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Asymmetric allylic substitution catalyzed by palladium–Yliphos complex

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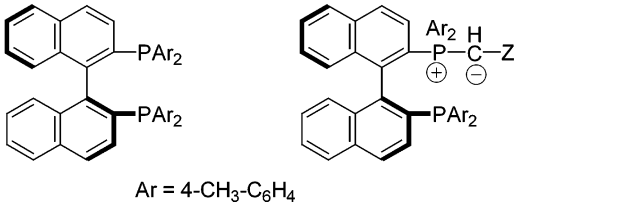
Abstract—Allylic substitution reactions catalyzed by Pd– or Pt–Yliphos complexes are examined. The reaction of 1,3-diphenyl-2-propenyl acetate with benzylamine proceeded in the presence of $Pd(dba)_2$–Yliphos to give *N*-benzyl-1,3-diphenyl-2-propenylamine in high yields with high enantioselectivities (up to 90% *ee*). Furthermore, the allylic alkylation of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate catalyzed by Pd–Yliphos complex resulted in high enantioselectivity (95% *ee*) in the presence of LiH as base.

1. Introduction

The asymmetric allylic substitution reaction by chiral metal complexes has attracted much attention in view of the high asymmetric induction and usefulness of the products.[1] Although many important results have been reported so far, recent approaches have been directed toward substrate-tailored catalyst systems. Recently, chiral bidentate ligands having different kinds of coordination sites have opened a new era in asymmetric reactions.[2,3]

We have already reported the preparation of chiral mono ylide–mono phosphine ligands (Yliphos, **2**) from diphosphine (TolBINAP, **1**) and also the preparation of their metal complexes.[4,5] These Yliphos–Pd(0) complexes were successfully applied to asymmetric allylic substitution reactions. Herein we wish to describe the details of this reaction.



(*S*)-**1**: (*S*)-TolBINAP (*S*)-**2a**: Z = CN ((*S*)-CN-TolYliphos)
(*S*)-**2b**: Z = CO_2Et ((*S*)-Et-TolYliphos)
(*S*)-**2c**: Z = $CO_2{}^tBu$ ((*S*)-^{t}Bu-TolYliphos)

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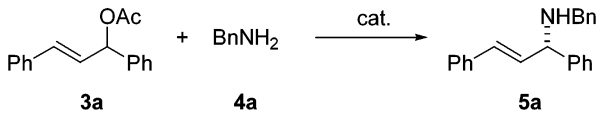
2. Results and discussion

2.1. Amination reaction

The reaction of 1,3-diphenyl-2-propenyl acetate **3a** with benzylamine **4a** (2.5 equiv. to **3a**) proceeded slowly in THF in low yield with good enantioselectivity (78% *ee*) using (*S*)-**2a**–Pd(0) complex as the catalyst (Scheme 1, Table 1, entry 6). The reaction conditions were then optimized (Table 1). In cyclohexane, acetonitrile, or dichloromethane, the enantiomeric excesses were somewhat low, while no reaction occurred in DMF or DMSO. Consequently, the reaction occurs either in toluene, THF, or dioxane. Using 2.5 equiv. of amine resulted in a low yield of the product, while increasing the amount of amine made the reaction proceed faster. With 20 equiv. of amine relative to **3a**, the yield of **5a** became 98% without any loss of enantiomeric excess (Table 1, entry 8). The reaction temperature did not strongly affect the yields and enantiomeric excesses (Table 1, entries 8–10). The combination of (*S*)-**2a** and $Pt(dba)_2$ showed no catalytic activity at all.

Next, the effect of a substituent on the ylide carbon was investigated. Three Yliphos ligands (*S*)-**2a**–**c** were used for this reaction, and cyano-substituted Yliphos **2a** (CN-TolYliphos) showed good results, while using



3a **4a** **5a**

Scheme 1.

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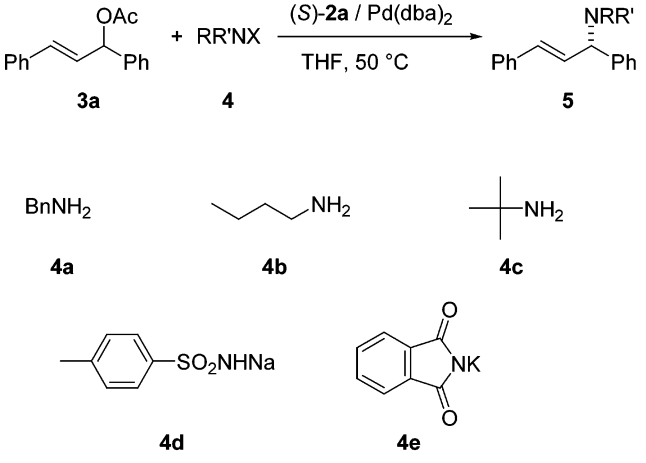
Table 1. Effects of reaction conditions on the reaction of **3a** and benzylamine **4a** catalyzed by (*S*)-**2a**/Pd(dba)$_2$[a]

Entry	Ligand	Solvent	Amount of **4a** (equiv. to **3a**)	Product **5a**	
				Yield (%)[b]	% *ee*[c]
1	(*S*)-**2a**	Cyclohexane	2.5	48	68
2	(*S*)-**2a**	Toluene	2.5	69	90
3	(*S*)-**2a**	1,4-Dioxane	2.5	46	87
4	(*S*)-**2a**	CH_2Cl_2	2.5	75	62
5	(*S*)-**2a**	CH_3CN	2.5	56	46
6	(*S*)-**2a**	THF	2.5	30	78
7	(*S*)-**2a**	THF	10	75	82
8	(*S*)-**2a**	THF	20	98	79
9[d]	(*S*)-**2a**	THF	20	99	84
10[e]	(*S*)-**2a**	THF	20	72	85
11	(*S*)-**2b**	THF	20	32	54
12	(*S*)-**2c**	THF	20	28	25

[a] A mixture of **3a** (0.25 mmol), **4a**, and catalyst (5 mol%, (*S*)-2/Pd(dba)$_2$) in solvent (1 mL) was stirred at 50°C for 48 h.
[b] Isolated yield based on **3a**.
[c] Determined by HPLC analysis using a Daicel Chiralcel OD-H column.
[d] At room temperature.
[e] At 0°C.

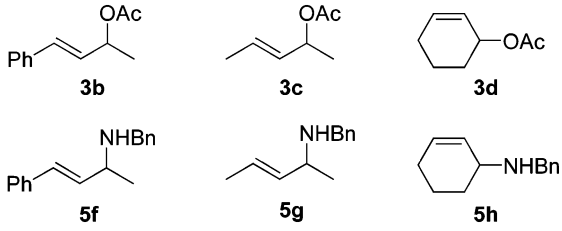
alkoxycarbonyl-substituted Yliphos **2b** or **2c** resulted in low yields with low selectivities (Table 1, entries 8, 11, and 12).

Various nitrogen nucleophiles were employed under standard reaction conditions in the presence of the (*S*)-**2a**–Pd(0) complex (Scheme 2 and Table 2). When primary amines **4a**–**c** were used, the bulkiness of the nucleophiles **4** substantially influenced the yields of the products. That is, the reactions of benzylamine and butylamine proceeded smoothly to give the product in almost quantitative yield with about 80% *ee*, while no reaction occurred with the use of *t*-butylamine as a substrate.

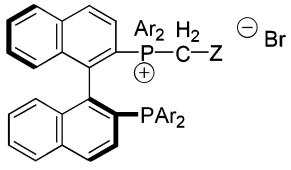


Scheme 2.

Several allylic substrates were tried for this amination: 1,3-diphenyl-2-propenyl acetate **3a** was converted to all corresponding allylamine derivatives in good yield with high enantiomeric excess. Less hindered substrate **3b** was converted to **5f** in good yield with low *ee* (95% yield, 5% *ee*), while **5g** was obtained from the reaction of 3-propen-2-yl acetate **3c** in 43% yield with no stereoselectivity. Furthermore, almost no reaction occurred on employing **3d** as a substrate.



From our previous study, Yliphos ligands (*S*)-**2a**–**c** coordinate to the metal center strongly via the phosphorus atom of the phosphine moiety and weakly via the anionic carbon atom of the ylide.[4] That is, Yliphos can act as a monodentate and/or a bidentate ligand. To obtain information on the coordination modes of Yliphos, monophosphine–monophosphonium compounds (*S*)-**2a**–**c**·HBr, Yliphos·HBr, precursors to Yliphos, were used for this reaction as ligands (Table 3), because Yliphos·HBr may coordinate only as a monodentate ligand. Interestingly, the enantiomeric excesses of the product **5a** from the reaction of **3a** with benzylamine **4a** were nearly similar using (*S*)-**2a**–**c**·HBr as a ligand, although substituted derivatives were different (Table 3). In the case of the reactions using (*S*)-**2a**–**c** as a ligand, enantiomeric excesses of the products were different (Table 1, entries 8, 10, and 11). These results indicate that Yliphos may not coordinate to the palladium center in monodentate fashion unlike Yliphos·HBr.



Ar = 4-CH_3-C_6H_4

(*S*)-**2a**·HBr: Z = CN ((*S*)-CN-TolYliphos·HBr)
(*S*)-**2b**·HBr: Z = CO_2Et ((*S*)-Et-TolYliphos·HBr)
(*S*)-**2c**·HBr: Z = $CO_2{}^t$Bu ((*S*)-^{t}Bu-TolYliphos·HBr)

Table 2. Several nucleophiles in catalytic allylic amination reaction[a]

Entry	Nucleophiles	Product			
			Yield (%)[b]	% *ee*[c]	Config.[d]
1	**4a**	**5a**	98	79	*S*
2[e]	**4a**	**5a**	99	84	*S*
3	**4b**	**5b**	Quant.	78	(−)
4[e]	**4b**	**5b**	Quant.	81	(−)
5	**4c**	**5c**	Trace	–	–
6	**4d**	**5d**	40	63	(−)
7	**4e**	**5e**	5	69	*S*

[a] A mixture of **3a** (0.25 mmol), **4** (5.0 mmol), and catalyst (5 mol%, (*S*)-**2a**/Pd(dba)$_2$) in THF (1 mL) was stirred at 50°C for 48 h.
[b] Isolated yield based on **3a**.
[c] Determined by HPLC analysis using a Daicel Chiralcel OD-H column.
[d] Determined by the sign of the optical rotation value and/or the retention time in chiral HPLC analysis.
[e] At room temperature.

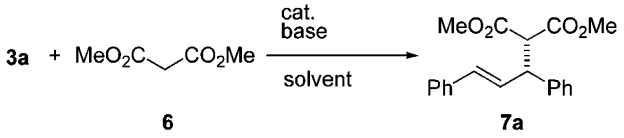
Table 3. Effect of ligand on the reaction of **3a** with **4a** by Pd complex[a]

Entry	Ligand	Yield (%)[b]	% *ee*[c]	Config.[d]
1	(*S*)-**2a**·HBr	76	83	*S*
2	(*S*)-**2b**·HBr	80	83	*S*
3	(*S*)-**2c**·HBr	42	82	*S*

[a] A mixture of **3a** (0.25 mmol), **4a** (5.0 mmol), and catalyst (5 mol%, ligand/Pd(dba)$_2$) in THF (1 mL) was stirred at 50°C for 48 h.
[b] Isolated yield based on **3a**.
[c] Determined by HPLC analysis using a Daicel Chiralcel OD-H column.
[d] Determined by the sign of the optical rotation value and/or the retention time in chiral HPLC analysis.

2.2. Alkylation reaction

Alkylation of **3a** using the anion of dimethyl malonate with NaH in THF resulted in poor selectivity using platinum– or palladium–Yliphos catalyst. The reaction solvent was optimized for the reaction of **3a** with **6** in the presence of potassium acetate and BSA with Pd(dba)$_2$–(*S*)-**2a** catalyst (Scheme 3 and Table 4). The reaction proceeded smoothly in THF or DMF, while higher selectivity was obtained in CH_3CN or CH_2Cl_2.

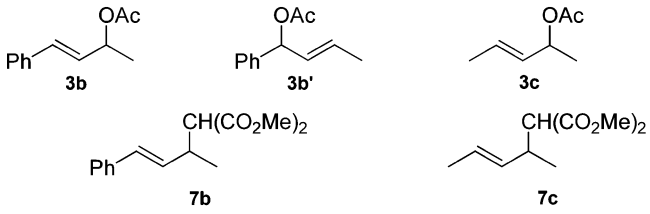


Scheme 3.

Next, the effect of the base was examined for the reaction of **3a** and **6** (Table 4). Using metal acetate combined with BSA as a base system, lithium acetate showed the best results among the metal acetates used. Diethylzinc, which is effective for the allylic alkylation using the BINAP–Pd complex,[6] showed low selectivity. Bases containing lithium were then tried for this catalysis. Lithium hydride gave excellent results, while other lithium compounds showed good but lower selectivities than lithium hydride. Sodium hydride and potassium hydride were not good bases for this reaction. Interestingly, the addition of LiCl to the NaH promoted reaction increased the enantiomeric excess of 70–81%. The reaction of **3a** with **6** in the presence of LiH proceeded smoothly at room temperature to give the alkylation product **7a** in 91% yield with 95% enantiomeric excess.

Using LiH as the base, the reaction conditions (catalyst ratio, ligand, amount of nucleophile, reaction temperature) were optimized. As shown in Table 4, the most favorable reaction conditions are room temperature, 2 mol% catalyst, and 3 equiv. of **6** to **3a**. CN–Yliphos (*S*)-**2a** is the best among the Yliphos ligands tested, while Yliphos ligands having an alkoxycarbonyl substituent showed moderate enantioselectivities.

When sterically less hindered allylic substrates **3b**, **3b′**, **3c** were employed, the selectivity and reactivity were lower as in the case of the amination reaction (**7b** from **3b**: 88% yield, **7b** from **3b′**: 84, **7c** from **3c**: 57% yield. Every product was racemic).



3. Conclusion

The activity of the Yliphos–Pd complexes for allylic substitution has been demonstrated. In the amination reaction, a higher concentration of amine accelerates the reaction, while LiH was the most effective base additive for alkylation. Further investigations on the utility of this unique Yliphos are in progress.

Table 4. Allylic alkylation reaction catalyzed by Pd complex[a]

Entry	Ligand	Solvent	Base	Yield[d]	% *ee*[b,c]
1	(*S*)-**2a**	THF	KOAc + BSA	99	32
2	(*S*)-**2a**	CH_3CN	KOAc + BSA	83	43
3	(*S*)-**2a**	DMF	KOAc + BSA	92	12
4	(*S*)-**2a**	CH_2Cl_2	KOAc + BSA	57	38
5	(*S*)-**2a**	THF	LiOAc + BSA	47	84
6	(*S*)-**2a**	THF	NaOAc + BSA	44	59
7	(*S*)-**2a**	THF	RbOAc + BSA	90	22
8	(*S*)-**2a**	THF	CsOAc + BSA	69	39
9	(*S*)-**2a**	THF	$ZnEt_2$	65	15
10	(*S*)-**2a**	THF	LiH	91	95
11	(*S*)-**2a**	THF	*n*-BuLi	92	73
12	(*S*)-**2a**	THF	LDA	65	73
13	(*S*)-**2a**	THF	CH_3Li	85	87
14	(*S*)-**2a**	THF	NaH	97	70
15	(*S*)-**2a**	THF	KH	94	14
16	(*S*)-**2a**	THF	NaH + LiCl	98	81
17[d]	(*S*)-**2a**	THF	LiH	33	87
18	(*S*)-**2b**	THF	LiH	81	61
19	(*S*)-**2c**	THF	LiH	43	64
20[e]	(*S*)-**2a**	THF	LiH	93	80
21[f]	(*S*)-**2a**	THF	LiH	87	91

[a] A mixture of **3a** (0.50 mmol), **6** (1.50 mmol), base (1.50 mmol), and catalyst (2 mol%, $Pd_2(dba)_3{\cdot}CHCl_3$+(*S*)-**2a**) in THF (2 mL) was stirred at room temperature for 24 h.
[b] Isolated yield based on **3a**. Absolute configuration of the product of each entry was (*R*).
[c] Determined by HPLC analysis using a Daicel Chiralcel OD-H column. Absolute configuration of the product of each entry was (*R*).
[d] At 0°C.
[e] 1 mol% of catalyst was used.
[f] 1.0 mmol of **6** was used.

4. Experimental

^{1}H NMR spectra were measured on a JEOL JNM-A400 (400 MHz) spectrometer using tetramethylsilane as the internal standard. IR spectra were measured on a Shimadzu IR-408. Optical rotations were recorded on a Horiba SEPA-200 spectrophotometer. Gas chromatographic analyses were conducted on a Shimadzu GC-8A (5% Silicone SE-30 on Chromosorb W (AW-DMCS 80–100 mesh), 2 m, 80–220°C). Liquid chromatographic analyses were conducted using Hitachi L-7100 (Daicel CHIRALCEL OD-H, 0.25 m). GC–MS spectra were measured on a Shimadzu QP-2000. HRMS (FAB) was measured on JEOL M-700 using *m*-nitrobenzyl alcohol as a matrix and PEG-200 as a calibration standard.

All reactions were carried out under an argon atmosphere. The solvents were distilled prior to use: diethyl ether, THF, dioxane, 1,2-dimethoxyethane, benzene and toluene were distilled over Na/benzophenone; acetonitrile and dichloromethane were distilled over P_2O_5; methanol and ethanol were distilled over Mg; chloroform, DMF, and DMSO were distilled over CaH_2. 1,3-Diphenyl-2-propenyl acetate **3a**,[7] 1-phenyl-2-butenyl acetate **3b**,[7] 2-acetoxy-3-pentene **3c**,[7] 2-cyclohexenyl acetate **3d**,[2a] phosphonium salts TolYliphos·HBr, (*S*)-**2a**–**c**·HBr,[4] TolYliphos (*S*)-**2a**–**c**,[4] $Pd(dba)_2$,[8] and $Pt(dba)_2$[9] were prepared according to literature methods. Other materials were purchased and used without further purification.

4.1. Asymmetric allylic amination reaction: general procedure

Under Ar, ligand ((*S*)-**2a**–**c**, (*S*)-**2a**–**c**·HBr, 0.025 mmol), $Pd(dba)_2$ (214 mg, 0.025 mmol), THF (1.0 mL) were mixed and stirred for 30 min in a 20 mL Schlenk tube. To this were added 1,3-diphenyl-2-propenyl acetate **3a** (126 mg, 0.50 mmol) and benzylamine **4a** (1.09 mL, 10.0 mmol), and the mixture was stirred at 50°C for 48 h. The reaction mixture was divided into saturated aqueous ammonium chloride and diethyl ether. Organic layer was dried over anhydrous magnesium sulfate, concentrated, and purified by column chromatography (silica gel, ethyl acetate:hexane = 1:4) to give **5a** as a colorless oil.

4.1.1. (*E*)-*N*-Benzyl-1,3-diphenyl-2-propenylamine 5a. Yield 99%; 84% *ee* (*S*) (Daicel Chiralcel OD-H, 1:99 2-propanol:hexane, 0.5 mL/min, UV 254 nm, 15.4 (*R*), 16.2 (*S*)); $[\alpha]_D^{25} = +21.0$ (*c* 1.4, $CHCl_3$) (lit.[10] $[\alpha]_D^{25} = +25$ (*c* 1.76, $CHCl_3$) for 96% *ee* (*S*)); ^{1}H NMR ($CDCl_3$) δ 1.70 (s, 1H), 3.77 (d, $J = 13.2$ Hz, 1H), 3.79 (d, $J = 13.2$ Hz, 1H), 4.40 (d, $J = 7.6$ Hz, 1H), 6.32 (dd, $J = 7.6$ and 15.8 Hz, 1H), 6.58 (d, $J = 15.8$ Hz, 1H), 7.13–7.52 (m, 15H).

4.1.2. (*E*)-*N*-Butyl-1,3-diphenyl-2-propenylamine 5b. Yield 100%; 81% *ee* (Daicel Chiralcel OD-H, 1:99 2-propanol:hexane, 0.5 mL/min, UV 254 nm, 9.4 (+), 10.2 (–)); $[\alpha]_D^{25} = -15.3$ (*c* 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.90 (t, $J = 7.4$ Hz, 3H), 1.27–1.39 (m, 2H),

1.49 (q, $J=7.4$ Hz, 2H), 1.74 (s, 1H), 2.54 (dt, $J=7.4$ and 11.4 Hz, 1H), 2.65 (dt, $J=7.4$ and 11.4 Hz, 1H), 4.35 (d, $J=7.4$ Hz, 1H), 6.30 (dd, $J=7.4$ and 15.8 Hz, 1H), 6.56 (d, $J=15.8$ Hz, 1H), 7.18–7.41 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 13.99, 20.43, 32.11, 47.37, 65.69, 126.34, 127.18, 127.22, 127.35, 128.42, 128.53, 130.10, 132.53, 136.83, 142.81; HRMS (FAB, in 3-nitrobenzyl alcohol) calcd. for $C_{19}H_{23}N$: 264.1752, found 264.1762.

4.1.3. (*E*)-*N*-(1,3-Diphenyl-2-propenyl)-4-methylbenzenesulfonamide 5d[11]. Yield 40%; 63% *ee* (Daicel Chiralcel OD-H, 20:80 2-propanol:hexane, 0.5 mL/min, UV 254 nm, 14.9 (–), 20.0 (+)); $[\alpha]_D^{25}=-7.0$ (*c* 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 3H), 4.99 (d, $J=7.2$ Hz, 1H), 5.11 (t, $J=7.2$ Hz, 1H), 6.07 (dd, $J=6.8$ and 15.6 Hz, 1H), 6.35 (d, $J=15.6$ Hz, 1H), 7.13–7.28 (m, 12H), 7.65–7.67 (m, 2H).

4.1.4. (*E*)-*N*-(1,3-Diphenyl-2-propenyl)phthalimide 5e[11]. Yield 5%; 69% *ee* (*S*) (Daicel Chiralcel OD-H, 1:99 2-propanol:hexane, 0.5 mL/min, UV 254 nm, 22.3 (*S*), 30.8 (*R*)); ^{1}H NMR ($CDCl_3$) δ 6.13 (d, $J=8.6$ Hz, 1H), 6.72 (d, $J=15.6$ Hz), 7.06 (dd, $J=8.6$ and 15.6 Hz, 1H), 7.23–7.49 (m, 10H), 7.70 (m, 2H), 7.83–7.85 (m, 2H).

4.1.5. (*E*)-*N*-Benzyl-1-phenyl-2-buten-3-ylamine 5f[12]. Yield 95%; 5% *ee* (Daicel Chiralcel OD-H, 1:99 2-propanol:hexane, 0.5 mL/min, UV 254 nm, 13.9 (+), 15.4 (–)); $[\alpha]_D^{25}=+1.3$ (*c* 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.26 (d, $J=6.4$ Hz, 3H), 1.54 (s, 1H), 3.37–3.48 (m, 1H), 3.73 (d, $J=13.2$ Hz, 1H), 3.84 (d, $J=13.2$ Hz, 1H), 6.11 (dd, $J=7.8$ and 15.8 Hz, 1H), 6.48 (d, $J=15.8$ Hz, 1H), 7.20–7.40 (m, 10H).

4.1.6. (*E*)-*N*-Benzyl-3-penten-2-ylamine 5g[13]. Yield 43%; $[\alpha]_D^{25}=0.0$ (*c* 2.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.07 (d, $J=6.8$ Hz, 3H), 1.62 (d, $J=6.8$ Hz, 3H), 1.93 (s, 1H), 3.10 (m, 1H), 3.59 (d, $J=13$ Hz, 1H), 3.71 (d, $J=13$ Hz, 1H), 5.26 (dd, $J=8$ and 15.2 Hz, 1H), 5.48 (dq, $J=6.8$ and 15.2 Hz, 1H), 7.1–7.3 (m, 5H).

4.2. Asymmetric allylic alkylation reaction: general procedure

Into a 20 mL Schlenk tube were added TolYliphos (5.0×10^{-3} mmol), $Pd(dba)_2$ (23 mg, 5.0×10^{-3} mmol) and THF (1.0 mL) under an argon atmosphere. After the mixture was stirred for 30 min, 1,3-diphenyl-2-propenyl acetate **3a** (63 mg, 0.25 mmol) was introduced. To this was added a mixture of dimethyl malonate **6** (0.09 mL, 0.75 mmol) and lithium hydride (4 mg, 0.75 mmol) in THF (1.0 mL). The resulting mixture was stirred for 24 h at room temperature. This reaction mixture was divided into saturated aqueous ammonium chloride and diethyl ether. The organic layer was dried over anhydrous magnesium sulfate, concentrated, and purified by column chromatography (silica gel, ethyl acetate/hexane = 1:4) to give **7a** as a colorless oil.

4.2.1. (*E*)-Dimethyl 1,3-diphenylprop-2-enylpropanedioate 7a. Yield 91%; 95% *ee* (*R*) (Daicel Chiralcel OD-H column, 1:99 2-propanol:hexane, 0.3 mL/min, UV 254 nm, 27.9 min (*R*), 29.2 min (*S*)); $[\alpha]_D^{25}=+17.4$ (*c* 1.1, EtOH) (lit.[14] $[\alpha]_D^{23}=+18.4$ (*c* 1.1, EtOH)); ^{1}H NMR ($CDCl_3$) δ 3.52 (s, 3H), 3.70 (s, 3H), 3.96 (d, $J=11.2$ Hz, 1H), 4.27 (dd, $J=8.2$ and 11.2 Hz, 1H), 6.33 (dd, $J=8.2$ and 16.0 Hz, 1H), 6.48 (d, $J=16.0$ Hz, 1H), 7.18–7.33 (m, 10H).

4.2.2. (*E*)-Dimethyl (1-styrylethyl)propanedioate 7b[15]. Yield 88%; $[\alpha]_D^{25}=+0.0$ (*c* 1.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.19 (d, $J=6.8$ Hz, 3H), 3.09–3.16 (m, 1H), 3.40 (d, $J=8.8$ Hz, 1H), 3.66 (s, 3H), 3.73 (s, 3H), 6.12 (dd, $J=8.0$ and 16.0 Hz, 1H), 6.45 (d, $J=16.0$ Hz, 1H), 6.90–7.30 (m, 5H).

4.2.3. (*E*)-Dimethyl (1-methyl-2-butenyl)propanedioate 7c[16]. Yield 57%; $[\alpha]_D^{25}=+0.0$ (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.99 (d, $J=6.8$ Hz, 3H), 1.58 (d, $J=6.8$ Hz, 3H), 2.79–2.85 (m, 1H), 3.19 (d, $J=8.8$ Hz, 1H), 3.62 (d, $J=14.8$ Hz, 6H), 5.24–5.30 (m, 1H), 5.41–5.48 (m, 1H).

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References

1. (a) Kagan, H. B.; Fiaud, J. C. *Top. Stereochem.* **1978**, *10*, 175; (b) Bosnish, B.; Fryzuk, M. D. *Top. Stereochem.* **1981**, *12*, 119; (c) Morrison, J. D. *Asymmetric Synthesis*; Academic Press Inc: New York, 1985; Vol. 5; (d) *Catalytic Asymmetric Synthesis*, Ojima, I., Ed.; VHC Publisher, Inc.; Weinheim, 1993; p. 2000; (e) Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H. *Comprehensive Asymmetric Catalysis I–III*; Springer: Berlin, 2000.
2. (a) Hayashi, T.; Kawatsura, M.; Uozumi, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1681–1687; (b) Kawatsura, M.; Uozumi, Y.; Ogasawara, M.; Hayashi, T. *Tetrahedron* **2000**, *56*, 2247–2257; (c) Kodama, H.; Taiji, T.; Ohta, T.; Furukawa, I. *Tetrahedron: Asymmetry* **2000**, *11*, 4009–4015; (d) Brown, J. M.; Hulmes, D. I.; Guiry, P. J. *Tetrahedron* **1994**, *50*, 4493–4506; (e) Vyskocil, S.; Smrcina, M.; Hanus, V.; Polasek, M.; Kocovsky, P. *J. Org. Chem.* **1998**, *63*, 7738–7748; (f) Martin, C. J.; Rawson, D. J.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1998**, *9*, 3723–3730.
3. (a) von Matt, P.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 566–567; (b) Evans, P. A.; Brandt, T. A. *Tetrahedron Lett.* **1996**, *37*, 9143–9146; (c) Zhang, W.; Hirao, T.; Ikeda, I. *Tetrahedron Lett.* **1996**, *37*, 4545–4548; (d) Chelucci, G.; Cabras, M. A.; Botteghi, C.; Basoli, C.; Marchetti, M. *Tetrahedron: Asymmetry* **1996**, *7*, 885–895; (e) Baldwin, I. C.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1995**, *6*, 1515–1518; (f) Wimmer, P.; Widhalm, M. *Tetrahedron: Asymmetry* **1995**, *6*, 657–660; (g) Rieck, H.; Helmchen, G. *Angew. Chem., Int. Ed. Engl.*

1995, *34*, 2687–2689; (h) Nakano, H.; Okuyama, Y.; Yanagida, M.; Hongo, H. *J. Org. Chem.* **2001**, *66*, 620–625; (i) Steinhagen, H.; Reggelin, M.; Helmchen, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2108–2110; (j) Anderson, J. C.; James, D. S.; Mathias, J. P. *Tetrahedron: Asymmetry* **1998**, *9*, 753–756.

4. Ohta, T.; Fujii, T.; Kurahashi, N.; Sasayama, H.; Furukawa, I. *Sci. Eng. Rev. Doshisha Univ.* **1998**, *39*, 133–141.
5. Recently, Yliphos (Z = H) was reported to act as a bidentate ligand in rhodium complex: Viau, L.; Lepetit, C.; Commenges, G.; Chauvin, R. *Organometallics* **2001**, *20*, 808–810.
6. Fuji, K.; Kinoshita, N.; Tanaka, K. *J. Chem. Soc., Chem. Commun.* **1999**, 1895–1896.
7. Auburn, P. R.; Mackenzie, P. B.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2033–2046.
8. Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253–266.
9. Cherwinski, W. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 1405–1409.
10. Sudo, A.; Saigo, K. *J. Org. Chem.* **1997**, *62*, 5508–5513.
11. Kodama, H.; Taiji, T.; Ohta, T.; Furukawa, I. *Synlett* **2001**, 385–387.
12. Selvakumar, K.; Valentini, M.; Woerle, M.; Pregosin, P. S.; Albinati, A. *Organometallics* **1999**, *18*, 1207–1215.
13. von Matt, P.; Loiseleur, O.; Koch, G.; Pfaltz, A.; Lefeber, C.; Feucht, T.; Helmchen, G. *Tetrahedron: Asymmetry* **1994**, *5*, 573–584.
14. Yamaguchi, M.; Shima, T.; Yamagishi, T.; Hida, M. *Tetrahedron: Asymmetry* **1991**, *2*, 663–666.
15. (a) Zhou, B.; Xu, Y. *J. Org. Chem.* **1988**, *53*, 4419–4421; (b) Pena-Cabrera, E.; Norrby, P. O.; Sjogren, M.; Vitagliano, A.; Felice, V. D.; Oslob, J.; Ishii, S.; O'Neill, D.; Akermark, B.; Helquist, P. *J. Am. Chem. Soc.* **1996**, *118*, 4299–4313.
16. Wiese, B.; Helmchen, G. *Tetrahedron Lett.* **1998**, *39*, 5727–5730.