Pergamon

Tetrahedron: *Asymmetry* 9 (1998) 1779–1787

TETRAHEDRON: *ASYMMETRY*

Synthesis and application of novel chiral phosphino-oxazoline ligands with 1,1′-binaphthyl skeleton

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Received 27 March 1998; accepted 31 March 1998

Abstract

C_1-Symmetric phosphino-oxazolines, (*S*,*S*)- and (*S*,*R*)-2-[4-(isopropyl)oxazol-2-yl]-2′-diphenylphosphino-1,1′-binaphthyl, which possess both phosphine and oxazoline moieties, were prepared from racemic binaphthol and enantiomerically pure (*S*)-(+)-2-amino-3-methyl-1-butanol in high yields. Reaction of 1,3-diphenyl-2-propenyl acetate with dimethyl sodiomalonate in the presence of 2 mol% of palladium catalysts bearing the new chiral ligands proceeded with high enantioselectivity to give allylic alkylation products of up to 91% ee.

1. Introduction

The progress of transition metal-catalyzed asymmetric synthesis has been linked closely with the development of chiral ligands.[1] The idea of C_2-symmetric bidentate ligands, which was originated by Kagan in the form of diop in 1971,[2] was an epoch-making concept, since their symmetry can greatly simplify the structure of their transition metal complexes and reduce the number of possible species. C_2-Symmetry is important for the design of efficient chiral ligands, and high enantioselectivity has actually been observed with the C_2-symmetric bidentate ligands.[1] However, as consumer demand grows for steric control in asymmetric reactions, a more elaborate design of chiral ligands is required in some cases. Recently, several new C_1-symmetric ligands have been reported to show fairly promising results.[3–5] One example is the monodentate phosphine ligand MOP, which has the axially chiral binaphthyl backbone and displays several unique features in catalytic asymmetric reactions.[6] The 1,1′-binaphthyl backbone has also been applied to several chiral ligands and used successfully in a wide range of reactions. Representative examples are binap,[7] binaphos,[5c] and boxax.[8]

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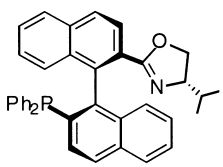
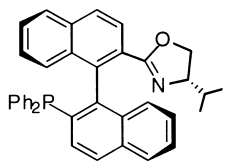
0957-4166/98/$19.00
PII: S0957-4166(98)00136-0

On the other hand, another approach to the C_1-symmetric chiral ligands can be seen in the development of so-called P–N ligands, which include phosphinophenyloxazolines[3] and their ferrocene analogues.[4] The phosphine (P donor) and the oxazoline (N donor) moieties in those ligands possess completely different electronic characteristics to each other, and they produce two distinctive coordination sites in the transition metal complexes upon their coordination. Based on this historical background, we designed and synthesized the new chiral phosphino-oxazoline ligands with binaphthyl skeletons **1a** and **1b**. Here we report their synthetic procedures and their application to the palladium-catalyzed asymmetric allylic alkylation.[9]



(*S,S*)-**1a**



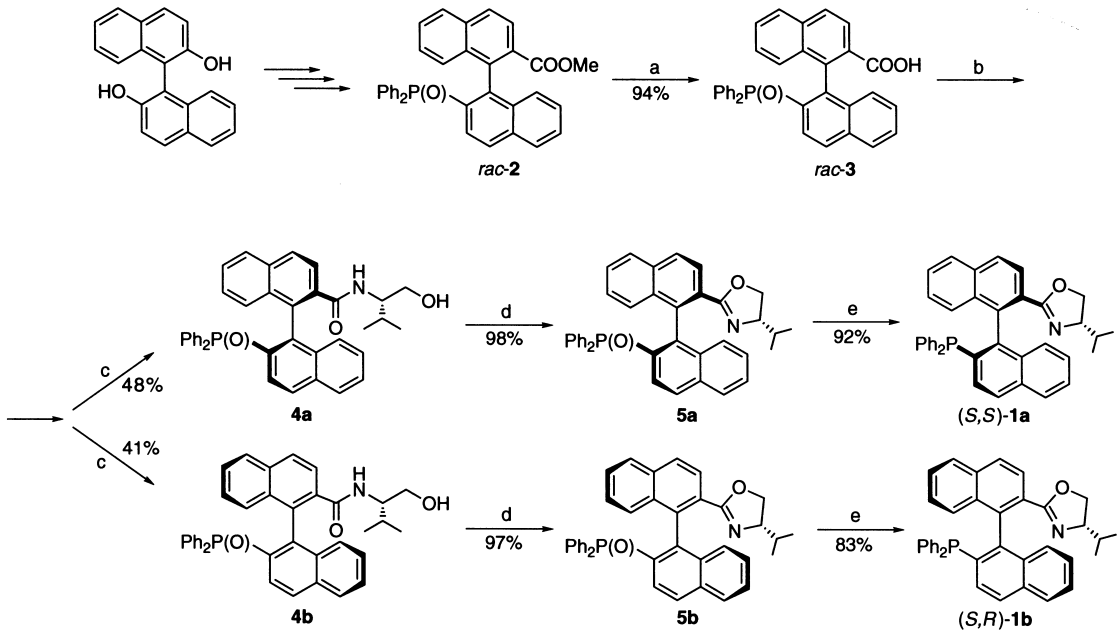
(*S,R*)-**1 b**

2. Results and discussion

2.1. Synthesis and characterization of phosphino-oxazoline ligands

A successful synthetic route to the new phosphino-oxazoline ligands is outlined in Scheme 1. All the reactions proceeded in excellent isolated yields and the final products were obtained readily from the known racemic compound, 2-methoxycarbonyl-2′-diphenylphosphinyl-1,1′-binaphthyl **2**,[10] on a multi-gram scale in 81% (for (*S,S*)-isomer **1a**) and 62% (for (*S,R*)-isomer **1b**) overall yield. The synthetic strategy described in Scheme 1 possesses several advantageous features: (1) it can furnish both (*S,S*)- and (*S,R*)-diastereomers at the same time; (2) the starting binaphthyl building block is racemic binaphthol, i.e. one can avoid using expensive enantiomerically pure binaphthyl compounds; (3) the synthetic procedures were performed on the compounds substituted with a diphenylphosphinyl group (phosphine oxide) as a phosphorus containing moiety until the final stage of the synthetic route. Thus, most of the intermediary products can be handled in air without loss of their purity and/or yield. This characteristic is especially important for scale-up of the reactions.

The starting methyl ester **2**, which was reported by us previously in an enantiomerically pure form, was obtained as a racemic compound from racemic binaphthol according to the reported procedures.[10] The racemic ester was hydrolyzed by a methanolic KOH solution to give racemic carboxylic acid **3** in 94% yield after recrystallization from hot chloroform. The carboxylic acid **3** was condensed with enantiomerically pure (*S*)-(+)-2-amino-3-methyl-1-butanol ((*S*)-valinol) in the presence of 1-hydroxylbenzotriazole (HOBt) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI) in DMF, which is a standard method widely used for peptide synthesis,[11] to give a mixture of a pair of diastereoisomeric amides **4a** and **4b** almost quantitatively. The diastereoisomers were readily separated by column chromatography on silica gel (eluent: hexane/EtOAc=1/5), and their absolute configurations were determined as (*S,S*) for **4a** (eluted first) and (*S,R*) for **4b** (eluted second) in comparison with the amide which was independently synthesized from enantiomerically pure (*S*)-**2** and (*S*)-valinol. The separated amides **4a** and **4b** were subjected to the oxazoline ring formation by treatment with triethylamine and methanesulfonyl chloride in the presence of a catalytic amount of 4-dimethylaminopyridine in dichloromethane. Both of the crude phosphinyl-oxazoline ligands **5a** and **5b** could be purified by silica gel column chromatography with hexane–EtOAc–NEt_3 as an eluent, and obtained in an analytically pure form in 98% and 97%



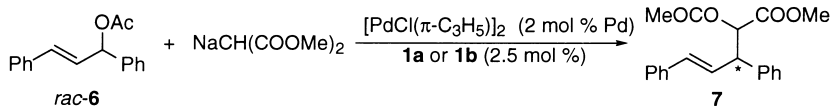
[a] KOH in MeOH–H_2O; [b] (*S*)-valinol, EDCI, HOBt in DMF; [c] Chromatography on silica gel with hexane/EtOAc; [d] MsCl, DMAP, Et_3N in CH_2Cl_2; [e] $HSiCl_3$, NEt_3 in refluxed toluene.

Scheme 1.

isolated yields, respectively. Addition of triethylamine to the eluent was essential for the protection of the oxazoline rings, which were sensitive to ring-opening under acidic conditions. The reduction of the phosphine-oxide in **5a** and **5b** was achieved by a standard silane reduction using trichlorosilane and triethylamine in refluxing toluene. Successive column chromatography under nitrogen and recrystallization from absolute ethanol (for **1a**) or Et_2O–CH_2Cl_2 (for **1b**) afforded the analytically pure phosphinooxazoline ligands (*S,S*)-**1a** and (*S,R*)-**1b** in 92% and 83% yield, respectively.

2.2. Palladium-catalyzed asymmetric allylic alkylation

Both of the diastereomeric ligands were examined in the enantioselective allylic substitution reaction catalyzed by palladium complexes.[9] It was found that a palladium complex generated in situ from $[PdCl(\pi\text{-}C_3H_5)]_2$ and **1b** (1.25 equiv. to Pd) was an effective catalyst for asymmetric allylic alkylation of racemic 1,3-diphenyl-2-propenyl acetate **6** with the sodium salt of dimethyl malonate (Scheme 2). The alkylation proceeded smoothly, even at −20°C, with high enantioselectivity to afford the product **7** whose enantiomeric excess was 91% (entry 6 in Table 1). The absolute configuration (*R*) was determined by comparison of the specific rotation ($[\alpha]_D^{20}$ +14.7 (*c* 1.10, EtOH) for the product from entry 4) with that reported for (*S*)-**7**[12] and the enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column (Chiralcel OD-H, hexane/2-propanol=98/2). The catalyst coordinated with **1a** showed slightly better catalytic activity (i.e. a faster reaction) than with **1b**, but the enantioselectivity was much lower. Interestingly, ligand **1a** has (*S*) axial chirality on the binaphthyl induced (*S*) configuration in product **7** (entry 1–3), while its diastereomeric ligand **1b** has (*R*) axial chirality induced (*R*) configuration (entry 4–6). This observation indicates that the axial chirality in ligands **1a** and **1b** is the more influential factor determining the stereochemical outcome in the allylic alkylation than the central chirality in the oxazoline unit.



Scheme 2.

Table 1
Asymmetric allylic alkylation of *rac*-**6** catalyzed by phosphino-oxazoline–palladium complexes[a]

entry	ligand	temp/°C	time/h	yield/%[b]	% ee[c] (config[d])
1	**1a**	20	3.5	>99	28 (*S*)
2	**1a**	0	1.5	>99	27 (*S*)
3	**1a**	–20	18	95	28 (*S*)
4	**1b**	20	2.0	>99	86 (*R*)
5	**1b**	0	24	87	85 (*R*)
6	**1b**	–20	48	>99	91 (*R*)

[a] The reaction was carried out in THF in the presence of 2 mol % of the catalyst generated *in situ* from $[PdCl(\pi\text{-}C_3H_5)]_2$ and the ligand. [b] Isolated yield by silica gel chromatography. [c] Determined by HPLC analysis with chiral stationary phase column, Daicel Chiralcel OD-H (hexane/2-propanol = 98/2). [d] Determined based on the sign of the specific rotation of the product **7**.[12]

3. Experimental

3.1. General

The reactions, which required anaerobic conditions, were carried out with standard Schlenk techniques under predried (P_2O_5; Merck, SICAPENT) nitrogen. Reaction progress was monitored by analytical thin-layer chromatography (TLC) using 0.25 mm Merck F-254 silica gel glass plates. Visualization of the TLC plates was achieved by an UV illumination. NMR spectra were recorded on a JEOL JNM LA500 spectrometer (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{31}P, 202 MHz). ^{1}H NMR chemical shifts are reported in ppm downfield of internal tetramethylsilane. ^{13}C NMR chemical shifts are relative to tetramethylsilane with the use of solvent resonances ($CDCl_3$, δ 77.05) as internal standards. ^{31}P NMR chemical shifts are externally referenced to 85% H_3PO_4. Optical rotations were measured on a JASCO DIP-370 polarimeter.

3.2. Materials

Compounds **2**,[11] $[PdCl(\pi\text{-}C_3H_5)]_2$,[13] and **6**[14] were prepared according to previous reports. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from sodium/benzophenone ketyl under N_2 prior to use. Dichloromethane was distilled from calcium hydride under nitrogen prior to use. Methanol (MeOH) was dried over magnesium methoxide, distilled, and stored over 4 Å molecular sieves. All other solvents were used as received. (*S*)-(+)-2-Amino-3-methyl-1-butanol (*S*-valinol) was prepared from (*S*)-valine and $LiAlH_4$. 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride, 1-hydroxybenzotriazole,

4-dimethylaminopyridine, methanesulfonyl chloride, and triethylamine were purchased from Nacalai Tesque, Japan, and used without purification. Trichlorosilane was purchased from Tokyo Chemical Industry Co. and used as received.

3.3. rac-2′-Diphenylphosphinyl-1,1′-binaphthyl-2-carboxylic acid **3**

To a methanol solution of **2** (5.00 g, 9.76 mmol in 150 mL) was added 30 mL of an aqueous KOH solution (40%), and the mixture was refluxed for 12 h. After cooling to 0°C, the reaction mixture was acidified to ca. pH=2 with conc HCl. The separated solid was extracted with $CHCl_3$ three times, and the combined organic layer was dried over anhydrous Na_2SO_4. After filtration, the filtrate was evaporated to dryness to give a slightly yellow residue. The crude material was recrystallized from hot chloroform to give the analytically pure compound as a white solid. Yield: 4.56 g (9.15 mmol, 94%). ^{1}H NMR ($CDCl_3$, 23°C): δ 6.21 (d, *J*=8.4 Hz, 1H), 6.66 (t, *J*=7.7 Hz, 1H), 6.98 (dt, *J*=3.0 and 7.7 Hz, 2H), 7.11–7.19 (m, 5H), 7.29 (t, *J*=8.4 Hz, 1H), 7.32 (dd, *J*=8.7 and 12.4 Hz, 1H), 7.52–7.55 (m, 3H), 7.63–7.66 (m, 2H), 7.72–7.78 (m, 3H), 7.90 (d, *J*=8.1 Hz, 1H), 7.93 (d, *J*=8.7 Hz, 1H), 7.94 (dd, *J*=2.7 and 8.7 Hz, 1H), 14.66 (br, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 23°C): δ 123.8 (s), 126.0 (s), 126.4 (d, J_{CP}=23.9 Hz), 126.9 (s), 127.1 (s), 127.5 (d, J_{CP}=9.2 Hz), 127.6 (s), 127.8 (s), 127.9 (d, J_{CP}=1.1 Hz), 128.1 (d, J_{CP}=13.0 Hz), 128.1 (d, J_{CP}=1.1 Hz), 128.2 (s), 128.8 (d, J_{CP}=12.5 Hz), 128.9 (s), 128.9 (d, J_{CP}=11.9 Hz), 129.6 (s), 129.8 (d, J_{CP}=4.9 Hz), 130.1 (s), 130.9 (d, J_{CP}=9.8 Hz), 131.5 (s), 131.8 (d, J_{CP}=3.3 Hz), 132.3 (d, J_{CP}=9.8 Hz), 132.7 (d, J_{CP}=2.7 Hz), 132.9 (s), 133.7 (d, J_{CP}=11.4 Hz), 134.9 (d, J_{CP}=2.2 Hz), 135.5 (s), 142.4 (d, J_{CP}=8.1 Hz), 171.5 (s). ^{31}P{^{1}H} NMR ($CDCl_3$, 22°C): δ 35.1 (s). Anal. calcd for $C_{33}H_{23}O_3P$: C, 79.51; H, 4.65. Found: C, 79.42; H, 4.58.

3.4. (S,S)- and (S,R)-N-(1-Hydroxymethyl-2-methylpropyl)-2′-diphenylphosphinyl-1,1′-binaphthyl-2-carboxylamide **4a** and **4b**

A mixture of **3** (4.49 g, 9.01 mmol), (*S*)-(+)-2-amino-3-methyl-1-butanol (1.86 g, 18.0 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (5.18 g, 27.0 mmol), and 1-hydroxybenzotriazole (4.87 g, 36.0 mmol) in *N*,*N*-dimethylformamide (500 mL) was stirred at 0°C for 30 min, and then at room temperature for 4 h. Most of the solvent was removed from the flask under reduced pressure. The resulting residue was diluted with $CHCl_3$, and washed with saturated NaCl solution twice. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo to leave a slightly yellow viscous oil, which contained both **4a** and **4b** as the main products. The two diastereomers were separated by column chromatography on silica gel (hexane/EtOAc=1/5 as an eluent). The (*S*,*S*)-isomer **4a**, which was eluted first, was further purified by recrystallization from chloroform/hexane, yielding colorless needles. Although the (*S*,*R*)-isomer **4b** was obtained as a colorless viscous oil after a second chromatography on silica gel (eluent: chloroform/acetone), an analytically pure compound could not be obtained because of the low crystallinity. **4a**: Yield: 2.53 g (4.34 mmol, 48%), mp 202–205°C. ^{1}H NMR ($CDCl_3$, 21°C): δ 0.96 (d, *J*=6.8 Hz, 3H), 1.03 (d, *J*=6.8 Hz, 3H), 1.95–2.05 (m, 1H), 3.14 (ddd, *J*=2.7, 5.9 and 11.7 Hz, 1H), 3.34 (ddd, *J*=4.9, 8.1 and 11.7 Hz, 1H), 3.54 (ddt, *J*=2.7, 4.6 and 8.8 Hz, 1H), 3.63 (br, 1H), 6.56 (d, *J*=8.5 Hz, 1H), 6.76 (dt, *J*=3.2 and 8.1 Hz, 2H), 6.85 (ddd, *J*=1.2, 6.8 and 8.5 Hz, 1H), 6.94 (dt, *J*=1.5 and 7.3 Hz, 1H), 7.07 (d, *J*=12.2, 1H), 7.09 (d, *J*=12.2 Hz, 1H), 7.17 (ddd, *J*=1.0, 6.8 and 8.3 Hz, 1H), 7.23 (d, *J*=8.5 Hz, 1H), 7.30 (ddd, *J*=1.2, 6.8 and 8.5 Hz, 1H), 7.47–7.58 (m, 6H), 7.66 (d, *J*=8.5 Hz, 1H), 7.78 (d, *J*=8.5 Hz, 1H), 7.82 (dd, *J*=1.5 and 11.5 Hz, 1H), 7.84 (d, *J*=11.5 Hz, 1H), 7.89 (d *J*=8.1 Hz, 1H), 7.94 (dd, *J*=2.4 and 8.8 Hz, 1H), 8.40 (d, *J*=9.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 22°C): δ 19.7 (s), 19.7 (s), 29.0 (s), 57.6 (s), 63.0 (s), 124.2 (s), 125.8 (s), 126.1 (s), 127.0 (s), 127.4 (d,

J_{CP}=13.0 Hz), 127.7 (d, J_{CP}=16.8 Hz), 127.7 (s), 127.9 (d, J_{CP}=13.0 Hz), 128.0 (s), 128.2 (d, J_{CP}=12.5 Hz), 128.6 (s), 128.7 (d, J_{CP}=11.9 Hz), 128.7 (s), 129.1 (s), 129.4 (s), 130.2 (d, J_{CP}=9.8 Hz), 130.7 (d, J_{CP}=2.7 Hz), 131.1 (d, J_{CP}=4.9 Hz), 131.5 (s), 132.0 (s), 132.1 (d, J_{CP}=9.2 Hz), 132.2 (s), 132.3 (s), 132.8 (s), 133.8 (d, J_{CP}=11.4 Hz), 134.5 (d, J_{CP}=2.2 Hz), 137.8 (s), 143.3 (d, J_{CP}=8.1 Hz), 170.1 (s). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 22°C): δ 30.1 (s). $[\alpha]^{20}_D$ −62.7 (*c* 1.01, $CHCl_3$). Anal. calcd for $C_{38}H_{34}O_3NP$: C, 78.20; H, 5.87; N, 2.40. Found: C, 77.90; H, 5.76; N, 2.48. **4b**: Yield: 2.17 g (3.72 mmol, 41%), mp 117–120°C. ^1H NMR ($CDCl_3$, 21°C): δ −0.10 (d, *J*=6.8 Hz, 3H), 0.53 (d, *J*=6.8 Hz, 3H), 1.16–1.25 (m, 1H), 3.51–3.59 (m, 2H), 3.71–3.74 (m, 1H), 4.24 (br, 1H), 6.58 (d, *J*=8.3 Hz, 1H), 6.73 (dt, *J*=3.2 and 7.8 Hz, 2H), 6.90–6.95 (m, 2H), 7.08–7.12 (m, 2H), 7.16 (d, *J*=8.8 Hz, 1H), 7.20 (t, *J*=7.1 Hz, 1H), 7.29 (t, *J*=7.1 Hz, 1H), 7.51–7.60 (m, 6H), 7.74 (d, *J*=8.5 Hz, 1H), 7.87 (d, *J*=11.5 Hz, 1H), 7.89 (d, *J*=11.5 Hz, 1H), 7.92 (d, *J*=8.3 Hz, 1H), 7.97 (d, *J*=8.8 Hz, 1H), 7.98 (dd, *J*=2.2 and 8.8 Hz, 1H), 8.28 (d, *J*=8.1 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23°C): δ 18.4 (s), 19.1 (s), 29.2 (s), 57.9 (s), 63.3 (s), 126.1 (s), 126.1 (d, J_{CP}=1.6 Hz), 127.0 (s), 127.3 (s), 127.3 (d, J_{CP}=12.5 Hz), 127.7 (s), 127.8 (s), 128.1 (s), 128.2 (d, J_{CP}=13.0 Hz), 128.6 (d, J_{CP}=11.9 Hz), 128.8 (d, J_{CP}=11.9 Hz), 128.9 (s), 129.0 (d, J_{CP}=9.8 Hz), 129.4 (s), 129.8 (s), 130.2 (d, J_{CP}=9.8 Hz), 130.7 (d, J_{CP}=3.3 Hz), 130.8 (d, J_{CP}=4.9 Hz), 131.2 (s), 132.0 (s), 132.1 (d, J_{CP}=9.2 Hz), 132.2 (s), 132.2 (d, J_{CP}=17.4 Hz), 133.3 (s), 133.3 (d, J_{CP}=11.4 Hz), 135.0 (d, J_{CP}=2.2 Hz), 136.3 (s), 143.0 (d, J_{CP}=8.7 Hz), 168.5 (s). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 23°C): δ 30.2 (s). $[\alpha]^{20}_D$ +39.8 (*c* 1.01, $CHCl_3$). Anal. calcd for $C_{38}H_{34}O_3NP$: C, 78.20; H, 5.87; N, 2.40. Found: C, 77.19; H, 5.97; N, 2.15.

3.5. (S,S)-2-[4-(Isopropyl)oxazol-2-yl]-2′-diphenylphosphinyl-1,1′-binaphthyl ***5a***

To a mixture of **4a** (2.27 g, 3.89 mmol), 4-dimethylaminopyridine (5.0 mg, 0.041 mmol), and triethylamine (791 mg, 1.09 mL, 7.82 mmol) in dichloromethane (50 mL) was added methanesulfonyl chloride (888 mg, 0.60 mL, 7.75 mmol) at 0°C, and the solution was stirred for 30 min at this temperature. Then another portion of triethylamine (3.56 g, 4.91 mL, 35.2 mmol) was added to the solution, and it was refluxed until the initially formed mesylate disappeared (checked by TLC). On cooling to room temperature, the reaction mixture was diluted with $CHCl_3$ and washed with an aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to give a slightly yellow residue, which was chromatographed on silica gel (elution with hexane/EtOAc/Et_3N=7/14/1) to give **5a** in pure form. Yield: 2.16 g (3.82 mmol, 98%), mp 221–225°C. ^1H NMR ($CDCl_3$, 21°C): δ 0.37 (d, *J*=6.8 Hz, 3H), 0.54 (d, *J*=6.8 Hz, 3H), 1.14–1.20 (m, 1H), 3.67–3.73 (m, 2H), 3.89–3.95 (m, 1H), 6.99 (dt, *J*=2.9 and 7.8 Hz, 2H), 7.02 (d, *J*=9.0 Hz, 1H), 7.15–7.22 (m, 4H), 7.24–7.29 (m, 4H), 7.37 (dt, *J*=1.5 and 7.3 Hz, 1H), 7.41 (ddd, *J*=2.0, 5.9 and 8.1 Hz, 1H), 7.45–7.48 (m, 1H), 7.60 (dd, *J*=1.2 and 11.7 Hz, 1H), 7.61 (d, *J*=11.7 Hz, 1H), 7.68 (d, *J*=8.5 Hz, 1H), 7.72 (d, *J*=8.3 Hz, 1H), 7.77 (dd, *J*=8.8 and 11.7 Hz, 1H), 7.84 (d, *J*=8.5 Hz, 1H), 7.87 (d, *J*=8.1 Hz, 1H), 7.92 (dd, *J*=1.7 and 8.8 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23°C): δ 17.8 (s), 18.6 (s), 32.8 (s), 69.7 (s), 72.9 (s), 125.6 (s), 126.4 (s), 126.6 (d, J_{CP}=3.6 Hz), 126.9 (s), 127.0 (d, J_{CP}=12.4 Hz), 127.1 (s), 127.2 (s), 127.6 (d, J_{CP}=3.1 Hz), 127.7 (s), 127.8 (d, J_{CP}=2.1 Hz), 128.5 (s), 128.9 (s), 128.9 (d, J_{CP}=11.4 Hz), 129.7 (s), 130.7 (d, J_{CP}=3.1 Hz), 131.0 (d, J_{CP}=3.1 Hz), 131.7 (d, J_{CP}=9.8 Hz), 132.1 (d, J_{CP}=9.8 Hz), 132.6 (s), 133.0 (s), 133.1 (s), 133.5 (s), 133.6 (s), 134.0 (s), 134.5 (d, J_{CP}=2.1 Hz), 134.8 (s), 136.4 (d, J_{CP}=4.7 Hz), 143.3 (d, J_{CP}=7.8 Hz), 162.3 (s). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 23°C): δ 27.5 (s). $[\alpha]^{20}_D$ −254 (*c* 1.01, $CHCl_3$). Anal. calcd for $C_{38}H_{32}O_2NP$: C, 80.69; H, 5.70; N, 2.48. Found: C, 80.44; H, 5.59; N, 2.33.

3.6. (S,R)-2-[4-(Isopropyl)oxazol-2-yl]-2′-diphenylphosphinyl-1,1′-binaphthyl **5b**

This compound was prepared from **4b** (2.17 g, 3.72 mmol), 4-dimethylaminopyridine (4.5 mg, 0.037 mmol), triethylamine (753 mg, 1.04 mL, 7.44 mmol), methanesulfonyl chloride (1.49 g, 1.01 mL, 13.0 mmol), and an additional portion of triethylamine (3.39 g, 4.67 mL, 33.5 mmol) in dichloromethane as described above. The final purification was performed by column chromatography on silica gel (elution with hexane/EtOAc/Et_3N=5/15/1). Yield: 2.03 g (3.59 mmol, 97%), mp 232–235°C. ^{1}H NMR ($CDCl_3$, 21°C): δ 0.54 (d, *J*=6.6 Hz, 3H), 0.59 (d, *J*=6.8 Hz, 3H), 1.44–1.53 (m, 1H), 3.45 (t, *J*=8.1 Hz, 1H), 3.69–3.74 (m, 1H), 3.96 (dd, *J*=8.3 and 9.8 Hz, 1H), 7.08–7.14 (m, 7H), 7.21 (ddd, *J*=1.0, 6.6 and 8.5 Hz, 1H), 7.24–7.27 (m, 2H), 7.36 (ddd, *J*=1.5, 6.6 and 8.1 Hz, 1H), 7.39–7.43 (m, 4H), 7.48 (t, *J*=7.1 Hz, 1H), 7.68 (d, *J*=8.5 Hz, 2H), 7.74 (dd, *J*=8.8 and 11.5 Hz, 1H), 7.88 (d, *J*=8.3 Hz, 1H), 7.91 (d, *J*=8.8 Hz, 1H), 7.93 (dd, *J*=2.0 and 8.5 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 23°C): δ 17.7 (s), 18.8 (s), 32.3 (s), 69.9 (s), 72.3 (s), 126.2 (d, J_{CP}=15.0 Hz), 126.7 (s), 126.8 (s), 126.8 (s), 127.2 (d, J_{CP}=11.9 Hz), 127.3 (s), 127.5 (d, J_{CP}=15.5 Hz), 127.5 (s), 127.7 (d, J_{CP}=2.6 Hz), 127.7 (d, J_{CP}=4.7 Hz), 128.6 (s), 128.8 (d, J_{CP}=11.9 Hz), 129.4 (s), 130.8 (s), 130.8 (d, J_{CP}=5.2 Hz), 131.6 (d, J_{CP}=15.5 Hz), 131.7 (d, J_{CP}=15.0 Hz), 132.9 (s), 133.2 (s), 133.3 (s), 133.5 (s), 133.5 (s), 133.7 (s), 133.9 (s), 134.0 (s), 134.2 (d, J_{CP}=2.6 Hz), 135.5 (d, J_{CP}=5.2 Hz), 143.2 (d, J_{CP}=7.8 Hz), 163.9 (s). ^{31}P{^{1}H} NMR ($CDCl_3$, 22°C): δ 28.0 (s). $[\alpha]^{20}_D$ +98.1 (*c* 1.00, $CHCl_3$). Anal. calcd for $C_{38}H_{32}O_2NP$: C, 80.69; H, 5.70; N, 2.48. Found: C, 80.13; H, 5.64; N, 2.51.

3.7. (S,S)-2-[4-(Isopropyl)oxazol-2-yl]-2′-diphenylphosphino-1,1′-binaphthyl **1a**

To a mixture of **5a** (2.00 g, 3.54 mmol) and triethylamine (10.7 g, 14.8 mL, 106 mmol) in toluene (60 mL) was added trichlorosilane (4.79 g, 3.57 mL, 35.4 mmol) at 0°C, and the solution was stirred for 30 min at this temperature. It was then refluxed for 2 h (checked with TLC) under nitrogen. After cooling to 0°C, the reaction mixture was diluted with Et_2O and quenched with a small amount of saturated aqueous $NaHCO_3$ solution. The resulting suspension was filtered through a pad of Celite and the filter cake was washed with Et_2O, then the filtrate was concentrated under reduced pressure. The crude product was chromatographed on silica gel (pretreated with an Et_2O/Et_3N solution) under a nitrogen atmosphere using Et_2O as an eluent to give analytically pure **1a**. Yield: 1.80 g (3.27 mmol, 92%), mp 152–155°C. ^{1}H NMR ($CDCl_3$, 22°C): δ 0.44 (d, *J*=6.6 Hz, 3H), 0.52 (d, *J*=6.8 Hz, 3H), 1.17–1.24 (m, 1H), 3.54 (t, *J*=7.8 Hz, 1H), 3.61 (ddd, *J*=6.6, 7.8 and 9.5 Hz, 1H), 3.78 (dd, *J*=7.8 and 9.5 Hz, 1H), 6.94 (d, *J*=8.1 Hz, 1H), 6.97 (ddd, *J*=1.2, 6.6 and 8.5 Hz, 1H), 7.06–7.28 (m, 12H), 7.37–7.43 (m, 2H), 7.49 (dd, *J*=2.9 and 8.5 Hz, 1H), 7.84 (d, *J*=8.5 Hz, 2H), 7.89 (d, *J*=8.3 Hz, 1H), 8.00 (d, *J*=8.8 Hz, 1H), 8.16 (d, *J*=8.5 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 23°C): δ 18.0 (s), 18.5 (s), 32.8 (s), 69.8 (s), 72.7 (s), 125.7 (d, J_{CP}=2.6 Hz), 126.1 (s), 126.1 (s), 126.5 (s), 126.7 (d, J_{CP}=2.6 Hz), 126.9 (s), 127.5 (s), 127.6 (d, J_{CP}=1.9 Hz), 127.8 (s), 127.8 (d, J_{CP}=5.7 Hz), 128.0 (d, J_{CP}=10.9 Hz), 128.1 (d, J_{CP}=7.2 Hz), 128.2 (s), 130.5 (d, J_{CP}=2.6 Hz), 133.0 (d, J_{CP}=8.3 Hz), 133.2 (s), 133.4 (s), 133.5 (d, J_{CP}=2.6 Hz), 133.5 (s), 133.8 (d, J_{CP}=20.2 Hz), 134.2 (s), 135.0 (d, J_{CP}=9.3 Hz), 137.7 (s), 137.8 (s), 138.5 (s), 138.7 (d, J_{CP}=18.6 Hz), 138.9 (s), 145.3 (d, J_{CP}=35.2 Hz), 162.7 (s). ^{31}P{^{1}H} NMR ($CDCl_3$, 23°C): δ −14.2 (s). $[\alpha]^{20}_D$ −142 (*c* 1.00, $CHCl_3$). Anal. calcd for $C_{38}H_{32}ONP$: C, 83.04; H, 5.87; N, 2.55. Found: C, 83.07; H, 5.95; N, 2.44.

3.8. (S,R)-2-[4-(Isopropyl)oxazol-2-yl]-2′-diphenylphosphino-1,1′-binaphthyl **1b**

This compound was prepared from **5b** (1.80 g, 3.18 mmol), triethylamine (10.3 g, 14.2 mL, 102 mmol) and trichlorosilane (4.32 g, 3.22 mL, 31.9 mmol) in toluene (55 mL) and purified as described above.

An analytically pure sample was obtained by recrystallization from Et_2O–CH_2Cl_2. Yield: 1.45 g (2.64 mmol, 83%), mp 165–167°C. ^{1}H NMR ($CDCl_3$, 22°C): δ 0.51 (d, *J*=6.8 Hz, 3H), 0.57 (d, *J*=6.8 Hz, 3H), 1.31–1.41 (m, 1H), 3.32 (t, *J*=8.1 Hz, 1H), 3.57 (ddd, *J*=6.3, 7.8 and 9.8 Hz, 1H), 3.69 (dd, *J*=8.1 and 9.8 Hz, 1H), 6.95 (d, *J*=8.5 Hz, 1H), 6.99–7.04 (m, 3H), 7.10–7.14 (m, 2H), 7.16–7.27 (m, 8H), 7.39 (ddd, *J*=1.2, 6.6 and 8.3 Hz, 1H), 7.43 (ddd, *J*=1.5, 6.3 and 8.3 Hz, 1H), 7.48 (dd, *J*=2.9 and 8.5 Hz, 1H), 7.84 (d, *J*=8.5 Hz, 2H), 7.89 (d, *J*=8.1 Hz, 1H), 7.99 (d, *J*=8.8 Hz, 1H), 8.13 (d, *J*=8.5 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 23°C): δ 17.7 (s), 18.6 (s), 32.4 (s), 70.0 (s), 72.0 (s), 126.2 (d, J_{CP}=8.8 Hz), 126.5 (d, J_{CP}=22.2 Hz), 126.8 (d, J_{CP}=2.6 Hz), 126.8 (s), 127.3 (d, J_{CP}=2.6 Hz), 127.6 (s), 127.6 (s), 127.7 (s), 127.9 (s), 128.0 (s), 128.0 (s), 128.0 (s), 128.0 (s), 128.1 (s), 128.2 (s), 130.2 (d, J_{CP}=2.1 Hz), 133.2 (d, J_{CP}=1.0 Hz), 133.3 (d, J_{CP}=2.6 Hz), 133.4 (d, J_{CP}=7.8 Hz), 133.5 (d, J_{CP}=20.2 Hz), 133.5 (d, J_{CP}=19.1 Hz), 134.1 (s), 134.8 (d, J_{CP}=10.9 Hz), 138.0 (s), 138.1 (s), 138.1 (s), 138.2 (d, J_{CP}=8.8 Hz), 144.9 (d, J_{CP}=34.7 Hz), 164.3 (s). ^{31}P{^{1}H} NMR ($CDCl_3$, 23°C): δ −14.7 (s). $[\alpha]^{20}_D$ +15.2 (*c* 1.00, $CHCl_3$). Anal. calcd for $C_{38}H_{32}ONP$: C, 83.04; H, 5.87; N, 2.55. Found: C, 82.88; H, 6.12; N, 2.49.

*3.9. Palladium-catalyzed asymmetric allylic alkylation of **6**: typical procedure*

To a mixture of $[PdCl(\pi\text{-}C_3H_5)]_2$ (1.0 mg, 2.7 μmol), **1b** (3.7 mg, 6.7 μmol) and *rac*-**6** (66.6 mg, 264 μmol) in THF (0.1 mL) was added a solution of the sodium salt of dimethyl malonate prepared from dimethyl malonate (66.1 mg, 0.50 mmol) and sodium hydride in THF (2 mL) at −78°C under nitrogen. The flask was then immersed in a bath maintained at −20°C and the solution was stirred for 48 h. The reaction mixture was quenched with a small amount of 5% HCl aqueous solution and evaporated to dryness under reduced pressure. The crude product was purified by preparative TLC on silica gel (eluent: hexane/EtOAc=4/1) to give **7** in pure form, quantitatively. The enantiomeric purity was detemined to be 91% ee by HPLC analysis with a chiral stationary phase column, Chiralcel OD-H (hexane/2-propanol=98/2).

Acknowledgements

This work was supported by ‘Research for the Future’ Program, the Japan Society for the Promotion of Science and a Grant-in-Aid for Scientific Research, the Ministry of Education, Japan.

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