Supporting Information

DESIGN AND SYNTHESIS OF A C_2-SYMMETRIC CHIRAL 1,2-BIS(DIPHENYLPHOSPHINO)BENZENE LIGAND VIA RHODIUM-CATALYZED INTRAMOLECULAR [2+2+2] CYCLOADDITION

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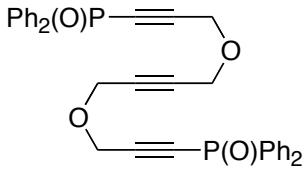
I. General

Anhydrous CH_2Cl_2 (No. 27,099-7) and $(CH_2Cl)_2$ (No. 28,450-5) were obtained from Aldrich and used as received. H_8-BINAP, Segphos, (*R*)-3-butyne-2-ol [(*R*)-**7**] were obtained from Takasago International Corporation. Solvents for the synthesis of substrates were dried over Molecular Sieves 4Å (Wako) prior to use. Alkenes **14a** and **14b** are commercially available. All other reagents were obtained from commercial sources and used as received. All reactions were carried out under an atmosphere of argon or nitrogen in oven-dried glassware with magnetic stirring.

II. Synthesis of Achiral Diphosphine 6a

Triyne Diphosphine Oxide 4a

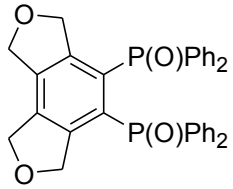


To a solution of 1,4-bis(prop-2-ynyloxy)but-2-yne (5.45 g, 33.6 mmol), CuI (0.213 g, 1.12 mmol) and Et_3N (9.37 mL, 67.2 mmol) in toluene (100 mL) was added chlorodiphenylphosphine (4.95 g, 22.4 mmol), and the mixture was stirred at room temperature for 20 h. The reaction was quenched by the addition of water and extracted with EtOAc. The organic layer was washed with saturated aqueous NH_4Cl and brine, dried over Na_2SO_4, and concentrated. The residue was dissolved in CH_2Cl_2 (80 mL) and 30% H_2O_2 (7 mL) was added to this solution at 0 °C. The mixture was stirred at room temperature for 3 h. The reaction was quenched by the addition of water and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by a silica gel column chromatography (EtOAc) afforded **4a** (2.12 g, 3.77 mmol, 33% yield based on chlorodiphenylphosphine) as a pale yellow oil. The corresponding mono-diphenylphosphinoyl triyne was also generated in 49% yield.

IR (neat) 3076, 3056, 2895, 2853, 2200, 1205 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.88–7.78 (m,

8H), 7.58–7.43(m, 12H), 4.44 (d, J = 3.0 Hz, 4H), 4.30 (s, 4H), ^{13}C NMR ($CDCl_3$, 125 MHz) δ 132.7, 132.45, 132.42, 131.8, 130.9, 130.8, 128.7, 128.6, 101.8, 101.6, 82.2, 82.0, 80.7 57.4, 56.85, 56.83, ^{31}P ($CDCl_3$, 121 MHz) δ 8.64; HRMS (ESI) calcd for $C_{34}H_{28}O_4P_2Na$ $[M+Na]^+$ 585.1355, found 585.1367.

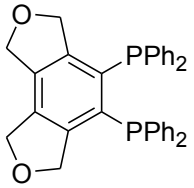
4,5-Bis(diphenylphosphinoyl)-1,3,6,8-tetrahydro-2,7-dioxa-*as*-indacene (5 a: Table 1, entry 2)



A CH_2Cl_2 (1.0 mL) solution of *rac*-BINAP (6.2 mg, 0.010 mmol) was added to a CH_2Cl_2 (0.5 mL) solution of $[Rh(cod)_2]BF_4$ (4.1 mg, 0.010 mmol) at room temperature, and the mixture was stirred for 30 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 1 h, the resulting solution was concentrated to dryness and redissolved in CH_2Cl_2 (0.5 mL). To this solution was added a solution of **4 a** (56.3 mg, 0.10 mmol) in CH_2Cl_2 (1.5 mL) at room temperature. After stirring at room temperature for 21 h, the resulting solution was concentrated and purified by a preparative TLC (EtOAc/MeOH = 70:3), which furnished **5a** (52.7 mg, 0.094 mmol, 94% yield) as a pale yellow solid.

Mp 165.8–167.1 °C; IR (KBr) 3056, 2850, 1437, 1196 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.42 (dd, J = 12.6, 8.0 Hz, 8H), 7.34 (t, J = 7.4 Hz, 4H), 7.23 (t, J = 7.4 Hz, 8H). 5.00 (s, 4H), 4.75 (s, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 146.95, 146.86, 146.8, 144.6, 137.7, 137.6, 133.5, 132.6, 131.9, 131.8, 131.5, 127.9, 127.8, 74.9, 70.8; ^{31}P ($CDCl_3$, 121 MHz) δ 5.02; HRMS (ESI) calcd for $C_{34}H_{28}O_4P_2Na$ $[M+Na]^+$ 585.1355, found 585.1357.

4,5-Bis(diphenylphosphanyl)-1,3,6,8-tetrahydro-2,7-dioxa-*as*-indacene (6a: Scheme 3)

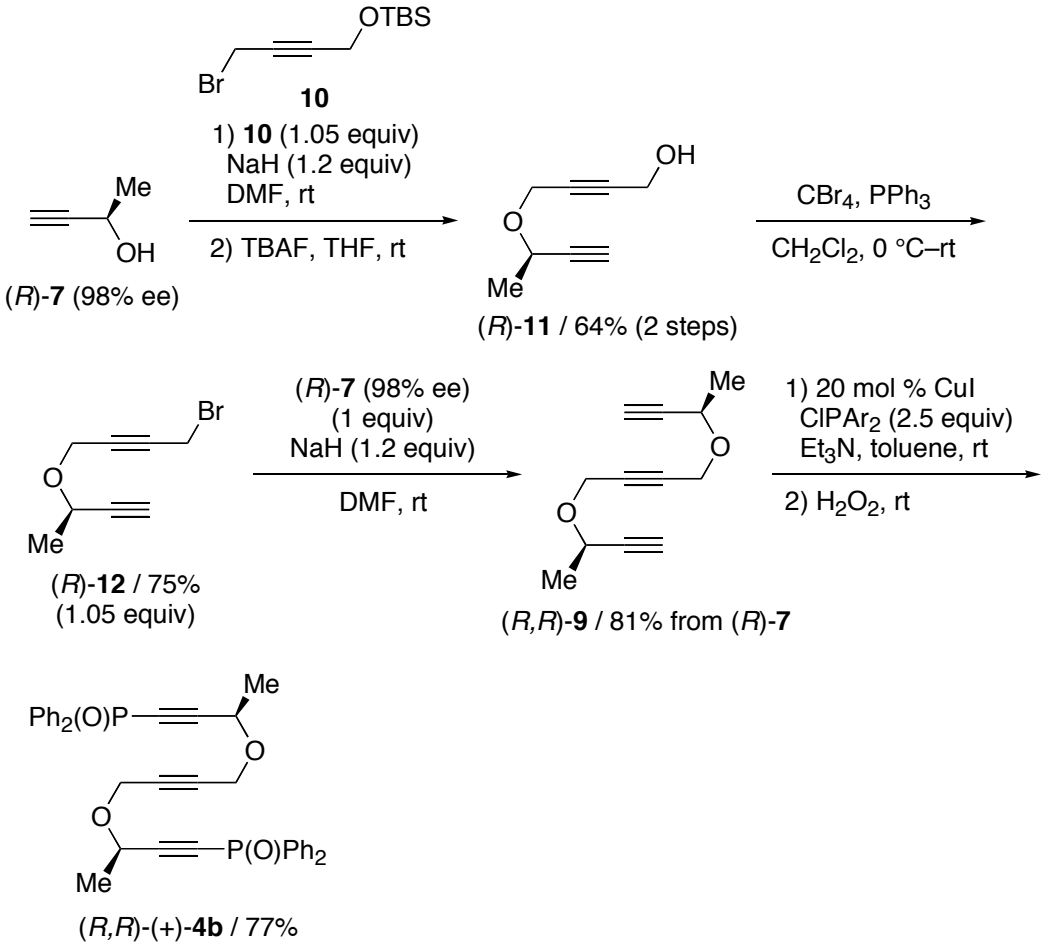


$HSiCl_3$ (0.670 g, 4.91 mmol) and *N,N*-dimethylaniline (118.0 mg, 0.97 mmol) was stirred in xylene (10 mL) at room temperature for 30 min. The mixture was added to **5a** (100.0 mg, 0.177 mmol) in xylene (4 mL) and stirred at 130 °C for 24 h. After the solution was cooled to room temperature, the reaction was quenched by the addition of 1 M aqueous sodium hydroxide and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by a preparative TLC (hexane/EtOAc = 1:1), which furnished **6a** (39.0 mg, 0.074 mmol, 42% yield) as a colorless solid.

Mp 87.2–88.9 °C; IR (KBr) 3067, 3051, 2848, 1583, 1479 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.33–7.11 (m, 20H), 4.87 (s, 4H), 4.02 (s, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 145.2, 135.3, 135.2, 132.9, 132.7, 132.6, 128.59, 128.55, 128.51, 128.4, 73.3, 71.2; ^{31}P ($CDCl_3$, 121 MHz) δ –11.0; HRMS (ESI) calcd for $C_{34}H_{28}O_2P_2Na$ $[M+Na]^+$ 553.1457, found 553.1461.

III. Synthesis of Chiral Diphosphine 6b

Triyne Diphosphine Oxide [(*R*,*R*)-(+)-4b: Scheme 4]



To a stirred suspension of NaH (55% in paraffin oil, 0.231 g, 5.30 mmol) in NMP (10 ml) at 0 °C was added an NMP (5 mL) solution of (*R*)-**7** (0.309 g, 4.41 mmol, 98% ee). The mixture was stirred at the same temperature for 1 h, and then **10** (1.22 g, 4.63 mmol) was added. The cold bath was removed, and the solution was stirred for 18 h. The reaction was quenched by the addition of water and saturated aqueous NH_4Cl and extracted with Et_2O. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was dissolved in THF (10 mL) and 1M TBAF (6.17 mL) was added to this solution at room temperature. The mixture was stirred at room temperature for 30 min and concentrated. To the residue was added saturated aqueous NH_4Cl and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by a silica gel column chromatography (hexane/EtOAc = 7:1) afforded (*R*)-**11** (0.393 g, 2.84 mmol, 64% yield) as a pale yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.44–4.341 (m, 2H), 4.336–4.23 (m, 3H), 2.47 (d, J = 2.0 Hz, 1H), 2.15 (s, 1H), 1.47 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 84.8, 82.6, 81.2, 73.7, 63.9, 55.9, 51.0, 21.8.

To a solution of (*R*)-**11** (0.393 g, 2.84 mmol), CBr_4 (1.13 g, 3.41 mmol) in CH_2Cl_2 (25 mL) was added PPh_3 (1.12 g, 4.26 mmol) at 0 °C, and the mixture was stirred at room temperature for 1 h.

The reaction was quenched by the addition of saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by a silica gel column chromatography (hexane/EtOAc = 20:1) afforded (*R*)-**12** (0.429 g, 2.13 mmol, 75% yield) as a pale yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.40 (dt, J = 15.8, 2.1 Hz, 1H), 4.37 (dq, J = 6.6, 2.1 Hz, 1H), 4.30 (dt, J = 15.8 Hz, 2.1 Hz, 1H), 3.95 (t, J = 2.1 Hz, 2H), 2.45 (d, J = 2.1 Hz, 1H), 1.47 (d, J = 6.6 Hz, 3H).

To a stirred suspention of NaH (55% in paraffin oil, 80.6 mg, 1.85 mmol) in DMF (5 ml) at 0 °C was added a DMF (2 mL) solution of (*R*)-**7** (0.108 g, 1.54 mmol). The mixture was stirred at the same temperature for 1 h, and then (*R*)-**12** (0.325 g, 1.62 mmol) was added. The cold bath was removed, and the solution was stirred for 3 h. The reaction was quenched by the addition of saturated aqueous NH_4Cl and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by a silica gel column chromatography (hexane/EtOAc= 20:1) afforded (*R*,*R*)-**9** (0.239 g, 1.24 mmol, 81% yield) as a collorless solid.

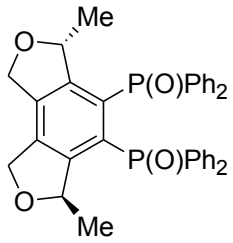
^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.44–4.24 (m, 4H), 4.39 (dq, J = 6.6 Hz, 2.0 Hz, 2H), 2.45 (d, J = 2.0 Hz, 2H), 1.47 (d, J = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 82.7, 82.0, 73.6, 63.8, 56.0, 21.8.

To a solution of (*R*,*R*)-(+)-**9** (0.100 g, 0.520 mmol), CuI (19.8 mg, 0.104 mmol), and Et_3N (0.47 mL, 3.38 mmol) in toluene (5 mL) was added chlorodiphenylphosphine (0.287 g, 1.30 mmol), and the mixture was stirred at room temperature for 20 h. The reaction was quenched by the addition of saturated aqueous NH_4Cl and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was dissolved in CH_2Cl_2 (8 mL) and 30% H_2O_2 (0.5 mL) was added to this solution at room temperature. The mixture was stirred at the same temperature for 3 h. The reaction was quenched by the addition of water and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by a preparative TLC (EtOAc) to afford (*R*,*R*)-(+)-**4b** (0.237 g, 1.23 mmol, 77% yield) as a pale yellow oil.

$[\alpha]^{25}_D$ +202.0° ($CHCl_3$, *c* 0.325); IR (neat) 3234, 3059, 2989, 2935, 2188, 1200 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.82 (dd, J = 13.7, 6.9 Hz, 8H), 7.58–7.53 (m, 4H), 7.51–7.45 (m, 8H), 4.57 (dq, J = 6.3, 1.5 Hz, 2H), 4.39–4.34 (m, 2H), 4.29–4.23 (m, 2H), 1.54 (d, J = 6.3 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 133.0, 132.40, 132.38, 132.0, 130.9, 130.8, 128.7, 128.6, 105.5, 105.3, 82.1, 80.7, 79.4, 64.3, 56.6, 21.1; ^{31}P ($CDCl_3$, 202 MHz) δ 8.59; HRMS (ESI) calcd for $C_{36}H_{32}O_4P_2Na$ $[M+Na]^+$ 613.1668, found 613.1685.

Diastereomeric mixture of **4b** (Table 2): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.90–7.72 (m, 8H), 7.64–7.40 (m, 12H), 4.62–4.52 (m, 2H), 4.43–4.32 (m, 2H), 4.31–4.21 (m, 2H), 1.54 (d, J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 132.9, 132.40, 132.37, 131.9, 130.9, 130.8, 128.7, 128.6, 105.6, 105.4, 82.1, 80.6, 79.3, 64.25, 64.23, 56.6, 21.1; ^{31}P ($CDCl_3$, 202 MHz) δ 8.74.

4,5-Bis(diphenylphosphinoyl)-3,6-dimethyl-1,3,6,8-tetrahydro-2,7-dioxa-as-indacene [(*R*,*R*)-(+)-5b: Scheme 5]

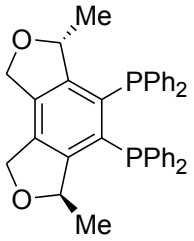


A CH_2Cl_2 (1.0 mL) solution of BIPHEP (39.2 mg, 0.075 mmol) was added to a CH_2Cl_2 (1.0 mL) solution of $[Rh(cod)_2]BF_4$ (30.5 mg, 0.075 mmol) at room temperature, and the mixture was stirred for 30 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 1 h, the resulting solution was concentrated to dryness and redissolved in $(CH_2Cl)_2$ (5.0 mL). To this solution was added a solution of (*R*,*R*)-(+)-**4b** (0.222 g, 0.376 mmol) in $(CH_2Cl)_2$ (20.0 mL) at room temperature. After stirring at room temperature for 24 h, the resulting solution was concentrated and purified by a preparative TLC (EtOAc/MeOH = 20:1), which furnished (*R*,*R*)-(+)-**5b** (0.151 g, 0.256 mmol, 68% yield, 98% ee) as a pale yellow solid.

Mp 154.5–155.8 °C; $[\alpha]^{25}_D$ +9.40° ($CHCl_3$, *c* 0.68, 98% ee); IR (KBr) 3055, 2972, 2926, 1437, 1194 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.56–7.46 (m, 7H), 7.42–7.37 (m, 4H), 7.32–7.26 (m, 3H), 7.18–7.13 (m, 2H), 7.06–7.00 (m, 4H), 5.35 (q, *J* = 6.3 Hz, 2H), 5.05 (d, *J* = 13.7 Hz, 2H), 4.93 (d, *J* = 13.7 Hz, 2H), 1.06 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.8, 151.7, 151.6, 138.2, 135.3, 134.5, 134.1, 133.3, 133.05, 132.97, 132.25, 132.17, 131.8, 131.3, 128.2, 128.1, 127.4, 127.3, 81.4, 68.9, 22.1; ^{31}P ($CDCl_3$, 202 MHz) δ 36.0; HRMS (ESI) calcd for $C_{36}H_{32}O_4P_2Na$ $[M+Na]^+$ 613.1668, found 613.1682; CHIRALPAK AD-H, hexane/2-PrOH = 80:20, 1.0 mL/min, retention times: 7.0 min (*S*,*S*-isomer) and 20.3 min (*R*,*R*-isomer).

Diastereomeric mixture of **5b** (Table 2): ^1H NMR ($CDCl_3$, 300 MHz) δ 7.77–7.68 (m, 20H), 5.73–5.56 (m, 1H), 5.35 (q, *J* = 6.0 Hz, 1H), 5.06 (d, *J* = 13.5 Hz, 2H), 4.93 (d, *J* = 13.5 Hz, 2H), 1.06 (d, *J* = 6.3 Hz, 3H), 0.94 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.7, 151.6, 151.5, 138.2, 138.1, 135.9, 135.2, 135.0, 134.3, 134.1, 133.2, 132.93, 132.88, 132.8, 132.13, 132.08, 132.06, 131.99, 131.96, 131.8, 131.71, 131.67, 131.31, 131.30, 131.2, 128.11, 128.05, 128.0, 127.96, 127.9, 127.8, 127.7, 127.32, 127.27, 127.2, 81.32, 81.29, 68.7, 68.2, 21.9, 20.8; ^{31}P ($CDCl_3$, 202 MHz) δ 36.6.

4,5-Bis(diphenylphosphanyl)-3,6-dimethyl-1,3,6,8-tetrahydro-2,7-dioxa-as-indacene [(*R*,*R*)-(+)-6b: Scheme 5]



$HSiCl_3$ (0.670 g, 4.91 mmol) and *i*Pr_2NH (0.659 g, 5.44 mmol) was stirred in xylene (8 mL) at room temperature for 30 min. One third of the mixture was added to diphosphine oxide **5b** (86.4 mg, 0.146 mmol) in xylene (3 mL) and stirred at 120 °C for 15 h. After the solution was cooled to room temperature, the reaction was quenched by the addition of 1 M aqueous sodium hydroxide and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by a preparative TLC (hexane/Et_3N = 7:1), which furnished diphosphine (*R*,*R*)-(+)-**6b** (20.9 mg, 0.037 mmol, 26% yield, 98% ee) as a yellow solid. The ee

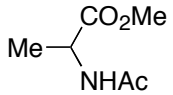
value of **6b** was determined after oxidation to **5b**.

Mp 123.4–125.0 °C; $[\alpha]^{25}_{D}$ +468.4° ($CHCl_3$, *c* 0.410, 98% ee); IR (KBr) 3069, 3053, 2971, 2925, 1435 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.54–7.16 (m, 20H), 4.92 (d, *J* = 13.2 Hz, 2H), 4.76 (d, *J* = 13.2 Hz, 2H), 3.92 (q, *J* = 6.1 Hz, 2H), 0.88 (d, *J* = 6.1 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 148.83, 148.81, 148.77, 137.0, 136.9, 136.8, 136.2, 135.2, 134.34, 134.31, 132.7, 132.62, 132.55, 132.1, 132.0, 131.9, 128.6, 128.53, 128.51, 128.45, 128.14, 128.12, 128.10, 79.1, 68.9, 22.5; ^{31}P ($CDCl_3$, 202 MHz) δ −7.46; HRMS (ESI) calcd for $C_{36}H_{32}O_2P_2Na$ $[M+Na]^+$ 581.1770, found 581.1794.

IV. Rh-Catalyzed Asymmetric Hydrogenation of Substituted Alkenes

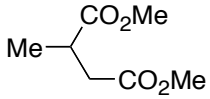
General procedure (Table 3): A $(CH_2Cl)_2$ (0.25 mL) solution of ligand (0.0033 mmol) was added to a $(CH_2Cl)_2$ (0.25 mL) solution of $[Rh(nbd)_2]BF_4$ or $[Rh(cod)_2]BF_4$ (0.0033 mmol) at room temperature, and the mixture was stirred at room temperature for 15 min. To this solution was added a solution of **13** (0.065 mmol) in $(CH_2Cl)_2$ (0.5 mL) at room temperature, and the solution was stirred at room temperature for 1 h. Then H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 16 h, the resulting solution was concentrated and passed through a silica gel plug to remove the catalyst. The ee values of the products **14** were determined by chiral HPLC analyses.

2-Acetylaminopropionic acid methyl ester (14a)[1]



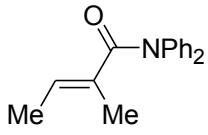
CHIRALPAK AD-H, hexane/2-PrOH = 90:10, 1.0 mL/min, retention times: 5.6 min (*R*-isomer) and 7.0 min (*S*-isomer).

2-Methylsuccinic acid dimethyl ester (14b)[1]



CHIRALPAK OD-H, hexane/2-PrOH = 98:2, 1.0 mL/min, retention times: 7.6 min (*R*-isomer) and 12.3 min (*S*-isomer).

2-Methylbut-2-enoic acid diphenylamide (13c)

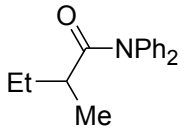


To a stirred solution of (*E*)-2-methylbut-2-enoic acid (1.00 g, 10.0 mmol) in CH_2Cl_2 (5 mL) was added thionyl chloride (1.1 mL, 15 mmol) at 0 °C, and the mixture was stirred at room temperature for 2 h, which furnished the corresponding crude acid chloride. The resulting solution was added to a solution of diphenylamine (1.86 g, 11.0 mmol), pyridine (20 mL), and CH_2Cl_2 (5 mL) at 0 °C, and the resulting mixture was stirred at room temperature for 48 h. The reaction was quenched by the addition of aqueous 1N HCl and extracted with CH_2Cl_2. The organic layer was washed with aqueous 1N NaOH and brine, dried over Na_2SO_4, and concentrated. The residue was purified by a

silica gel column chromatography (hexane/EtOAc = 2:1) to give **17c** (0.502 g, 2.00 mmol, 20% yield) as a colorless solid.

Mp 89.3–90.3 °C; IR (KBr) 3063, 3037, 2971, 2921, 1644 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.31 (t, J = 7.7 Hz, 4H), 7.19 (t, J = 6.9 Hz, 2H), 7.13 (d, J = 8.0 Hz, 4H), 6.02 (q, J = 6.9 Hz, 1H); 1.63 (s, 3H), 1.55 (d, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 173.2, 143.8, 133.1, 132.6, 129.0, 127.1, 126.1, 13.8, 13.6.; HRMS (ESI) calcd for $C_{17}H_{17}NONa$ $[M+Na]^+$ 274.1202, found 274.1200.

(–)-2-Methyl-*N*,*N*-diphenyl-butyramide (14c)

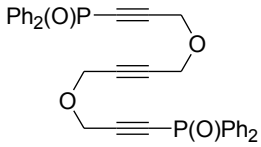


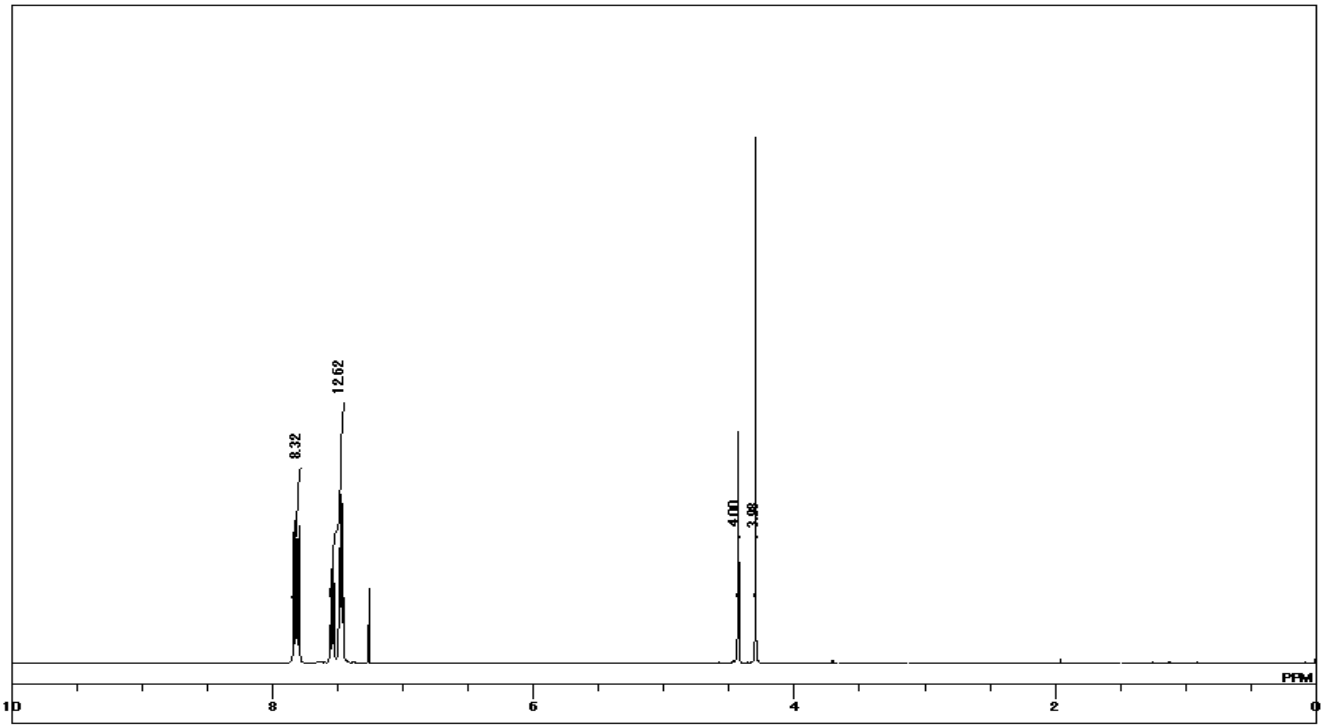
Mp 64.4–65.4 °C; IR (KBr) 3089, 2969, 2930, 2871, 1656 cm^{-1}; $[\alpha]^{25}_D$ –100.6° ($CHCl_3$, c 0.64, 52% ee); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.58–7.05 (m, 10H), 2.54–2.45 (m, 1H), 1.84–1.70 (m, 1H), 1.44–1.33 (m, 1H), 1.13 (d, J = 6.9 Hz, 3H), 0.90 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 177.1, 143.0, 129.7, 128.7, 127.6, 126.5, 125.9, 39.0, 27.7, 17.9, 12.0; HRMS (ESI) calcd for $C_{17}H_{19}NONa$ $[M+Na]^+$ 276.1359, found 276.1366. CHIRALPAK AD-H, hexane/2-PrOH = 98:2, 0.8 mL/min, retention times: 21.8 min [major isomer with (*R*,*R*)-**10b**] and 23.2 min [minor isomer with (*R*,*R*)-**10b**].

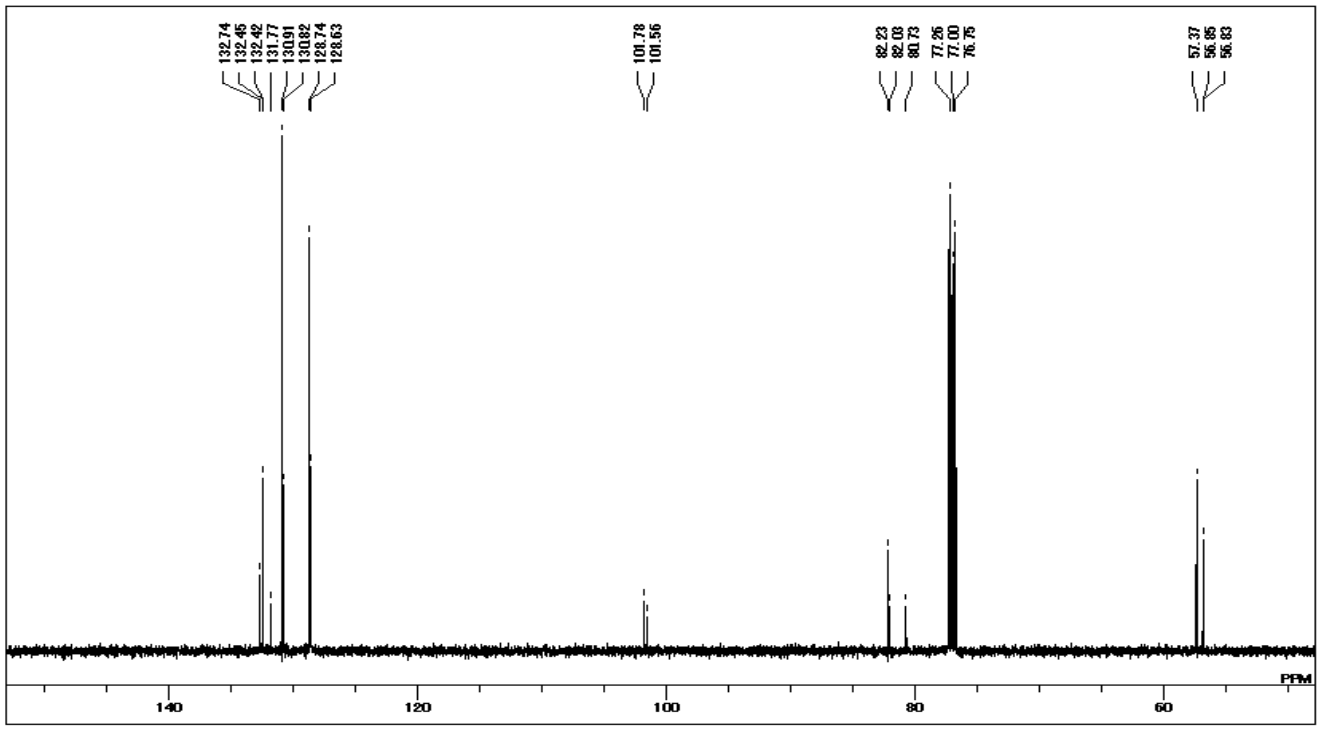
V. Reference

(1) F. Mori, N. Fukawa, K. Noguchi, and K. Tanaka, *Org. Lett.*, 2011, **13**, 362.

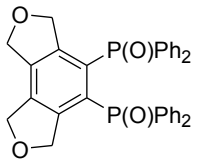
Triyne Diphosphine Oxide 4a

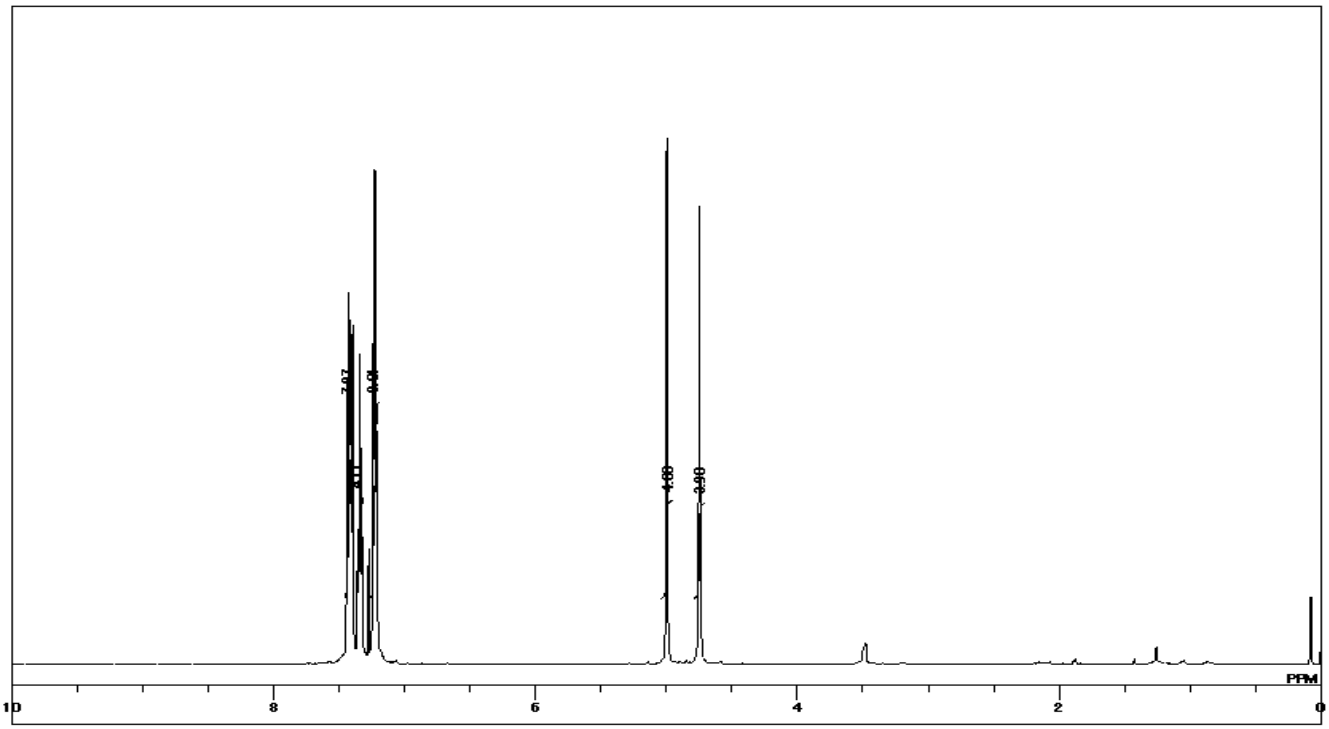


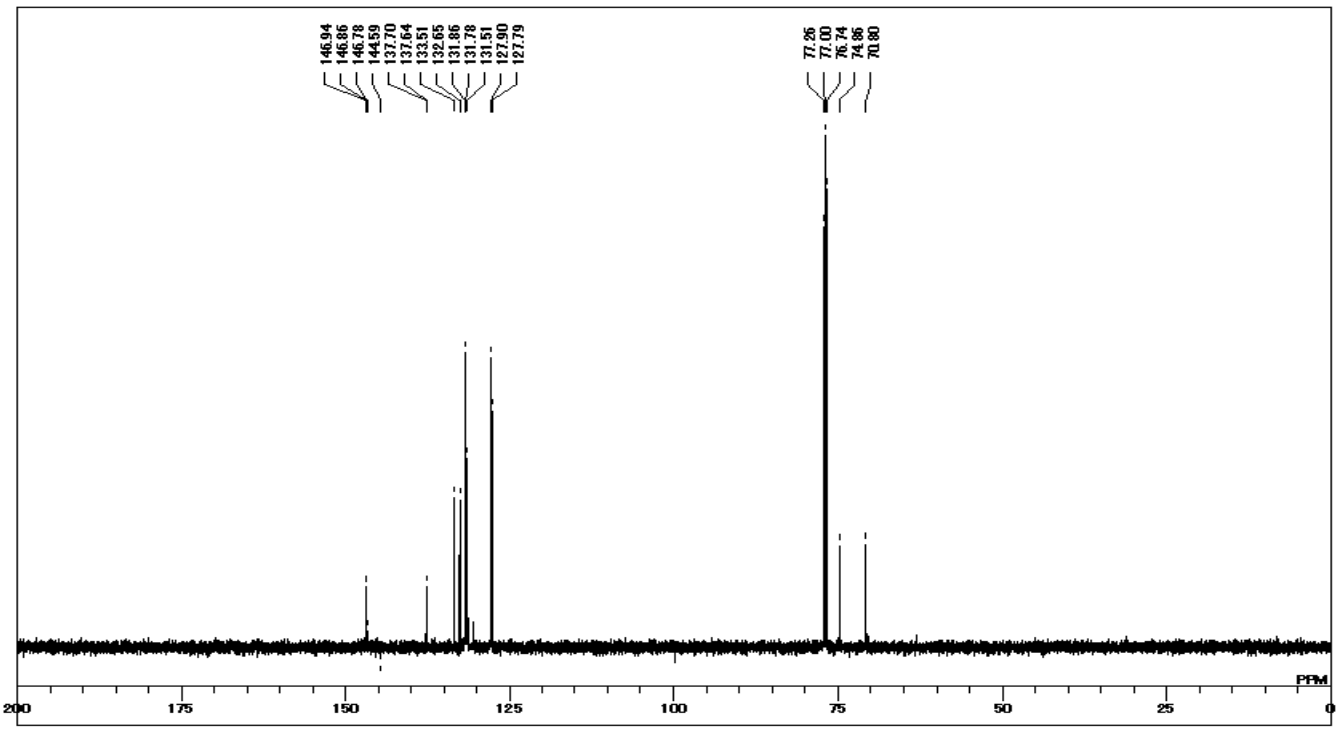




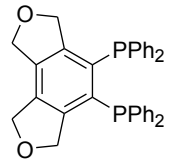
Diphosphine oxide 5a

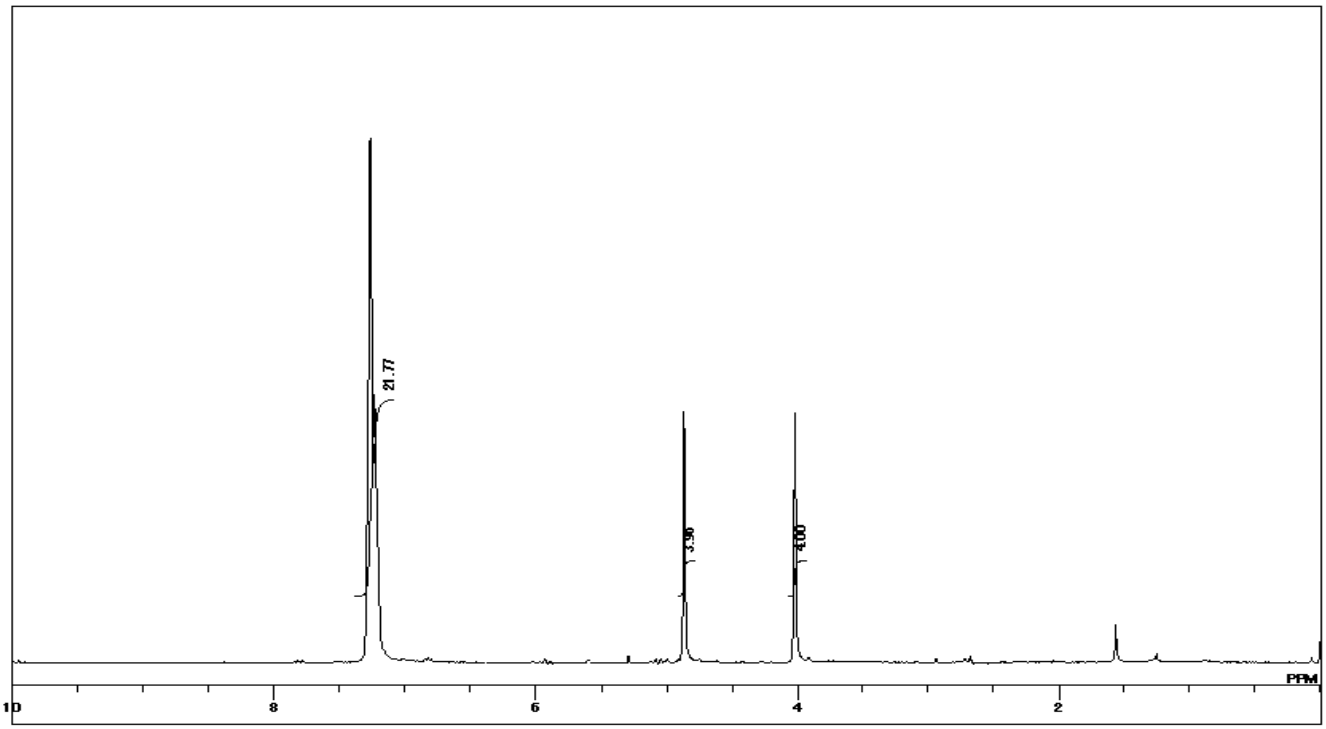


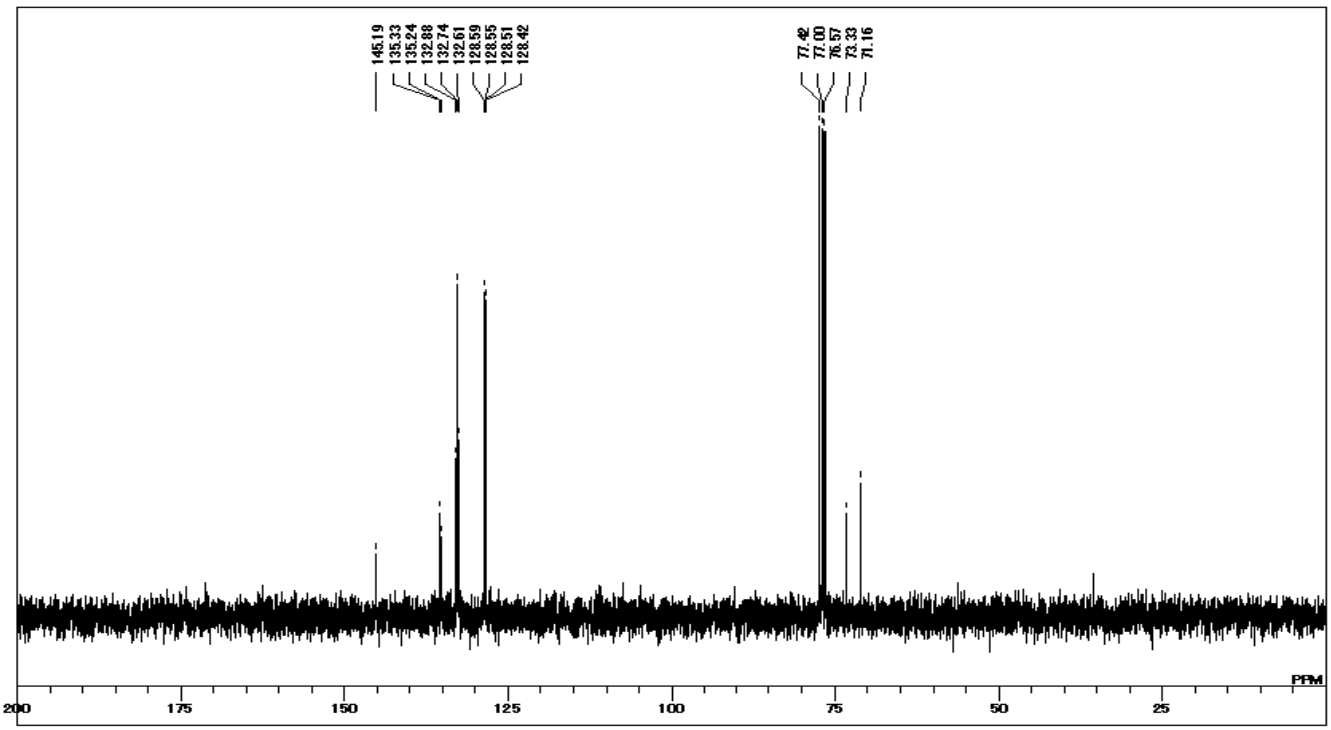




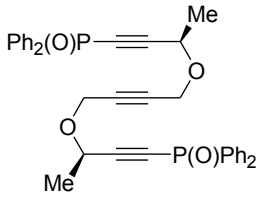
Diphosphine 6a

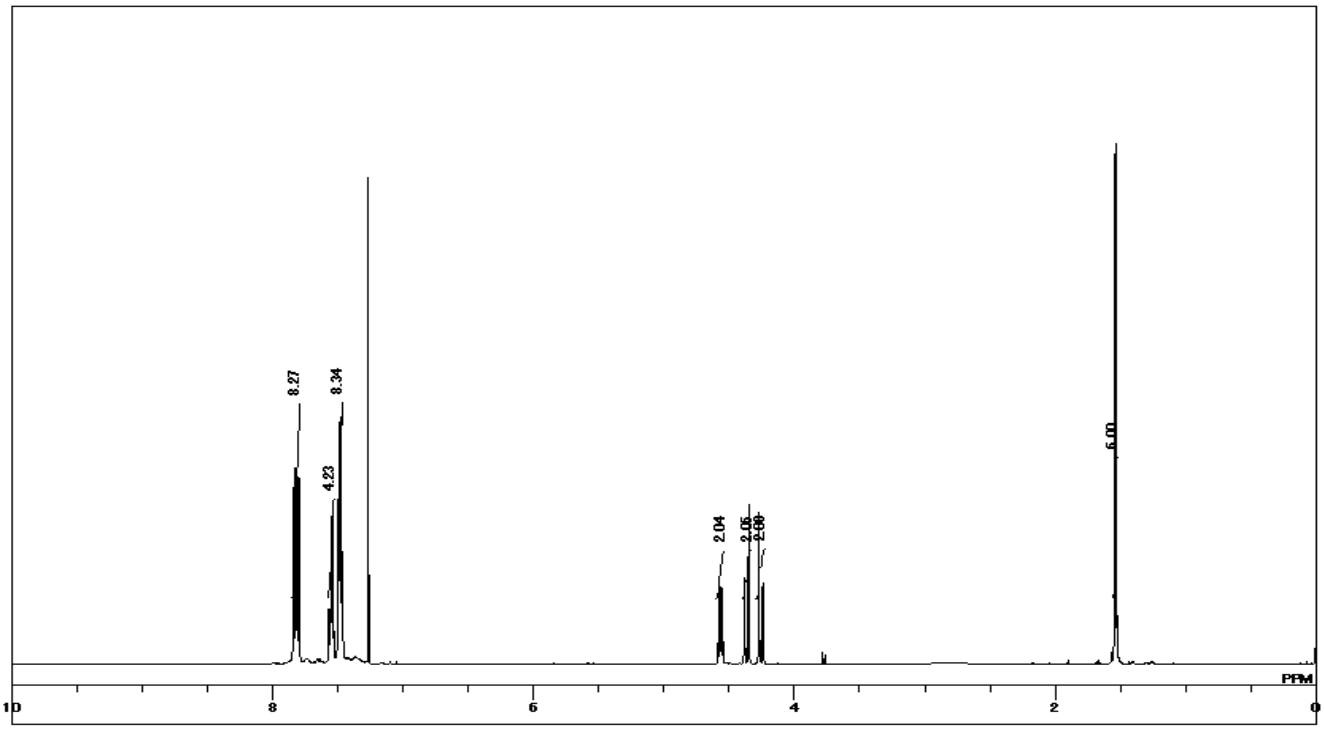


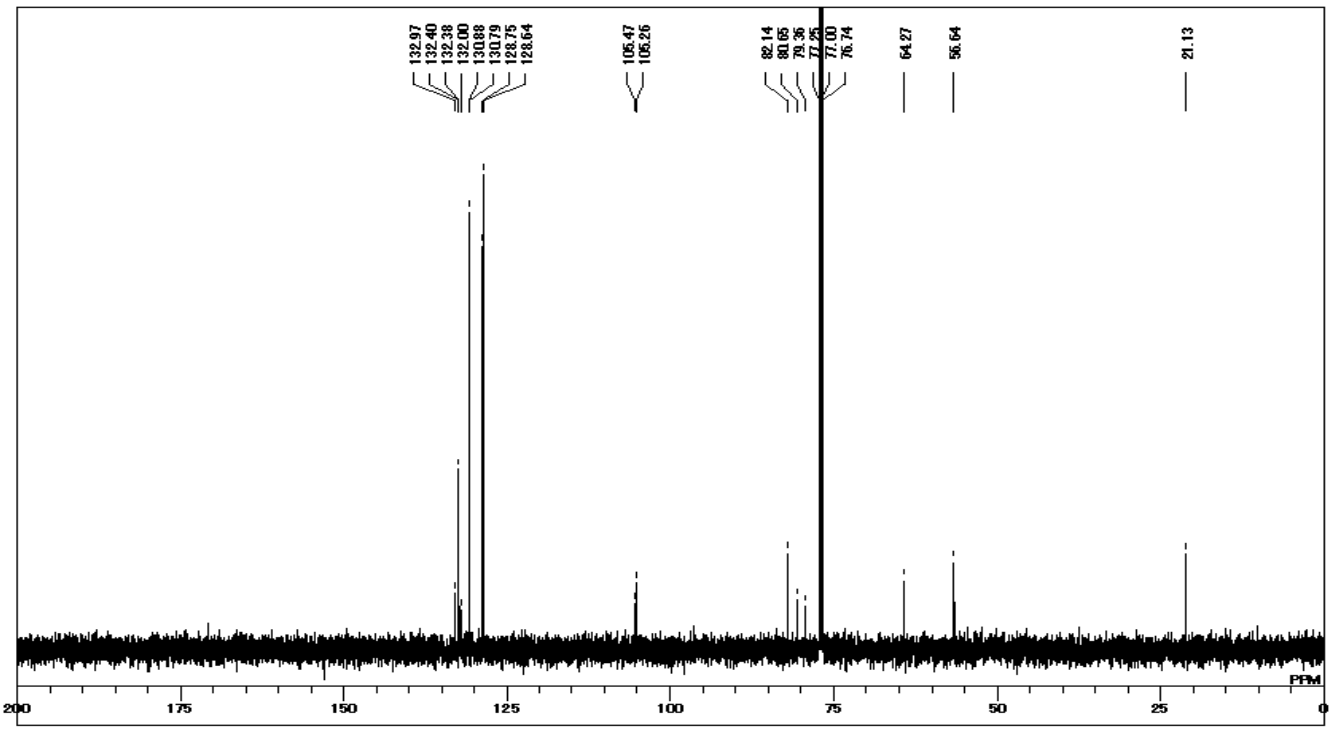




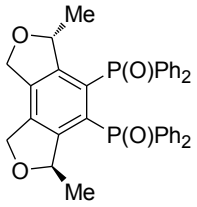
Chiral Triyne Diphosphine Oxide (*R*,*R*)-(+)-4b

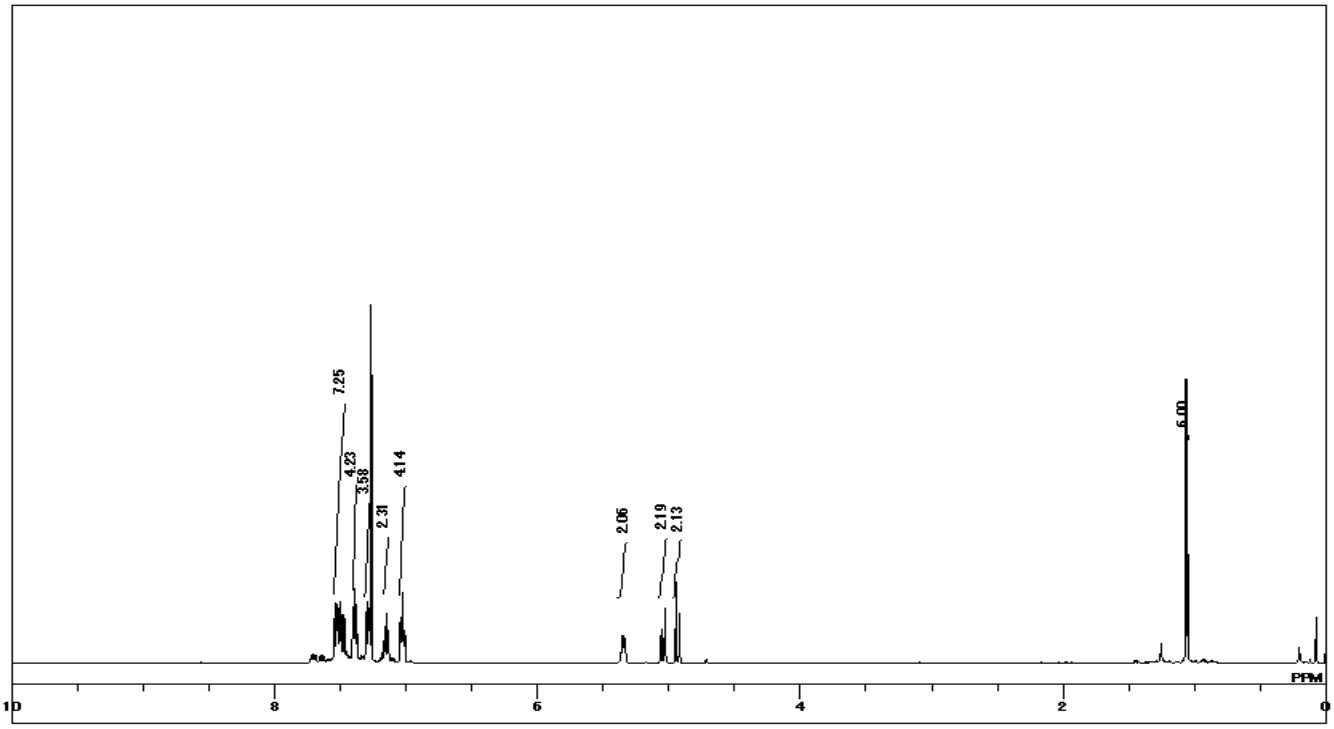


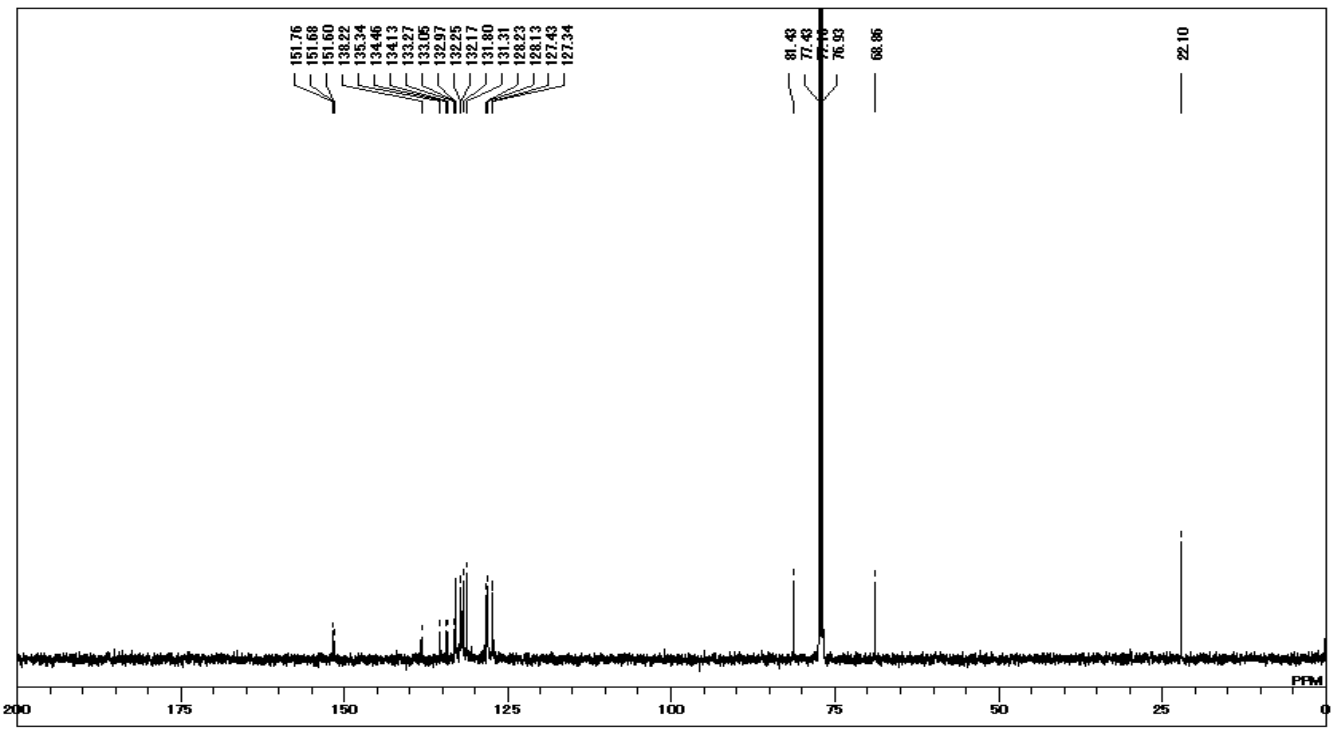




Chiral Diphosphine Oxide (*R*,*R*)-(+)-5b







Chiral Diphosphine (*R*,*R*)-(+)-6b