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An N–Ar axially chiral mimetic. A new approach to ligand design for asymmetric catalysis

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Abstract—A new-type chiral ligand, (*S*)-*N*-[2-(diphenylphosphino)naphthyl]-2-(pyrrolidinylmethyl)piperidine mimicking N–Ar axial chirality, has been developed. This chiral ligand was found to exhibit 99% ee with the use of (*E*)-1,3-diphenyl-2-propenyl acetate as the standard substrate, and achieved slightly better results than the Pfaltz and Trost ligands with the use of (*E*)-1-phenyl-3-trimethylsilyl-2-propenyl acetate as the substrate, in the palladium-catalyzed asymmetric allylic substitution.

1. Introduction

In the course of our studies in relation to organic chemistry based on the N–Ar axis,[1,2] we became very interested in the development of a new chiral ligand[3] mimicking N–Ar axial chirality. We designed the ligand **1** on the following concept: the ligand **1** may have two diastereomers due to the N–Ar axis and the chiral carbon in solution (Fig. 1). But, if the N–Ar axis in **1** is configurationally flexible, and the complexation of **1** and a metal is largely reflected by the asymmetric center of pyrrolidinyl group **A** in **1**, one of the two diastereomer complexes due to the N–Ar axis, is expected to be selectively formed (**2a** in Fig. 2), leading to the creation of favorable asymmetric environment. The outcome of this complexation was rationalized by the destabilization of **2b** over **2a** due to an unfavorable interaction in the former between the pendant substituent and the naphthalene ring. Some ligands which are structurally similar to our envisioned ligand **1**, have been reported by Miyano and Hattori,[4] Hiroi,[5] Guiry,[6] and Mino;[7] however, the ability of their ligands was inadequate: even in the standard palladium-catalyzed asymmetric allylic substitution employing (*E*)-1,3-diphenyl-2-propenyl acetate as the substrate and dimethyl malonate as the pronucleophile, the asymmetric induction was moderate.

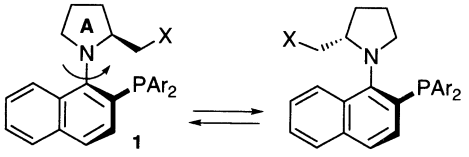


Figure 1.

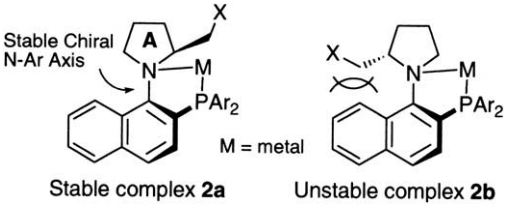
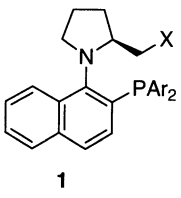


Figure 2.



1a: X=OBn, Ar=Ph
1b: X=NMePh, Ar=Ph
1c: X=NBn_2, Ar=Ph
1d: X=pyrrolidinyl, Ar=Ph
1e: X=pyrrolidinyl, Ar=4-tolyl
1f: X=pyrrolidinyl, Ar=4-CF_3-C_6H_4
1g: X=pyrrolidinyl, Ar=2-naphthyl

2. Results and discussion

The ligands **1a–g** were selected as the test ligands. The preparation of **1d** is representatively shown in Scheme 1. Treatment of the lithium amide generated from the diamine **4** with **3** in THF at 0°C afforded the coupling product **5**, according to the Miyano–Hattori protocol.[8] The phosphinyl group in **5** was then reduced with $HSiCl_3$ in *p*-xylene at 140°C to provide the ligand **1d** in 59% yield (2 steps). The diastereomers of **1d** due to the N–Ar axis and the chiral carbon were not observed by TLC, and by determining the NMR coalescence temperature, an N–Ar rotation barrier of ca. 13 kcal/mol at 0°C was calculated for **1d**. The interconversion process between **1dA** and **1dB** (Fig. 3) may consist not only of the rotation around the N–Ar bond but

Keywords: N–Ar axial chirality; chiral mimetic; P,N-ligand; palladium-catalyzed allylic substitution; asymmetric catalyst.

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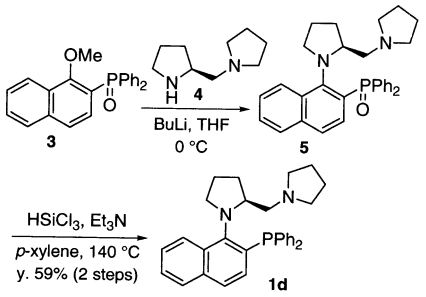


Scheme 1. The representative preparation **1d**.

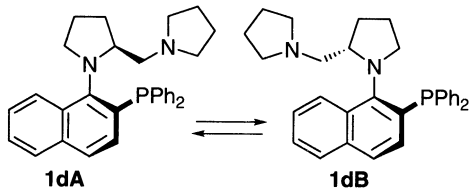
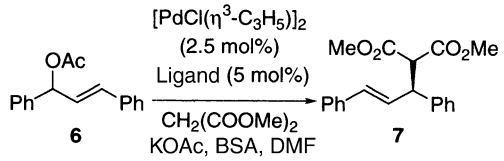


Figure 3. The exchange process between **1dA** and **1dB**.

Table 1. Ligand evaluation in the standard system



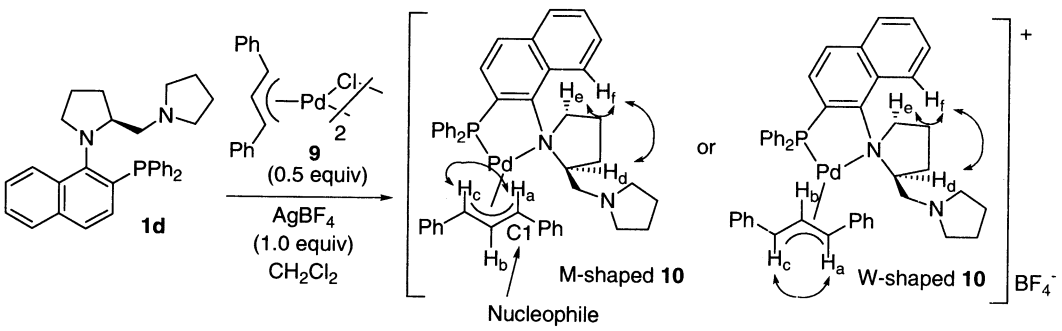
Entry	Ligand	Temperature (°C)	Time (h)	Yield (%)	ee (%)
1	**1a**	−10	24	68	57
2	**1b**	−10	24	69	86
3	**1c**	−10	24	69	83
4	**1d**	−10	24	81	91
5	**1e**	−10	24	61	90
6	**1f**	−10	24	89	90
7	**1g**	−10	24	42[a]	89
8	**1d**	−40	72	49[a]	95

[a] The starting material **6** was recovered in 35–40% yield.

also inversion of the nitrogen atom. The nitrogen atom inversion barrier has been reported to be 4–7 kcal/mol in many acyclic amines and 7 kcal/mol in *N*-methyl pyrrolidine,[9] and so the interconversion process shown in Fig. 3 should mostly arise from the restricted rotation of the N–Ar bond. Thus, these observations suggest that the N–Ar axis in **1d** is configurationally flexible. The other ligands **1a**–**c** and **1e**–**g** were also prepared in an analogous manner. The behavior of **1a**–**c** and **1e**–**g** in TLC and NMR was similar to that of **1d**.

In our initial studies concerning asymmetric catalysis using the ligands **1a**–**g**, we concentrated on a palladium-catalyzed asymmetric allylic substitution. The ligands **1a**–**g** were evaluated in the standard test system,[10] employing (*E*)-1,3-diphenyl-2-propenyl acetate (**6**) as the substrate and dimethyl malonate as the pronucleophile.[11] The catalyst was generated by mixing $[PdCl(\eta^3\text{-}C_3H_5)]_2$ and the ligand (1:1, in 5 mol% of Pd and 5 mol%, respectively), and the nucleophile was generated from dimethyl malonate, *N*,*O*-bis(trimethylsilyl)acetamide (BSA)[12] and a catalytic amount of KOAc. The results are shown in Table 1. All of the ligands evaluated functioned as a chiral ligand (entries 1–7). Among them, the ligand **1d** showed better asymmetric induction, yielding the product **7** with 91% ee in DMF at −10°C (entry 4). Reducing the reaction temperature from −10 to −40°C increased the ee of **7** from 91 to 95% ee (entry 8). Unfortunately, this upgrade in enantioselectivity was accompanied with a decrease in yield from 81 to 49%.[13,14] The absolute configuration of **7** was determined by comparison of the specific rotation with that reported for (*S*)-**7**.[15]

In an attempt to explain the enantioselectivity observed with the ligand **1d**, we carried out NMR studies on the cationic palladium(II) 1,3-diphenylallyl complex. The η^3-1,3-diphenylallyl palladium tetrafluoroborate salt **10** by the reaction of **1d** with di-μ-chloro-bis(1,3-diphenyl-π-allyl)-dipalladium complex **9** was prepared according to the literature precedent (Scheme 2).[16] The ^{1}H NMR spectra of the complex **10** gave sharp signals at 25°C (Fig. 4).[17] It can be seen that **10** exists as only one isomer complex at 25°C: for example, the central proton H_b (6.59 ppm, dd) appeared as only one signal due to one diastereomer complex. Furthermore, NOEs were observed between H_a and H_c, H_d and H_f, and H_e and H_f, respectively (Scheme 2): using COSY and DQF-COSY experiments, these protons were identified. On the basis of this finding, **10** can be assigned to be M-shaped **10** or W-shaped **10**. The fact that the complex was originated from one of the diastereomers, was reconfirmed by ^{31}P{^{1}H} NMR with a single resonance at 37.75 ppm. Treatment of **10** with dimethyl malonate, BSA and KOAc in CH_2Cl_2 gave the product **7** in 87% ee, which is the same as the ee value obtained from the catalytic reaction (see, Ref. 13). Taking these results and the observed absolute configuration of the product **7** into consideration, the reaction intermediate can be assumed to be M-shaped **10**,



Scheme 2.

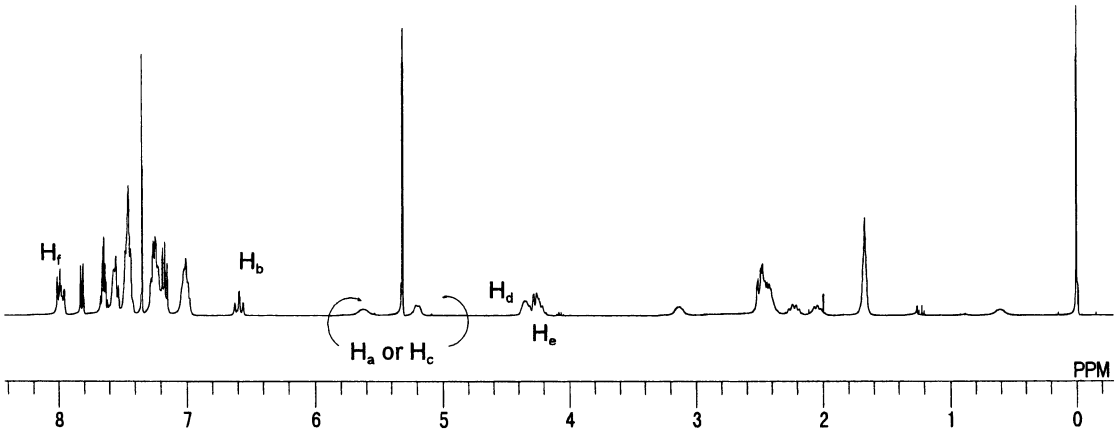


Figure 4. ^{1}H NMR spectrum of complex **10**.

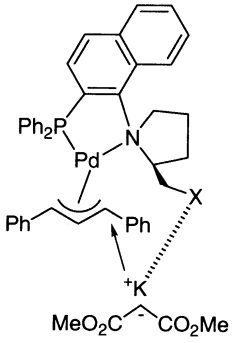
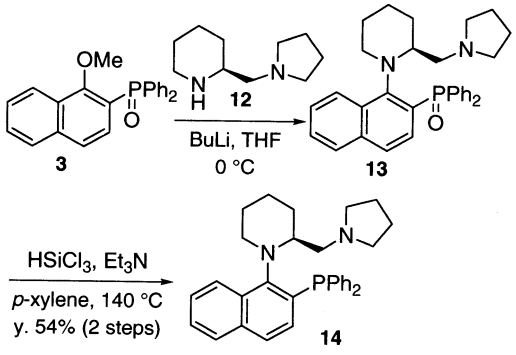


Figure 5. Possible model for the coordinative interaction.

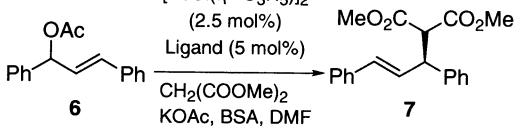
because due to the *trans* effect arising from the fact that the pyrrolidinyl group acts as donor while the phosphinyl group acts as π-acceptor,[18] the preferential alkylation should proceed from the back side of the palladium catalyst at the allyl terminus C^1 (Scheme 2). Furthermore, since the case of the pendant nitrogen-containing substituents in **1b–d** showed much better asymmetric induction than the case of the oxygen-containing substituent in **1a** (entry 1 vs 2–4, Table 1), coordinative interaction[19] between the pendant X and the nucleophile was suggested in the M-shaped intermediate (Fig. 5).[20]

In order to gain better asymmetric induction, we focused on the preparation of another ligand **14** having a pendant pyrrolidinyl group. The ligand **14** was prepared as shown in Scheme 3 and evaluated in the standard test system as



Scheme 3. Preparation of **14**.

Table 2. Ligand evaluation in the standard system



Entry	Solvent	Temperature (°C)	Time (h)	Yield (%)	ee (%)
1	DMF	−10	24	80	96
2	DMF	−40	72	43[a]	98
3	CH_3CN	−10	24	95	96
4	Toluene	−10	24	97	98
5	CF_3–C_6H_5	−10	19	98	99

[a] The starting material **6** was recovered in 32% yield.

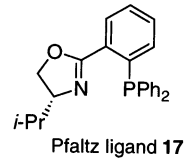
shown in Table 2.[21] As can be seen, **14** (y. 80%, 96% ee, entry 1, Table 2) was found to be more effective than **1d** (y. 81%, 91% ee, entry 4, Table 1). When the reaction temperature was reduced from −10 to −40°C, a decrease in yield from 80 to 43% was observed although the ee of **7** from 96 to 98% ee was increased (entry 1 vs 2). In order to improve this result, further reactions in various solvents were examined. α,α,α-Trifluorotoluene,[22] a less coordinated solvent, gave the best results with 98% yield and 99% ee (entry 5).

With these positive results, we finally examined the reaction of (*E*)-1-phenyl-3-trimethylsilyl-2-propenyl acetate[23] (**15**) using our ligand **14** and the Trost ligand[24] **18** (Table 3). Romero reported that no enantioselectivity was observed in the reaction with the use of the Pfaltz ligand[25] **17** (entry 2).[23] In the case of our ligand **14**, asymmetric induction was 6% ee (entry 1).[26] On the other hand, in the case of Trost ligand **18**, no reaction occurred at 40°C for 48 h (entry 3).

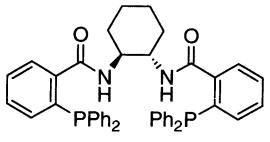
3. Conclusion

Our ligand **14** can be considered to be one of the best ligands for the standard asymmetric allylic alkylation described in the literature to date, and was found to exhibit slightly better results in the reaction employing (*E*)-1-phenyl-3-trimethylsilyl-2-propenyl acetate (**15**) as the substrate (Scheme 3), compared with the Pfaltz and Trost ligands. Using our

Table 3. Regioselective asymmetric allylic substitution



Pfaltz ligand **17**



Trost ligand **18**

Entry	Ligand	Temperature (°C)	Time (h)	Yeild (%)	ee (%)
1	**14**	40	24	79	6
2[a]	**17**	rt	–[b]	91	0
3	**18**	40	48	NR[c]	–

[a] Romero's results.[23]
[b] The reaction time was not reported by Romero.[23]
[c] No reaction was occurred.

ligands[27] and related mimetics,[28] further application to other asymmetric reactions is now in progress in our laboratory.

4. Experimental

All melting points (mp) were determined on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were measured on a JASCO FT/IR-230 diffraction grating IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured on a JEOL AL-400 NMR spectrometer, operating at 400 MHz for ^{1}H NMR and at 100 MHz at ^{13}C NMR. ^{1}H and ^{13}C NMR spectra were reported in δ units, parts per million (ppm) downfield from tetramethylsilane (δ=0). ^{31}P{^{1}H} NMR spectra were measured on a JEOL JMN-ECP500 NMR spectrometer, operating at 202 MHz with H_3PO_4 or $P(OMe)_3$ as an external standard. EI MS spectra were measured on a JEOL JMS-DX-303 instrument. Specific rotations (in deg cm^3 g^{-1} L^{-1}) were determined on a JASCO DIP-1000 digital polarimeter. Enantiomeric excesses (ee) were determined by HPLC analysis using a chiral stationary phase column (DAICEL CHIRALPAK AD, hexane/2-propanol=25/1).

1-Methoxy-2-(diphenylphosphinyl)naphthalene[8] (**3**), (*E*)-1,3-diphenyl-2-propenyl acetate[29] (**6**), (*E*)-1-phenyl-3-trimethylsilyl-2-propenyl acetate[23] (**15**) and di-μ-chloro-bis(1,3-diphenyl-π-allyl)dipalladium complex[16] **9** were prepared according to the known procedure. All reagents were available from commercial sources and used without further purification. In general, all reactions were performed in dry solvents under an argon atmosphere. THF was distilled under an argon atmosphere from Na/benzophenone ketyl. Other solvents were available from commercial sources and used without further purification. Silica gel column chromatography was performed on Kanto Chemical Silica gel 60 (spherical, 100–210 μm).

4.1. Typical procedure for preparation of ligand 1a–g and 14

4.1.1. (*S*)-*N*-[2-(Diphenylphosphino)naphthyl]-2-(pyrrolidinylmethyl)piperidine (14). To a stirred solution of (*S*)-2-(pyrrolidinylmethyl)piperidine (**12**) (1.51 g, 8.98 mmol) in THF (20.0 mL) was gradually added BuLi (5.6 mL, 8.90 mmol, 1.59 M solution in hexane) at 0°C, and the mixture was stirred for 20 min at the same temperature. To this solution was then added 1-methoxy-2-(diphenylphosphinyl)naphthalene (**3**) (2.17 g, 4.98 mmol) at 0°C. The whole mixture was stirred for 30 min at rt, quenched with water and extracted with EtOAc. The organic extracts were successively washed with saturated aq. NH_4Cl and brine, dried (Na_2SO_4) and concentrated. Purification by silica gel column (benzene/Et_3N, 50:1) gave a mixture (2.22 g) of 1-(*S*)-*N*-[2-(diphenylphosphinyl)-naphthyl]-2-(pyrrolidinylmethyl)piperidine (**13**) and small amounts of impurities. This mixture was used for the next step without further separation: ^{1}H NMR (DMSO-d_6): δ=0.70–2.15 (m, 17H), 2.80–2.94 (br, 1H), 3.47–3.64 (br, 1H), 6.92 (dd, *J*=12.2, 8.8 Hz, 1H), 7.41–8.01 (m, 14H), 8.27 (d, *J*=8.8 Hz, 1H). IR (nujol): ν=1735, 1558, 1201, 1114 cm^{-1}. EI MS: *m*/*z*=494 (M$^+$), 410 (bp), 201, 84. This mixture was dissolved in *p*-xylene (20.0 mL), and Et_3N (5.5 mL, 39.4 mmol) and $HSiCl_3$ (4.0 mL, 39.6 mmol) were added at 0°C. The whole mixture was heated at 140°C for 2 h. After being cooled to rt, the reaction mixture was carefully poured into 10% NaOH, and the whole mixture was extracted with EtOAc. The organic extracts were successively washed with water and brine, dried (Na_2SO_4), and concentrated. Purification by silica gel column (benzene/Et_3N, 50:1) gave (*S*)-*N*-[2-(diphenylphosphino)naphthyl]-2-(pyrrolidinylmethyl)piperidine (**14**) (1.27 g, 54% in 2 steps) as a pale yellow amorphous. $[\alpha]_D^{25}$=+38.6° (*c* 0.785, benzene). ^{1}H NMR (DMSO-d_6): δ=0.81–3.09 (m, 18H), 3.58–4.05 (m, 1H), 6.79–8.31 (m, 16H). IR (nujol): ν=1739, 1434 cm^{-1}. EI MS: *m*/*z*=478 (M$^+$), 394 (bp), 233, 183, 84. Anal. Calcd for $C_{32}H_{35}N_2P$: C, 80.30; H, 7.37; N, 5.85. Found: C, 80.02; H, 7.63; N, 5.67.

4.1.2. (*S*)-*N*-[2-(Diphenylphosphino)naphthyl]-2-(benzyloxymethyl)pyrrolidine (1a). Typical procedure afforded **1a** in 72% yield (2 steps) as a pale yellow amorphous. $[\alpha]_D^{25}$=+107° (*c* 1.10, benzene). ^{1}H NMR ($CDCl_3$, 55°C): δ=1.90–2.08 (m, 3H), 2.31–2.45 (m, 1H), 3.19–3.44 (m, 4H), 4.20 (s, 2H), 4.12–4.35 (br, 1H), 7.05 (br d, *J*=6.3 Hz, 3H), 7.13–7.33 (m, 13H), 7.39–7.48 (m, 2H), 7.57 (d, *J*=8.5 Hz, 1H), 7.81 (br d, *J*=6.8 Hz, 1H), 8.08 (br s, 1H). ^{13}C NMR ($CDCl_3$, 55°C): δ=25.29, 30.35, 54.69, 63.36, 72.94, 74.67, 125.6, 126.2, 127.0, 127.2, 128.0, 128.1, 128.2, 128.3, 133.5, 133.7, 133.9, 135.6, 138.8. IR (nujol): ν=1433, 1094 cm^{-1}. EI MS: *m*/*z*=410 (M$^+$−Bn), 394, 380, 91 (bp). Anal. Calcd for $C_{34}H_{32}NOP$: C, 81.41; H, 6.43; N, 2.79. Found: C, 81.11; H, 6.64; N, 2.88.

4.1.3. (*S*)-*N*-[2-(Diphenylphosphino)naphthyl]-2-(*N*-methyl-*N*-phenylaminomethyl)pyrrolidine (1b). Typical procedure afforded **1b** in 38% yield (2 steps) as a pale yellow amorphous. $[\alpha]_D^{25}$=+52° (*c* 0.77, benzene). ^{1}H NMR ($CDCl_3$, 50°C): δ=1.86–2.12 (m, 4H), 2.32 (br s, 1H), 2.67 (br s, 3H), 3.16–3.53 (m, 3H), 4.35 (br s, 1H), 6.34 (br s, 2H), 6.49–6.55 (m, 1H), 6.96 (br s, 2H), 7.10 (br

s, 1H), 7.18–7.37 (m, 10H), 7.39–7.54 (m, 3H), 7.62 (d, J=8.5 Hz, 1H), 7.84 (br d, J=7.6 Hz, 1H). IR (nujol): ν=1477, 1026 cm^{-1}. EI MS: m/z=380 (M^+−CH_2NMePh, bp), 233. Anal. Calcd for $C_{34}H_{33}N_2P$: C, 81.57; H, 6.64; N, 5.60. Found: C, 81.49; H, 6.75; N, 5.30.

4.1.4. (*S*)-*N*-[2-(Diphenylphosphino)naphthyl]-2-(*N*,*N*-dibenzylaminomethyl)pyrrolidine (1c). Typical procedure afforded **1c** in 47% yield (2 steps) as a pale yellow amorphous. $[\alpha]_D^{25}$=+21° (c 0.56, benzene). ^1H NMR ($CDCl_3$, 55°C): δ=1.20–1.48 (m, 2H), 1.66–1.95 (m, 3H), 2.20–2.42 (m, 3H), 3.03 (br d, J=13.7 Hz, 2H), 3.18–3.26 (m, 1H), 3.38 (d, J=13.7 Hz, 2H), 4.06–4.29 (br, 1H), 7.01–7.33 (m, 21H), 7.36–7.50 (m, 2H), 7.57 (d, J=8.5 Hz, 1H), 7.81 (d, J=8.1 Hz, 1H), 7.97 (br s, 1H). IR (nujol): ν=1434, 1069 cm^{-1}. EI MS m/z=590 (M^+), 499, 380 (bp), 233, 91. Anal. Calcd for $C_{41}H_{39}N_2P$: C, 83.36; H, 6.65; N, 4.74. Found: C, 83.08; H, 6.92; N, 4.60.

4.1.5. (*S*)-*N*-[2-(Diphenylphosphino)naphthyl]-2-(pyrrolidinylmethyl)pyrrolidine (1d). Typical procedure afforded **1d** in 59% yield (2 steps) as a pale yellow amorphous. $[\alpha]_D^{25}$=+107° (c 0.36, benzene). ^1H NMR ($CDCl_3$, 50°C): δ=1.41–1.57 (m, 4H), 1.89–2.50 (m, 10H), 3.21–3.33 (m, 2H), 4.14 (br s, 1H), 7.08 (dd, J=8.5, 3.1 Hz, 1H), 7.17–7.37 (m, 10H), 7.37–7.50 (m, 2H), 7.57 (d, J=8.5 Hz, 1H), 7.75–7.84 (m, 1H), 8.08 (br s, 1H). ^{13}C NMR ($CDCl_3$, 50°C): δ=23.58, 25.13, 31.74, 54.47, 62.17, 62.19, 63.21, 63.29, 124.7, 125.5, 126.0, 126.2, 128.0, 128.1, 128.2, 128.3, 128.5, 131.0, 133.4, 133.6, 133.8, 135.5, 139.2, 139.4. IR (nujol): ν=1433, 1154 cm^{-1}. EI MS: m/z=464 (M^+), 380 (bp), 233, 183, 84. Anal. Calcd for $C_{31}H_{33}N_2P$: C, 80.14; H, 7.16; N, 6.03. Found: C, 80.28; H, 7.11; N, 5.94.

4.1.6. (*S*)-*N*-[2-(Di-*p*-tolylphosphino)naphthyl]-2-(pyrrolidinylmethyl)pyrrolidine (1e). Typical procedure afforded **1d** in 46% yield (2 steps) as a pale yellow amorphous. $[\alpha]_D^{25}$=+118° (c 1.36, benzene). ^1H NMR ($CDCl_3$, 55°C): δ=1.88–2.52 (m, 14H), 2.32 (s, 3H×2), 3.21–3.36 (br, 2H), 4.13 (br s, 1H), 7.03–7.25 (m, 9H), 7.40–7.45 (m, 2H), 7.55 (d, J=8.5 Hz, 1H), 7.73–7.82 (m, 1H), 8.09 (br s, 1H). IR (nujol): ν=1496, 1148, 1090 cm^{-1}. EI MS: m/z=408 (M^+−pyrrolidinylmethyl, bp), 84. Anal. Calcd for $C_{33}H_{37}N_2P$: C, 80.46; H, 7.57; N, 5.69. Found: C, 80.18; H, 7.75; N, 5.71.

4.1.7. (*S*)-*N*-{2-[Bis(*p*-trifluoromethylphenyl)phosphino]-naphthyl}-2-(pyrrolidinylmethyl)pyrrolidine (1f). Typical procedure afforded **1f** in 40% yield (2 steps) as a pale yellow amorphous. $[\alpha]_D^{25}$=+102° (c 1.22, benzene). ^1H NMR (C_6D_6, 65°C): δ=1.24–1.41 (m, 4H), 1.80–2.19 (m, 7H), 2.30–2.44 (m, 2H), 2.48–2.57 (m, 1H), 3.32 (br s, 2H), 4.23 (br s, 1H), 7.04 (dd, J=8.5, 3.2 Hz, 1H), 7.08–7.39 (m, 10H), 7.43 (d, J=8.5 Hz, 1H), 7.63 (d, J=7.8 Hz, 1H), 8.17 (br s, 1H). IR (nujol): ν=1321, 1164, 1127 cm^{-1}. EI MS: m/z=600 (M^+), 581, 516 (M^+−pyrrolidinylmethyl, bp), 301. Anal. Calcd for $C_{33}H_{31}F_6N_2P$: C, 66.00; H, 5.20; N, 4.66. Found: C, 66.04; H, 5.36; N, 4.62.

4.1.8. (*S*)-*N*-[2-(Dinaphthylphosphino)naphthyl]-2-(pyrrolidinylmethyl)pyrrolidine (1g). Typical procedure afforded **1g** in 41% yield (2 steps) as a pale yellow amorphous. $[\alpha]_D^{25}$=+51° (c 1.12, benzene). ^1H NMR ($CDCl_3$, 55°C): δ=1.26 (br s, 2H), 1.89–2.55 (m, 12H), 3.34 (br s, 2H), 4.18 (br s, 1H), 7.20 (dd, J=8.5, 3.1 Hz, 2H), 7.35–7.51 (m, 8H), 7.57 (d, J=8.5 Hz, 1H), 7.67 (dd, J=7.6, 7.3 Hz, 2H), 7.70–7.85 (m, 6H), 8.11 (br s, 1H). IR (nujol): ν=1498, 1134, 1075 cm^{-1}. EI MS: m/z=564 (M^+), 480 (M^+−pyrrolidinylmethyl, bp), 84. Anal. Calcd for $C_{39}H_{37}N_2P$: C, 82.95; H, 6.60; N, 4.96. Found: C, 82.68; H, 6.59; N, 4.95.

4.2. Typical procedure for allylic alkylation

To a stirred solution of (*E*)-1,3-diphenyl-2-propenyl acetate (**6**) (101 mg, 0.400 mol) in α,α,α-trifluorotoluene (1.2 mL) were added ligand **14** (9.3 mg, 0.0200 mmol), $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (3.7 mg, 0.0100 mmol), potassium acetate (2.0 mg, 0.0200 mmol), dimethyl malonate (0.14 mL, 1.24 mmol) and *N*,*O*-bis(trimethylsilyl)acetamide (0.33 mL, 1.30 mmol) at 0°C. The reaction mixture was stirred for 19 h at the same temperature (monitored by TLC). After usual work-up, purification by silica gel column (hexane/EtOAc, 10:1, the silica gel was pretreated with 3% Et_3N in hexane) gave (*E*)-methyl 2-carbomethoxy-3,5-diphenylpent-4-enoate (**7**) (119 mg, 98%, 99% ee) as a colorless oil.

4.2.1. [(*S*)-*N*-[2-(Diphenylphosphino)naphthyl]-2-(pyrrolidinylmethyl)pyrrolidine}-[1,3-diphenyl-π-allyl]palladium] tetrafluoroborate (10). To a stirred solution of $[PdCl(\eta^3\text{-}PhCHCHCHPh)]_2$ (32.0 mg, 0.0478 mmol) and ligand **1d** (44.4 mg, 0.0956 mmol) in CH_2Cl_2 (7.5 mL) was added $AgBF_4$ (29.2 mg, 0.135 mmol) at 0°C. The mixture was stirred for 8 h at rt, and the formed silver chloride was removed by filtration. The filtrate was concentrated. Recrystallization (CH_2Cl_2/hexane) gave complex **10** (32.5 mg, 89%) as pale yellow powders. ^1H NMR (CD_2Cl_2): δ=0.61 (br s, 1H), 1.62–1.76 (m, 4H), 1.98–2.15 (m, 1H), 2.15–2.30 (m, 1H), 2.35–2.58 (m, 6H), 3.14 (br s, 1H), 4.18–4.41 (m, 3H), 5.20 (br d, J=12.3 Hz, 1H), 5.54–5.68 (br, 1H), 6.59 (dd, J=12.3, 12.3 Hz, 1H), 6.95–7.08 (m, 4H), 7.17 (dd, J=8.5, 7.5 Hz, 2H), 7.23–7.30 (m, 6H), 7.40–7.52 (m, 6H), 7.52–7.62 (m, 3H), 7.62–7.69 (m, 2H), 7.82 (d, J=8.5 Hz, 1H), 7.94–8.04 (m, 2H). ^{13}C NMR (CD_2Cl_2): δ=23.04, 24.73, 32.85, 55.90, 60.52, 64.84, 70.00, 108.8, 108.9, 122.8, 125.9, 126.8, 127.1, 127.3, 127.8, 127.9, 128.3, 128.6, 128.8, 129.0, 129.1, 129.3, 129.3, 130.3, 130.4, 130.5, 130.6, 131.1, 131.4, 131.7, 131.8, 135.3, 135.4, 135.7, 137.5, 151.5, 151.7. ^{31}P NMR (CD_2Cl_2): δ=37.75. ESI MS: m/z=cation 571 (M−PhCHCHCHPh−BF_4).

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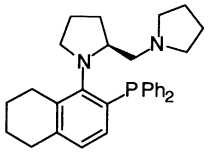

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