



Phosphine-oxazoline ligands with an axial-unfixed biphenyl backbone: the effects of the substituent at oxazoline ring and P phenyl ring on Pd-catalyzed asymmetric allylic alkylation

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ABSTRACT

A novel kind of chiral phosphine-oxazoline ligands **3** with an axial-unfixed biphenyl backbone bearing different substituent on oxazoline ring and P phenyl ring was prepared. These ligands exist as a mixture of two diastereomers in equilibrium in solution. Upon coordinated to Pd(II), however, only one of the two possible kinds of diastereomer complexes with different axial chirality was formed. These compounds as chiral ligands were applied in Pd-catalyzed asymmetric allylic alkylation with high reaction activity and enantioselectivity. Meanwhile, the asymmetric catalytic behavior was affected obviously by the substituent at oxazoline ring and P phenyl ring. The best result, up to 92.3% ee and 99% yield, was obtained with the ligand **3c** having two phenyl groups on P and a phenyl group on oxazoline ring in this asymmetric catalysis reaction.

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1. Introduction

Transition metal-catalyzed asymmetric synthesis is one of the most interesting and challenging fields in the modern organic chemistry.¹ Since chiral ligand is one of the origins of asymmetric induction, the design and synthesis of novel chiral ligands are always the key issues in the development of efficient catalysis systems.² Among the various chiral ligands, axially chiral biaryl ligands draw much attention because they exhibit excellent chirality transfer properties.³ In view of atom economy, traditional axial-fixed ligands require inconvenient enantiomer resolution or diastereomer separation in their synthetic processes, and generally, only one enantiomeric or diastereomeric pure form of the ligands works effectively in catalytic asymmetric reactions for industrial uses. Whereas the axial flexible ligands can afford completely a single enantiomeric or diastereomeric metal catalyst on complexing process without any ligand wasting.⁴ Chiral oxazoline ligands derived from readily available amino acids have found widespread use in metal-catalyzed asymmetric reactions, and extensive efforts have been devoted to the preparation of their efficient structural derivatives.⁵ Recently, we had reported a novel *C*₂-symmetric bisoxazoline ligand **1** bearing an axial-unfixed biphenyl backbone (Fig. 1).⁶ These ligands exist as an equilibrium mixture of diastereomers in solution as a result of rotation around the internal bond of the biphenyl. When these ligands coordinated to metal, interestingly, only one of the two

possible diastereomeric complexes were formed and showed excellent enantioselectivities in metal-catalyzed asymmetric reactions.

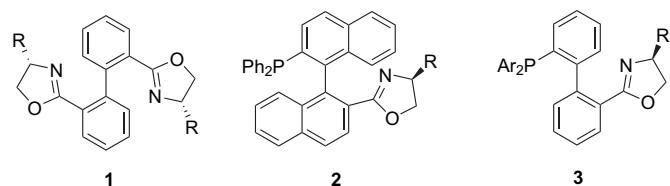
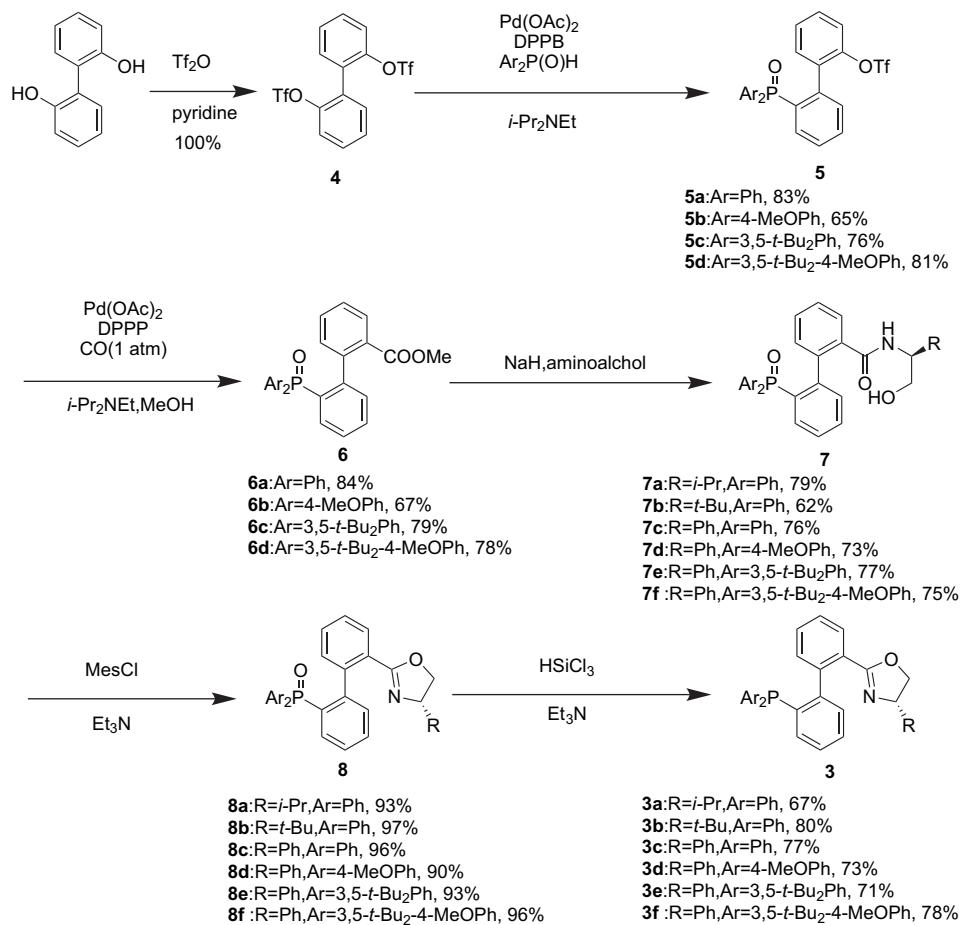


Figure 1. Chiral axial oxazoline ligands.

Ever since PHOX ligands were introduced by Pflatz, Helmchen, and Williams,⁷ which showed excellent reactivity and enantioselectivity in many asymmetric reactions, structure modification of these ligands has been continuing by introducing chiral elements into the ligand backbone.^{5i,1} Several groups including us had independently developed a novel kind of chiral phosphine-oxazoline ligands **2** with an axial-fixed binaphthyl backbone (Fig. 1).^{8,9} These chiral P,N-ligands were successfully employed in metal-catalyzed asymmetric reactions and showed excellent enantioselectivities. Taking into account of the advantages of chiral P,N-chelating binaphthyl ligands **2** and axial-unfixed biphenyl ligand **1** with high usage efficiency and unnecessary resolution process, we designed a novel kind of chiral phosphine-oxazoline ligands **3** (*R*=*i*-Pr, *t*-Bu, Ar=Ph) with an axial-unfixed biphenyl backbone (Fig. 1), which showed excellent reactivity and enantioselectivity in Pd-catalyzed allylic alkylation.¹⁰ In order to further explore the effect of the substituent at the oxazoline ring and P

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Scheme 1. Synthesis of axial-unfixed biphenyl phosphine-oxazoline ligands.

phenyl ring, we report here the synthesis and complexation of **3a–f**, and their application in the Pd-catalyzed asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate with excellent reaction activity and enantioselectivity.

2. Results and discussions

2.1. Ligands preparation

Ligands were prepared from 2,2'-dihydroxybiphenyl as illustrated in Scheme 1. 2,2'-Dihydroxybiphenyl was treated with trifluoromethanesulfonic anhydride (Tf_2O) in the presence of pyridine to give triflate **4** in quantitative yield. Then Pd-catalyzed insertion reactions of **4** with different diarylphosphine oxides were carried out smoothly to afford compounds **5** in 65–83% yield. Next, in the presence of methanol, Pd-catalyzed carboxylation reactions of **5** with CO gave monocarboxylic acid esters **6** in 67–84% yield. In the presence of a catalytic amount of sodium hydride, the reaction of compounds **6** with amino alcohol afforded amide compounds **7** in 62–79% yield. Then, compounds **7** were treated with methanesulfonfonyl chloride in the presence of triethylamine to give cyclic chiral monooxazoline compounds **8** in 90–97% yield. Finally, the reduction of **8** with trichlorosilane afforded the novel chiral ligands **3** in 67–80% yield, which are stable enough to be purified by silica gel column chromatography. The final ligands were obtained in 21–39% overall yield after six steps.

2.2. Behavior of the ligands in solution

The behavior of ligands **3** in solution was then investigated. As shown in Table 1, all of the ligands exist as two diastereomers in solution

Table 1
Diastereomeric ratio of ligands and complexes

	a	b	c	d	e	f
(<i>aS</i>)- 3 :(<i>aR</i>)- 3	52:48	53:47	51:49	53:47	55:45	56:44
(<i>aS</i>)- 10 :(<i>aR</i>)- 10	100:0	100:0	100:0	100:0	100:0	100:0

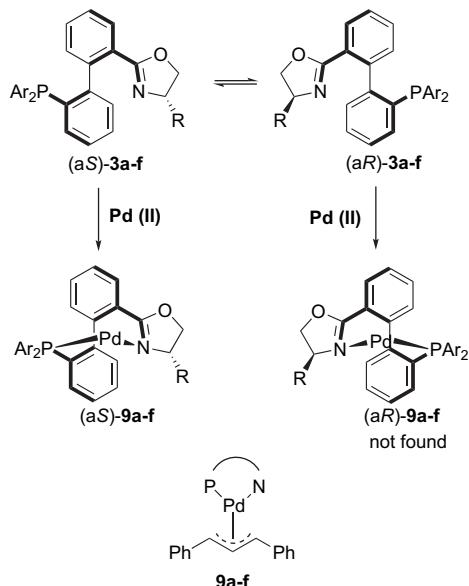
Determined by ^1H NMR and ^{31}P NMR in CDCl_3 at 24 °C.

according to their ^1H NMR and ^{31}P NMR in CDCl_3 . If the temperature was changed, the ratio of the two diastereomers was also changed. This indicated that the ligands exist in an equilibrium due to the rotation around the internal bond of the biphenyl backbone (Scheme 2). It was also found that either the bulkiness of the substituents on the oxazoline ring or the substituent on the P phenyl ring had little effect on the ratio of the two diastereomers for the derivatives **3a–f**.

2.3. Complexation behavior of ligands with Pd(II)

The complexation behavior of ligands **3a–f** with Pd(II) using complex $[\text{Pd}(\eta^3\text{-1,3-diphenylallyl})\text{Cl}]_2$ in solution was then examined. Upon coordinated to the Pd complex, interestingly, all of the ligands gave only one of the two possible diastereomer complexes **9a–f** with different axial chirality in CDCl_3 , respectively, according to their ^1H NMR and ^{31}P NMR spectra (Scheme 2 and Table 1).

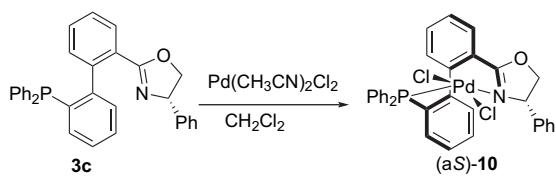
It was reported that the absolute configuration of 2,2'-bridged biphenyl compounds could be determined by their CD spectrum.¹¹ We chose **9a** and **9b** as representatives to determine their absolute axial chirality configuration by CD spectrum. Both **9a** and **9b** displayed negative Cotton effect at 260 nm. The results suggested that



Scheme 2. Complexation behavior of ligands 3a-f.

the axial chirality of both **9a** and **9b** was characterized as *S* configuration, which were in contrast with the spectra in the literature of axially chiral biphenyl compounds. The axial configurations of **9c–f** were assigned by comparison of their ^1H NMR spectrum with that of **9a** and **9b**.

We also attempted to confirm the complex configuration by single-crystal X-ray analysis. Unfortunately, we could not obtain crystals of **9a–f** suitable for X-ray diffraction analysis. So, the complex **10** was obtained by complexing ligand **3c** with $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ in CH_2Cl_2 (Scheme 3), which could be easily crystallized from CH_2Cl_2 /hexane and afforded crystals suitable for X-ray diffraction analysis. The X-ray diffraction analysis revealed that the ligand **3c** coordinated $\text{Pd}(\text{II})$ with phosphorus and nitrogen atoms, as illustrated in Figure 2, and the complex **10** has an *S* configuration. This result was in accord with that determined by CD spectrum.

Scheme 3. Synthesis of complex **10**.

Furthermore, we found that all of the complexes **9a–f** exist in two diastereomeric intermediates with *W*- and *M*-types observed in their ^1H and ^{31}P NMR spectra. With **9a–b** as representatives, two diastereomeric intermediates with *W*- and *M*-type were observed in the ratio of 54:46, and 58:42, respectively (Scheme 4). According to their NOE spectrum, the major was assigned as *W*-type because there are NOE observations between the proton of the substituent on oxazoline and H^a , and the minor was assigned as *M*-type because there are no NOE observations (Scheme 4).

2.4. Application in Pd-catalyzed asymmetric alkylation

Pd-catalyzed asymmetric allylic alkylation as one of the important C–C bond forming asymmetric reactions has been investigated using various chiral phosphine-oxazoline ligands.^{12,13} We also chose this reaction as the model reaction in this paper. The

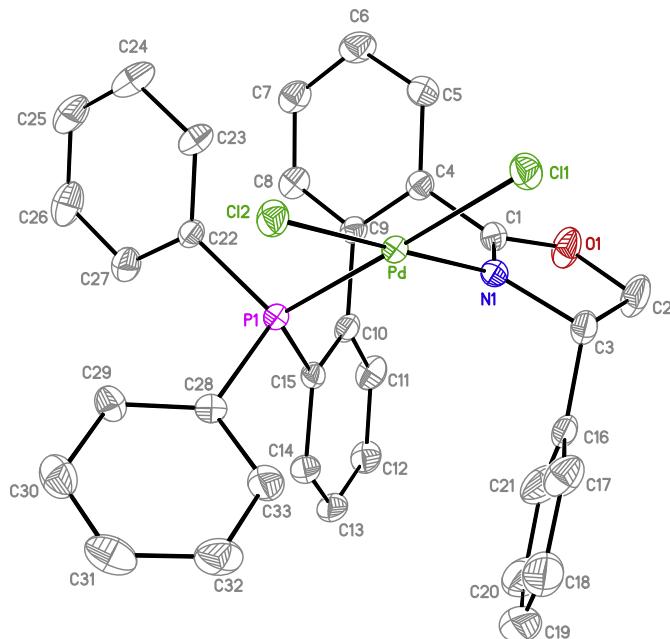
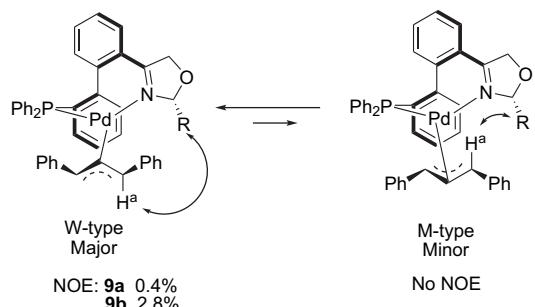


Figure 2. ORTEP view of complex (aS)-10.

Scheme 4. NOE model of **9a–b**.

reaction was carried out by using 1,3-diphenyl-2-propenyl acetate as a typical substrate, bis(trimethylsilyl)acetamide (BSA) as a base, and dimethyl malonate as a nucleophile. The results are summarized in Table 2.

Initially, screening of solvents and additives was carried out. Although THF afforded the highest ee in the reactions without any additives (entries 1–3), CH_2Cl_2 was the suitable solvent when additive was added (entry 5 vs entries 3, 4). The results also showed that LiOAc was better than NaOAc or KOAc (entries 5–7), NaBARF (sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate) was also an efficient additive in this reaction (entry 8), while Cs_2CO_3 gave good yield and moderate enantioselectivity (entry 9). From the above results, it is obvious that CH_2Cl_2 was the suitable solvent and LiOAc was the suitable additive.

Then, the temperature effect was investigated. Whether the temperature rised (entry 10) or decreased (entries 11, 12), the reaction activity and enantioselectivity changed dramatically. When the temperature decreased to -20°C (entry 12), the reaction almost ceased. The results showed that the suitable reaction temperature was 20°C .

Next, the phosphine-oxazoline ligands bearing different substituents on the oxazoline ring and different aryl groups on P atom were investigated. Almost all of the ligands afforded full conversion. Ligand **3c** led to the highest enantioselectivity (92.3% ee, entry 14), whereas ligand **3a** with *i*-Pr (entry 5) or ligand **3b** with *t*-Bu

Table 2
Pd-catalyzed asymmetric allylic alkylation^a

Entry	Ligand	Additive	Solvent	T (°C)	Time (h)	Yield ^b (%)	%ee ^c (config) ^d
1	3a	None	CH ₂ Cl ₂	20	48	68	85.7 (S)
2	3a	None	Toluene	20	48	62	83.7 (S)
3	3a	None	THF	20	48	76	86.3 (S)
4	3a	LiOAc	THF	20	24	99	85.5 (S)
5	3a	LiOAc	CH ₂ Cl ₂	20	24	99	86.5 (S)
6	3a	NaOAc	CH ₂ Cl ₂	20	24	99	81.5 (S)
7	3a	KOAc	CH ₂ Cl ₂	20	24	99	83.2 (S)
8	3a	NaBARF	CH ₂ Cl ₂	20	3	99	83.7 (S)
9	3a	Cs ₂ CO ₃	CH ₂ Cl ₂	20	3	99	53.0 (S)
10	3a	LiOAc	CH ₂ Cl ₂	35	24	99	56.0 (S)
11	3a	LiOAc	CH ₂ Cl ₂	0	24	80	60.5 (S)
12	3a	LiOAc	CH ₂ Cl ₂	-20	24	Trace	Nd ^e
13	3b	LiOAc	CH ₂ Cl ₂	20	24	99	90.0 (S)
14	3c	LiOAc	CH ₂ Cl ₂	20	24	99	92.3 (S)
15	3d	LiOAc	CH ₂ Cl ₂	20	24	99	67.7 (S)
16	3e	LiOAc	CH ₂ Cl ₂	20	24	99	75.5 (S)
17	3f	LiOAc	CH ₂ Cl ₂	20	24	99	85.3 (S)

^a Conducted with 1,3-diphenyl-2-propenyl acetate (1 mmol), dimethyl malonate (3 mmol), BSA (3 mmol), and LiOAc (20 μ mol) in 3 mL of solvent under nitrogen in the presence of the catalyst, which was prepared from ligand (30 μ mol) and $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}_2]$ (13 μ mol) in 1 mL solvent for 1 h before use.

^b Isolated yield.

^c Determined by HPLC (Chiralcel OD).

^d Determined by comparing the sign of its optical rotation with literature data.

^e Not determined.

(entry **13**) gave 86.5% ee and 90.0% ee, respectively. Notably, the different aryl groups on P have great influence on the enantioselectivity, ligand **3d–f** gave 67.7% ee, 75.5% ee and 85% ee, respectively (entries 15–17). The results showed that the substituents on oxazoline ring have a slight effect on the enantioselectivity, whereas the substituents on the P phenyl ring have a significant effect on this reaction.

Finally, the reactivities of the two diastereomers of intermediate **9** were discussed. For the asymmetric allylic alkylation, it is known that, the W-type intermediate leads to the product of *R* configuration and the M-type one leads to the product of *S* configuration, because the *trans* effect directs nucleophilic attack to the allylic terminus *trans* to phosphorus atom.¹⁴ In the present case, the *S* configured product was obtained with all of the ligands **3**. This result suggested that the two conformers may have different reactivity with the nucleophile. The minor M-type diastereomer of **9** has much more reactivity than the major W-type one (Scheme 4), due to the position *trans* to the phosphorus atom becoming more cationic caused by the steric repulsion between the substituent on oxazoline ring and phenyl group.

3. Conclusions

In conclusion, we have developed a novel chiral phosphine-oxazoline ligand **3** with an axial-unfixed biphenyl backbone bearing different substituents on oxazoline ring and P phenyl ring. These ligands exist as a mixture of two diastereomers in equilibrium in solution. Upon coordinated to Pd(II), only one of the two possible kinds of diastereomer complexes with different axial chirality was formed. These compounds were applied as chiral ligands in Pd-catalyzed asymmetric allylic alkylation and the effects of the substituents were examined. The best result was obtained with the ligand **3c** having two phenyl groups on P and a phenyl group on

oxazoline ring, which afforded 92.3% ee. Furthermore, the stability and reactivity of intermediates **9** were discussed.

4. Experimental

4.1. General

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen. The reaction solvents were distilled prior to use (toluene and dichloromethane were distilled from CaH₂, THF was distilled from Na). The commercially available reagents were used without further purification. Column chromatography was run on silica gel (100–200 mesh). Melting points were measured on an X-4 microscopic melting point apparatus and are uncorrected. ¹H, ¹³C, and ³¹P NMR spectra were recorded on a Varian MERCURY plus-400 spectrometer. The ee values were determined by HPLC using a Daicel Chiralcel OD-H column. HRMS was performed on a Micromass LCTTM at the Analysis and Research Center of East China University of Science and Technology.

4.2. Synthesis of biphenyl-2,2'-diyl bis(trifluoromethanesulfonate) **4**

2,2'-Dihydroxyl biphenyl (4.30 g, 23 mmol) was dissolved in a solution of dry pyridine (7.0 mL) in dry CH₂Cl₂ (70 mL) under N₂. To this solution was added Tf₂O (13.0 g, 46 mmol) slowly at 0 °C. The reaction was carried out at 0 °C for 3 h, at which time TLC indicated that the reaction was completed. The reaction mixture was diluted with CH₂Cl₂ and washed subsequently with 1 M HCl, 1 M NaHCO₃, and brine. The CH₂Cl₂ solution was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified by column chromatography with ethyl acetate and petroleum ether (1:9) as eluent to afford biphenyl-2,2'-diyl bis(trifluoromethanesulfonate) (10.3 g, 100%, white solid). Mp 35–36 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.44 (dd, *J*=1.5, 8.1 Hz, 2H), 7.48 (dd, *J*=2.2, 7.3 Hz, 2H), 7.51 (td, *J*=1.5, 7.3 Hz, 2H), 7.56 (ddd, *J*=2.2, 8.1, 7.3 Hz, 2H).

4.3. General procedure for the synthesis of **5**

Biphenyl-2,2'-diyl bis(trifluoromethanesulfonate) (**4**) (1.9 g, 4.1 mmol), Pd(OAc)₂, DPPB (88 mg, 0.21 mmol), and diarylphosphine oxide (4.8 mmol) were added to a two-neck flask under N₂. To this flask were added dry DMSO (20 mL) and DIPEA (2.9 mL, 16 mmol). The reaction mixture was heated to 100 °C for 8 h, at which time TLC indicated that the reaction was completed. The reaction mixture was diluted with CH₂Cl₂ and washed subsequently with 1 M HCl, 1 M NaHCO₃, and brine. The CH₂Cl₂ solution was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified by column chromatography with ethyl acetate and petroleum ether as eluent to afford compound **5**.

4.3.1. Compound 5a. 83% yield, white powder. Mp 120–122 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.90–6.93 (m, 1H), 7.23–7.26 (m, 2H), 7.28–7.32 (m, 2H), 7.37–7.56 (m, 10H), 7.58–7.64 (m, 1H), 7.65–7.71 (m, 2H).

4.3.2. Compound 5b. 65% yield, pale yellow solid. Mp 106–108 °C. ¹H NMR (400 MHz, CDCl₃): δ 3.79 (s, 3H), 3.84 (s, 3H), 6.77–6.83 (m, 2H), 6.90–6.98 (m, 3H), 7.22–7.27 (m, 2H), 7.32–7.48 (m, 6H), 7.50–7.60 (m, 3H). HRMS (Micromass LCT) calcd for C₂₇H₂₂F₃O₆PS (M+H)⁺: 563.0905; found: 563.0893.

4.3.3. Compound 5c. 76% yield, white powder. Mp 147–149 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.24 (s, 18H), 1.28 (s, 18H), 6.90–6.94

(m, 1H), 7.15–7.24 (m, 2H), 7.33–7.46 (m, 7H), 7.50–7.60 (m, 4H). HRMS (Micromass LCT) calcd for $C_{41}H_{50}F_3O_4PS$ ($M+H$)⁺: 727.3198; found: 727.3170.

4.3.4. Compound 5d. 81% yield, white powder. Mp 114–115 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.32 (s, 18H), 1.35 (s, 18H), 3.66 (s, 3H), 3.70 (s, 3H), 7.00–7.03 (m, 1H), 7.18–7.25 (m, 1H), 7.35–7.47 (m, 9H), 7.55–7.60 (m, 1H). HRMS (Micromass LCT) calcd for $C_{43}H_{54}F_3O_6PS$ ($M+H$)⁺: 787.3409; found: 787.3397.

4.4. General procedure for the synthesis of 6

A mixture of triflates **5** (11.3 mmol), Pd(OAc)₂ (381.7 mg, 1.70 mmol), DPPP (701.1 mg, 1.70 mmol), MeOH (60 mL), DMSO (90 mL), and Et₃N (24 mL) was saturated with CO and freeze-pumped for three times, and then stirred under a CO atmosphere at 70 °C. The reaction mixture was monitored by TLC for full conversion. After cooling to room temperature, the mixture was concentrated at reduced pressure. The residue was diluted with CH₂Cl₂ and washed with 1 M HCl and brine. The organic phase was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel eluted with ethyl acetate and petroleum ether to afford esters **6**.

4.4.1. Compound 6a. 84% yield, white powder. Mp 93–95 °C. ¹H NMR (400 MHz, CDCl₃): δ 3.64 (s, 3H), 7.18–7.27 (m, 6H), 7.33–7.65 (m, 12H).

4.4.2. Compound 6b. 67% yield, pale yellow powder. Mp 60–64 °C. ¹H NMR (400 MHz, CDCl₃): δ 3.56 (s, 3H), 3.78 (s, 3H), 3.79 (s, 3H), 6.78–6.84 (m, 4H), 6.92–6.95 (m, 1H), 7.04–7.18 (m, 6H), 7.24–7.38 (m, 4H), 7.92–7.96 (m, 1H). HRMS (Micromass LCT) calcd for $C_{28}H_{25}O_5P$ ($M+H$)⁺: 473.1518; found: 473.1527.

4.4.3. Compound 6c. 79% yield, white powder. Mp 69–72 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.24 (s, 18H), 1.25 (s, 18H), 3.68 (s, 3H), 7.05–7.21 (m, 4H), 7.32–7.54 (m, 9H), 7.73–7.77 (m, 1H). HRMS (Micromass LCT) calcd for $C_{42}H_{53}O_3P$ ($M+H$)⁺: 637.3811; found: 637.3804.

4.4.4. Compound 6d. 78% yield, white powder. Mp 75–78 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.32 (s, 18H), 1.35 (s, 18H), 3.64 (s, 3H), 3.65 (s, 3H), 3.67 (s, 3H), 7.09–7.18 (m, 4H), 7.33–7.52 (m, 7H), 7.77–7.81 (m, 1H). HRMS (Micromass LCT) calcd for $C_{44}H_{57}O_5P$ ($M+H$)⁺: 697.4022; found: 697.4017.

4.5. General procedure for the synthesis of 7

A solution of L-amino alcohol (3.0 mmol) in THF (8.0 mL) was added to a two-neck flask, which charged with NaH (60 mg, 1.5 mmol) at 0 °C. After stirring at rt for 1 h, at which time white precipitate emerged, the mixture was cooled to 0 °C again and a solution of **6** (1.0 mmol) in THF (8.0 mL) was added. The reaction mixture was stirred at rt overnight and monitored by TLC for full conversion. The reaction was quenched with water and concentrated at reduced pressure. The residue was diluted with CH₂Cl₂ and washed with 1 M HCl and brine. The organic phase was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel eluted with ethyl acetate and petroleum ether to afford esters **7**.

4.5.1. Compound 7a. 79% yield, viscous oil. ¹H NMR (400 MHz, CDCl₃) (major/minor=55:45 in CDCl₃): δ 0.40 (d, J =7.0 Hz, 3H), 0.75 (d, J =6.6 Hz, 3H), 0.98 (d, J =7.0 Hz, 3H), 1.01 (d, J =7.0 Hz, 3H), 1.52–1.67 (m, 1H), 1.89–2.00 (m, 1H), 2.44 (t, J =6.6 Hz, 1H), 3.23–3.35 (m, 2H), 3.60–3.74 (m, 3H), 6.11 (d, J =7.7 Hz, 1H), 6.14 (d, J =7.7 Hz, 1H),

6.62–6.68 (m, 2H), 7.17–7.62 (m, 25H), 7.68 (dd, J =0.7, 7.7 Hz, 1H), 7.70–7.77 (m, 4H), 8.40 (dd, J =0.7, 9.2 Hz, 1H), 8.83 (d, J =8.4 Hz, 1H).

4.5.2. Compound 7b. 62% yield, viscous oil. ¹H NMR (400 MHz, CDCl₃) (major/minor=58:42 in CDCl₃): δ 0.61 (s, 9H), 1.03 (s, 9H), 3.28–3.35 (m, 1H), 3.50–3.57 (m, 1H), 3.72–3.90 (m, 4H), 6.12 (dd, J =1.1, 7.3 Hz, 1H), 6.15 (dd, J =0.7, 7.7 Hz, 1H), 6.60 (d, J =1.1, 7.7 Hz, 1H), 6.68 (td, J =1.1, 7.3 Hz, 1H), 7.18–7.81 (m, 30H), 8.13 (d, J =9.9 Hz, 1H), 8.44 (d, J =8.8 Hz, 1H).

4.5.3. Compound 7c. 76% yield, white foam. ¹H NMR (400 MHz, CDCl₃) (major/minor=56:44 in CDCl₃): δ 3.32–3.41 (m, 3H), 3.47–3.57 (m, 2H), 3.72–3.90 (m, 1H), 6.64 (d, J =7.7 Hz, 1H), 6.72 (d, J =7.3 Hz, 1H), 7.18–7.81 (m, 42H), 8.18 (d, J =9.9 Hz, 1H), 8.48 (d, J =8.8 Hz, 1H).

4.5.4. Compound 7d. 73% yield, viscous oil. ¹H NMR (400 MHz, CDCl₃) (major/minor=62:38 in CDCl₃): δ 3.83 (s, 3H), 3.84 (s, 3H), 3.88 (s, 3H), 3.89 (s, 3H), 4.95–5.03 (m, 1H), 6.15 (d, J =7.8 Hz, 1H), 6.21 (dd, J =7.8, 17.6 Hz, 1H), 6.54 (d, J =8.0 Hz, 1H), 6.73 (dt, J =1.2, 8.0 Hz, 1H), 6.83 (dt, J =1.2, 8.0 Hz, 1H), 6.89–7.69 (m, 42H).

4.5.5. Compound 7e. 77% yield, white foam. ¹H NMR (400 MHz, CDCl₃) (major/minor=55:45 in CDCl₃): δ 1.19 (s, 18H), 1.22 (s, 18H), 1.24 (s, 18H), 1.28 (s, 18H), 3.28–3.35 (m, 3H), 3.50–3.57 (m, 2H), 4.95–5.10 (m, 1H), 5.98–6.04 (m, 1H), 6.46–6.59 (m, 2H), 6.91–7.85 (m, 34H), 8.56–9.72 (m, 1H). ³¹P NMR (161 MHz, CDCl₃): δ 35.2, 33.9.

4.5.6. Compound 7f. 75% yield, white foam. ¹H NMR (400 MHz, CDCl₃) (major/minor=52:48 in CDCl₃): δ 1.26 (s, 18H), 1.30 (s, 18H), 1.32 (s, 18H), 1.35 (s, 18H), 3.26–3.37 (m, 3H), 3.51–3.56 (m, 2H), 3.72 (s, 3H), 3.75 (s, 3H), 4.93–5.10 (m, 1H), 5.98–6.04 (m, 1H), 6.46–6.59 (m, 2H), 7.16–7.71 (m, 36H), 9.56–9.72 (m, 1H). ³¹P NMR (161 MHz, CDCl₃): δ 35.4, 34.3.

4.6. General procedure for the synthesis of compound 8

To a solution of **7** (0.9 mmol), triethylamine (0.44 mL, 3.1 mmol) in dichloromethane (6.0 mL) was added methanesulfonyl chloride (90 μ L) at 0 °C. The mixture was stirred for 30 min and then the resulting mixture was warmed to room temperature. The reaction was monitored with TLC for a full conversion. The reaction was quenched with water and diluted with CH₂Cl₂ and washed with 1 M HCl and brine. The organic phase was dried over Na₂SO₄ and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel eluted with ethyl acetate/petroleum ether to afford ligands **8**.

4.6.1. Compound 8a. 93% yield, viscous oil. ¹H NMR (400 MHz, CDCl₃) (major/minor=52:48 in CDCl₃): δ 0.81 (d, J =1.5 Hz, 3H), 0.83 (d, J =1.5 Hz, 3H), 0.84 (d, J =3.7 Hz, 3H), 0.85 (d, J =3.7 Hz, 3H), 1.55–1.64 (m, 1H), 1.66–1.77 (m, 1H), 3.74 (t, J =8.4 Hz, 1H), 3.79–3.88 (m, 3H), 4.01 (dd, J =11.9, 12.8 Hz, 1H), 4.15 (t, J =8.5 Hz, 1H), 7.10–7.18 (m, 5H), 7.18–7.65 (m, 29H), 7.69–7.75 (m, 2H). ³¹P NMR (161 MHz, CDCl₃): δ 28.6, 29.3.

4.6.2. Compound 8b. 97% yield, viscous oil. ¹H NMR (400 MHz, CDCl₃) (major/minor=55:45 in CDCl₃): δ 0.77 (s, 9H), 0.82 (s, 9H), 3.78–3.85 (m, 3H), 3.95 (d, J =7.7 Hz, 1H), 3.96 (d, J =9.9 Hz, 1H), 4.11 (t, J =13.6 Hz, 1H), 7.05–7.64 (m, 34H), 7.71 (dd, J =1.5, 11.4 Hz, 1H), 7.73 (dd, J =1.1, 11.4 Hz, 1H). ³¹P NMR (161 MHz, CDCl₃): δ 28.3, 29.0.

4.6.3. Compound 8c. 96% yield, white foam. ¹H NMR (400 MHz, CDCl₃) (major/minor=56:44 in CDCl₃): δ 3.90 (t, J =8.0 Hz, 1H), 3.93 (t, J =8.0 Hz, 1H), 4.39 (dd, J =8.0, 10.4 Hz, 1H), 4.54 (dd, J =8.0,

10.4 Hz, 1H), 5.17 (t, J =4.0 Hz, 1H), 5.20 (t, J =4.0 Hz, 1H), 7.07–7.72 (m, 46H). ^{31}P NMR (161 MHz, CDCl_3): δ 28.1, 28.7. HRMS (Micromass LCT) calcd for $\text{C}_{33}\text{H}_{26}\text{NO}_2\text{P}$ ($\text{M}+\text{H}$) $^+$: 500.1779; found: 500.1764.

4.6.4. Compound 8d. 90% yield, viscous oil. ^1H NMR (400 MHz, CDCl_3) (major/minor=66:34 in CDCl_3): δ 3.84 (s, 3H), 3.85 (s, 3H), 3.87 (s, 3H), 3.88 (s, 3H), 3.88–3.97 (m, 2H), 4.84–4.90 (m, 2H), 5.21–5.28 (m, 2H), 6.10 (dd, J =1.2, 7.6 Hz, 1H), 6.16 (dd, J =1.2, 7.6 Hz, 1H), 6.68–7.60 (m, 38H), 9.70 (dd, J =1.6, 8.0 Hz, 1H), 9.80 (dd, J =1.6, 8.0 Hz, 1H). ^{31}P NMR (161 MHz, CDCl_3): δ 32.17, 32.19. HRMS (Micromass LCT) calcd for $\text{C}_{35}\text{H}_{30}\text{NO}_4\text{P}$ ($\text{M}+\text{H}$) $^+$: 560.1991; found: 560.1990.

4.6.5. Compound 8e. 93% yield, white foam. ^1H NMR (400 MHz, CDCl_3) (major/minor=58:42 in CDCl_3): δ 1.18 (s, 18H), 1.22 (s, 18H), 1.23 (s, 18H), 1.24 (s, 18H), 3.82 (t, J =9.2 Hz, 1H), 4.00 (t, J =9.2 Hz, 1H), 4.58 (dd, J =7.8, 17.6 Hz, 1H), 4.65 (dd, J =7.8, 17.6 Hz, 1H), 5.18 (t, J =9.2 Hz, 1H), 5.29 (t, J =9.2 Hz, 1H), 7.05–7.56 (m, 36H), 7.71 (dd, J =1.6, 8.0 Hz, 1H), 7.75 (dd, J =1.6, 8.0 Hz, 1H). ^{31}P NMR (161 MHz, CDCl_3): δ 28.46, 29.67. HRMS (Micromass LCT) calcd for $\text{C}_{49}\text{H}_{58}\text{NO}_2\text{P}$ ($\text{M}+\text{H}$) $^+$: 724.4283; found: 724.4299.

4.6.6. Compound 8f. 96% yield, white foam. ^1H NMR (400 MHz, CDCl_3) (major/minor=66:34 in CDCl_3): δ 1.27 (s, 18H), 1.32 (s, 18H), 1.33 (s, 18H), 1.34 (s, 18H), 3.60 (s, 3H), 3.65 (s, 3H), 3.66 (s, 3H), 3.66 (s, 3H), 3.83 (t, J =8.8 Hz, 1H), 4.03 (t, J =8.8 Hz, 1H), 4.60 (dd, J =7.8, 17.6 Hz, 1H), 4.70 (dd, J =7.8, 17.6 Hz, 1H), 5.15 (t, J =9.2 Hz, 1H), 5.29 (t, J =9.2 Hz, 1H), 7.04–7.56 (m, 32H), 7.70 (dd, J =1.6, 8.0 Hz, 1H), 7.75 (dd, J =1.6, 8.0 Hz, 1H). ^{31}P NMR (161 MHz, CDCl_3): δ 28.57, 29.56. HRMS (Micromass LCT) calcd for $\text{C}_{51}\text{H}_{62}\text{NO}_4\text{P}$ ($\text{M}+\text{H}$) $^+$: 784.4495; found: 784.4489.

4.7. General procedure for the synthesis of compound 3

HSiCl_3 (4.2 mL, 39.6 mmol) was added to a solution of **8** (1.3 g, 1.98 mmol) and Et_3N (9.4 mL, 39.6 mmol) in dried and degassed toluene (25 mL) under nitrogen atmosphere, and the mixture was heated under reflux overnight. After cooling to 0 °C, 30% NaOH aq (60 mL) was added, and the mixture was stirred at 60 °C until the organic and aqueous layers became clear. The organic product was extracted with degassed EtOAc (3×30 mL), and the combined organic layer was washed with water (2×20 mL), brine successively and dried over anhydrous Na_2SO_4 . The organic layer was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel eluting with $\text{EtOAc}/\text{hexane}=20:1$ to afford ligands **3**.

4.7.1. Compound 3a. 67% yield, viscous oil. ^1H NMR (400 MHz, CDCl_3) (major/minor=52:48 in CDCl_3): δ 0.79 (d, J =6.6 Hz, 3H), 0.80 (d, J =7.0 Hz, 3H), 0.81 (d, J =7.0 Hz, 3H), 0.84 (d, J =7.0 Hz, 3H), 1.52–1.61 (m, 1H), 1.62–1.71 (m, 1H), 3.69 (t, J =8.4 Hz, 1H), 3.80–3.90 (m, 3H), 4.01 (dd, J =6.6, 8.1 Hz, 1H), 4.09 (dd, J =8.4, 9.5 Hz, 1H), 6.87 (d, J =7.7 Hz, 1H), 6.89 (d, J =7.7 Hz, 1H), 7.07–7.38 (m, 32H), 7.88 (dd, J =1.5, 7.7 Hz, 1H), 7.89 (dd, J =1.5, 7.7 Hz, 1H). ^{31}P NMR (161 MHz, CDCl_3): δ -14.87, -14.96. HRMS (EI) calcd for $\text{C}_{30}\text{H}_{28}\text{NOP}$: 449.1910; found: 449.1905.

4.7.2. Compound 3b. 80% yield, viscous oil. ^1H NMR (400 MHz, CDCl_3) (major/minor=53:47 in CDCl_3): δ 0.73 (s, 9H), 0.81 (s, 9H), 3.75–3.89 (m, 3H), 3.93–4.06 (m, 3H), 6.83 (d, J =8.0 Hz, 1H), 6.88 (d, J =8.0 Hz, 1H), 7.07–7.39 (m, 32H), 7.88 (dd, J =1.5, 7.7 Hz, 1H), 7.89 (dd, J =1.5, 7.7 Hz, 1H). ^{31}P NMR (161 MHz, CDCl_3): δ -14.95, -15.02. HRMS (EI) calcd for $\text{C}_{31}\text{H}_{30}\text{NOP}$: 463.2067; found: 463.2064.

4.7.3. Compound 3c. 77% yield, white foam. ^1H NMR (400 MHz, CDCl_3) (major/minor=51:49 in CDCl_3): δ 3.39 (dd, J =6.0, 11.2 Hz,

1H), 3.59 (dd, J =4.8, 11.2 Hz, 1H), 3.71 (dd, J =6.0, 11.2 Hz, 1H), 3.80 (dd, J =4.8, 11.2 Hz, 1H), 5.28–5.37 (m, 2H), 6.15 (d, J =6.8, 1H), 6.29 (d, J =6.8, 1H), 6.65 (t, J =8.0 Hz, 2H), 6.77 (d, J =8.0 Hz, 2H), 6.91–7.47 (m, 38H), 7.81 (dd, J =1.6, 8.0 Hz, 1H), 7.91 (dd, J =1.6, 8.0 Hz, 1H). ^{31}P NMR (161 MHz, CDCl_3): δ -12.69, -12.85. HRMS (Micromass LCT) calcd for $\text{C}_{33}\text{H}_{26}\text{NOP}$ ($\text{M}+\text{H}$) $^+$: 484.1830; found: 484.1833.

4.7.4. Compound 3d. 73% yield, viscous oil. ^1H NMR (400 MHz, CDCl_3) (major/minor=66:34 in CDCl_3): δ 3.73 (s, 3H), 3.75 (s, 3H), 3.78 (s, 3H), 3.80 (s, 3H), 3.92 (t, J =8.8 Hz, 1H), 4.01 (t, J =8.8 Hz, 1H), 4.48 (dd, J =7.8, 17.6 Hz, 1H), 4.61 (dd, J =7.8, 17.6 Hz, 1H), 5.21 (t, J =9.2 Hz, 1H), 5.26 (t, J =9.2 Hz, 1H), 6.57 (dd, J =2.4, 8.8, 2H), 6.65 (dd, J =2.4, 8.8, 2H), 6.78 (d, J =8.8, 4H), 7.07–7.81 (m, 34H). ^{31}P NMR (161 MHz, CDCl_3): δ -13.78, -13.92. HRMS (Micromass LCT) calcd for $\text{C}_{35}\text{H}_{30}\text{NO}_3\text{P}$ ($\text{M}+\text{H}$) $^+$: 544.2042; found: 544.2048.

4.7.5. Compound 3e. 71% yield, white foam. ^1H NMR (400 MHz, CDCl_3) (major/minor=55:45 in CDCl_3): δ 1.12 (s, 18H), 1.17 (s, 18H), 1.21 (s, 18H), 1.22 (s, 18H), 3.82 (t, J =9.2 Hz, 1H), 3.96 (t, J =9.2 Hz, 1H), 4.43 (dd, J =7.8, 17.6 Hz, 1H), 4.55 (dd, J =7.8, 17.6 Hz, 1H), 5.21 (t, J =9.2 Hz, 1H), 5.24 (t, J =9.2 Hz, 1H), 6.72 (dd, J =3.2, 8.0 Hz, 2H), 6.91 (d, J =3.2 Hz, 1H), 7.00–7.46 (m, 33H), 7.91 (dd, J =1.6, 8.0 Hz, 1H), 8.00 (dd, J =1.6, 8.0 Hz, 1H). ^{31}P NMR (161 MHz, CDCl_3): δ -9.35, -9.97. HRMS (Micromass LCT) calcd for $\text{C}_{49}\text{H}_{58}\text{NOP}$ ($\text{M}+\text{H}$) $^+$: 708.4334; found: 708.4344.

4.7.6. Compound 3f. 78% yield, white foam. ^1H NMR (400 MHz, CDCl_3) (major/minor=56:44 in CDCl_3): δ 1.21 (s, 18H), 1.26 (s, 18H), 1.29 (s, 18H), 1.30 (s, 18H), 3.63 (s, 3H), 3.64 (s, 3H), 3.65 (s, 3H), 3.66 (s, 3H), 3.83 (t, J =8.8 Hz, 1H), 3.94 (t, J =8.8 Hz, 1H), 4.43 (dd, J =7.8, 17.6 Hz, 1H), 4.56 (dd, J =7.8, 17.6 Hz, 1H), 5.21 (t, J =9.2 Hz, 1H), 5.24 (t, J =9.2 Hz, 1H), 6.68 (d, J =3.2, 2H), 6.97–7.36 (m, 30H), 7.90 (dd, J =1.6, 8.0 Hz, 1H), 8.00 (dd, J =1.6, 8.0 Hz, 1H). ^{31}P NMR (161 MHz, CDCl_3): δ -12.01, -12.07. HRMS (Micromass LCT) calcd for $\text{C}_{51}\text{H}_{62}\text{NO}_3\text{P}$ ($\text{M}+\text{H}$) $^+$: 768.4546; found: 768.4537.

4.8. General procedure for the synthesis of complex 9

Ligand **3** (0.030 mmol) and complex $[\text{Pd}(\eta^3\text{-1,3-diphenylallyl})\text{Cl}_2]$ (**9**) (0.017 mmol) were dissolved in CD_2Cl_2 (0.75 mL) under N_2 . After stirring at rt for 30 min, the mixture was transferred to NMR tube and analyzed by ^1H NMR and ^{31}P NMR.

4.8.1. Complex 9a. ^1H NMR (400 MHz, CD_2Cl_2) (major/minor=54:46 in CD_2Cl_2): δ 0.08 (d, J =6.9 Hz, 3H), 0.38 (d, J =7.0 Hz, 3H), 0.51 (d, J =7.0 Hz, 3H), 0.71 (d, J =7.0 Hz, 3H), 1.40–1.50 (m, 1H), 1.77–1.86 (m, 1H), 2.38–2.48 (m, 1H), 3.34 (t, J =9.4 Hz, 1H), 3.80–3.97 (m, 4H), 4.85 (d, J =12.3 Hz, 1H), 4.94 (d, J =10.9 Hz, 1H), 5.68–5.80 (m, 2H), 5.88 (d, J =7.7 Hz, 1H), 5.91 (d, J =8.0 Hz, 1H), 6.53–7.86 (m, 58H). ^{31}P NMR (161 MHz, CD_2Cl_2): δ 24.80, 28.80.

4.8.2. Complex 9b. ^1H NMR (400 MHz, CD_2Cl_2) (major/minor=58:42 in CD_2Cl_2): δ 0.43 (s, 9H), 0.64 (s, 9H), 2.2 (br s, 1H), 3.09 (t, J =9.4 Hz, 3H), 3.68 (dd, J =5.4, 10.5 Hz, 1H), 3.87 (dd, J =9.1, 10.5 Hz, 1H), 3.96–4.03 (m, 2H), 4.80 (d, J =12.3 Hz, 1H), 4.94 (d, J =11.2 Hz, 1H), 5.53 (t, J =10.9 Hz, 1H), 5.83–5.93 (m, 3H), 6.54 (dd, J =11.2, 13.1 Hz, 1H), 6.58–7.87 (m, 55H). ^{31}P NMR (161 MHz, CD_2Cl_2): δ 25.21, 29.10.

4.9. General procedure for palladium-catalyzed asymmetric allylic alkylation

A mixture of ligand (30 μmol) and $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}_2]$ (4.60 mg, 12.5 μmol) in dry dichloromethane (1 mL) was stirred at room temperature under nitrogen for 1 h, and the resulting green solution was added to a mixture of 1,3-diphenyl-2-propenyl acetate (0.252 g, 1.00 mmol) and lithium acetate (0.0020 g, 20 μmol) in dry

dichloromethane (2 mL) via a cannula, followed by the addition of dimethyl malonate (0.396 g, 3.00 mmol) and BSA (0.613 g, 3.00 mmol). The reactions were carried out at room temperature and monitored by TLC for the disappearance of 1,3-diphenyl-2-propenyl acetate. Then the solvent was evaporated and the resulting mixture was extracted with ether (20 mL). The extract was washed twice with ice-cold saturated NH_4Cl aqueous solution (25 mL) and then dried over anhydrous Na_2SO_4 . After removal of the ether, the residue was purified on silica gel column chromatography with hexane/ethyl acetate (8:1) to afford pure product. Viscous oil. ^1H NMR (400 MHz, CDCl_3): δ 3.51 (s, 3H), 3.69 (s, 3H), 3.94 (d, $J=10.8$ Hz, 1H), 4.25 (dd, $J=8.8, 10.8$ Hz, 1H), 6.32 (dd, $J=8.4, 15.6$ Hz, 1H), 6.46 (d, $J=15.6$ Hz, 1H), 7.17–7.32 (m, 10H). The enantiomeric excess was determined by HPLC on a Chiralpak OD-H column, hexane/2-propanol=98:2, flow rate=0.5 mL/min.

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Supplementary data

Supplementary data associated with this article can be found in online version, at doi:10.1016/j.tet.2009.09.053.

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