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Asymmetric Kumada–Corriu cross-coupling reaction with $Pd_2(dba)_3$ and an N–Ar axially chiral mimetic-type ligand catalyst

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Abstract—A catalyst comprised of $Pd_2(dba)_3 \cdot CHCl_3$ and an N–Ar axially chiral mimetic-type ligand, (*S*)-*N*-[2-(diphenylphosphanyl)naphthalene-1-yl]-2-(piperidinylmethyl)piperidine, provides good enantioselectivities for the asymmetric Kumada–Corriu cross-coupling reaction of 1-phenylethylmagnesium chloride and *E*-β-bromostyrene derivatives with which it is more difficult to achieve high enantioselectivity. Furthermore, in the case of styrene derivatives bearing both vinyl and aryl bromide groups, the chemoselective asymmetric cross-coupling reaction of the vinyl bromide group is observed. This N–Ar axially chiral mimetic-type ligand allows easy synthesis of a wide variety of analogues, and starting from the initial ligand, the enantioselectivity of coupling products is improved by modifying the structure in the ligand.

1. Introduction

Catalytic asymmetric carbon–carbon bond formation with metal–chiral ligand complexes, is one of the most important reactions in synthetic organic chemistry. The development of new chiral ligands for use in asymmetric catalysis has continued to undergo rapid growth. For testing the new ligands, standard palladium-catalyzed asymmetric allylic substitution with the use of (*E*)-1,3-diphenyl-2-propenyl acetate as the substrate and dimethyl malonate as the pronucleophile, has been quite often examined.[1] A large number of ligands, which exhibit enantioselectivity of more than 90%, have been reported.[1] However, there are some successful examples of other catalytic asymmetric reactions with these new ligands.[2] Therefore, it is very important to develop versatile chiral ligands, which afford good enantioselectivity in a variety of reactions.

We have recently developed a novel chiral ligand **1** mimicking N–Ar axial chirality, in which a chiral carbon center induces a preferred conformation **2a** by rotation around an N–Ar bond which is fixed by formation of a chelate structure with metal (Figs. 1 and 2).[3] Among the designed ligands **1**, **1i** has been found to exhibit 99% ee in the standard palladium-catalyzed asymmetric allylic substitution.[3] These results prompted us to explore further application of the ligand **1**. Our interest in this ligand focused on its use in the asymmetric Kumada–Corriu cross-coupling reaction[4] of 1-phenylethylmagnesium chloride with alkenyl halides, which has met with success using Kumada's P,N-ligands.[5] Some ligands have been developed for the asymmetric cross-coupling reaction of 1-phenylethylmagnesium chloride with alkenyl halides, but the best substrate exhibiting more than 80% ee was vinyl bromide.[6] One type of substrate with which it has been more difficult to achieve high selectivity is a styrene derivative such as

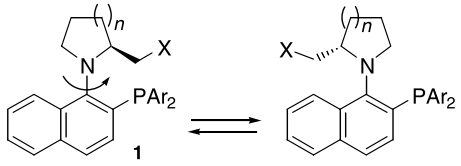

Figure 1.

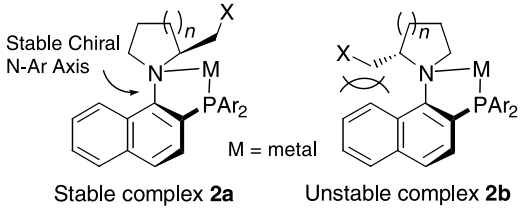

Figure 2.

Keywords: Kumada–Corriu cross-coupling reaction; N–Ar Axially chiral mimetic-type ligand; Enantioselectivity.
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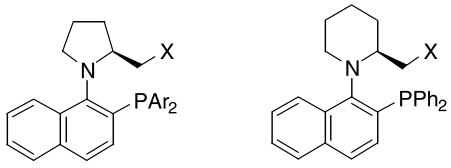
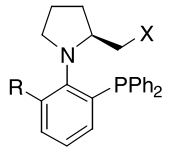
E-β-bromostyrene.[7] There are, to date, only two examples by Knochel[8] and Saigo[9] that give good enantioselectivity with *E*-β-bromostyrene. Herein we would like to report our investigation of this reaction using *E*-β-bromostyrene derivatives as substrates with the ligand **1** mimicking N–Ar axial chirality.[10] The results obtained with the ligand **1** are, to the best of our knowledge, the third best enantioselectivity in the reported literature. Additionally, the ligand **1** is appealing, because it allows easy synthesis of a wide variety of analogues.

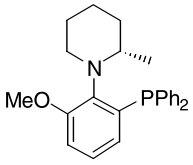


1a: X=OMOM, Ar=Ph
1b: X=OBn, Ar=Ph
1c: X=O*t*-Bu, Ar=Ph
1d: X=pyrrolidinyl, Ar=Ph
1e: X=NBn_2, Ar=Ph
1f: X=OBn, Ar=*p*-tolyl
1g: X=pyrrolidinyl, Ar=*p*-tolyl
1h: X=pyrrolidinyl, Ar=2-naphthyl

1i: X=pyrrolidinyl
1j: X=piperidinyl



1k: X=OBn, R=Me
1l: X=pyrrolidinyl, R=OMe



1m

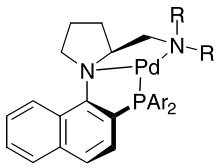
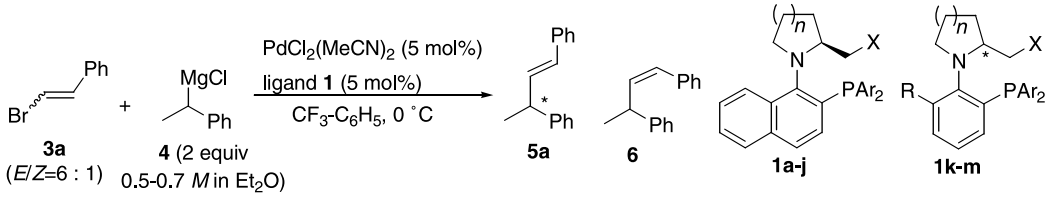


Figure 3. Internal coordination of the pendant nitrogen group.

2. Results and discussion

We began to screen a variety of the ligands **1** in the asymmetric cross-coupling reaction of 1-phenylethylmagnesium chloride (**4**) with β-bromostyrene (*E*/*Z*=6:1, **3a**). The results are shown in Table 1. Reactions were carried out with $PdCl_2(CH_3CN)_2$ (5 mol%), the ligand **1** (5 mol%), and 1-phenylethylmagnesium chloride (**4**) (2 equiv, 0.5–0.7 mol/L in Et_2O) in α,α,α-trifluorotoluene[11] at 0 °C. The use of other solvents such as toluene, chlorobenzene, THF, Et_2O, isopropyl ether, *t*-butyl methyl ether, dioxane, DME, and CH_2Cl_2, gave less satisfactory results. First, the effect of a pendant substituent X with the pyrrolidine-based ligands **1a–e** was examined.[12] As shown in entries 1–5, the pendant substituent played an important role. The ligands **1a–c** possessing a pendant oxygen group exhibited faster reaction rate than **1d** and **1e** possessing a pendant nitrogen group. Among the oxygen-containing ligands **1a–c**, the ligand **1b** bearing the pendant BnO group, gave better results (entry 2, 66% yield, 66% ee). The ee of **5a** was determined by HPLC analysis (Daicel Chiralcel OD), and its absolute configuration was determined by comparison with the reported **5a**.[8] The inhibition of the reactivity observed with the ligands **1d** and **1e** possessing

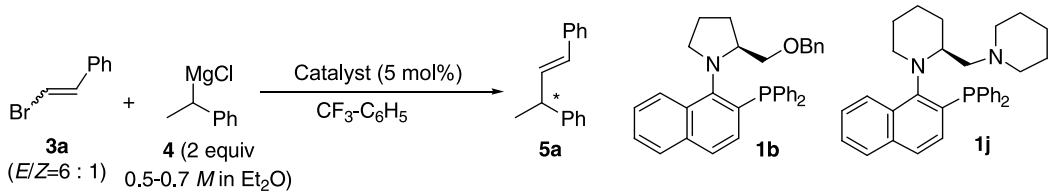
Table 1. Initial ligand screening[a]



Entry[b]	Ligand **1**	X	*n*	Ar	R	Time (h)	Yield of **5a** (%)	ee[c] of **5a** (%)	Absolute configuration
1	**1a**	OMOM	1	Ph	—	1	59	7	*R*
2	**1b**	OBn	1	Ph	—	1	66	66	*S*
3	**1c**	O*t*-Bu	1	Ph	—	1	42	47	*S*
4	**1d**	Pyrrolidinyl	1	Ph	—	24	35	62	*S*
5	**1e**	NBn_2	1	Ph	—	24	20	9	*R*
6	**1i**	Pyrrolidinyl	2	Ph	—	1	53	61	*S*
7[d]	**1i**	Pyrrolidinyl	2	Ph	—	24	25	52	*S*
8	**1j**	Piperidinyl	2	Ph	—	1	58	66	*S*
9	**1f**	OBn	1	*p*-Tolyl	—	24	15	9	*S*
10	**1g**	Pyrrolidinyl	1	*p*-Tolyl	—	24	37	65	*S*
11	**1h**	Pyrrolidinyl	1	2-Naphthyl	—	24	43	56	*S*
12	**1k**	OBn	1	Ph	Me	24	42	63	*S*
13	**1l**	Pyrrolidinyl	1	Ph	MeO	24	26	69	*S*
14	**1m**	H	2	Ph	MeO	1	52	7	*S*

[a] The reactions were performed using 5 mol% of $PdCl_2(MeCN)_2$ and the ligand **1**, a 6:1 mixture of *E*- and *Z*-β-bromostyrene **3a**, and 2 equiv of the Grignard reagent **4** in CF_3–C_6H_5 at 0 °C.
[b] In all entries, a small amount of **6** was obtained with no enantioselectivity (for example, **1d** afforded **6** with 2% yield and 0% ee).
[c] Determined by HPLC analysis.
[d] 1-Phenylethylmagnesium bromide was used.

Table 2. Further screening of reaction conditions with the ligand **1b** and **1j**[a]

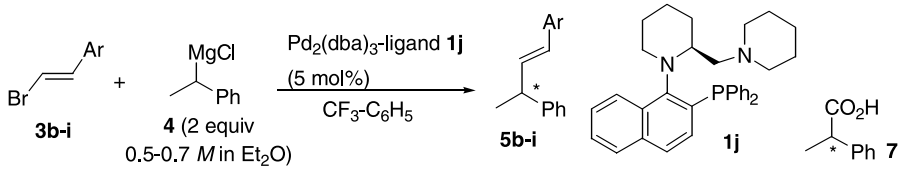


Entry[b]	Catalyst	Additive	Temperature (°C)	Time (h)	Yield of **5a** (%)	ee[c] of **5a** (%)	Absolute configuration
1	$PdCl_2(MeCN)_2$/**1b**	—	−10	24	NR[d]	—	—
2	$PdCl_2(MeCN)_2$/**1j**	—	−10	12	66	71	*S*
3	$PdCl_2(MeCN)_2$/**1j**	—	−20	24	NR[d]	—	—
4	$Pd_2(dba)_3\cdot CHCl_3$/ **1j**	—	−20	2	67	74	*S*
5[e]	$Pd_2(dba)_3\cdot CHCl_3$/ **1j**	—	−30	7	64	76	*S*
6	$Pd_2(dba)_3\cdot CHCl_3$/ **1j**	LiCl[f]	−30	12	61	73	*S*
7	$Pd_2(dba)_3\cdot CHCl_3$/ **1j**	LiI[f]	−30	24	9	47	*S*
8	$Pd_2(dba)_3\cdot CHCl_3$/ **1j**	$ZnCl_2$[f]	−30	24	Trace	—	—
9	$Pd_2(dba)_3\cdot CHCl_3$/ **1j**	—	−40	24	Trace	—	—
10	$[PdCl(\eta^3\text{-}C_3H_5)]_2$ /**1j**	—	0	1	68	58	*S*
11	$Ni(cod)_2$/**1j**	—	0	15	56	0	—

[a] The reactions were performed using 5 mol% of metal complex and the ligand **1**, a 6:1 mixture of *E*- and *Z*-β-bromostyrene **3a**, and 2 equiv of the Grignard reagent **4** in CF_3–C_6H_5.
[b] In all entries, a small amount of **6** was obtained.
[c] Determined by HPLC analysis.
[d] No reaction occurred.
[e] The use of 7.5–10 mol% of the ligand **1j** gave the same results.
[f] One molar equivalent of the additive was used.

the pendant nitrogen substituent, a strong coordinating group, is considered to be due to the internal coordination of the pendant nitrogen group to palladium (Fig. 3). Molecular modeling studies suggested that the piperidine based-ligand **1i** avoids such a problem, because coordination of the pendant nitrogen group to the internal palladium seemed to be torsionally unfavorable. As expected, replacement of the piperidine ring on the naphthalene ring enhanced the reaction rate, and the chemical yield was increased from 35 to 53% (entries 4 vs 6). The use of 1-phenylethylmagnesium bromide in place of the corresponding chloride decreased both chemical yield and enantioselectivity (entries 6 vs 7). Furthermore, employing the piperidine-based ligand **1j** possessing the pendant piperidinyl group gave better results (58% yield, 66% ee) than **1i** (entries 6 vs 8). The effects of the diarylphosphino groups, the aromatic parts and so on were also examined (entries 9–14), but their replacements gave less satisfactory results.

Table 3. Substrate generality[a]

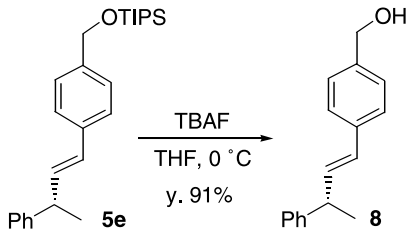


Entry	Ar	Temperature (°C)	Time (h)	Yield of **5** (%)	ee[b] of **5** (%)	Absolute configuration
1	4-Me-C_6H_4– (**3b**)	−20	4	73[c] (**5b**)	78	*S*
2	4-*i*-Pr-C_6H_4– (**3c**)	−20	6	75[c] (**5c**)	80	*S*
3	4-Cl-C_6H_4– (**3d**)	−10	2	80[c] (**5d**)	71	*S*
4	4-TIPSOCH$_2$-C_6H_4– (**3e**)	−10	18	61[d] (**5e**)	73	*S*
5	4-MeO-C_6H_4– (**3f**)	0	24	NR[e]	—	—
6	3-MeO-C_6H_4– (**3g**)	0	24	NR[e]	—	—
7	2-Br-C_6H_4– (**3h**, *E*/*Z*=17:1)	−20	24	22[c,f] (**5h**)	60	*S*
8[g]	3-Br-C_6H_4– (**3i**, *E*/*Z*=23:1)	−20	9	65[c] (**5i**)	70	*S*

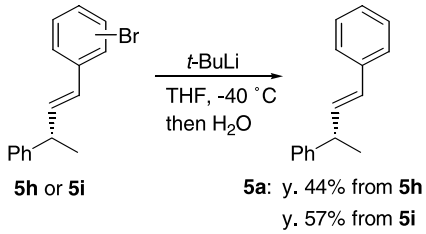
[a] The reactions were performed using 2.5 mol% of $Pd_2(dba)_3\cdot CHCl_3$, 5 mol% of the ligand **1j**, an *E*-isomer of the bromostyrene **3** except for **3h** and **3i**, and 2 equiv of the Grignard reagent **4** in CF_3–C_6H_5.
[b] Determined by HPLC analysis.
[c] The desired product **5** was obtained as a mixture with 2,3-diphenylbutane. The chemical yield was calculated on the basis of ^1H NMR analysis of the mixture.
[d] Yield of **8** after desilylation.
[e] No reaction occurred.
[f] Remainder of mass balance was the unreacted starting bromostyrene **3h**.
[g] Since the use of (*E*)-1-bromo-2-(4-bromophenyl)ethene as a substrate gave a mixture of the cross-coupling product and a small amount of unknown impurities, the chemical yield and ee of the cross-coupling product could not be determined.

Thus, in terms of both chemical yield and enantioselectivity, the two ligands **1b** and **1j** were chosen as candidates for the next screening. The effect of temperature on the reaction was examined (entries 1–3, Table 2). In the case of the ligand **1b**, lowering the temperature from 0 to −10 °C resulted in no reaction (entry 1). On the other hand, in the case of the ligand **1j**, the enantioselectivity was improved (entry 2: 71% ee). Further intensive screening of other palladium and nickel complexes (entries 4, 10 and 11) established that $Pd_2(dba)_3 \cdot CHCl_3$ is the most effective complex. Thus, the reaction was found to proceed at lower temperature (< −10 °C), and the best enantioselectivity (76% ee) was observed at −30 °C (entry 5). The use of the additives such as LiCl, LiI, and $ZnCl_2$ with the best catalyst gave less satisfactory results (entries 6–8).

Using the best $Pd_2(dba)_3$-ligand **1j** catalyst, we examined the cross-coupling reaction with several *E*-β-bromostyrenes as shown in Table 3. Styrene derivatives bearing *p*-methyl (**3b**), *p*-isopropyl (**3c**), *p*-chloro (**3d**) and *p*-triisopropylsilyloxymethyl (**3e**) groups were found to be employable, giving the corresponding products in good enantioselectivities (entries 1–4, up to 80% ee). Unfortunately, the reaction with **3f** and **3g** bearing an electron-donating group did not proceed (entries 5 and 6).[13] The coupling product **5e** with 73% ee was transformed into lipoxygenase inhibitor[14] **8**, as shown in Scheme 1. The ee of **5b–e** were determined by HPLC analysis (Daicel Chiralcel OD), and their absolute configurations were determined by HPLC analysis (Daicel Chiralpak AD) after conversion of **5b–e** to the commercially available carboxylic acid **7**. Finally, the asymmetric cross-coupling reaction with the styrene derivatives **3h** and **3i** bearing both vinyl and aryl bromide groups was examined as shown in entries 7 and 8, because it is important to control the chemoselectivity in the Pd-catalyzed Grignard cross-coupling.[15] The styrene derivatives **3h** and **3i** underwent the selective substitution of the vinyl bromide group to give the corresponding mono-coupling product **5h** and **5i**, respectively, although conversion of the reaction with *ortho*-substituted bromostyrene **3h** was low. Their ee and absolute configurations were determined by HPLC analysis after conversion to **5a** as shown in Scheme 2.



Scheme 1. Conversion to lipoxygenase inhibitor **8**.



Scheme 2. Debromination of **5h** and **5i**.

Based on the previous ^1H and ^{31}P NMR study[3] of the Pd-ligand **1d** complex, which is similar to the Pd-ligand **1j** complex, and the absolute configuration of the product **5** obtained by using the Pd-ligand **1j** catalyst, enantiomeric induction in the present system can be understood by assuming the transition state in Figure 4. At first, oxidative addition of the styryl bromide **3** to the Pd-ligand **1j** complex occurs. Next, the pendant nitrogen group of **1j** coordinates with the Mg atom of the Grignard reagent **4** (Fig. 4). This coordination allows to undergo enantiomerselective transmetalation, thus giving the observed *S*-product.

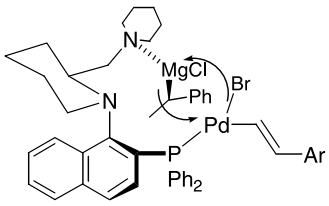


Figure 4. Possible model for asymmetric induction.

3. Conclusion

We have shown that an N–Ar axially chiral mimetic-type ligand is efficient in the asymmetric Kumada–Corriu cross-coupling reaction[16–18] of 1-phenylethylmagnesium chloride with *E*-β-bromostyrene derivatives. Starting from the initial ligand, the enantioselectivity was improved by modifying the structure in the ligand. These findings validate the usefulness of ligand tuning for optimization. Further application to other catalytic asymmetric reactions is now in progress.

4. Experimental

4.1. General

IR spectra were measured on a SHIMADZU FTIR-8100 and 84005 diffraction grating IR spectrophotometer. ^1H and ^{13}C NMR spectra were measured on a JEOL JNM-EX-270 NMR spectrometer, operating at 270 MHz for ^1H NMR and at 68 MHz at ^{13}C NMR. ^1H and ^{13}C NMR spectra were reported in δ units, parts per million (ppm) downfield from tetramethylsilane ($\delta=0$). EI and FAB MS spectra were measured on a JEOL JMS-SX-102A instrument. Specific rotations (in deg cm^3 g^{-1} L^{-1}) were determined on a JASCO DIP-1000 digital polarimeter.

1-Methoxy-2-(diarylphosphinyl)naphthalene,[19] (*S*)-2-(benzyloxymethyl)pyrrolidine,[20] (*S*)-2-(*t*-butoxymethyl)-pyrrolidine[21] and 1,1-dibromo-2-(2-bromophenyl)ethene[22] were prepared according to the known procedure. (*S*)-2-Methylpiperidine and 1-bromo-2-phenylethene (*E*/*Z*=6:1) were commercially available. The syntheses of the ligands **1b**, **1d**, **1e**, **1g**, **1h** and **1i** were previously reported by us.[3] The known (*E*)-1-bromo-2-arylethene shown below were prepared according to our published procedure.[23] Their physical data were comparable to those of the corresponding literature: (*E*)-1-bromo-2-(4-tolyl)ethene[24] (**3b**), (*E*)-1-bromo-2-(4-isopropylphenyl)ethene[23] (**3c**), (*E*)-1-bromo-2-(4-chlorophenyl)ethene[24] (**3d**), (*E*)-1-bromo-2-(4-hydroxymethylphenyl)ethene,[23] (*E*)-1-bromo-2-(4-methoxyphenyl)-ethene[24] (**3f**), (*E*)-1-bromo-2-(3-methoxyphenyl)ethene[24]

(**3g**). 2,3-Diphenylbutane, and optically active and racemic 2-phenylpropionic acid were commercially available.

All reagents were available from commercial sources and used without further purification. In general, all reactions were performed under an argon atmosphere. α,α,α-Trifluorotoluene was distilled from Na under a nitrogen atmosphere. THF, Et_2O, DME, and 1,4-dioxane, were distilled from Na/benzophenone ketyl under a nitrogen atmosphere. CH_2Cl_2 was distilled from CaH_2 under a nitrogen atmosphere. Other solvents were available from commercial sources and used without further purification. Silica gel column chromatography was performed on Fuji silysia PSQ 60B, unless otherwise noted.

4.1.1. (*S*)-2-(Piperidinylmethyl)piperidine. The title compound was prepared according to the similar procedure reported.[25] The physical data were comparable to the commercially available racemate. $[\alpha]_D^{26}=+33°$ (*c* 8.17, dioxane).

4.2. Representative procedure for the synthesis of ligand 1

4.2.1. (*S*)-*N*-[2-(Diphenylphosphanyl)naphthalen-1-yl]-2-(piperidinylmethyl)piperidine (1j). First step: to a stirred solution of (*S*)-2-(piperidinylmethyl)piperidine (700 mg, 3.84 mmol) in THF (4.0 mL) was gradually added BuLi (2.53 mL, 4.00 mmol, 1.58 M solution in hexane) at −30 °C, and the mixture was stirred for 2 h at the same temperature. To this solution was then added a solution of 1-methoxy-2-(diphenylphosphinoyl)naphthalene (680 mg, 1.90 mmol) in THF (2.0 mL) at −30 °C. The whole mixture was stirred for 1 h at the same temperature, 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 (Fuji Silysia Chromatorex NH, EtOAc/hexane=1:5) gave a mixture (724 mg) of 1-(*S*)-*N*-[2-(diphenylphosphonyl)naphthalen-1-yl]-2-(piperidinylmethyl)piperidine and small amounts of impurities. This mixture was used for the next step without further separation. IR (neat): $\nu=1308$, 1254, 1192, 1161 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta=0.75$–1.15 (m, 8H), 1.24–1.45 (m, 2H), 1.60–1.94 (m, 7H), 2.46 (dd, $J=13.3$, 5.9 Hz, 1H), 2.92 (brd, $J=11.1$ Hz, 1H), 3.36 (dd, $J=11.1$, 11.1 Hz, 1H), 3.51–3.62 (br, 1H), 6.97 (dd, $J=12.1$, 8.6 Hz, 1H), 7.35–7.57 (m, 10H), 7.65–7.87 (m, 4H), 8.23 (d, $J=8.4$ Hz, 1H). ^{13}C NMR ($CDCl_3$): 24.29, 24.90, 25.47, 25.63, 31.38, 54.80, 56.09, 60.55, 62.23, 125.15, 125.42, 125.62, 126.21, 127.02, 127.95, 128.13, 128.65, 129.02, 129.22, 129.77, 130.74, 131.09, 131.23, 131.37, 131.94, 132.07, 134.15, 134.65, 135.09, 135.22, 135.66, 136.22, 136.63, 155.14. FABMS: $m/z=509$ ($M^+ +1$). Second step: the above mixture was dissolved in *p*-xylene (7.0 mL), and Et_3N (2.10 mL, 15.1 mmol) and $HSiCl_3$ (1.4 mL, 14 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 (Fuji Silysia Chromatorex NH, hexane/EtOAc=20:1) gave (*S*)-*N*-[2-(diphenylphosphanyl)naphthyl]-2-(pyrrolidinylmethyl)piperidine (**1j**) (505 mg, 54% in 2 steps) as a colorless amorphous. $[\alpha]_D^{28}=+115°$ (*c* 1.60, dioxane). IR (nujol): $\nu=1300$, 1275, 1206, 1159 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta=0.83$–2.22 (m, 18H), 2.66 (brd, $J=11.5$ Hz, 1H×4/5), 3.01 (brd, $J=11.2$ Hz, 1H×1/5), 3.30 (brdd, $J=11.5$, 10.6 Hz, 1H×4/5), 3.45–3.53 (br, 1H×1/5), 3.55–3.73 (br, 1H×4/5), 4.13–4.28 (br, 1H×1/5), 6.89 (dd, $J=8.6$, 2.4 Hz, 1H×4/5), 7.09 (dd, $J=8.6$, 3.8 Hz, 1H×1/5), 7.14–7.57 (m, 13H), 7.72–7.77 (m, 1H×1/5), 7.81 (dd, $J=6.3$, 3.5 Hz, 1H×4/5), 8.05 (dd, $J=6.3$, 3.5 Hz, 1H×4/5), 8.63 (dd, $J=6.3$, 3.5 Hz, 1H×1/5). ^{13}C NMR ($CDCl_3$): 24.05, 24.29, 24.41, 25.27, 25.71, 25.93, 26.02, 27.47, 29.75, 31.59, 32.34, 54.10, 54.32, 54.93, 55.10, 57.17, 57.38, 59.20, 61.70, 62.50, 62.59, 124.80, 124.94, 125.49, 125.57, 125.78, 125.95, 126.02, 126.71, 127.44, 127.90, 127.97, 128.00, 128.13, 128.17, 128.27, 128.37, 128.63, 129.50, 131.91, 132.72, 133.00, 133.29, 133.54, 133.80, 133.95, 134.10, 134.26, 134.54, 134.66, 135.01, 135.19, 136.92, 137.40, 137.60, 138.35, 138.54, 138.81, 139.00, 139.63, 139.87, 150.99, 151.30, 153.92, 154.28. FABMS: $m/z=493$ ($M^+ +1$). Anal. Calcd for $C_{33}H_{37}N_2P$: C, 80.46; H, 7.57; N, 5.69. Found: C, 80.27; H, 7.56; N, 5.85.

4.2.2. (*S*)-*N*-[2-(Diphenylphosphanyl)naphthalen-1-yl]-2-(methoxymethoxymethyl)pyrrolidine (1a). The representative 2-step procedure was used to afford the title ligand **1a** (yield 35%) as a colorless viscous oil. $[\alpha]_D^{24}=+98°$ (*c* 0.41, THF). IR (neat): $\nu=1374$, 1362, 1078 cm^{-1}. ^1H NMR ($CDCl_3$, 55 °C): $\delta=1.93$–2.06 (br, 3H), 2.30–2.46 (br, 1H), 3.15 (s, 3H), 3.20–3.32 (br, 2H), 3.38 (d, $J=6.3$ Hz, 2H), 4.16–4.28 (br, 1H), 4.34 (s, 2H), 7.07 (dd, $J=1.5$, 3.2 Hz, 1H), 7.24–7.34 (br, 10H), 7.44 (dd, $J=1.5$, 3.2 Hz, 2H), 7.57 (d, $J=7.6$ Hz, 1H), 7.80 (dd, $J=1.5$, 3.2 Hz, 1H), 7.99–8.12 (br, 1H). ^{13}C NMR ($CDCl_3$): 25.15, 30.32, 54.72, 55.07, 63.43, 63.55, 71.83, 96.66, 124.44, 125.72, 126.24, 126.32, 128.11, 128.19, 128.23, 128.32, 128.62, 130.92, 133.43, 133.59, 133.73, 133.89, 135.59. FABMS: $m/z=456$ ($M^+ +1$). Anal. Calcd for $C_{29}H_{30}NO_2P$: C, 76.46; H, 6.64; N, 3.07. Found: C, 76.75; H, 6.48; N, 3.11.

4.2.3. (*S*)-*N*-[2-(Diphenylphosphanyl)naphthalen-1-yl]-2-(*t*-butoxymethyl)pyrrolidine (1c). The representative 2-step procedure was used to afford the title ligand **1c** (yield 44%) as a colorless amorphous. $[\alpha]_D^{27}=+115°$ (*c* 2.26, dioxane). IR (neat): $\nu=1374$, 1362, 1078 cm^{-1}. ^1H NMR ($CDCl_3$, 50 °C): $\delta=0.93$ (s, 9H), 1.91–2.06 (m, 3H), 2.26–2.43 (br, 1H), 3.09–3.31 (m, 4H), 4.00–4.14 (br, 1H), 7.05 (br d, $J=8.4$ Hz, 1H), 7.21–7.33 (m, 10H), 7.43 (br dd, $J=4.2$, 4.2 Hz, 2H), 7.57 (d, $J=8.4$ Hz, 1H), 7.77–7.84 (br, 1H), 7.96–8.12 (br, 1H). ^{13}C NMR ($CDCl_3$): 25.05, 27.54, 30.33, 54.70, 54.76, 64.04, 64.12, 65.65, 72.17, 124.67, 125.52, 126.15, 126.22, 128.04, 128.08, 128.15, 128.25, 128.36, 128.65, 130.73, 133.38, 133.50, 133.67, 133.80, 135.68, 139.02, 139.25, 150.32, 150.65. FABMS: $m/z=468$ ($M^+ +1$). Anal. Calcd for $C_{31}H_{34}NOP$: C, 79.63; H, 7.33; N, 3.00. Found: C, 79.39; H, 7.35; N, 3.24. The physical data of the coupling product in the first step, (*S*)-*N*-[2-(diphenylphosphinoyl)naphthalen-1-yl]-2-(*t*-butoxymethyl)pyrrolidine, with small amounts of inseparable impurities are shown below. This mixture was used for the second step, the reduction reaction, without further separation. IR (neat): $\nu=1387$, 1364, 1196, 1115 cm^{-1}. ^1H

NMR ($CDCl_3$): δ=0.89 (s, 9H), 1.70–1.82 (m, 3H), 2.04–2.20 (br, 1H), 2.71–2.89 (br, 1H), 2.96–3.05 (m, 1H), 3.11 (dd, J=9.1, 4.1 Hz, 1H), 3.23–3.35 (br, 1H), 4.16–4.31 (br, 1H), 7.16 (dd, J=12.7, 8.6 Hz, 1H), 7.37–7.60 (m, 9H), 7.65–7.81 (m, 4H), 7.84 (d, J=7.8 Hz, 1H), 8.23 (br d, J=7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): 24.60, 27.35, 29.45, 54.02, 64.32, 64.50, 71.93, 124.78, 124.98, 125.41, 126.02, 127.38, 127.87, 128.06, 128.49, 129.31, 129.50, 130.79, 130.83, 130.88, 130.92, 131.21, 131.35, 131.63, 131.77, 133.72, 133.92, 135.25, 135.48, 136.72, 136.75, 152.08, 152.14. FABMS: m/z=484 (M^++1).

4.2.4. (*S*)-*N*-[2-(Di-*p*-tolylphosphanyl)naphthalen-1-yl]-2-(benzyloxymethyl)pyrrolidine (1f). The representative 2-step procedure was used to afford the title ligand **1f** (yield 48%) as a colorless viscous oil. $[\alpha]_D^{24}$=+81° (c 0.47, THF). IR (neat): ν=1374, 1308, 1113 cm^{-1}. ^{1}H NMR ($CDCl_3$, 50 °C): δ=1.90–2.09 (br, 3H), 2.22–2.45 (m, 7H), 3.20–3.41 (m, 4H), 4.10–4.30 (br, 3H), 6.98–8.25 (m, 19H). ^{13}C NMR ($CDCl_3$): 21.32, 25.24, 30.26, 54.63, 63.22, 63.32, 72.88, 74.61, 125.58, 126.04, 126.15, 127.02, 127.22, 127.90, 127.98, 129.01, 129.11, 133.44, 133.58, 133.74, 133.88, 137.84, 137.95, 138.81. FABMS: m/z=530 (M^++1). Anal. Calcd for $C_{36}H_{36}NOP$: C, 81.64; H, 6.85; N, 2.64. Found: C, 81.35; H, 6.70; N, 2.65. The physical data of the coupling product in the first step, (*S*)-*N*-[2-(di-*p*-tolylphosphinoyl)naphthalen-1-yl]-2-(benzyloxymethyl)pyrrolidine, with small amounts of inseparable impurities are shown below. This mixture was used for the second step, the reduction reaction, without further separation. IR (neat): ν=1383, 1310, 1186, 1113 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.56–1.73 (br, 1H), 1.78–1.94 (m, 2H), 2.12–2.29 (br, 1H), 2.36 (s, 6H), 2.80–2.99 (br, 1H), 3.11–3.27 (m, 2H), 3.28–3.46 (br, 1H), 4.11 (s, 2H), 4.27–4.48 (br, 1H), 7.03 (br d, J=6.8 Hz, 2H), 7.11–7.32 (m, 8H), 7.36–7.67 (m, 7H), 7.83 (d, J=8.1 Hz, 1H), 8.14–8.24 (br, 1H). ^{13}C NMR ($CDCl_3$): 21.58, 24.81, 29.57, 54.21, 63.38, 72.56, 73.88, 124.80, 124.99, 125.47, 125.73, 126.88, 126.95, 127.43, 127.87, 128.69, 128.75, 128.83, 128.88, 128.93, 129.50, 129.69, 130.34, 130.81, 131.34, 131.48, 131.67, 131.81, 132.40, 136.72, 138.71, 141.19, 141.23, 141.27, 151.86. FABMS: m/z=546 (M^++1).

4.2.5. (*S*)-*N*-[2-(Diphenylphosphanyl)-6-methylphenyl]-2-(benzyloxymethyl)pyrrolidine (1k). The representative 2-step procedure was used to afford the title ligand **1l** (yield 50%) as a colorless viscous oil. $[\alpha]_D^{24}$=+50° (c 0.647, THF). IR (neat): ν=1095 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.49–1.90 (m, 3.5H), 1.99–2.20 (m, 1.2H), 2.27 (s, 3H), 2.60–2.80 (m, 0.6H), 2.85 (dd, J=7.6, 7.6 Hz, 0.9H), 3.09–3.36 (m, 2H), 3.64–3.80 (m, 0.8H), 4.27 (s, 2H), 6.61–6.84 (br, 0.8H), 7.01 (dd, J=7.4, 7.4 Hz, 1H), 6.97–7.40 (16.2H). FABMS: m/z=466 (M^++1). EIMS: m/z=344 (M^+−CH_2OBn, bp), 91. HRMS (M^+−CH_2OBn): calcd for $C_{23}H_{23}NP$: 344.1568; found: 344.1549. The physical data of the coupling product in the first step, (*S*)-*N*-[2-(diphenylphosphinoyl)-6-methylphenyl]-2-(benzyloxymethyl)pyrrolidine, with small amounts of inseparable impurities are shown below. This mixture was used for the second step, the reduction reaction, without further separation. IR (neat): ν=1454, 1418, 1200, 1113 cm^{-1}. ^{1}H NMR ($CDCl_3$, 50 °C): δ=1.30–1.51 (br, 1H), 1.54–1.72 (m, 2H), 1.90–2.05 (m, 2H), 2.29 (s, 3H), 2.43–2.68 (br, 1H), 2.88–3.04 (br, 1H), 3.12–3.23 (m, 2H), 4.22 (s, 2H), 6.89–7.02 (m, 2H), 7.06–7.13 (m, 2H), 7.15–7.49 (m, 9H), 7.61–7.76 (m, 5H). FABMS: m/z=482 (M^++1).

4.2.6. (*S*)-*N*-[2-(Diphenylphosphanyl)-6-methoxylphenyl]-2-(pyrrolidinylmethyl)pyrrolidine (1l). The representative 2-step procedure was used to afford the title ligand **1l** (yield 31%) as a colorless viscous oil. The physical data were comparable to those reported.[18a]

4.2.7. (*S*)-*N*-[2-(Diphenylphosphanyl)-6-methoxylphenyl]-2-methylpiperidine (1m). The representative 2-step procedure was used to afford the title ligand **1m** (yield 30%) as a colorless amorphous. $[\alpha]_D^{25}$=−23° (c 3.51, dioxane). IR (neat): ν=1283, 1258 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=0.67 (d, J=6.3 Hz, 3H), 1.03–1.35 (m, 4H), 1.48 (brd, J=8.3 Hz, 1H), 1.60–1.68 (br, 1H), 2.46 (brd, J=11.1 Hz, 1H), 2.94 (ddd, J=11.1, 11.1, 3.3 Hz 1H), 3.20–3.32 (m, 1H), 3.77 (s, 3H), 6.36 (brd, J=8.1 Hz 1H), 6.81 (d, J=8.1 Hz, 1H), 7.02 (dd, J=8.1, 8.1 Hz, 1H), 7.22–7.36 (m, 10H). ^{13}C NMR ($CDCl_3$): 20.03, 20.08, 25.40, 25.84, 35.20, 52.41, 54.98, 55.18, 111.90, 124.71, 126.09, 126.11, 127.77, 127.82, 127.87, 127.92, 133.87, 134.12, 134.18, 134.42, 138.04, 138.22, 138.91, 139.12, 141.67, 141.79, 141.82, 141.97, 158.83, 158.86. FABMS: m/z=390 (M^++1). Anal. Calcd for $C_{25}H_{28}NOP$: C, 77.10; H, 7.25; N, 3.60. Found: C, 76.96; H, 7.33; N, 3.41. The physical data of the coupling product in the first step, (*S*)-*N*-[2-(diphenylphosphinoyl)-6-methoxylphenyl]-2-methylpiperidine, with small amounts of inseparable impurities are shown below. This mixture was used for the second step, the reduction reaction, without further separation. IR (nujol): ν=1283, 1267, 1190 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=0.52 (d, J=6.4 Hz, 3H), 0.83–1.00 (m, 1H), 1.08–1.34 (m, 4H), 1.79–1.91 (br, 1H), 2.87–2.95 (m, 2H), 3.16–3.30 (m, 1H), 3.80 (s, 3H), 6.62 (ddd, J=13.5, 7.3, 1.6 Hz, 1H), 6.99–7.10 (m, 2H), 7.36–7.50 (m, 6H), 7.73–7.83 (m, 4H). ^{13}C NMR ($CDCl_3$): 19.75, 24.88, 25.42, 34.06, 54.29, 55.19, 55.85, 115.59, 115.62, 125.50, 125.73, 125.88, 126.06, 127.62, 127.73, 127.80, 127.90, 130.48, 130.50, 130.52, 130.54, 131.19, 131.32, 131.56, 131.69, 133.53, 134.00, 135.07, 135.55, 144.08, 144.15, 159.84, 159.99. FABMS: m/z=406 (M^++1).

4.2.8. (*E*)-1-Bromo-2-(4-triisopropylsilyloxymethylphenyl)ethene (3e). To a stirred solution of (*E*)-1-bromo-2-(4-hydroxymethylphenyl)ethene (134 mg, 0.632 mmol) and imidazole (94.2 mg, 1.37 mmol) in DMF (0.6 mL) was gradually added TIPSCl (240 mg, 1.24 mmol) at 0 °C. The reaction mixture was stirred for 1.5 h at rt and purified directly by silica gel column (hexane) to gave 1-bromo-2-(4-triisopropylsilyloxymethylphenyl)ethene (**3e**) (230 mg, 99%) as a colorless oil. IR (neat): ν=1462, 1094 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=0.97–1.24 (m, 3H), 1.09 (d, J=5.6 Hz, 18H), 4.81 (s, 2H), 6.74 (d, J=14.0 Hz, 1H), 7.09 (d, J=14.0 Hz, 1H), 7.26 (d, J=8.3 Hz, 2H), 7.31 (d, J=8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ=12.00, 18.01, 64.63, 105.68, 125.73, 125.87, 134.23, 136.82, 141.71. EIMS: m/z=370 (M^+), 368 (M^+), 325 (bp), 195. HRMS: m/z calcd for $C_{18}H_{29}^{79}BrOSi$: 368.1171; found: 368.1180.

4.3. Representative procedure for the stereoselective synthesis of (*E*)-1-bromo-2-arylethene (3)[23]

4.3.1. 1-Bromo-2-(2-bromophenyl)ethene (3h). To a stirred solution of 1,1-dibromo-2-(2-bromophenyl)ethene (580 mg, 1.72 mmol) and EtOAc (302 mg, 3.44 mmol) in THF (5.7 mL) was gradually added $LiAlH_4$ (130 mg, 3.44 mmol) at −40 °C. The mixture was stirred for 8 h at the same temperature and quenched with a small amount of acetone. To the mixture was then added $Na_2SO_4 \cdot 10H_2O$. The whole mixture was stirred for 1 h at rt and filtered to remove white precipitates. After concentration, purification by silica gel column (hexane) gave 1-bromo-2-(2-bromophenyl)ethene (**3h**) (283 mg, 65%) as a 17:1 mixture of *E*- and *Z*-isomers. a colorless oil. IR (neat): ν=1605, 1462, 1435 cm^{-1}. ^1H NMR ($CDCl_3$): δ=6.76 (d, J=14.0 Hz, 1H), 7.15 (ddd, J=7.7, 7.7, 1.6 Hz, 1H), 7.27 (ddd, J=7.7, 7.7, 1.2 Hz, 1H), 7.39 (dd, J=7.7, 1.6 Hz, 1H), 7.43 (d, J=14.0 Hz, 1H), 7.55 (dd, J=7.7, 1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ=109.14, 122.63, 126.95, 127.53, 129.44, 132.99, 135.78, 136.03. EIMS: m/z=264 (M^+), 262 (M^+), 260 (M^+), 181 (bp), 75. HRMS: m/z calcd for $C_8H_6^{79}Br_2$: 259.8836; found: 259.8839.

4.3.2. 1,1-Dibromo-2-(3-bromophenyl)ethene. The published procedure[26] was used to afford the title dibromoalkene (yield 99%) as a pale yellow oil. IR (neat): ν=1589, 1560, 1470 cm^{-1}. ^1H NMR ($CDCl_3$): δ=7.23 (dd, J=7.6, 7.9 Hz, 1H), 7.41 (s, 1H), 7.43 (d, J=7.9 Hz, 1H), 7.47 (d, J=7.6 Hz, 1H), 7.68 (s, 1H). ^{13}C NMR ($CDCl_3$): δ=91.37, 122.31, 126.85, 129.79, 131.01, 131.34, 135.24, 137.08. EIMS: m/z=344 (M^+), 342 (M^+), 340 (M^+, bp) 338 (M^+), 261, 180. HRMS: m/z calcd for $C_8H_5^{79}Br_3$: 337.7941; found: 337.7953.

4.3.3. (*E*)-1-Bromo-2-(3-bromophenyl)ethene (3i). The above representative procedure was used to afford the title bromoalkene (yield 65%, *E*/*Z*=23: 1) as a colorless oil. IR (neat): ν=1605, 1593, 1562, 1475, 1470 cm^{-1}. ^1H NMR ($CDCl_3$): δ=6.80 (d, J=14.0 Hz, 1H), 7.04 (d, J=14.0 Hz, 1H), 7.18–7.24 (m, 2H), 7.38–7.48 (m, 2H). ^{13}C NMR ($CDCl_3$): δ=108.13, 122.82, 124.61, 128.85, 130.17, 131.03, 135.62, 137.75. EIMS: m/z=264 (M^+), 262 (M^+, bp), 260 (M^+), 102, 75. HRMS: m/z calcd for $C_8H_6^{79}Br_2$: 259.8836; found: 259.8823.

4.4. Representative procedure for the cross-coupling with $PdCl_2(MeCN)_2$-the ligand 1j catalyst (entry 2, Table 2)

1-Phenylethylmagnesium chloride (2.10 mL, 1.50 mmol, 0.70 mol/L in Et_2O) was added to the mixture of $PdCl_2(MeCN)_2$ (9.3 mg, 0.036 mmol) and the ligand **1j** (18.2 mg, 0.0369 mmol) in α,α,α-trifluorotoluene (2.10 mL) at 0 °C, and the solution was stirred at the same temperature for 30 min (CAUTION: stirring at 0 °C for 30 min for the favorable complexation of Pd and ligand **1j** is needed.). To the solution was added β-bromostyrene (*E*/*Z*=6:1, **3a**) (133 mg, 0.727 mmol) at −10 °C. The resulting solution was stirred for 6 h at −10 °C. After usual work-up, purification by silica gel column (hexane) afforded (*S*)-(*E*)-1,3-diphenyl-1-butene (**5a**) (105 mg, 69%, 71% ee) as a colorless oil. The ee was determined by HPLC analysis (Daicel chiralcel OD, hexane/*i*-PrOH=100:1, 0.3 mL/min, 254 nm): t_R/min=34.9 (*S*), 37.1 (*R*). The absolute configuration was determined by comparison of the reported specific rotation.[8] The physical data were comparable to those reported.[8]

4.5. Representative procedure for the cross-coupling reaction with $Pd_2(dba)_3$-the ligand 1j catalyst (entry 5, Table 2)

1-Phenylethylmagnesium chloride (2.10 mL, 1.50 mmol, 0.70 mol/L in Et_2O) was added to the mixture of $Pd_2(dba)_3 \cdot CHCl_3$ (19.1 mg, 0.0180 mmol) and the ligand **1j** (18.2 mg, 0.0369 mmol) in α,α,α-trifluorotoluene (2.10 mL) at −30 °C, and the solution was stirred at the same temperature for 30 min. To the solution was added β-bromostyrene (*E*/*Z*=6:1, **3a**) (133 mg, 0.727 mmol) at −30 °C. The resulting solution was stirred for 7 h at −30 °C. After usual work-up, purification by silica gel column (hexane) afforded (*S*)-(*E*)-1,3-diphenyl-1-butene (**5a**) (96.9 mg, 64%, 76% ee) as a colorless oil. The ee was determined by HPLC analysis with Daicel chiralcel OD. The absolute configuration was determined by comparison of the reported specific rotation.[8] The physical data were comparable to those reported.[8]

4.5.1. (*S*)-(*E*)-1-(4-Tolyl)-3-phenyl-1-butene (5b). Yield 73%, 78% ee. The desired product **5b** was obtained as a mixture with 2,3-diphenylbutane. The chemical yield of **5b** was calculated on the basis of ^1H NMR analysis of the mixture. The protons of these compounds were assigned, respectively, by comparison with the authentic sample (±)-**5b**, which was prepared by Wittig olefination of 2-phenylpropionaldehyde with $Ph_3P{=}CH$(4-tolyl), and commercially available 2,3-diphenylbutane. The ee was determined by HPLC analysis with Daicel chiralcel OD (hexane/*i*-PrOH=200:1), and its absolute configuration was determined by HPLC analysis with Daicel Chiralpak AD (hexane/*i*-PrOH/TFA=9:1:0.1) after conversion ((i) OsO_4, NMO, *t*-BuOH–H_2O, (ii) RuO_2, $NaIO_4$, CCl_4-MeCN–H_2O, 0 °C) of **5b** to 2-phenylpropionic acid **7** of known configuration. Physical data of the authentic sample (±)-(*E*)-**5b**. A colorless oil. IR (neat): ν=1603, 1456, 967 cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.46 (d, J=6.9 Hz, 3H), 2.32 (s Hz, 3H), 2.87 (sept, J=6.9 Hz, 1H), 3.57–3.68 (m, 1H), 6.33–6.37 (m, 2H), 7.06–7.35 (m, 9H). EIMS: m/z= 222 (M^+), 207 ($M^+ - CH_3$, bp). HRMS (M^+): calcd for $C_{17}H_{18}$ 222.1409; found: 222.1401.

4.5.2. (*S*)-(*E*)-1-(4-Isopropylphenyl)-3-phenyl-1-butene (5c). Yield 75%, 80% ee. The desired product **5c** was obtained as a mixture with 2,3-diphenylbutane. The chemical yield of **5c** was calculated on the basis of ^1H NMR analysis of the mixture. The protons of these compounds were assigned, respectively, by comparison with the authentic sample (±)-**5c**, which was prepared by Wittig olefination of 2-phenylpropionaldehyde with $Ph_3P{=}CH$(4-*i*-Pr-C_6H_4), and commercially available 2,3-diphenylbutane. The ee was determined by HPLC analysis with Daicel chiralcel OD (hexane/*i*-PrOH=200:1), and its absolute configuration was determined by HPLC analysis with Daicel Chiralpak AD (hexane/*i*-PrOH/TFA=9:1:0.1) after conversion of **5c** to 2-phenylpropionic acid **7** of known

configuration. Physical data of the authentic sample (±)-(*E*)-**5c**. A colorless oil. IR (neat): ν=1603, 1453, 968 cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.23 (d, J=6.9 Hz, 3H×2), 1.45 (d, J=7.1 Hz, 3H), 2.87 (sept, J=6.9 Hz, 1H), 3.62 (dt, J=6.9, 6.9 Hz, 1H), 6.28–6.46 (m, 2H), 7.10–7.34 (m, 9H). ^{13}C NMR ($CDCl_3$): 21.34, 24.04, 33.88, 42.56, 126.00, 126.04, 126.44, 127.20, 128.23, 128.33, 134.21, 135.08, 145.66, 147.72. EIMS: m/z=250 (M^+), 207 (bp). HRMS (M^+): calcd for $C_{19}H_{22}$ 250.1722; found: 250.1715.

4.5.3. (*S*)-(*E*)-1-(4-Chlorophenyl)-3-phenyl-1-butene (5d). Yield 80%, 71% ee. The desired product **5d** was obtained as a mixture with 2,3-diphenylbutane. The chemical yield of **5d** was calculated on the basis of ^1H NMR analysis of the mixture. The protons of these compounds were assigned, respectively, by comparison with the known **5d**[27] and commercially available 2,3-diphenylbutane. The ee was determined by HPLC analysis with Daicel chiralcel OD (hexane/*i*-PrOH=200:1), and its absolute configuration was determined by HPLC analysis with Daicel Chiralpak AD (hexane/*i*-PrOH/TFA=9:1:0.1) after conversion of **5d** to 2-phenylpropionic acid **7**.

4.5.4. (*S*)-(*E*)-1-(4-Hydroxymethylphenyl)-3-phenyl-1-butene (8). The ee of **5e** was determined by HPLC analysis with Daicel chiralpak AD (hexane/*i*-PrOH=20:1), and its absolute configuration was determined by HPLC analysis with Daicel Chiralpak AD (hexane/*i*-PrOH/TFA=9:1:0.1) after conversion of **5e** to 2-phenylpropionic acid of known configuration. Since the desired product **5e** was obtained as a mixture with 2,3-diphenylbutane, the desilylation was performed without further separation. The solution of the above mixture and TBAF (187 mg, 0.717 mmol) in THF (1.2 mL) were stirred for 1 h at 0 °C, and purified directly by silica gel column (EtOAc/hexane=1:2) to gave (*S*)-(*E*)-1-(4-hydroxymethylphenyl)-3-phenyl-1-butene (**8**) (81 mg, 61%, 2 steps, 73% ee) as a pale yellow oil. $[\alpha]_D^{23}=-36°$ (*c* 2.08, THF). IR (neat): ν=1491, 1451, 1011 cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.46 (d, J=7.1 Hz, 3H), 1.68–1.76 (br, 1H), 3.58–3.67 (m, 1H), 4.63 (s, 2H), 6.34–6.43 (m, 2H), 7.17–7.35 (m, 9H). ^{13}C NMR ($CDCl_3$): δ=21.26, 42.59, 65.12, 126.14, 126.23, 127.12, 127.20, 128.03, 128.40, 135.29, 136.98, 139.52, 145.46. EIMS: m/z=238 (M^+), 115 (bp). Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.27; H, 7.68.

4.5.5. (*S*)-(*E*)-1-(2-Bromophenyl)-3-phenyl-1-butene (5h). Yield 22%, 60% ee. The desired product **5h** was obtained as a mixture with 2,3-diphenylbutane. The chemical yield of **5h** was calculated on the basis of ^1H NMR analysis of the mixture. The protons of these compounds were assigned, respectively, by comparison with the known **5h**[28] and commercially available 2,3-diphenylbutane. The ee and absolute configuration were determined by HPLC analysis with Daicel chiralcel OD and OD-H (hexane/*i*-PrOH=400:1) after conversion (*t*-BuLi, THF, −40 °C) of **5h** to **5a**.

4.5.6. (*S*)-(*E*)-1-(3-Bromophenyl)-3-phenyl-1-butene (5i). Yield 65%, 70% ee. The desired product **5i** was obtained as a mixture with 2,3-diphenylbutane. The chemical yield of **5i** was calculated on the basis of ^1H NMR analysis of the mixture. The protons of these compounds were assigned, respectively, by comparison with the authentic sample (±)-**5i**, which was prepared by Wittig olefination of 2-phenylpropionaldehyde with Ph_3P=CH(3-Br-C_6H_4), and commercially available 2,3-diphenylbutane. The ee and absolute configuration were determined by HPLC analysis with Daicel chiralcel OD and OD-H (hexane/*i*-PrOH=400:1) after conversion (*t*-BuLi, THF, −40 °C) of **5i** to **5a** of known configuration. Physical data of the authentic sample (±)-**5i**. A colorless oil. IR (neat): ν=1591, 1558, 1493, 1474, 1450 cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.46 (d, J=6.9 Hz, 3H), 3.63 (dq, J=6.9, 6.9 Hz, 1H), 6.27–6.44 (m, 2H), 7.08–7.37 (m, 8H), 7.50 (s, 1H). EIMS: m/z=288 (M^+), 286 (M^+), 207 (bp), 192, 130. HRMS (M^+): calcd for $C_{16}H_{15}^{79}Br$: 286.0357; found: 286.0369.

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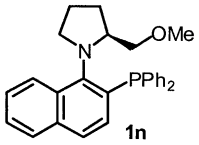

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