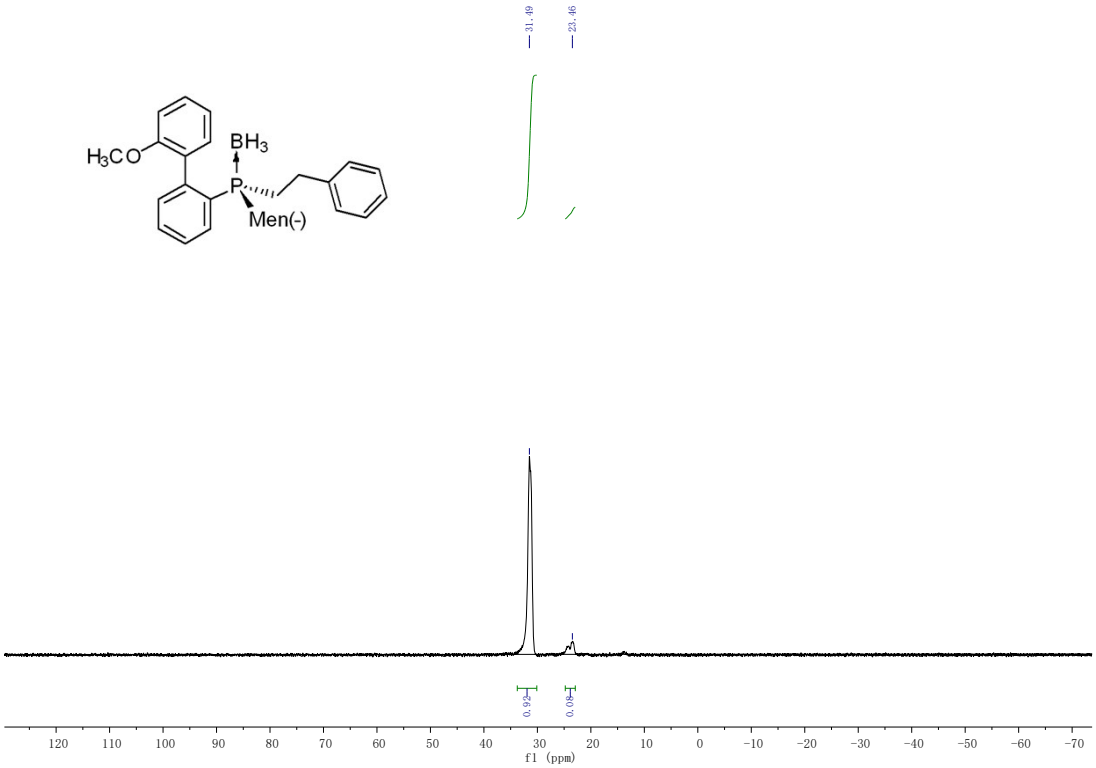

155.45
135.14
131.64
131.59
130.98
130.34
130.32
129.98
129.97
129.36
128.39
128.34
128.22
125.89
125.79
118.47
118.09
109.06
108.97
76.27
76.01
75.76
54.15
53.99
53.69
52.22
52.18
51.58
51.54
42.58
42.47
33.51
33.37
33.36
32.10
31.98
26.97
23.57
21.30
20.32
20.26
13.53
12.92
H3CO
BH3
P
OCH3
Men(-)
f1 (ppm)

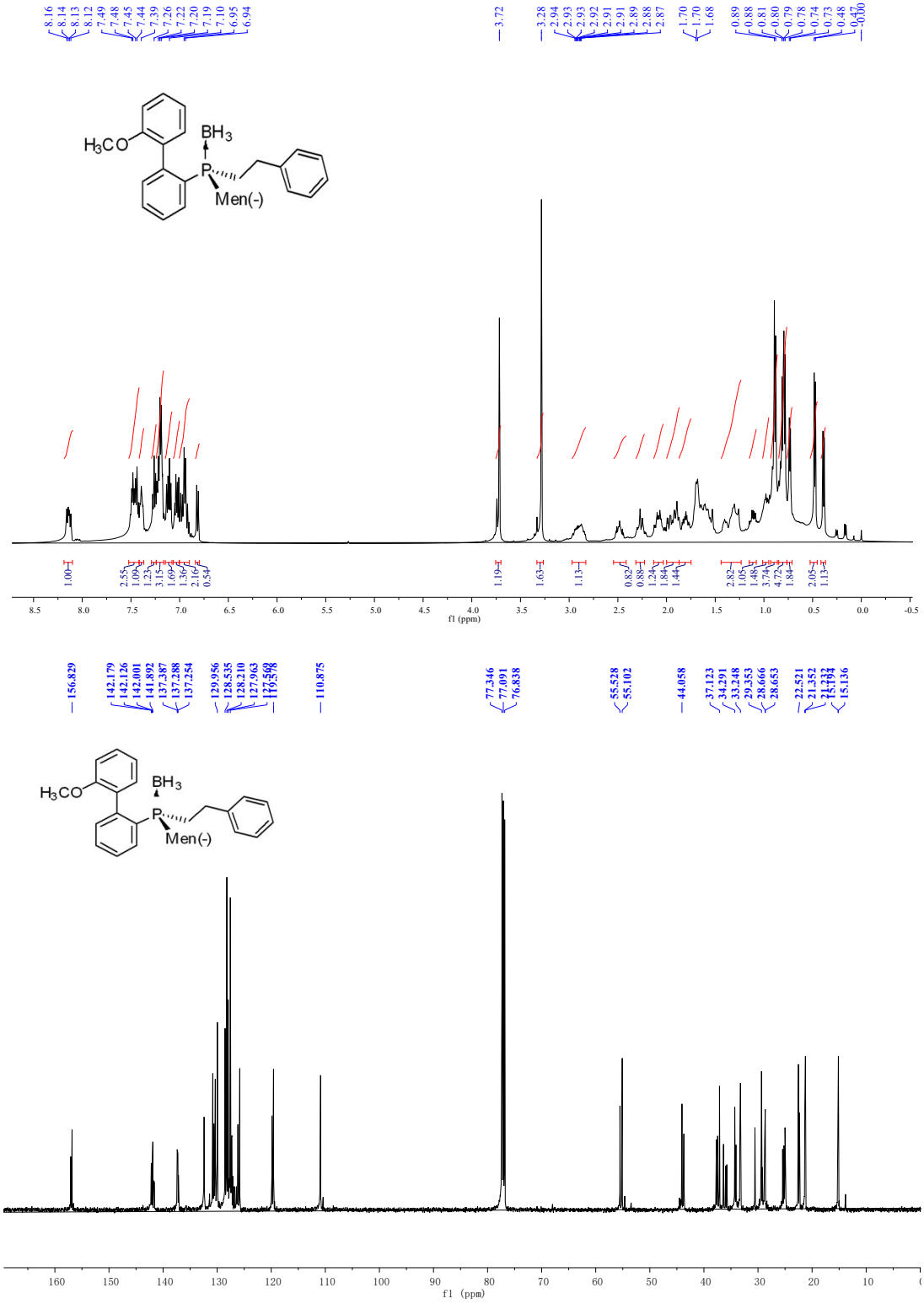
(R_P/S_P)-(–)-Menthyl ethyl (2'- methoxy -1,1-biphenyl-2-yl) phosphine borane (6h/6h')



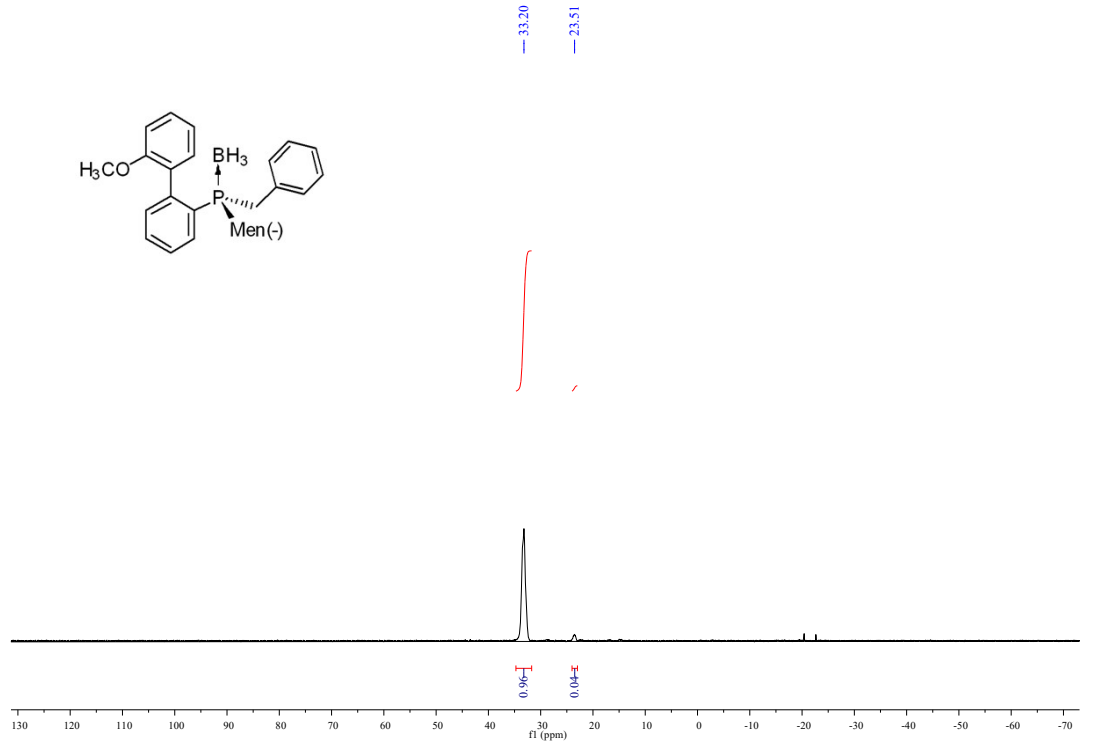


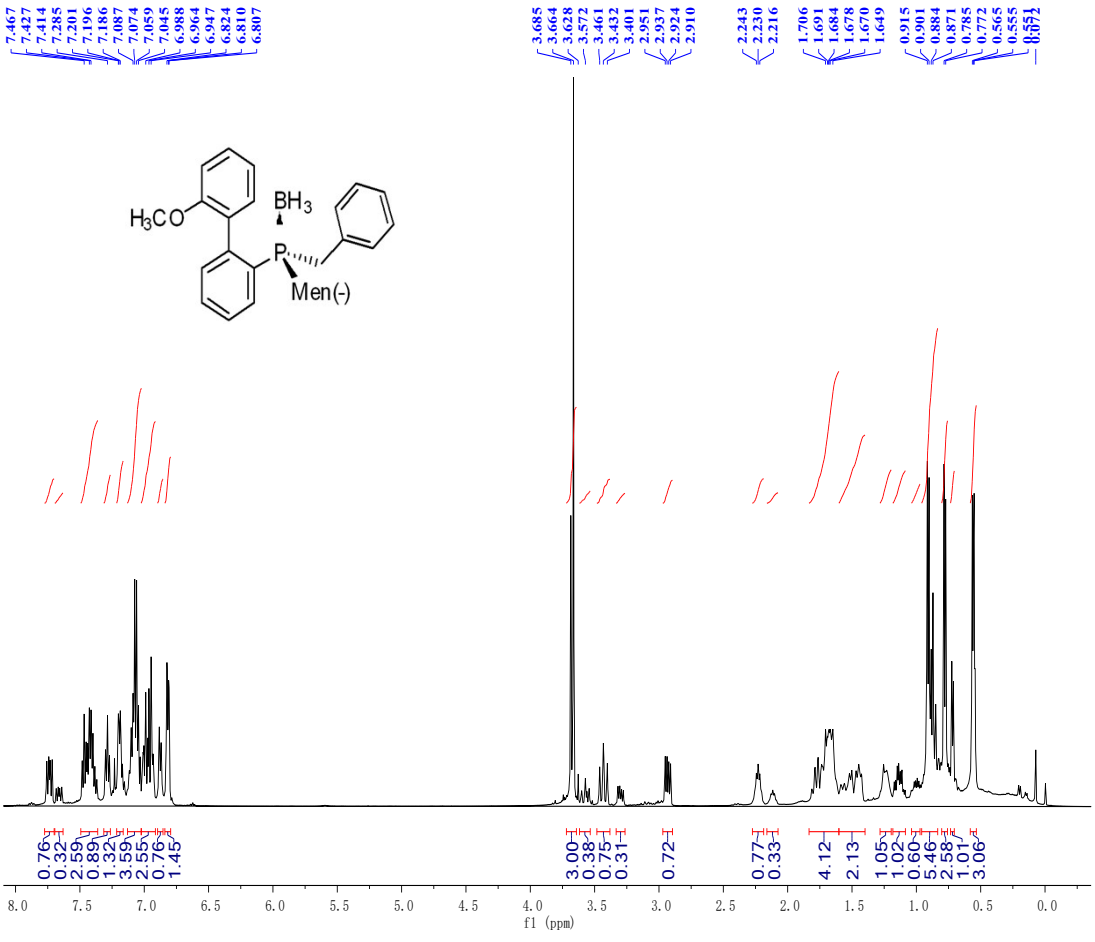
(R_P/S_P)-(–)-Menthyl phenylethyl (2'- methoxy -1,1-biphenyl-2-yl) phosphine borane (6i/6i')

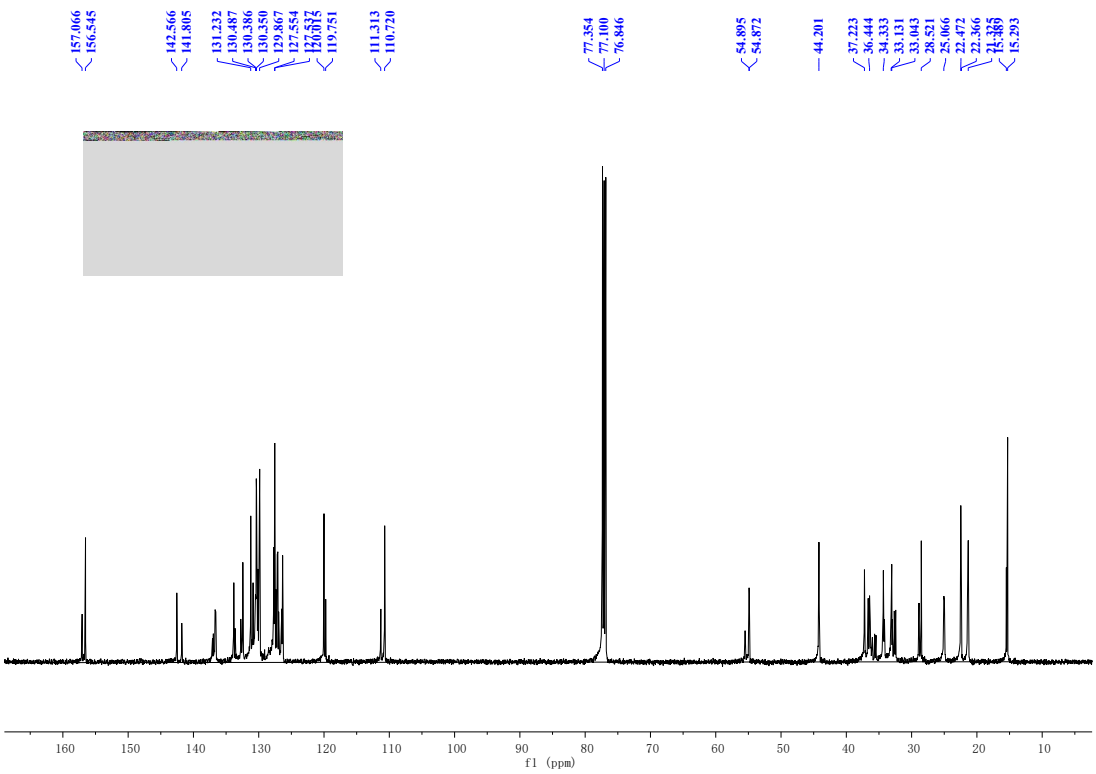




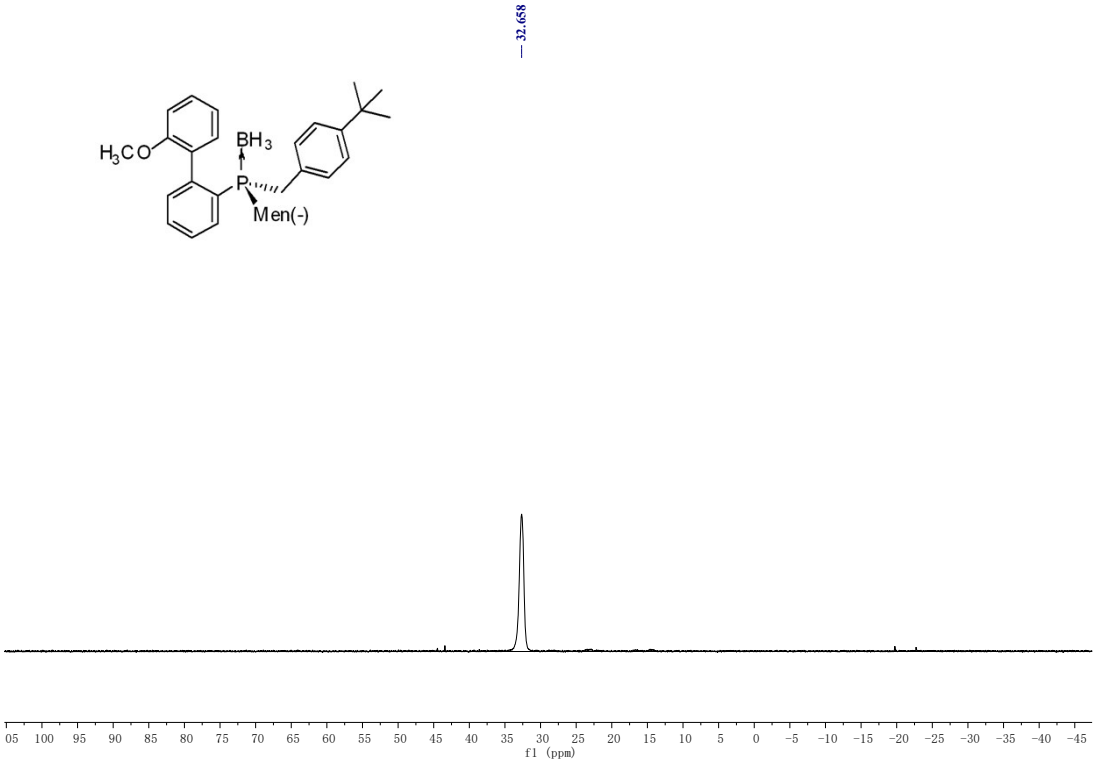
(R_P/S_P)-(–)-Menthyl benzyl (2'- methoxy-1,1-biphenyl-2-yl) phosphine borane (6j/6j')

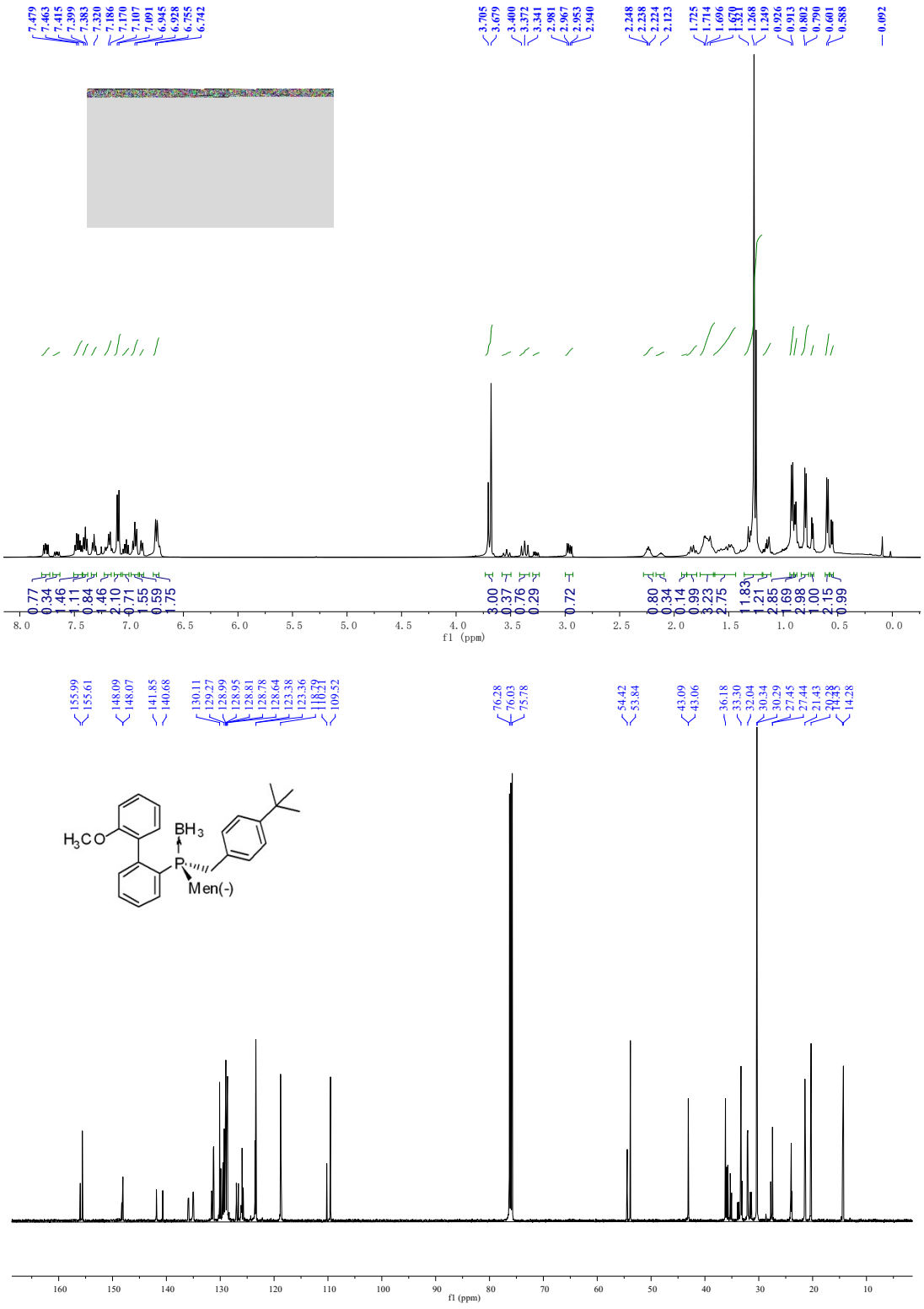

33.20
23.51
H3CO
BH3
P
Men(-)
0.96
0.04
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm)


7.467 7.427 7.414 7.285 7.201 7.196 7.186 7.087 7.074 7.059 7.045 6.988 6.964 6.947 6.824 6.810 6.807
3.685 3.664 3.628 3.572 3.461 3.432 3.401 2.951 2.937 2.924 2.910
2.243 2.230 2.216
1.706 1.691 1.684 1.678 1.670 1.649
0.915 0.901 0.884 0.871 0.785 0.772 0.565 0.555
H3CO
BH3
P
Men(-)
0.76 0.32 2.59 0.89 1.32 3.59 2.55 0.76 1.45
3.00 0.38 0.75 0.31 0.72 0.77 0.33 4.12 2.13 1.05 1.02 0.60 5.46 2.58 1.01 3.06
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)

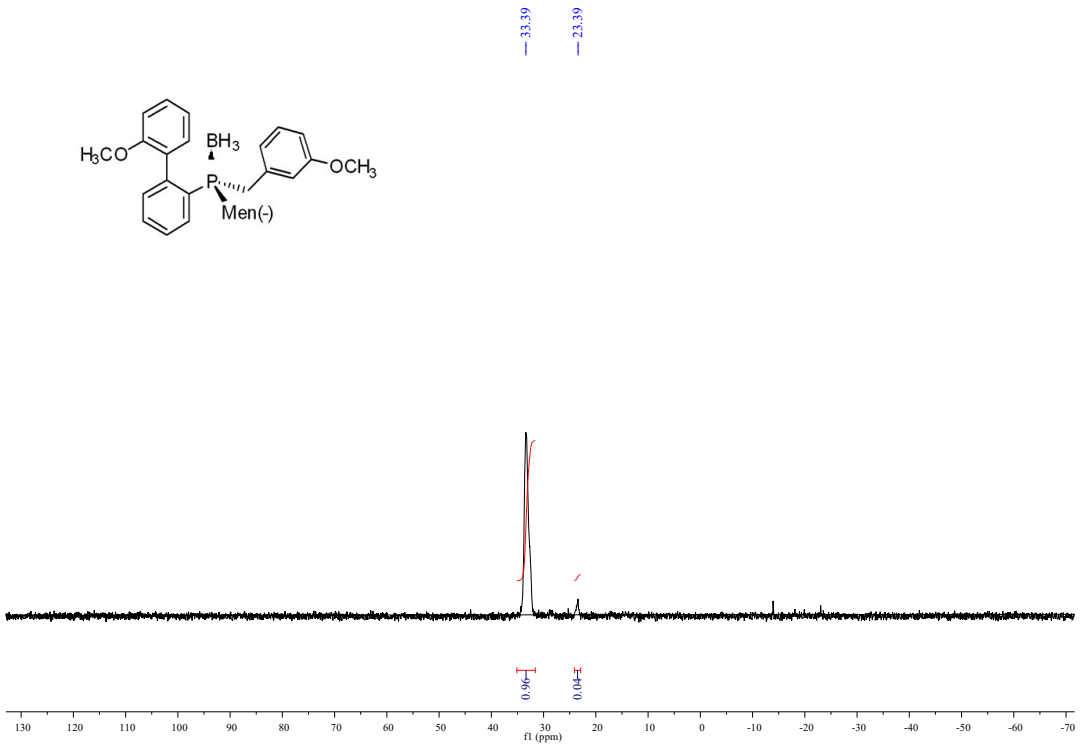


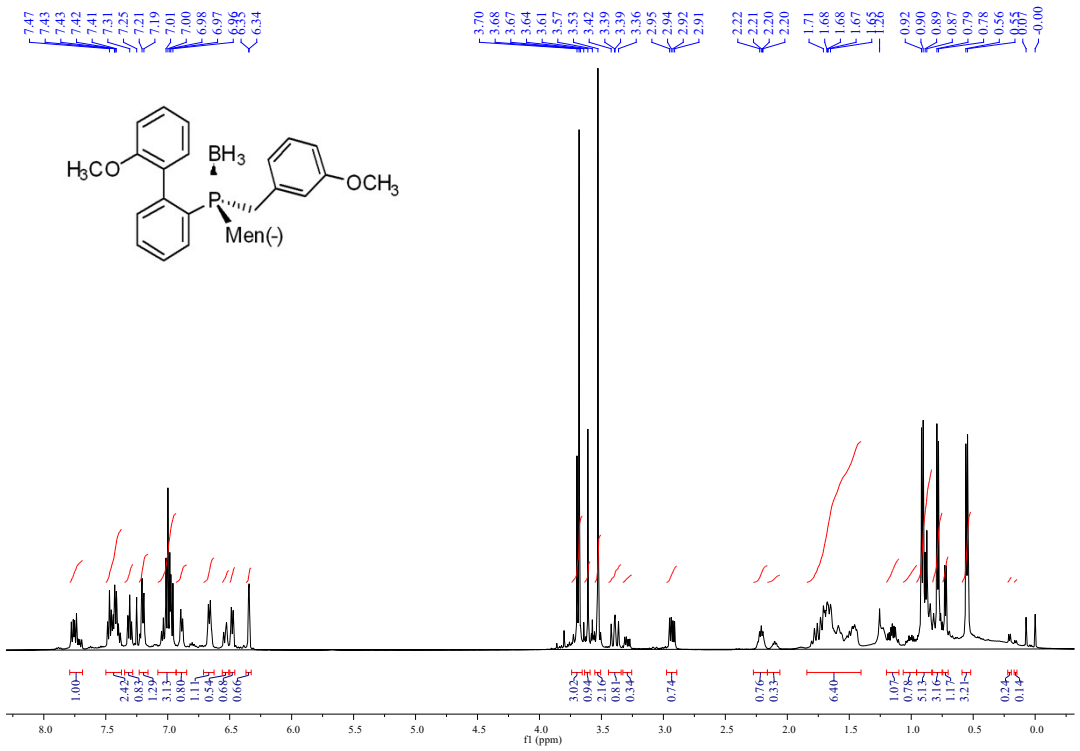
(R_P)-(–)-Menthyl *p*-tert-butylbenzyl (2'-methoxy-1,1-biphenyl-2-yl) phosphine borane (R_P-6k)

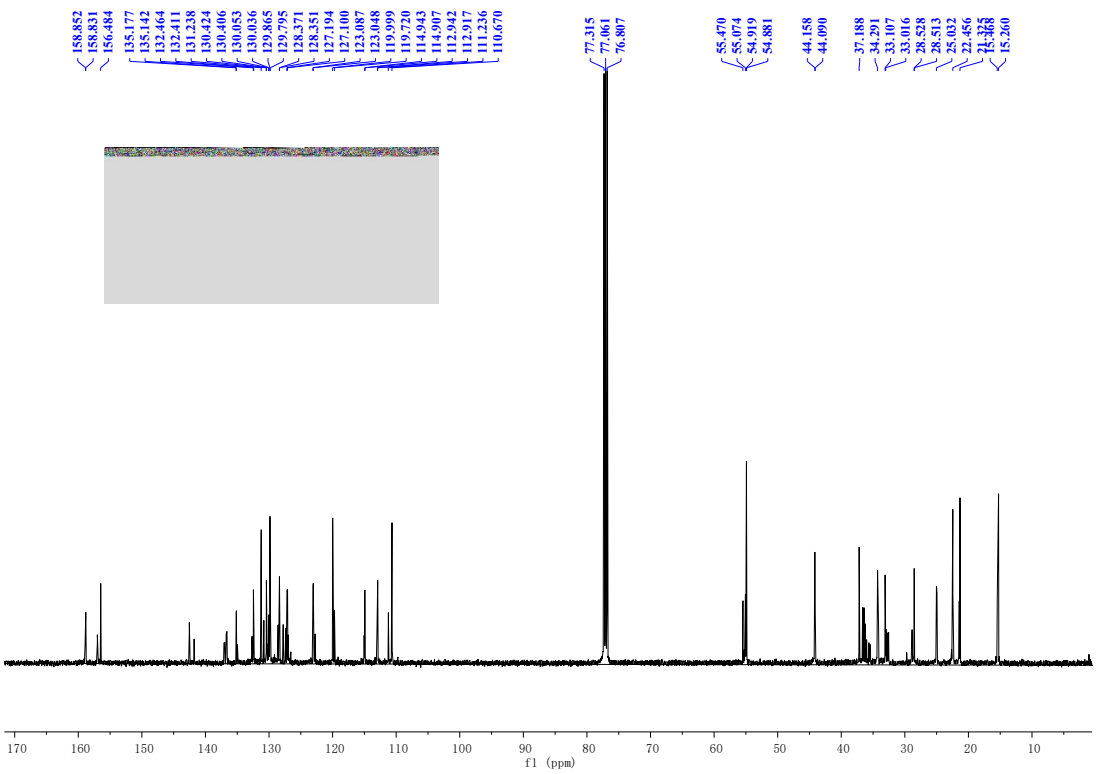




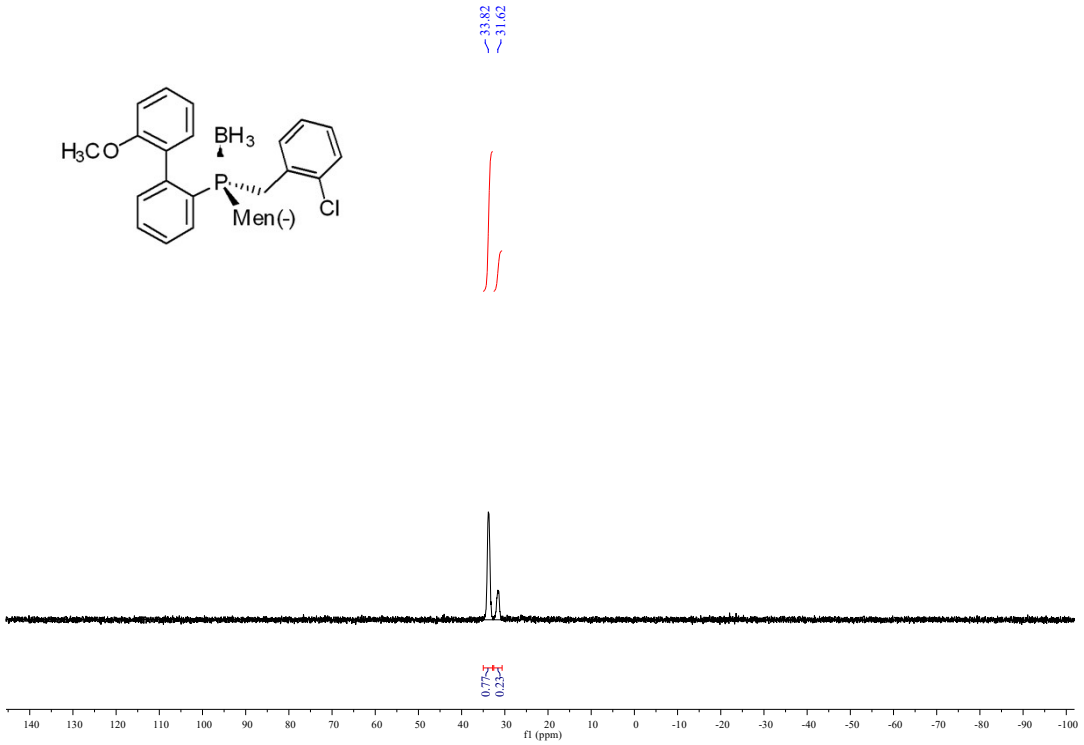
(R_P/S_P)-(–)-Menthyl *m*-methoxybenzyl (2'-methoxy-1,1-biphenyl-2-yl) phosphine borane (6l/6l')

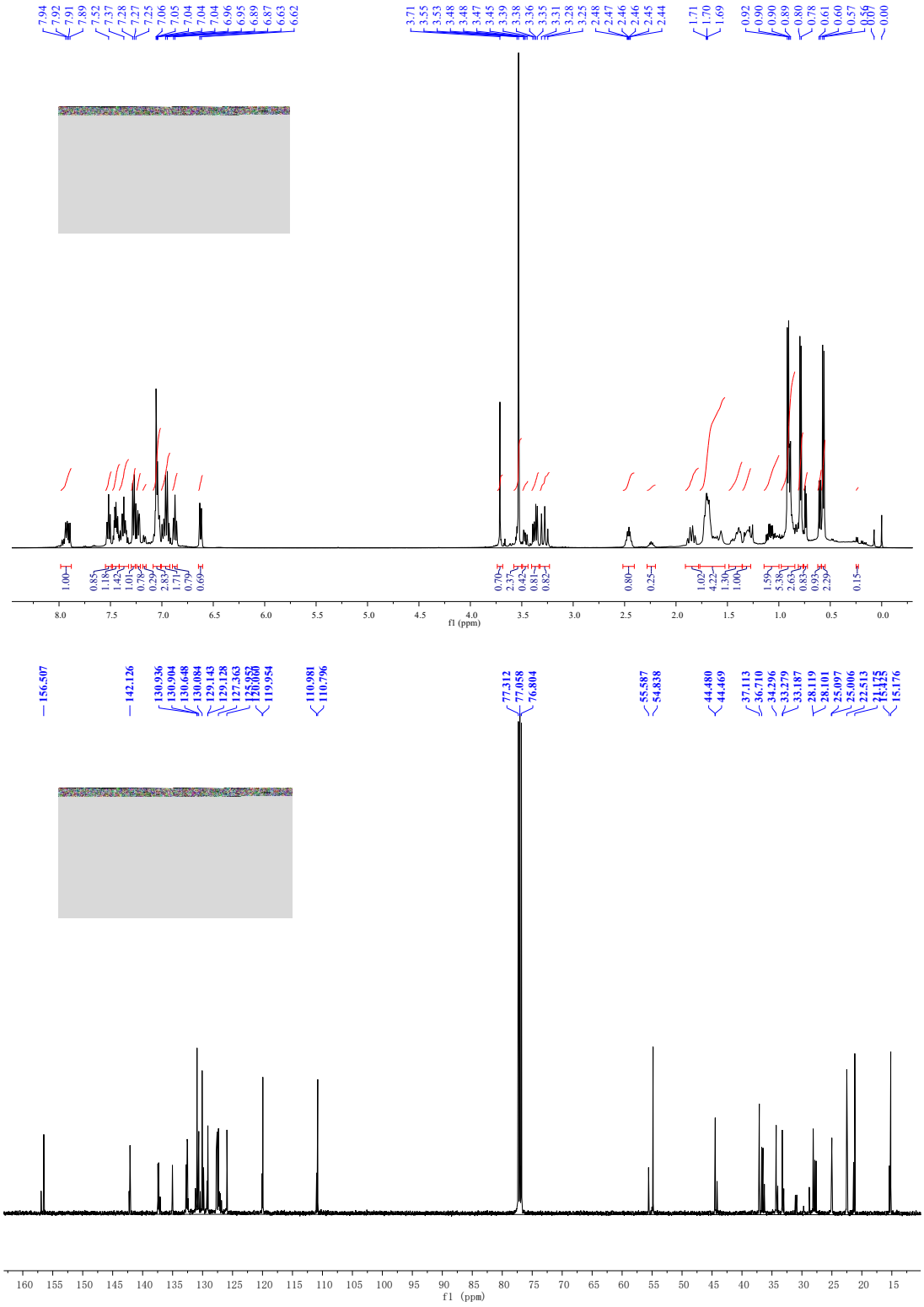

33.39
23.39
H3CO
BH3
OCH3
P
Men(-)
0.96
0.04
f1 (ppm)


7.47
7.43
7.43
7.42
7.41
7.31
7.25
7.21
7.19
7.01
7.00
6.98
6.97
6.36
6.34
3.70
3.68
3.67
3.64
3.61
3.57
3.53
3.42
3.39
3.39
3.36
2.95
2.94
2.92
2.91
2.22
2.21
2.20
2.20
1.71
1.68
1.68
1.67
1.65
1.26
0.92
0.90
0.89
0.87
0.79
0.78
0.56
0.55
0.07
-0.00
H3CO
BH3
OCH3
P
Men(-)
1.00
2.42
0.83
1.29
3.13
0.80
1.11
0.54
0.68
0.66
3.02
0.94
2.16
0.81
0.34
0.74
0.76
0.33
6.40
1.07
0.78
5.13
3.16
1.17
3.21
0.24
0.14
f1 (ppm)

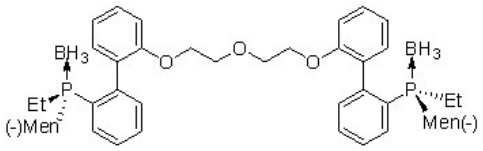


(R_P)-(–)-Menthyl *o*-chloride benzyl (2'-methoxy -1,1-biphenyl-2-yl) phosphine borane (R_P -6m)

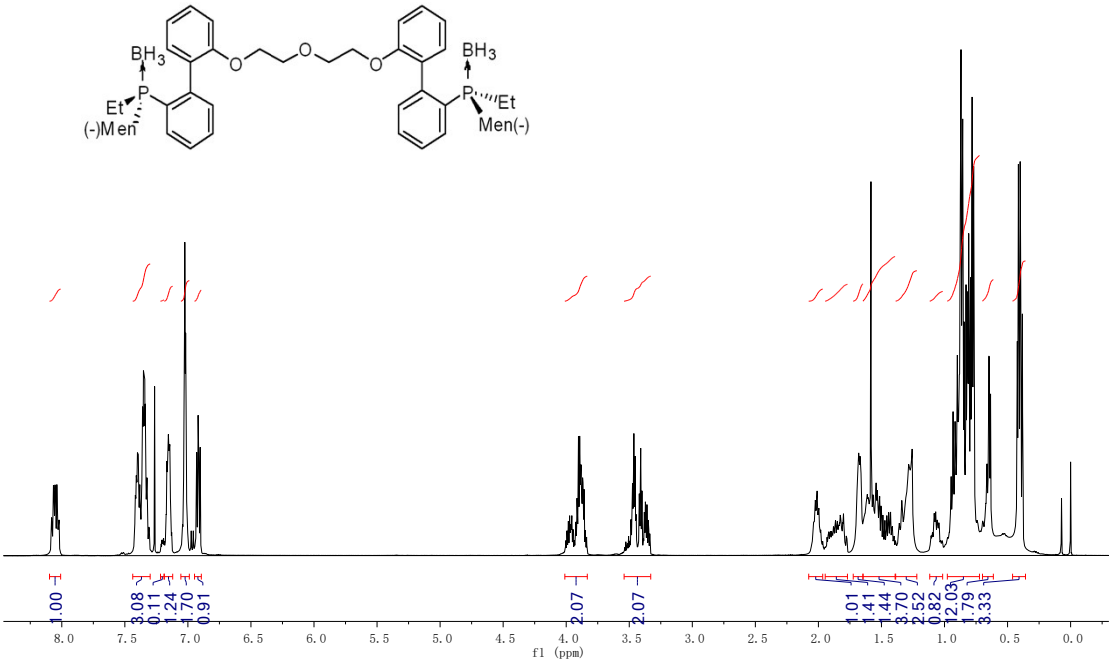


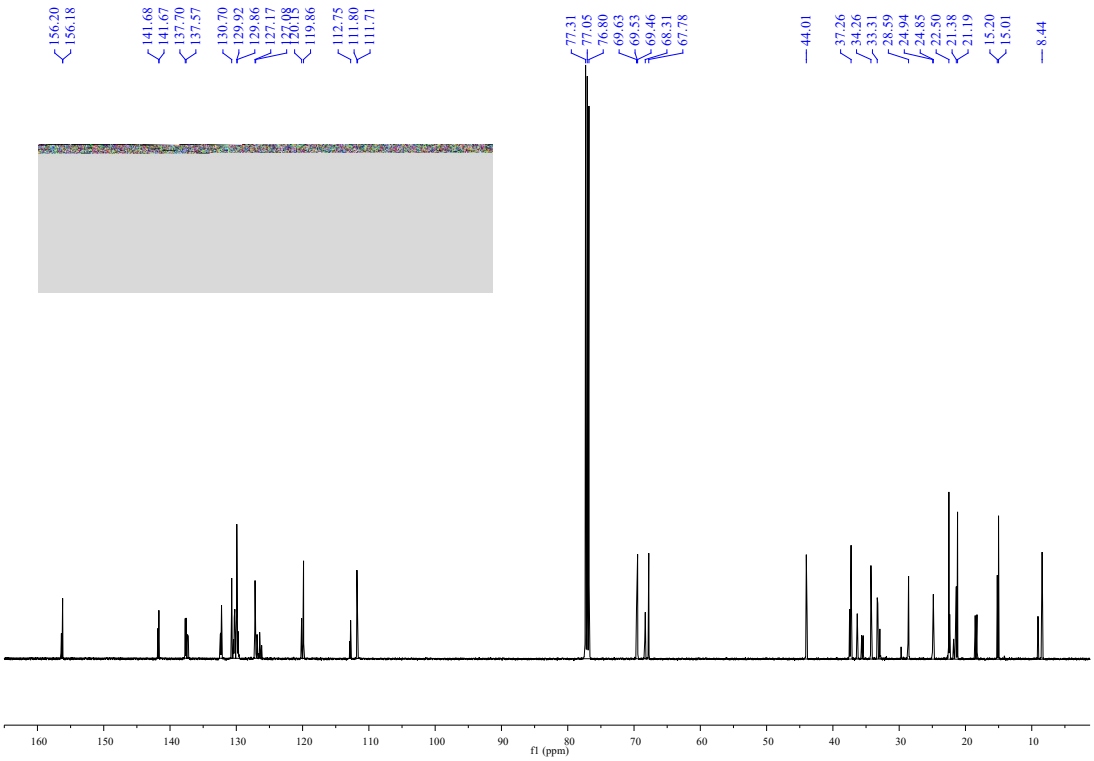


R_P,R_P-Diethylene glycol di[2-(-)-menthyl ethylphosphino-1,1'-biphenyl-2'-yl)] ether diborane (9a)

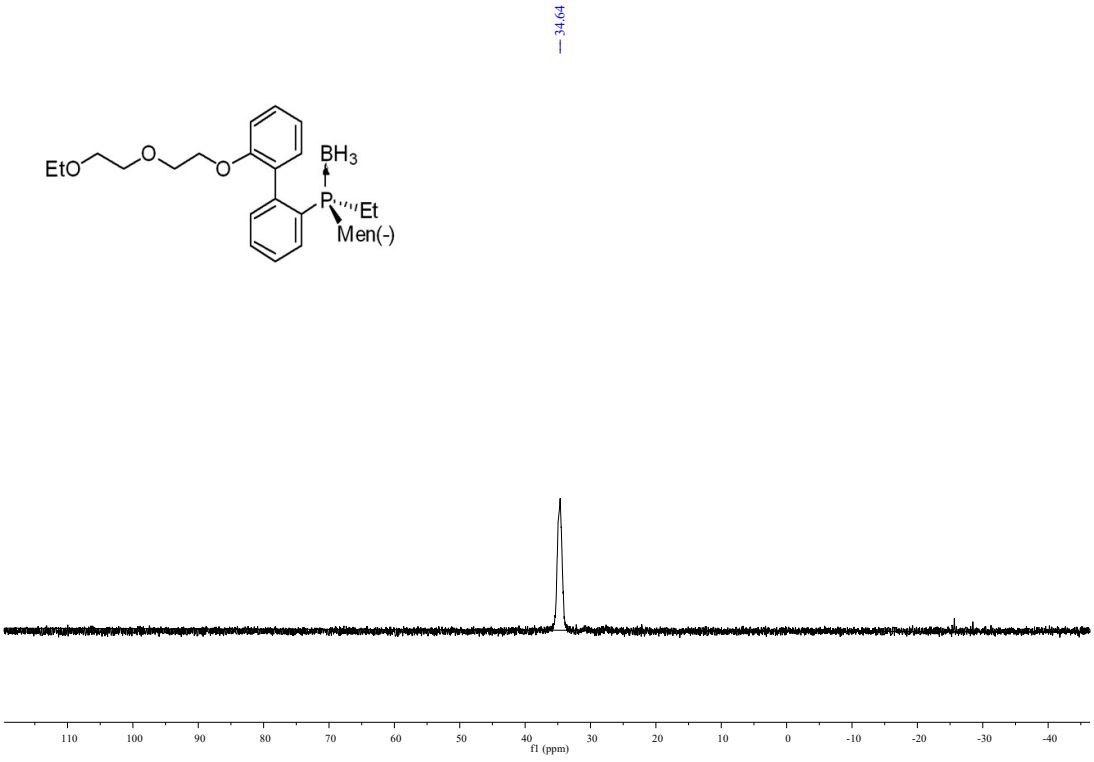

BH3
P
Et
(-)Men
O
O
O
BH3
P
Et
Men(-)

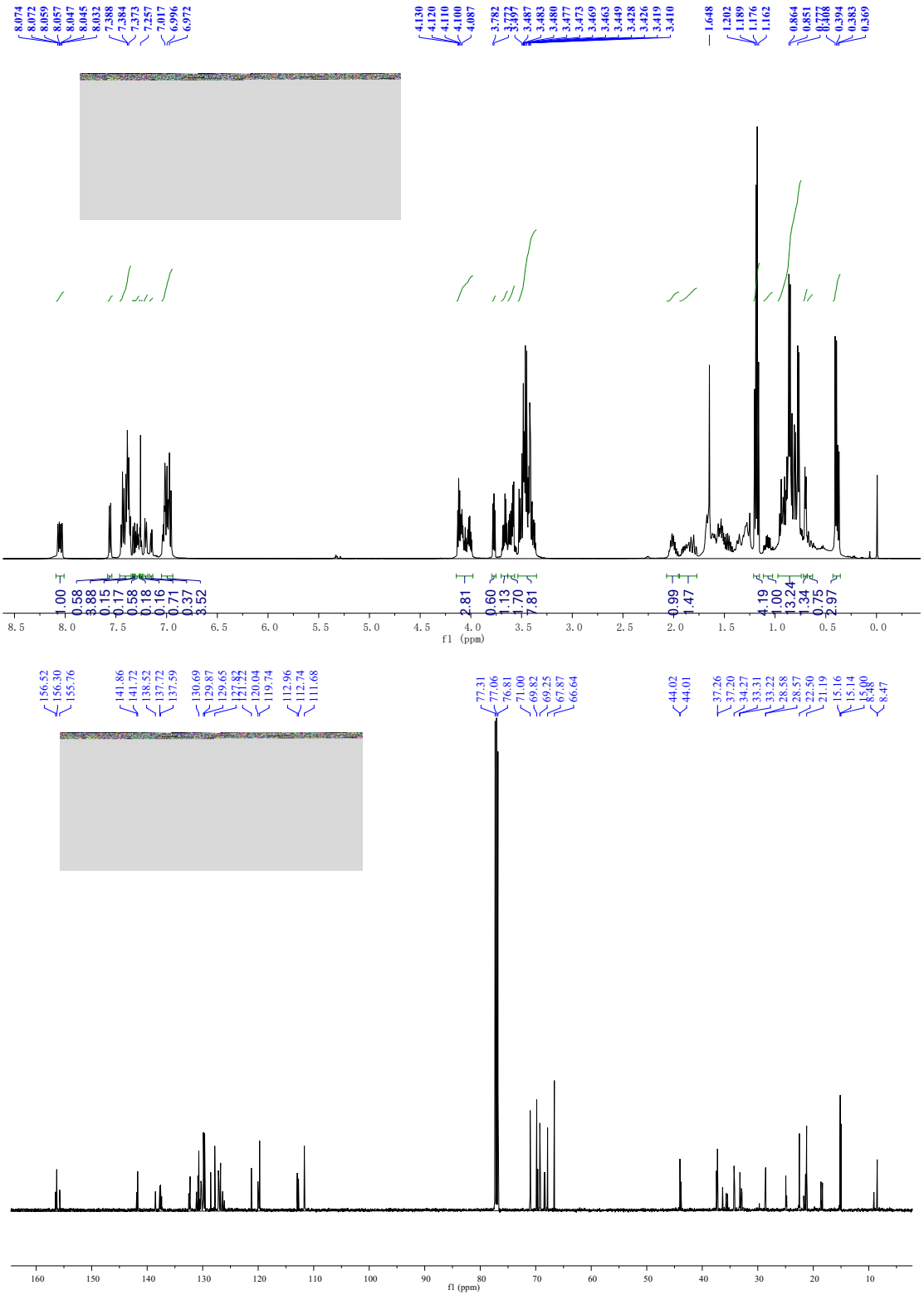
34.68
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
f1 (ppm)
8.066
8.063
8.054
8.049
8.039
8.036
7.360
7.356
7.353
7.349
7.345
7.342
7.338
7.264
7.024
7.021
7.018
7.013
6.919
3.903
3.893
3.886
3.882
3.878
3.870
3.463
3.453
3.409
2.024
2.015
2.010
2.002
1.996
1.583
0.874
0.869
0.861
0.856
0.844
0.422
0.414
0.409
0.400
0.396
0.000


BH3
P
Et
(-)Men
O
O
O
BH3
P
Et
Men(-)
1.00
3.08
0.11
1.24
1.70
0.91
2.07
2.07
1.01
1.41
1.44
3.70
2.52
0.82
12.03
1.79
3.33
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)

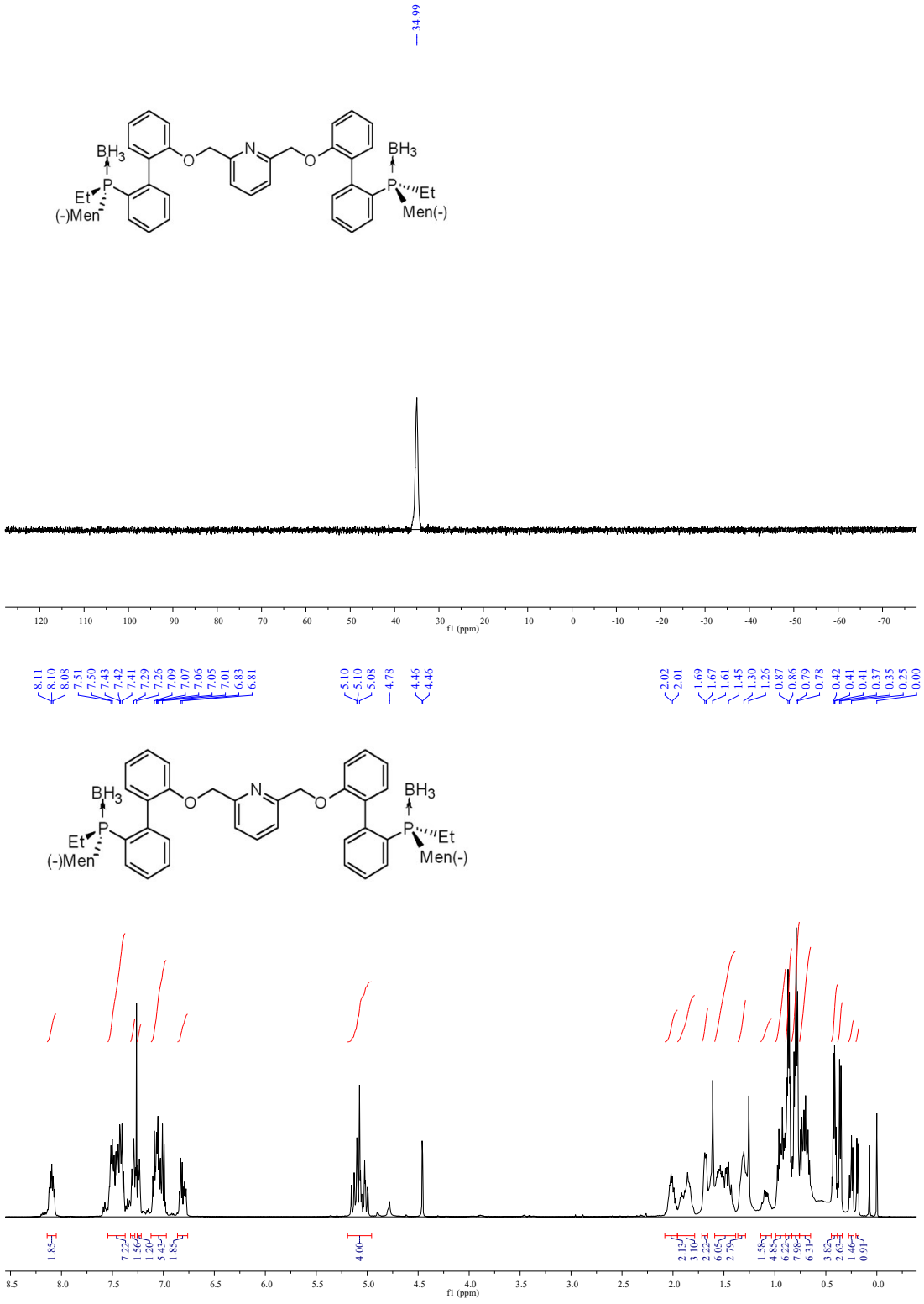


R_P-(-)-Menthyl 2'-ethoxyethoxyethoxy-1,1'-biphenyl-2-yl ethylphosphine borane (10a)

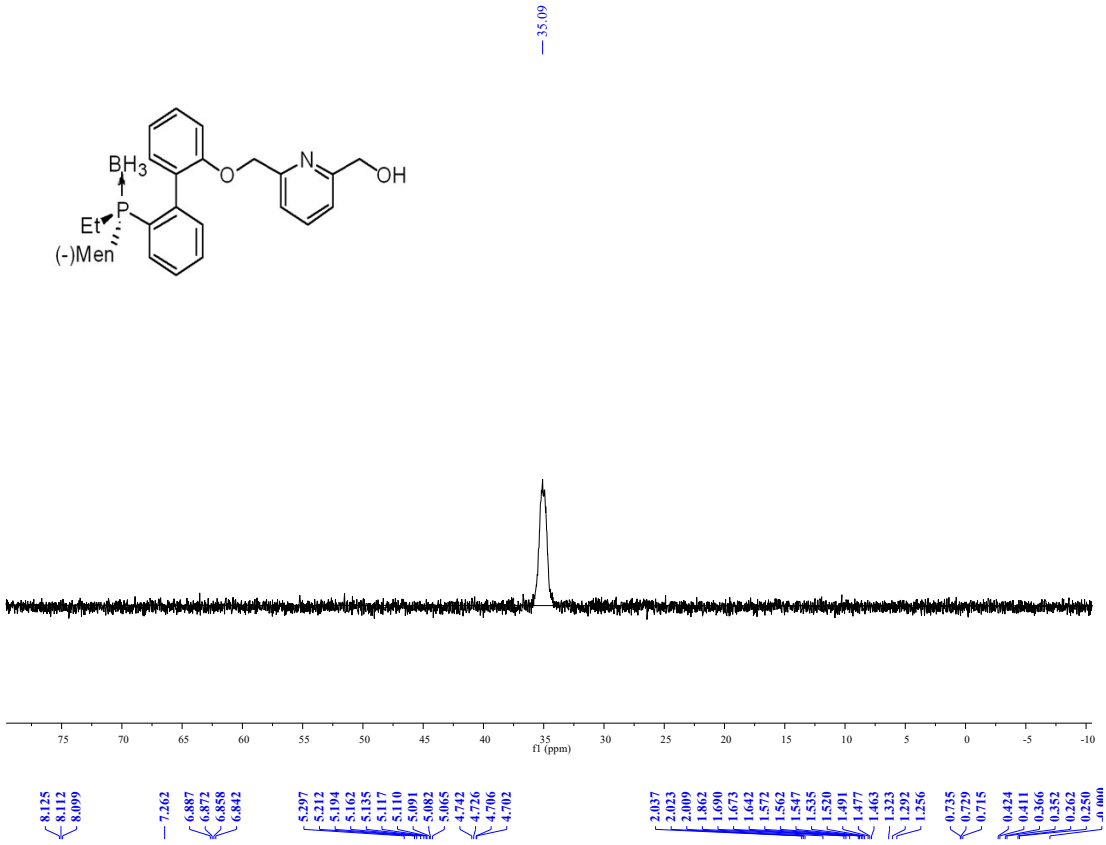


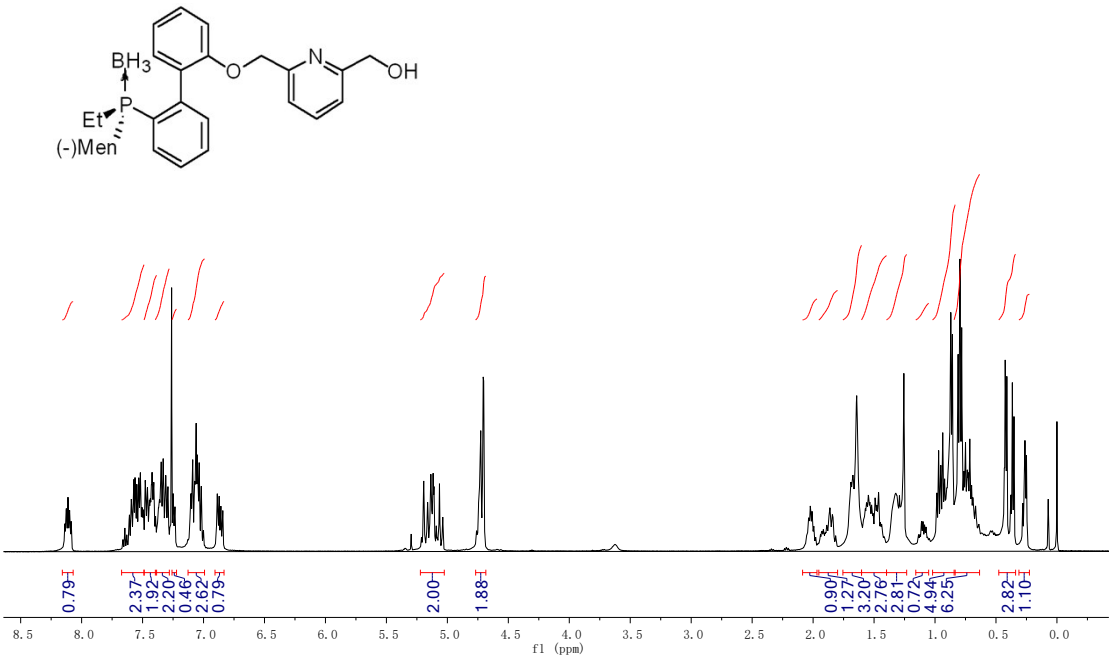


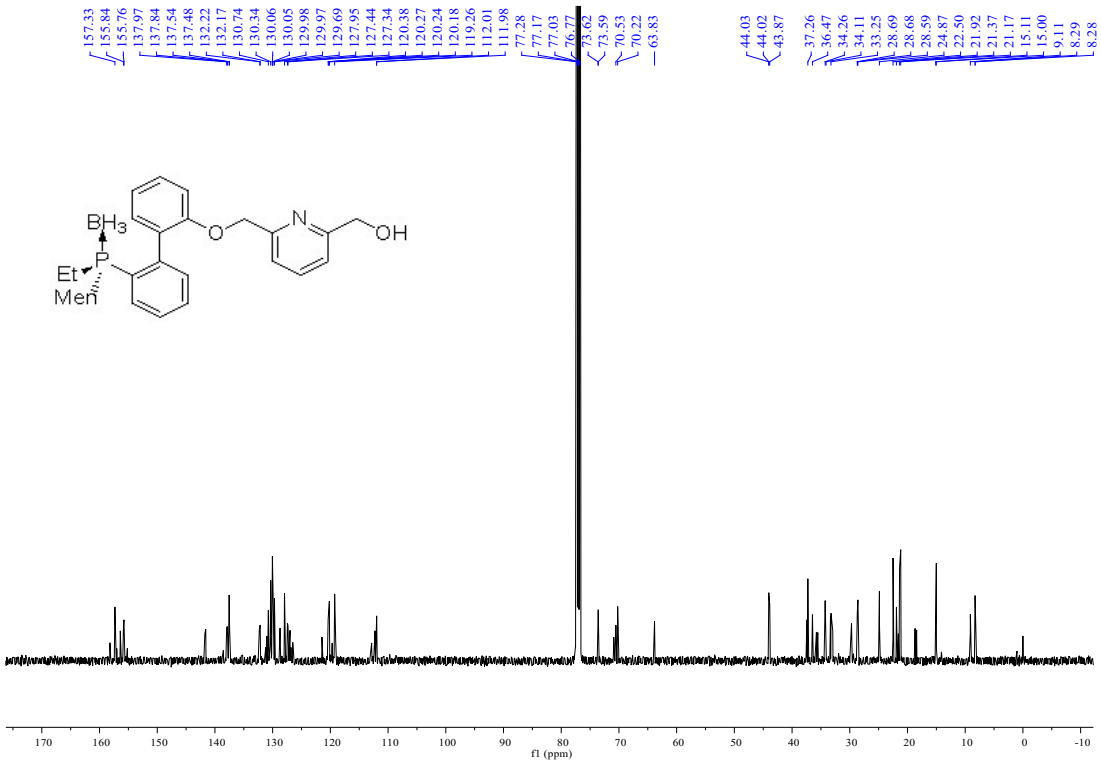
R_P,R_P-2,6-Di[2-(-)-menthyl ethylphosphino-1,1'-biphenyl-2'-oxymethyl]Pyridine diborane (9b)



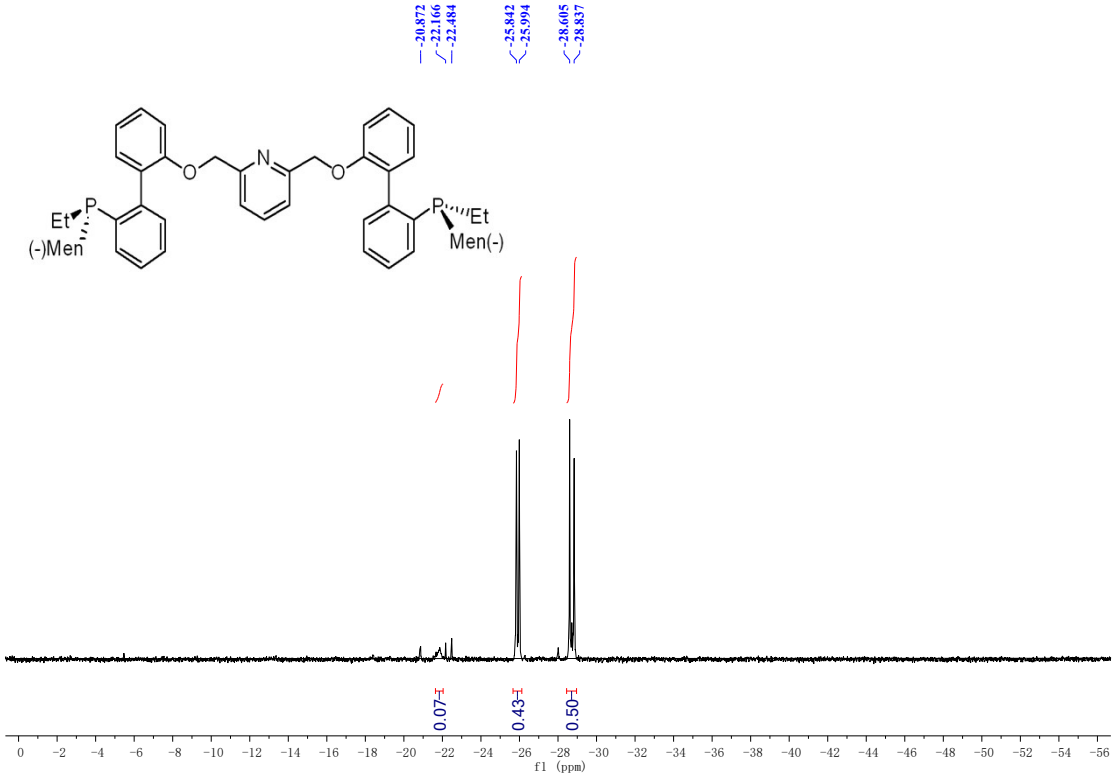
***R*P-2-[2-(-)-Menthyl ethyl phosphino-1,1'-biphenyl-2'-oxymethyl] 6-hydroxymetnylpyridine borane (10b)**

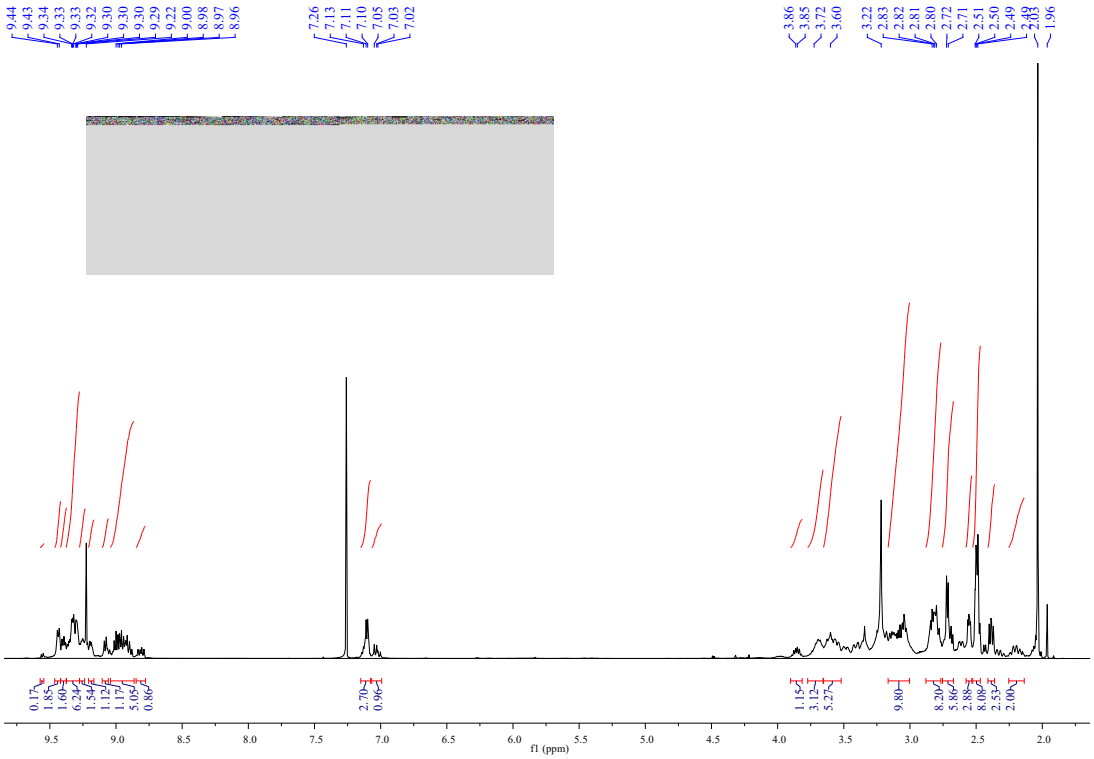

35.09
BH3
P
Et
(-)Men
O
N
OH
f1 (ppm)
8.125
8.112
8.099
7.262
6.887
6.872
6.858
6.842
5.297
5.212
5.194
5.162
5.135
5.117
5.110
5.091
5.082
5.065
4.742
4.726
4.706
4.702
2.037
2.023
2.009
1.862
1.690
1.673
1.642
1.572
1.562
1.547
1.535
1.520
1.491
1.477
1.463
1.333
1.292
1.256
0.735
0.729
0.715
0.424
0.411
0.366
0.352
0.262
0.250


BH3
P
Et
(-)Men
O
N
OH
0.79
2.37
1.92
2.26
0.46
2.62
0.79
2.00
1.88
0.90
1.27
3.20
2.76
2.81
0.72
4.94
6.25
2.82
1.10
f1 (ppm)

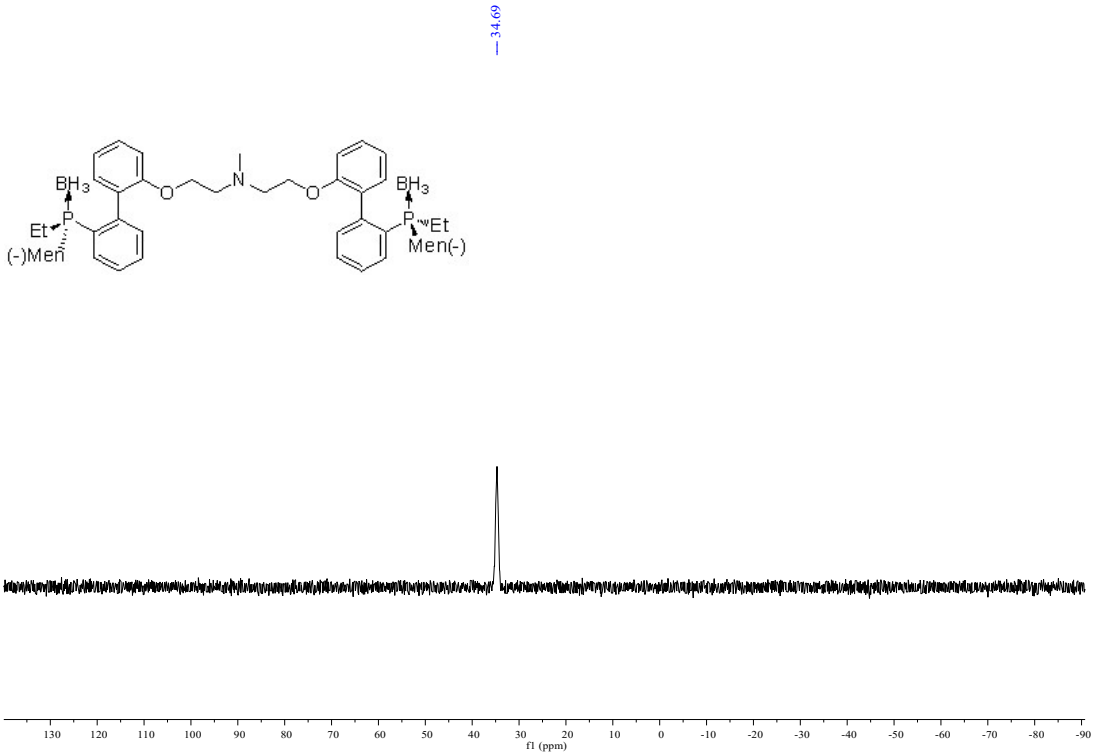


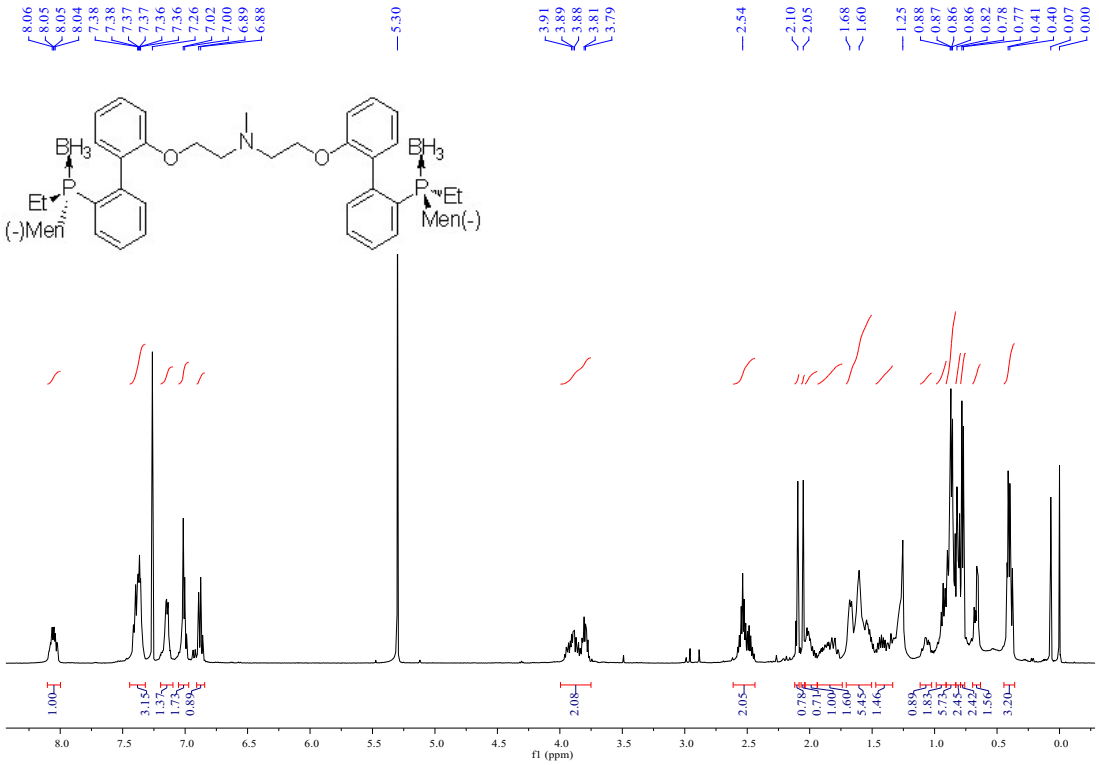
***R*P,*R*P-2,6-Di[2-(-)-menthyl ethylphosphino-1,1'-biphenyl-2'-oxymethyl]pyridine (12b)**

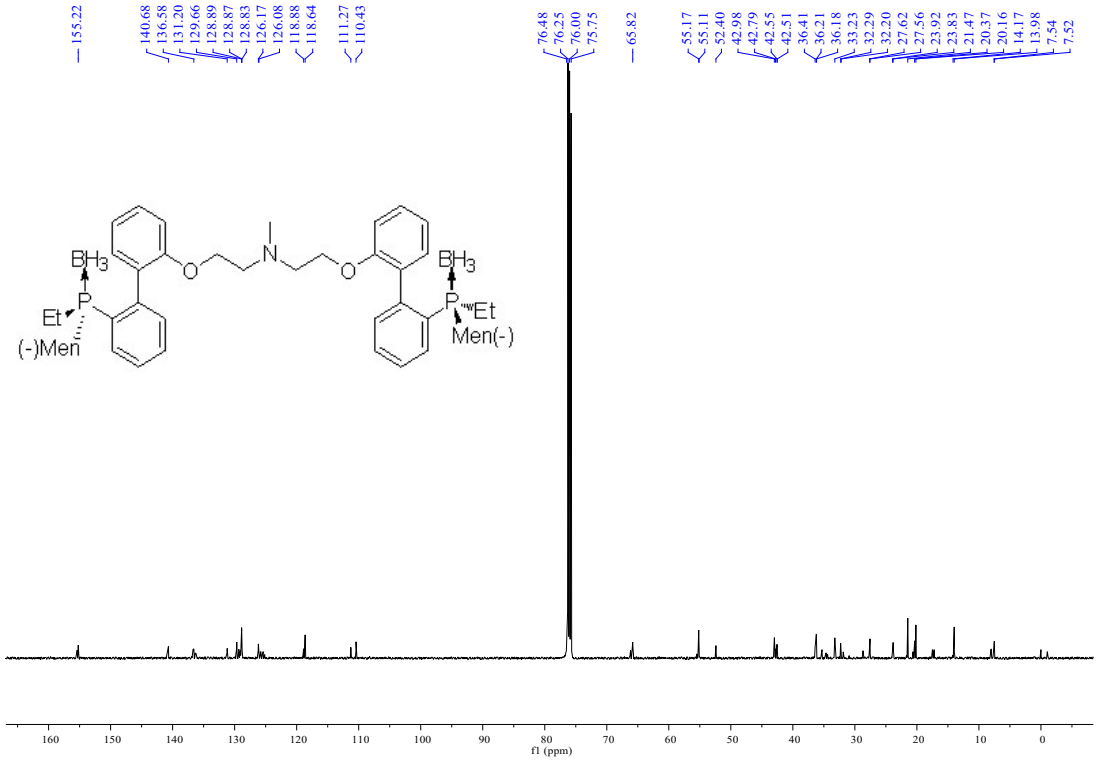




R_P,R_P-Di[2-(-)-menthyl ethylphosphino-1,1'-biphenyl-2'-oxyethyl] methylamine diborane(9c)

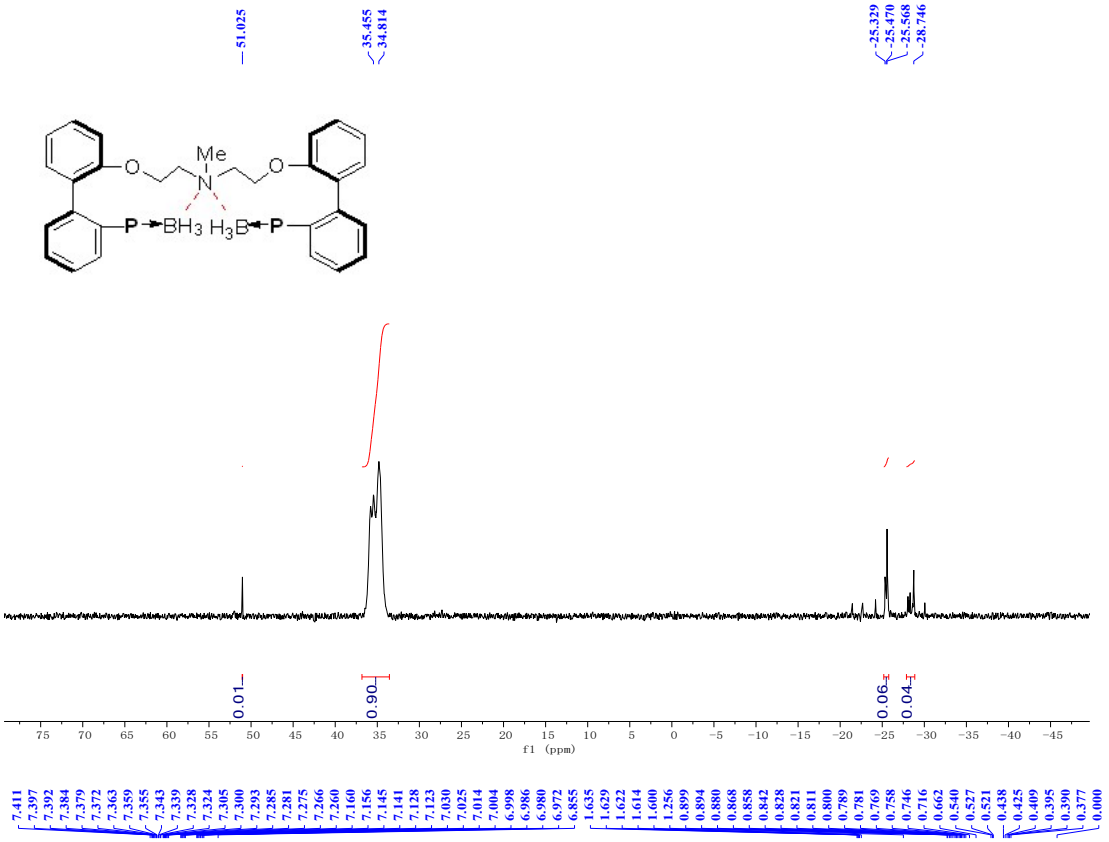


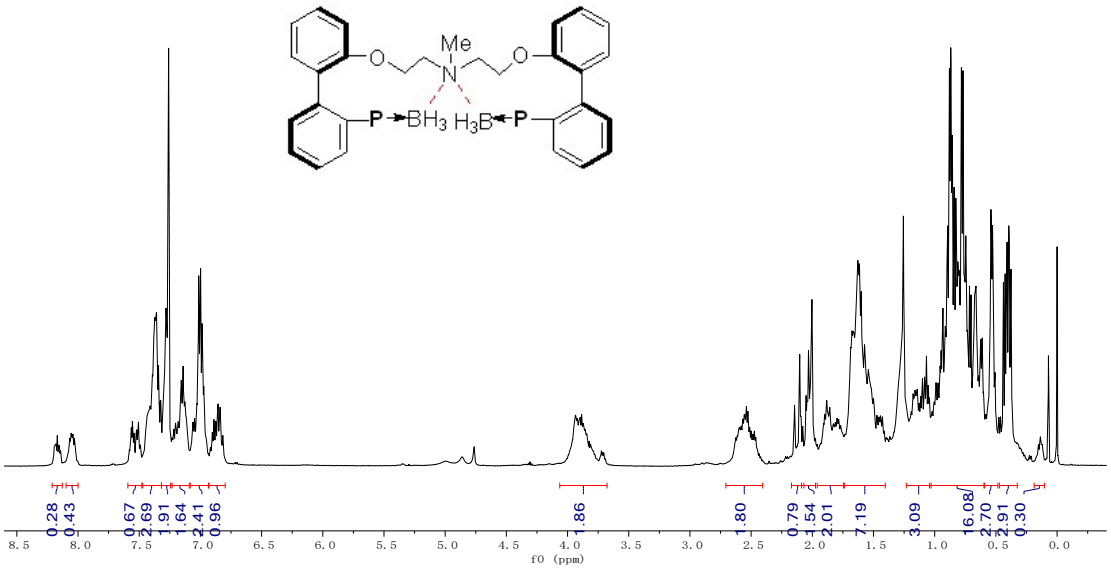




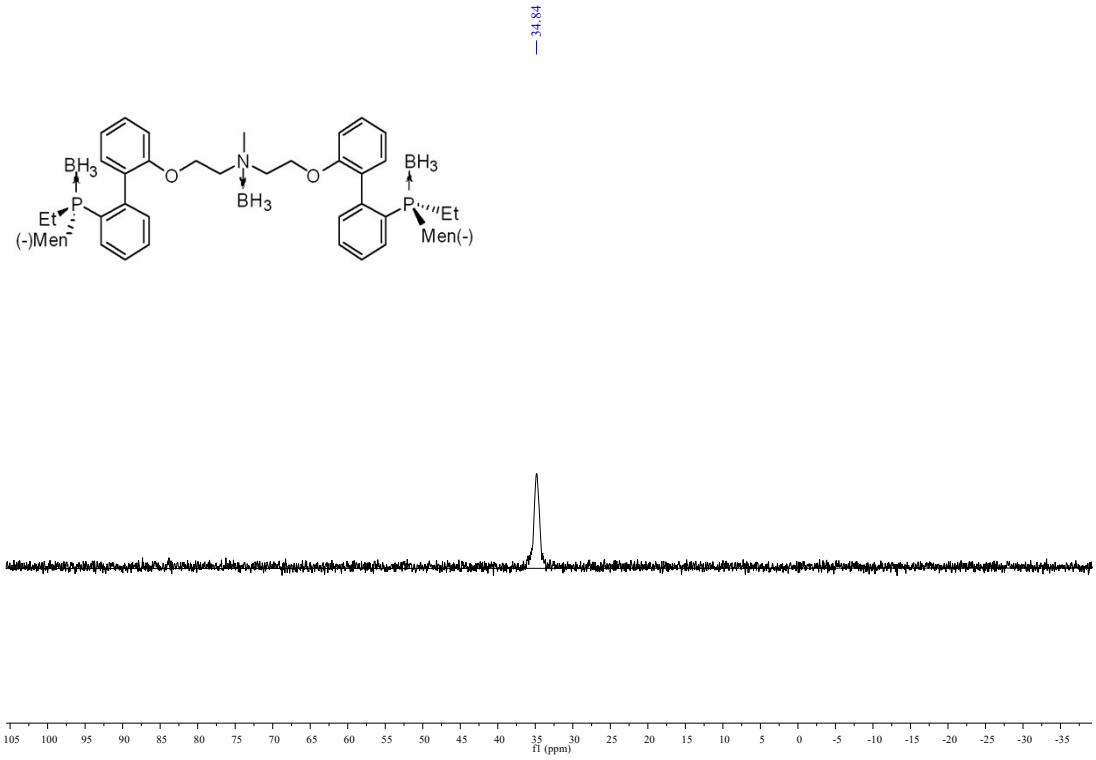
R_P,R_P-Di[2-(-)-menthyl ethylphosphino-1,1'-biphenyl-2'-oxyethyl] methylamine diborane (9c)

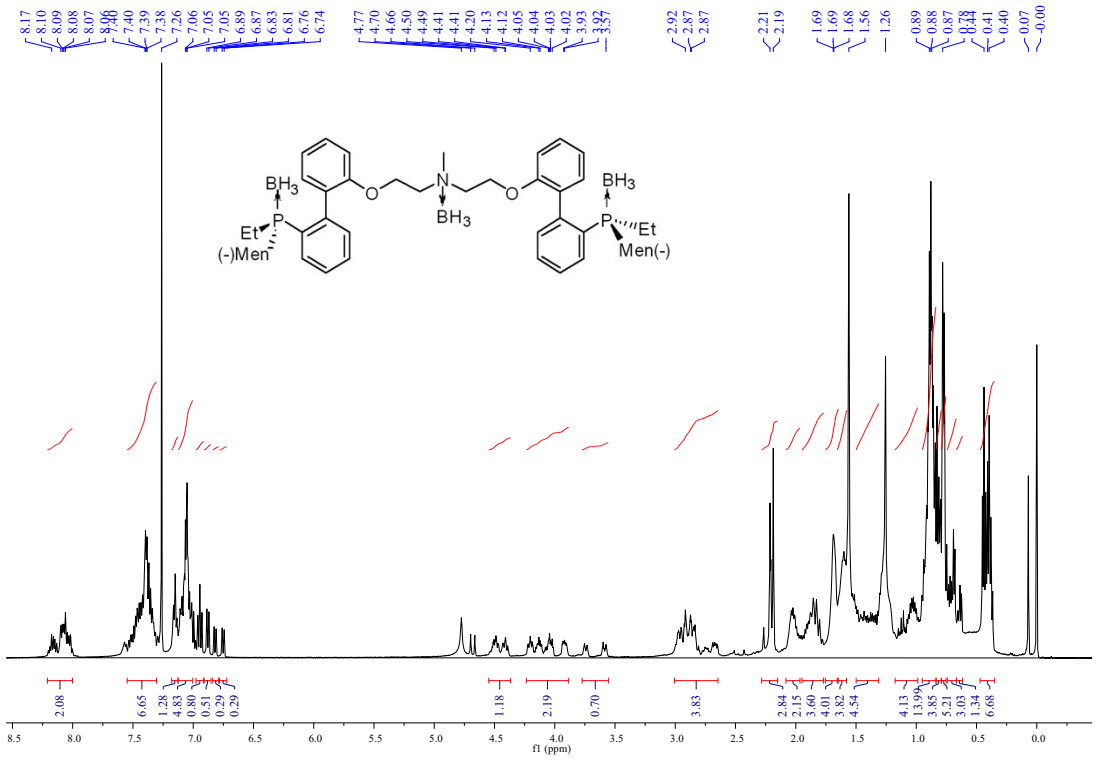
/ R_P,R_P-Di[2-(-)-menthyl ethylphosphino-1,1'-biphenyl-2'-oxyethyl] methylamine (12c)

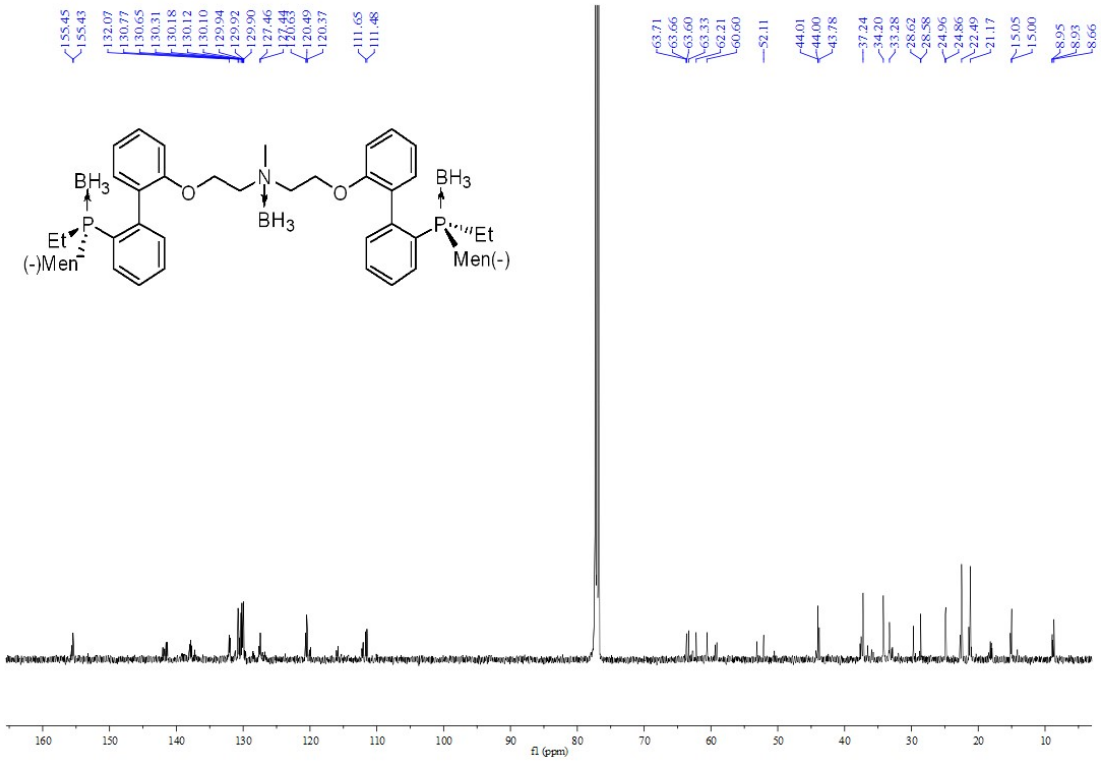




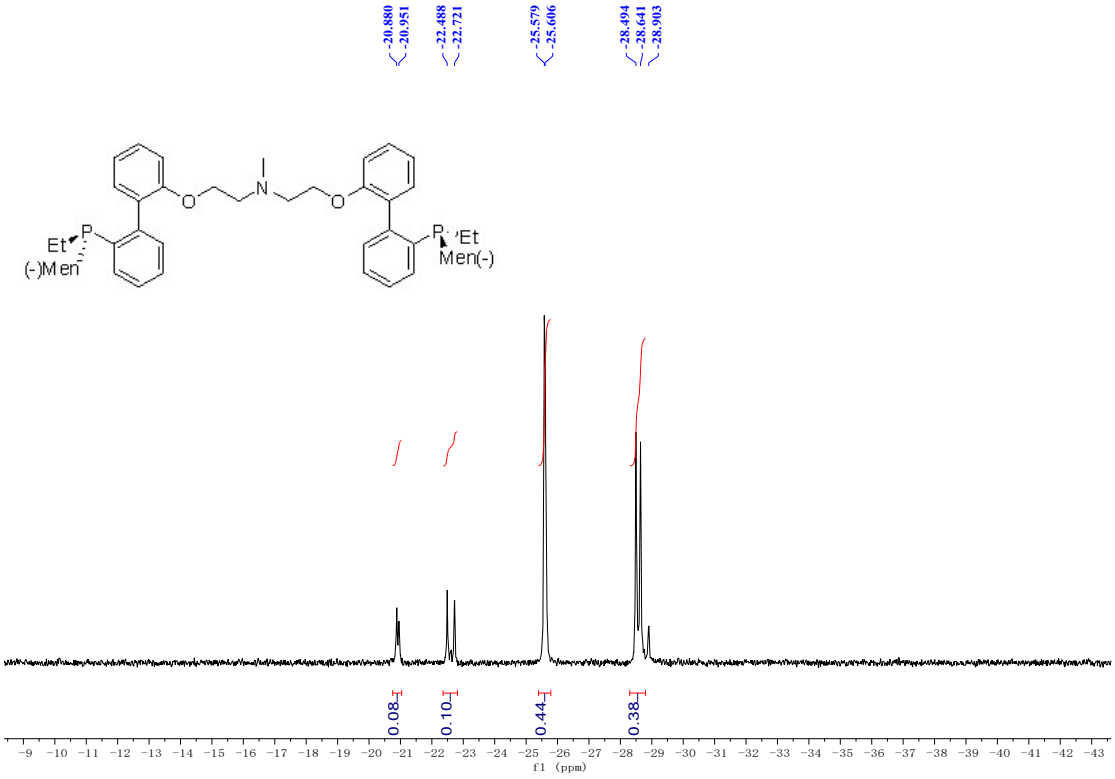
R_P,R_P-Di[2-(-)-menthyl ethylphosphino-1,1'-biphenyl-2'-oxyethyl] methylamine triborane (11c)

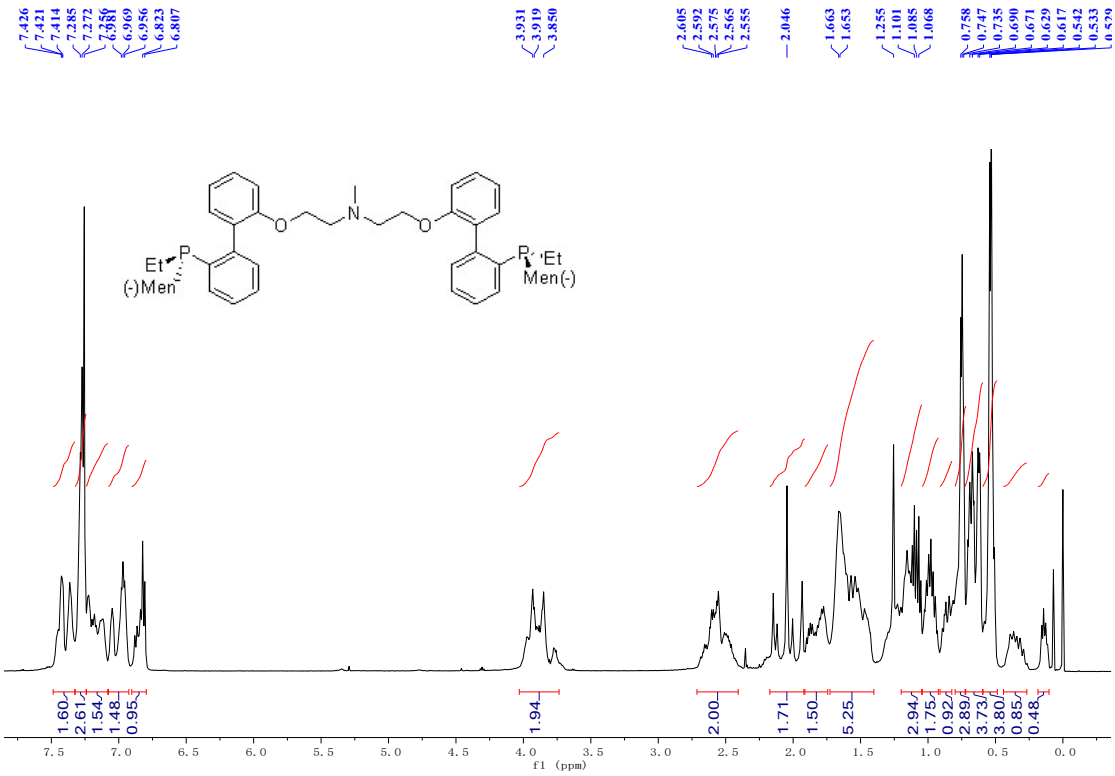

34.84
BH3
P
Et
(-)Men
O
N
BH3
O
BH3
P
Et
Men(-)
f1 (ppm)


8.17
8.10
8.09
8.08
8.07
7.40
7.39
7.38
7.26
7.06
7.05
7.05
6.89
6.87
6.83
6.81
6.76
6.74
4.77
4.70
4.66
4.50
4.49
4.41
4.41
4.20
4.13
4.12
4.05
4.04
4.03
4.02
3.93
2.92
2.87
2.87
2.21
2.19
1.69
1.69
1.68
1.56
1.26
0.89
0.88
0.87
0.41
0.40
0.07
-0.00
BH3
P
Et
(-)Men
O
N
BH3
O
BH3
P
Et
Men(-)
2.08
6.65
1.28
4.83
0.80
0.51
0.29
0.29
1.18
2.19
0.70
3.83
2.84
2.15
3.60
4.01
3.82
4.54
4.13
13.99
3.85
5.21
3.03
1.34
6.68
f1 (ppm)



***R*P,*R*P-Di[2-(-)-menthyl ethylphosphino-1,1'-biphenyl-2'-oxyethyl] methylamine (12c)**




7.426
7.421
7.414
7.285
7.272
6.969
6.956
6.823
6.807
3.931
3.919
3.850
2.605
2.592
2.575
2.565
2.555
2.046
1.663
1.653
1.255
1.101
1.085
1.068
0.758
0.747
0.735
0.690
0.671
0.629
0.617
0.542
0.533
Et
(-)Men
P
O
N
O
P
Et
Men(-)
1.60
2.61
1.54
1.48
0.95
1.94
2.00
1.71
1.50
5.25
2.94
1.75
0.92
2.89
3.73
3.80
0.85
0.48
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)