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The synthesis of phosphine oxide-linked bis(oxazoline) ligands and their application in asymmetric allylic alkylation

Yu Jin, Da-Ming Du *

School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081, China

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ABSTRACT

The phosphine oxide-linked bis(oxazoline) ligands were designed and synthesized in two ways. One is the coupling of Grignard reagent derived from 2-(2-bromophenyl)oxazoline with phenylphosphonic dichloride, another route is the condensation of bis(2-formylphenyl)(phenyl)phosphine oxide with chiral amino alcohols followed by NBS oxidation. These new bis(oxazoline) ligands were applied in Pd-catalyzed asymmetric allylic alkylation reactions and good yields and enantioselectivities were obtained with diphenyl substituted ligand (up to 95% ee).

1. Introduction

Oxazoline ligand has been recognized as one type of the 'privileged ligands' owing to its ready synthesis, modular nature, and successful applications in various catalytic asymmetric reactions. The design, synthesis and applications of chiral oxazoline ligands have gained much attention in recent years.[1] Many types of ligands with diverse scaffolds have been synthesized from commercially available amino alcohols in a few steps. Among the various ligands, some ligand scaffolds can be used in a variety of different asymmetric transformations, while other ligand scaffolds only can be applied in specific reactions. To the best of our knowledge, there is no universal oxazoline ligand suitable for every organic reaction or every substrate. This situation makes the design of novel oxazoline ligands and studies on the relationship of ligand structure and enantioselectivity still a challenging task.

In recent years, the C_2-symmetric chiral bis(oxazoline) ligands **L1**–**L4** with diphenyl bridging backbone (Fig. 1) have been studied extensively because of their excellent applicability to metal cation in combination with stereochemical discrimination. Due to the different bridging linkers, the corresponding bis(oxazoline) ligands have demonstrated different applications in asymmetric reactions.[2–4] For example, ligand **L1** with the bridging linker is NH, which was reported by our group[2] and Guiry's group,[3] these diphenylamine-linked ligands were successfully applied to many asymmetric reactions, such as asymmetric Henry reaction, Michael addition, Friedel–Crafts alkylation, Nozaki–Hiyama–Kishi reaction and so on. The ligand **L2** with the bridging linker is O atom was reported in 2002 by Gómez and co-workers, this diphenyl ether-linked ligand was applied to the asymmetric allylic alkylation and up to 89% ee was obtained.[4a] The good enantioselectivity in asymmetric allylic alkylation was also obtained with diphenyl sulfide-linked ligand **L3**.[4b] Other bridging groups such as phenylphosphine has also been synthesized and applied in asymmetric allylic alkylation.[4c] The bis(oxazoline) ligands containing phosphite linker[5a] or phosphite, phosphinite, and phosphane side arms[5b] were also reported. However, to our knowledge, the synthesis and studies on phosphine oxide-linked bis(oxazoline) ligands have not appeared, although phosphine oxide has well properties to activate some Lewis acids such as allysilane.[5c,5d] In this paper, we designed and synthesized a series of phosphine oxide-linked bis(oxazoline) ligands **L5**–**L9** and studied their applications in Pd-catalyzed asymmetric allylic alkylation reactions.

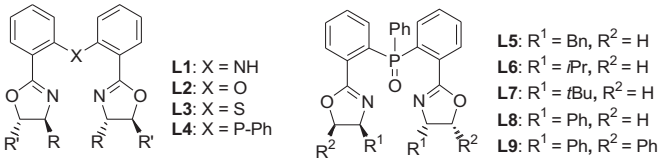

Fig. 1. C_2-symmetric chiral bis(oxazoline) ligands with diphenyl bridging backbone.

* Corresponding author. Tel./fax: +0 86 10 68914985; e-mail address: dudm@bit.edu.cn (D.-M. Du).

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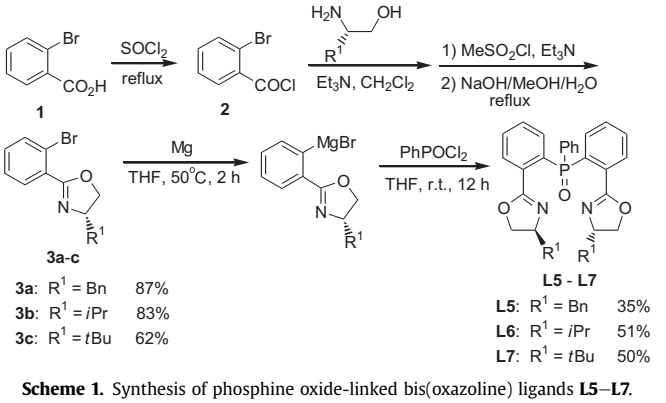
2. Results and discussion

2.1. Synthesis of phosphine oxide-linked bis(oxazoline) ligands

The synthesis of oxazoline has been widely described in the literature and the method of acid derivatives reacting with chiral amino alcohols followed by cyclization was the most widely used method.[6] At first, we designed to synthesize the phosphine oxide-linked bis(oxazoline) ligands through mono-oxazoline coupling. This approach consists of the synthesis of mono-oxazoline semi-ligand, then two equal parts are joined through a Ph–P(O) bridging. The synthesis of mono-oxazoline **3** was initiated from 2-bromobenzoic acid **1**, which was converted into the corresponding acid chloride **2** by refluxing in thionyl chloride. Without further purification, the acid chloride was treated with chiral amino alcohols and Et_3N in CH_2Cl_2, followed by methanesulfonyl chloride, and then refluxed under basic conditions to yield the mono-oxalzoines **3a**–**c**.[7] The products **3** were then converted to corresponding Grignard reagents and the later reacted with phenylphosphonic dichloride ($PhPOCl_2$) to give the corresponding bis(oxazoline) ligands **L5**–**L7** (as shown in Scheme 1).

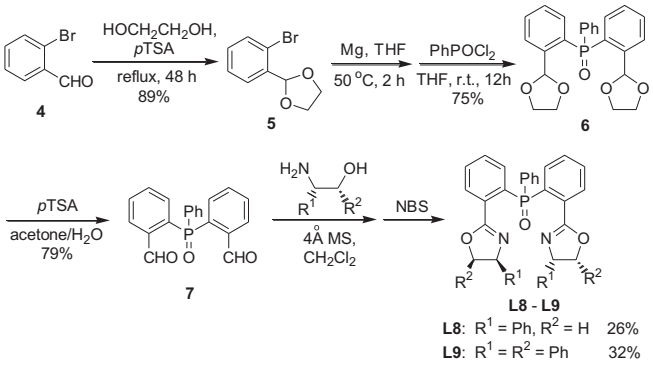


Scheme 1. Synthesis of phosphine oxide-linked bis(oxazoline) ligands **L5**–**L7**.

To our disappointment, the bis(oxazoline) ligands **L8** and **L9** cannot be synthesized through the above Grignard reagent coupling method, this may be ascribed to the active benzyl hydrogens in mono-oxazolines when the substituents in 4- or/and 5-position are phenyl. So we designed another route to synthesize the phosphine oxide-linked bis(oxazoline) ligands **L8** and **L9**. This approach was based on the synthesis of the bis(2-formylphenyl)(phenyl)phosphine oxide bridging linker, followed by the formation of the chiral oxaziline rings. The synthetic route started with 2-bromobenzaldehyde **4**, which was protected by ethylene glycol to yield **5**,[8a] Compound **5** was converted to Grignard reagent,[8b,8c] coupling with $PhPOCl_2$ and then deprotection to afford the corresponding dicarboxyaldehyde **7**.[8d] The latter was transformed into **L8** or **L9** by reacted with corresponding chiral amino alcohols in CH_2Cl_2 in the presence of 4 Å molecular sieves and subsequently oxidized by the *N*-bromosuccinimide (NBS) (as shown in Scheme 2).[9]

2.2. Pd-catalyzed asymmetric allylic alkylation

Allylic alkylation is one of the most versatile methods for forming different types of carbon–carbon and carbon–heteroatom bonds.[10] In order to evaluate the asymmetric catalytic activity of the new ligands, we decided to investigate the asymmetric allylic alkylation reaction. Ligand **L5** was used first in order to establish the optimal reaction conditions for allylic alkylation, in which *rac*-1,3-dipenylpropen-1-yl acetate was chosen as the substrate and dimethyl malonate as the nucleophile (3 equiv) in the presence of

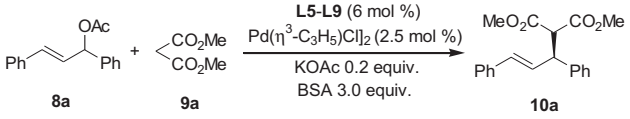


Scheme 2. Synthesis of phosphine oxide-linked bis(oxazoline) ligands **L8**–**L9**.

N,*O*-bis(trimethylsilyl)acetamide (BSA) (3 equiv) and KOAc (acted as BSA activator) (0.2 equiv).

After screening different solvents (as shown in Table 1), we found that the best solvent was $CHCl_3$, although in which the reactivity was lower than toluene, the enantioselectivity was much higher (up to 60% ee) (Table 1, entry 4 vs entry 8). In protic solvent such as ethanol, there was no conversion at all (Table 1, entry 7). In $CHCl_3$, we then studied the effects of ligands **L5**–**L9** in asymmetric allylic alkylation and found that the reactivity and enantioselectivity were highly depended on the substituent group of oxazoline moiety; the steric bulkiness of the substituent on the oxazoline affected the asymmetric induction in this allylic alkylation. To our delight, when the substituent was Ph, both the reactivity and the enantioselectivity were greatly improved. Ligand **L9** synthesized from (1*R*,2*S*)-1,2-dipheny1-2-aminoethanol was regarded as the best ligand because of the best enantioselectivity (94% ee) (Table 1, entry 12). Owing to the long reaction time, we further raised the reaction temperature to improve the activity. The reaction time could be reduced to 3 days when it was performed at 40 °C and the yield was enhanced to 99% with slightly decrease of the enantioselectivity (from 94% to 92% ee) (Table 1, entries 13).

Table 1
Screening of solvents, ligands and temperature in asymmetric allylic alkylation[a]

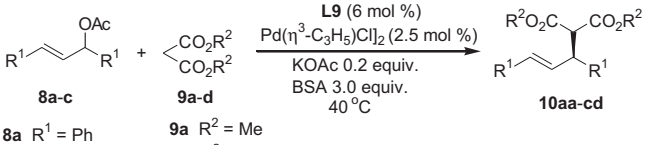


Entry	Ligand	Solvent	Time(day)	Yield(%)[b]	ee(%)[c]
1	**L5**	CH_2Cl_2	8	55	33
2	**L5**	CCl_4	8	29	40
3	**L5**	$ClCH_2CH_2Cl$	8	trace	n.d.
4	**L5**	Toluene	8	59	50
5	**L5**	THF	8	18	17
6	**L5**	Et_2O	8	trace	n.d.
7	**L5**	EtOH	8	0	n.d.
8	**L5**	$CHCl_3$	8	57	60
9	**L6**	$CHCl_3$	8	23	15
10	**L7**	$CHCl_3$	14	20	30
11	**L8**	$CHCl_3$	8	89	89
12	**L9**	$CHCl_3$	8	73	94
13[d]	**L9**	$CHCl_3$	3	99	92

[a] The reaction was conducted with (*E*)-1,3-diphenylprop-2-en-1-yl acetate **8a** (0.5 mmol) and dimethyl malonate **9a** (1.5 mmol) in solvent (3 mL) at room temperature.
[b] Isolated yield.
[c] Determined by HPLC using a ChiralpakIA column with *n*-hexane/2-propanol (90:10) as eluent.
[d] The temperature of the reaction is 40 °C.

With the optimized reaction conditions in hand, we further screened the substrate scope using the ligand **L9** in the asymmetric allylic alkylation reaction. The results are summarized in Table 2. These reactions demonstrated the broad applicability of ligand **L9** to different substrates. Different malonates with various allylic substrates are all tolerated and good yields and enantioselectivities were obtained (Table 2, entries 1–12). Diisopropyl malonate gave lower reactivity and enantioselectivity than dibenzyl malonate (Table 2, entries 3, 7, 11 vs entries 4, 8, 12). Electron-withdrawing groups in phenyl of *rac*-1,3-dipenylpropen-1-yl acetate could improve the activity of the allylic alkylation with the reaction time reducing at least one day. We further evaluated alkyl allylic acetate, using 1-cyclohexenyl acetate as substrate, but no reaction occurred under optimized conditions even after 7 days, this phenomenon may be ascribed to its low reactivity.

Table 2
Scope of substrates for Pd-**L9**-catalyzed asymmetric allylic alkylation[a]



8a-c **9a-d** **10aa-cd**

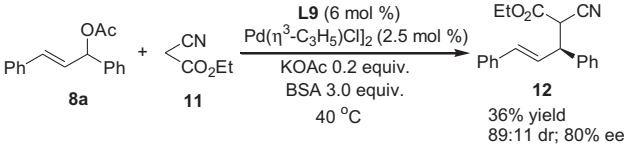
8a R^1 = Ph
8b R^1 = 4-ClC_6H_4
8c R^1 = 4-BrC_6H_4

9a R^2 = Me
9b R^2 = Et
9c R^2 = *i*Pr
9d R^2 = Bn

Entry	Product	Time(day)	Yield (%)[b]	ee (%)[c]
1	**10aa**	3	99	92
2	**10ab**	3	99	88
3	**10ac**	7	16	74
4	**10ad**	2	>99	92
5	**10ba**	2	99	93
6	**10bb**	1	99	85
7	**10bc**	5	73	87
8	**10bd**	1	>99	95
9	**10ca**	2	>99	92
10	**10cb**	1	>99	81
11	**10cc**	5	71	87
12	**10cd**	1	>99	95

[a] The reaction was conducted with allyl acetate substrate **8** (0.5 mmol) and nucleophile **9** (1.5 mmol) in $CHCl_3$ (2 mL) at 40 °C using **L9** (6 mol %) and [Pd(η^3-C_3H_5)Cl]$_2$ (2.5 mol %) as catalyst.
[b] Isolated yield.
[c] Determined by HPLC by using a ChiralpakIA column.

Further substrate scope was also investigated as shown in Scheme 3. (*E*)-1,3-diphenylprop-2-en-1-yl acetate **8a** reacted with ethyl 2-cyanoacetate **11** to afford (*E*)-ethyl 2-cyano-3,5-diphenylpent-4-enoate **12** in 36% yield (89:11 dr; major diastereomer 80% ee). In order to elucidate the nature of this type of ligand, especially the function of O atom, we also used various other nucleophiles, such as indole, benzylamine, cyclohenanone and 4-hydroxycoumarin, but they all did not take place the alkylation substitution or no asymmetric induction.



Scheme 3. Asymmetric allylic alkylation with 2-cyanoacetate as the nucleophile.

Yamagishi and co-worker reported the synthesis of phosphine-linked bis(oxazoline) ligands and applied their Pd(II) complexes in asymmetric alkylation reaction.[4c] The phosphine-linked bis(oxazoline) ligands are very similar to ligands **L6** and **L7**. These ligands coordinated to Pd(II) ion as bidentate P,N-ligands rather than bidentate N,N-ligands to give a stereogenic phosphorus atom. The difference of our ligands with Yamagishi's ligands is the presence of the oxide to the P atom. The presence of oxide may prohibit the coordination of P atom to Pd, but the weak interaction between the O atom and the Pd may be existed. The oxide may function as an additional chelating point to coordinate with Pd and stabilize the complex. On the basis of the absolute configurations of the products, a possible transition-state for the asymmetric allylic alkylation reaction was proposed (Fig. 2). The nucleophile attacks the η^3-allyl complex as illustrated in Fig. 2 to afford the *S* configured product. The effort was directed to have a crystal structure of the complex, but we failed to obtain it at present time.

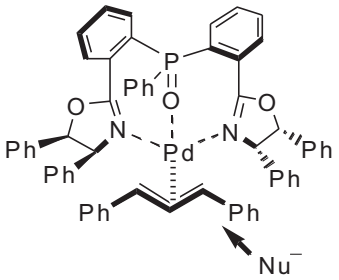


Fig. 2. Proposed transition-state model.

3. Conclusions

In conclusion, we have designed and synthesized the phosphine oxide-linked bis(oxazoline) ligands **L5**–**L9** in two ways and applied them in Pd-catalyzed asymmetric allylic alkylation reactions of (*E*)-1,3-diarylprop-2-en-1-yl acetate with malonates. Good enantioselectivities and yields were obtained with ligand **L9** (up to 95% ee, 99% yield). When the nucleophile was 2-cyanoacetate, we could get the corresponding product with 80% ee and 89:11 dr. Further application of these ligands in other asymmetric transformations is under way in our laboratory.

4. Experimental section

4.1. General remarks

Commercially available compounds were used without further purification. Solvents were dried according to standard procedures. Column chromatography was carried out using silica gel (200–300 mesh). Melting points were measured with a XT-4 melting point apparatus without correction. The ^{1}H NMR spectra were recorded with Varian Mercury-plus 400 MHz or Bruker Avance DRX 500 MHz spectrometers, while ^{13}C NMR spectra were recorded at 100 or 125 MHz, respectively. Infrared spectra were obtained with a Perkin Elmer Spectrum One spectrometer. The ESI-MS spectra were obtained with Bruker APEX IV Fourier Transform mass spectrometer. Optical rotations were measured with WZZ-3 spectrometer. The enantiomeric excesses of the products were determined by chiral HPLC using Agilent HP 1200 instrument with Daicel ChiralpakIA or IB columns.

4.2. Synthesis of phosphine oxide-linked bis(oxazoline) ligands L5–L7

*4.2.1. (4S)-4-Benzyl-2-(2-bromophenyl)-4,5-dihydrooxazole (**3a**).*[7a] To a round bottom flask, the 2-bromobenzoic acid **1** (1.01 g, 5 mmol) and thionyl chloride (10 mL) were added, and

the mixture were refluxed at 80 °C for 4 h. The redundant $SOCl_2$ was removed under vacuum to give dark yellow oil. The oil was dissolved in CH_2Cl_2 (35 mL), and added dropwise to a solution of (*S*)-phenylalaninol (756 mg, 5 mmol), Et_3N (2.8 mL, 20 mmol), and CH_2Cl_2 (10 mL) at 0 °C. After the completion of addition, the mixture was warmed to room temperature and stirred overnight.

To this mixture, methanesulfonyl chloride (464 mg, 6 mmol) was added via syringe at 0 °C. After the completion of addition, the mixture was warmed to room temperature and stirred for 4 h. The reaction was quenched by addition of saturated ammonium chloride (aq), and the mixture was extracted with CH_2Cl_2 (3×20 mL). Then the mixture was concentrated, and the residue was dissolved in the 1:1 (v/v) mixture of MeOH and water (6 mL), and refluxed in the presence of NaOH (400 mg, 10 mmol) for another 4 h. After removing MeOH under vacuum, the mixture was extracted with CH_2Cl_2 (3×20 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude product was purified by silica gel column chromatography using petroleum ether–EtOAc 5:1 (v/v) as eluent to afford **3a** as yellow oil (1.27 g, 87% yield).

*4.2.2. (4S)-2-(2-Bromophenyl)-4-isopropyl-4,5-dihydrooxazole (**3b**).*[7a] Prepared according to the general procedure outlined for **3a** using 2.01 g (10 mmol) 2-bromobenzoic acid **1** and 1.03 g (10 mmol) (*S*)-valinol. The product was obtained as yellow oil (2.22 g, 83% yield).

*4.2.3. (4S)-2-(2-Bromophenyl)-4-tert-butyl-4,5-dihydrooxazole (**3c**).*[7b] Prepared according to the general procedure outlined for **3a** using 1.01 g (5 mmol) 2-bromobenzoic acid **1** and 586 mg (5 mmol) (*S*)-*tert*-leucinol. The product was obtained as yellow oil (868.9 mg, 62% yield).

*4.2.4. Bis(oxazoline) ligand (**L5**).* To a flame dried Schlenk tube, the crumbs of Mg (72 mg, 3 mmol) were added under argon, followed by addition of THF (2 mL). Then the solution of **3a** (948.6 mg, 3 mmol) in THF (2 mL) was added at 50 °C. After the completion of addition, the mixture was refluxed for 2 h. After the disappearance of the crumbs of Mg, the mixture was cooled to room temperature. Then the solution of phenylphosphonic dichloride (195 mg, 1 mmol) in THF (2 mL) was added, and the mixture was stirred at room temperature for overnight. The reaction was quenched by addition of water (10 mL) and the mixture was extracted with CH_2Cl_2 (3×10 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude product was purified by silica gel column chromatography using CH_2Cl_2–MeOH 50:1 (v/v) as eluent to afford **L5** as yellow soild (205.9 mg, 35% yield). Mp 52–54 °C, $[\alpha]_D^{20}=-70.4$ (*c* 1.00, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ 2.58 (dd, *J*=9.0, 13.5 Hz, 2H, CH_2), 3.03–3.08 (m, 2H, CH_2), 3.73 (t, *J*=8.0 Hz, 1H, CH), 3.78 (t, *J*=8.0 Hz, 1H, CH_3), 3.97–4.01 (m, 2H, CH), 4.15–4.23 (m, 1H, CH), 4.29–4.38 (m, 1H, CH), 7.13 (d, *J*=7.0 Hz, 2H, ArH), 7.17 (d, *J*=7.5 Hz, 2H, ArH), 7.19–7.31 (m, 6H, ArH), 7.38–7.42 (m, 2H), 7.44–7.49 (m, 3H), 7.53–7.60 (m, 4H), 7.79 (d, *J*=7.5 Hz, 1H, ArH), 7.81 (d, *J*=7.5 Hz, 1H, ArH),7.86 (dd, *J*=3.5, 7.5 Hz, 2H, ArH) ppm. ^{13}C NMR(100 MHz, $CDCl_3$): 40.9, 67.66, 67.70, 72.2, 126.1, 128.0 (d, $^3J_{CP}$=12.4 Hz), 128.18, 128.22, 128.91, 128.93, 129.7 (d, $^3J_{CP}$=12.3 Hz), 129.8 (d, $^3J_{CP}$=12.0 Hz), 130.3 (d, $^2J_{CP}$=9.0 Hz), 130.5 (d, $^2J_{CP}$=9.2 Hz), 130.83, 130.86, 130.89, 130.91, 131.18, 131.20, 131.74 (d, $^2J_{CP}$=8.9 Hz), 131.75, 132.1 (d, $^2J_{CP}$=9.6 Hz), 132.38 (d, $^1J_{CP}$=108.2 Hz), 133.23 (d, $^1J_{CP}$=102.9 Hz), 133.41 (d, $^2J_{CP}$=10.4 Hz), 133.44 (d, $^1J_{CP}$=102.6 Hz), 134.0, 138.01, 138.03, 163.7 (d, $^3J_{CP}$=3.2 Hz), 164.0 (d, $^3J_{CP}$=3.3 Hz) ppm. ^{31}P NMR (85% H_3PO_4 as external standard): 31.7 ppm. IR (KBr): ν 3058, 3025, 2894, 1722, 1659, 1603, 1588, 1563, 1495, 1471, 1453, 1437, 1357, 1284, 1247, 1201, 1130, 1108, 1061, 1030, 960, 918, 774, 737, 699 cm^{-1}. HRMS (EI): calcd for $C_{38}H_{34}N_2O_3P$ $[M+H]^+$ 597.23016, found: 597.22906.

*4.2.5. Bis(oxazoline) ligand (**L6**).* Prepared according to the general procedure outlined for **L5** using the crumbs of Mg (199 mg, 8.29 mmol), $PhPOCl_2$ (538 mg, 2.76 mmol) and compound **3b** (2.22 g, 8.29 mmol). The product was obtained as yellow solid (709 mg, 51% yield). Mp 47–49 °C, $[\alpha]_D^{20}=-58.0$ (*c* 1.00, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 0.77 (d, *J*=6.4 Hz, 3H, CH_3), 0.80 (d, *J*=6.0 Hz, 3H, CH_3), 0.86 (d, *J*=5.6 Hz, 3H, CH_3), 0.91 (d, *J*=5.6 Hz, 3H, CH_3), 1.66 (br s, 2H, CH), 3.52–3.54 (m, 1H), 3.69–3.76 (m, 3H), 4.00 (br s, 2H), 7.41–7.63 (m, 10H, ArH), 7.83–7.85 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 18.3, 18.4, 19.1, 19.2, 32.7, 70.6, 70.7, 72.7, 72.8, 127.8 (d, $^3J_{CP}$=12.3 Hz), 129.5 (d, $^3J_{CP}$=12.3 Hz), 129.6 (d, $^3J_{CP}$=12.2 Hz), 130.3 (d, $^2J_{CP}$=9.0 Hz), 130.5 (d, $^2J_{CP}$=9.1 Hz), 132.1 (d, $^2J_{CP}$=9.4 Hz), 130.71, 130.75, 130.78, 131.0, 131.1, 132.1 (d, $^2J_{CP}$=9.6 Hz), 133.4 (d, $^1J_{CP}$=103.1 Hz), 133.5 (d, $^2J_{CP}$=10.6 Hz), 133.6 (d, $^2J_{CP}$=10.0 Hz), 133.7 (d, $^1J_{CP}$=102.4 Hz), 133.9 (d, $^1J_{CP}$=108.1 Hz), 163.2 (d, $^3J_{CP}$=3.3 Hz), 163.4 (d, $^3J_{CP}$=3.3 Hz) ppm. ^{31}P NMR (85% H_3PO_4 as external standard): 31.8 ppm. IR (KBr): ν 3058, 2958, 2923, 2871, 1725, 1664, 1588, 1560, 1467, 1437, 1353, 1309, 1246, 1203, 1129, 1108, 1063, 963, 906, 770, 739, 696 cm^{-1}. HRMS (ESI): calcd for $C_{30}H_{34}N_2O_3P$ $[M+H]^+$ 501.23016, found: 501.23062.

*4.2.6. Bis(oxazoline) ligand (**L7**).* Prepared according to the general procedure outlined for **L5** using the crumbs of Mg (68 mg, 2.85 mmol), $PhPOCl_2$ (195 mg, 1 mmol) and compound **3c** (804.9 mg, 2.85 mmol). The product was obtained as yellow solid (246 mg, 50% yield). Mp 69–71 °C, $[\alpha]_D^{20}=-106.8$ (*c* 1.00, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 0.79 (s, 9H, 3 CH_3), 0.83 (s, 9H, 3 CH_3), 3.46 (t, *J*=8.8 Hz, 1H, CH), 3.67 (t, *J*=8.8 Hz, 1H, CH), 3.85 (t, *J*=8.8 Hz, 4H, CH), 7.42–7.52 (m, 8H, ArH), 7.67–7.73 (m, 1H, ArH), 7.79–7.89 (m, 4H, ArH) ppm. ^{13}C NMR(100 MHz, $CDCl_3$): 25.86, 25.94, 33.4, 33.5, 68.8, 68.9, 76.0, 127.8 (d, $^3J_{CP}$=12.4 Hz), 129.6 (d, $^3J_{CP}$=12.0 Hz), 129.7 (d, $^3J_{CP}$=11.5 Hz), 130.1 (d, $^2J_{CP}$=9.1 Hz), 130.5 (d, $^2J_{CP}$=8.9 Hz), 130.8, 131.0, 132.3 (d, $^2J_{CP}$=9.7 Hz), 133.5 (d, $^1J_{CP}$=102.9 Hz), 133.867 (d, $^2J_{CP}$=11.4 Hz), 133.874 (d, $^1J_{CP}$=103.0 Hz), 134.0 (d, $^1J_{CP}$=108.3 Hz), 163.0 (d, $^3J_{CP}$=2.7 Hz), 163.2 (d, $^3J_{CP}$=2.2 Hz) ppm. ^{31}P NMR (85% H_3PO_4 as external standard): 31.8 ppm. IR (KBr): ν 3059, 2954, 2903, 2867, 1727, 1663, 1589, 1566, 1477, 1437, 1394, 1356, 1248, 1190, 1130, 1108, 1066, 1027, 963, 904, 767, 739, 695 cm^{-1}. HRMS (ESI): calcd for $C_{32}H_{38}N_2O_3P$ $[M+H]^+$ 529.26146, found: 529.26207.

4.3. Synthesis of phosphine oxide-linked bis(oxazoline) ligands (L8 and L9)

*4.3.1. 2-(2-Bromophenyl)-1,3-dioxolan (**5**).* This was a modified procedure according to literature.[8a] To a round bottom flask, the2-bromobenzaldehyde (3.70 g, 20 mmol), ethylene glycol (1.73 mL, 25 mmol), *p*-toluenesulfonic acid (60.2 mg, 0.35 mmol) and toluene (30 mL) were added, and the mixture was heated at reflux with a Dean Stark Trap for 24 h. The reaction was monitored by TCL. After the completion of the reaction, the mixture was cooled to room temperature, and the KOH–EtOH solution was added until white solid appeared. Then the organic phase was washed with water and brine, dried over anhydrous K_2CO_3, and concentrated under vacuum. The crude product was purified by silica gel column chromatography using petroleum ether–EtOAc 100:1 (v/v) as eluent. The product was obtained as yellow oil (4.08 g, 89% yield).

*4.3.2. Bis[2-(1,3-dioxolan-2-yl)phenyl](phenyl) phosphine oxide (**6**).* This was a modified procedure according to literature.[8b,8c] To a flame dried Schlenk tube, the crumbs of Mg (427.2 mg, 17.8 mmol) were added under argon, followed by addition of THF (6 mL). Then the solution of 2-(2-bromophenyl)-1,3-dioxolan **5** (4.08 g,

17.8 mmol) in THF (6 mL) was added at 50 °C. After the completion of addition, the mixture was heated at reflux for 2 h. After the disappearance of the crumbs of Mg, the mixture was cooled to room temperature. Then the solution of $PhPOCl_2$ (1.74 g, 8.9 mmol) in THF (6 mL) was added, and the mixture was stirred at room temperature for overnight. The reaction was quenched by addition of water (20 mL) and the mixture was extracted with CH_2Cl_2 (3×20 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude product was purified by silica gel column chromatography using petroleum ether–EtOAc 1:1 (v/v) as eluent. The product was obtained as yellow soild **6** (2.82 g, 75% yield). Mp 157–160 °C ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81–3.85 (m, 2H, CH_2), 3.95–4.01 (m, 2H, CH_2), 6.55 (s, 2H, CH), 7.03–7.09 (m, 2H, ArH), 7.26–7.33 (m, 2H, ArH), 7.43–7.63 (m, 7H, ArH), 7.85 (dd, J=7.6 Hz, 1.8 Hz, 2H, ArH) ppm.

*4.3.3. Bis(2-formylphenyl)(phenyl)phosphine oxide (**7**)..*[8d] To a round bottom flask, bis[2-(1,3-dioxolan-2-yl)phenyl](phenyl)phosphine oxide **6** (4.58 g, 10.85 mmol), pTSA (356 mg, 2 mmol) and acetone (80 mL) were added. After the solid was dissolved, water (0.8 mL) was added. Then the mixture was heated at reflux for 2 h. The reaction was monitored by TLC. After the completion of the reaction, the mixture was cooled to room temperature, and the acetone was removed under vacuum. The residue was dissolved in CH_2Cl_2 (20 mL), washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude product was purified by silica gel column chromatography using petroleum ether–EtOAc 1:1 (v/v) as eluent. The product was obtained as yellow solid (2.87 g, 79% yield). Mp 170–172 °C ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.21–7.28 (m, 2H, ArH), 7.53–7.77 (m, 9H), 8.17–8.23 (m, 2H, ArH) 10.74 (s, 2H, CHO) ppm.

*4.3.4. Bis(oxazoline) ligand (**L8**).* In a round bottom flask equipped with a bubbler, compound **7** (334.3 mg, 1 mmol) was dissolved in dry CH_2Cl_2 (10 mL). (*S*)-2-phenylglycinol (302.4 mg, 2 mmol) was added and followed by 4 Å molecular sieves (1 g). The mixture was stirred at room temperature for overnight. *N*-bromsuccinimide (356 mg, 2 mmol) was added while the reaction mixture was cooled with a water bath. After 1 h, the solid byproducts and the molecular sieves were removed by filtration and the filtrate was washed with aqueous saturated $NaHCO_3$ solution, $Na_2S_2O_5$ solution and brine. The organic phase was dried with anhydrous $MgSO_4$, filtrated and concentrated to dryness. The crude product was purified by silica gel column chromatography using CH_2Cl_2–MeOH 50:1 (v/v) as eluent to afford **L8** as white solid (146 mg, 26% yield). Mp 89–91 °C, $[\alpha]_D^{20}$=−53.2 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83–3.97 (m, 2H, CH), 4.37–4.53 (m, 2H, CH), 4.91–5.13 (m, 2H, CH), 7.18–7.27 (m, 8H, ArH), 7.37–7.65 (m, 10H, ArH), 7.69–7.84 (m, 3H, ArH), 7.96–7.81 (m, 2H, ArH) ppm. ^{13}C NMR(100 MHz, $CDCl_3$): 69.9, 70.0, 74.9, 75.0, 126.8, 126.9, 127.2, 127.8, 128.0, 128.1, 128.36, 128.41, 129.85 (d, $^3J_{CP}$=12.3 Hz), 129.91 (d, $^3J_{CP}$=12.5 Hz), 130.0 (d, $^3J_{CP}$=13.4 Hz), 130.8 (d, $^2J_{CP}$=8.9 Hz), 130.89, 130.98, 131.04, 131.3 (d, $^2J_{CP}$=11.3 Hz), 131.6, 131.7, 132.2 (d, $^2J_{CP}$=9.7 Hz), 133.49 (d, $^2J_{CP}$=10.9 Hz), 133.58 (d, $^2J_{CP}$=10.6 Hz), 133.61 (d, $^1J_{CP}$=107.9 Hz), 133.7 (d, $^1J_{CP}$=103 Hz), 133.8 (d, $^1J_{CP}$=101.7 Hz), 164.9 (d, $^3J_{CP}$=3.3 Hz), 165.1 (d, $^3J_{CP}$=3.7 Hz) ppm. ^{31}P NMR (85% H_3PO_4 as external standard): 34.1 ppm. IR (KBr): ν 3060, 3030, 2924, 2854, 1712, 1659, 1630, 1588, 1578, 1565, 1496, 1467, 1450, 1438, 1359, 1303, 1193, 1130, 1109, 1060, 949, 761, 735, 695 cm^{-1}. HRMS (EI): calcd for $C_{36}H_{30}N_2O_3P$ [M+H] 569.19886, found: 569.19923.

*4.3.5. Bis(oxazoline) ligand (**L9**).* Prepared according to the general procedure outlined for **L8** using compound **7** (2.67 g, 8 mmol) and (1*R*,2*S*)-2-amino-1,2-dipheny1ethanol (3.41 g, 16 mmol). The product was obtained as white solid (1.85 g, 32% yield). Mp 117–119 °C, $[\alpha]_D^{20}$=−303.2 (*c* 0.50, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.29 (d, J=10.0 Hz, 1H, CH), 5.45 (d, J=10.0 Hz, 1H, CH), 5.70 (d, J=9.2 Hz, 2H, CH), 6.60 (d, J=6.0 Hz, 2H, ArH), 6.72 (s, 2H, ArH), 6.83–6.96 (m, 13H, ArH), 7.12–7.42 (m, 10H, ArH), 7.60–7.71 (m, 3H, ArH), 7.89–7.97 (m, 2H, ArH), 8.22–8.24(m, 1H, ArH). ^{13}C NMR(100 MHz, $CDCl_3$): 73.5, 73.7, 85.4, 85.8, 126.1, 126.2, 126.7, 126.8, 127.0, 127.2, 127.7, 127.9 (d, $^3J_{CP}$=12.6 Hz), 129.8 (d, $^3J_{CP}$=12.3 Hz), 129.9 (d, $^3J_{CP}$=12.3 Hz), 130.2 (d, $^2J_{CP}$=8.8 Hz), 130.7, 130.8, 131.0 (d, $^2J_{CP}$=8.9 Hz), 131.1, 131.2, 132.1 (d, $^2J_{CP}$=9.7 Hz), 133.5 (d, $^2J_{CP}$=10.5 Hz), 133.7 (d, $^1J_{CP}$=108.8 Hz), 134.2 (d, $^1J_{CP}$=102.1 Hz), 134.5 (d, $^2J_{CP}$=11.1 Hz), 134.7 (d, $^1J_{CP}$=103.3 Hz), 135.5, 136.0, 137.5, 137.7, 164.6 (d, $^3J_{CP}$=3.2 Hz), 165.3 (d, $^3J_{CP}$=3.2 Hz) ppm. ^{31}P NMR (85% H_3PO_4 as external standard): 33.8 ppm. IR (KBr): ν 3059, 3029, 2932, 1712, 1663, 1604, 1587, 1564, 1496, 1454, 1437, 1330, 1284, 1192, 1109, 959, 919, 893, 738, 698 cm^{-1}. HRMS (ESI): calcd for $C_{48}H_{38}N_2O_3P$ [M+H] 721.26146, found: 721.26131.

4.4. The catalytic asymmetric allylic alkylation

4.4.1. General procedure. To a flame dried Schlenk tube, [Pd(η^3-C_3H_3)Cl]$_2$ (4.6 mg, 0.0125 mmol) and ligand **L9** (21.6 mg, 0.03 mmol) were added under argon, followed by addition of $CHCl_3$ (2 mL). The solution was stirred at 40 °C for 0.5 h. Then (*E*)-1,3-diphenylprop-2-en-1-yl acetate (126 mg, 0.5 mmol) was added, and the mixture was stirred for 10 min before the addition of nucleophile (1.5 mmol), BSA (0.37 mL, 1.5 mmol) and anhydrous KOAc (10 mg, 0.10 mmol). After being stirred for indicated time, water (10 mL) was added and the mixture was extracted with CH_2Cl_2 (3×10 mL). and the combined organic phase was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by flash chromatography using petroleum ether–EtOAc 20:1 (v/v) as eluent to afford the desired product.

*4.4.2. Dimethyl 2-[(1S,2E)-1,3-diphenyl-2-propen-1-yl]malonate (**10aa**).* Prepared according to the general procedure using (*E*)-1,3-diphenyl-2-propen-1-yl acetate (126 mg, 0.5 mmol) and dimethyl malonate (0.17 mL, 1.5 mmol), while the reaction time was 3 days. The desired product was obtained as colorless oil (160 mg, 99% yield). The ee was determined by chiral HPLC with a Daicel ChiralpakIA column (*n*-hexane/2-propanol=90:10, flow rate 0.5 mL/min, detection at 254 nm, minor enantiomer t_R=15.9 min, major enantiomer t_R=19.3 min). $[\alpha]_D^{30}$=−11.3 (*c*=2.3, CH_2Cl_2; 92% ee). (Ref. 11 $[\alpha]_D^{20}$=−11.2, c=1.04, $CHCl_3$; 86% ee), ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.50 (s, 3H, CH_3), 3.69 (s, 3H, CH_3), 3.96 (d, J=10.8 Hz, 1H, CH), 4.27 (t, J=9.6 Hz, 1H, CH), 6.33 (dd, J=15.6, 8.8 Hz, 1H,=CH), 6.48 (d, J=16.0 Hz, 1H,=CH), 7.16–7.30 (m, 10H, ArH) ppm.

*4.4.3. Diethyl 2-[(1S,2E)-1,3-diphenyl-2-propen-1-yl]malonate (**10ab**).* Prepared according to the general procedure using (*E*)-1,3-diphenyl-2-propen-1-yl acetate (126 mg, 0.5 mmol) and diethyl malonate (0.23 mL, 1.5 mmol), while the reaction time was 3 days. The desired product was obtained as colorless oil (174 mg, 99% yield). The ee was determined by chiral HPLC with a Daicel ChiralpakIA column (*n*-hexane/2-propanol=90:10, flow rate 0.5 mL/min, detection at 254 nm, minor enantiomer t_R=15.6 min, major enantiomer t_R=19.5 min). $[\alpha]_D^{30}$=−8.6 (*c*=3.9, CH_2Cl_2; 88% ee). (Ref. 12 $[\alpha]_D^{25}$=−17.2, c=1.02, $CHCl_3$; 97% ee). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.98 (t, J=6.8 Hz, 3H, CH_3), 1.18 (t, J=6.8 Hz, 3H, CH_3), 3.92–3.96 (m, 3H, CH+CH_2), 4.12–4.19 (m, 2H, CH_2), 4.27 (t, J=9.6, Hz, 1H, CH), 6.35 (dd, J=15.6, 8.4 Hz, 1H,=CH), 6.48 (d, J=15.6 Hz, 1H,=CH), 7.16–7.31 (m, 10H, ArH) ppm.

*4.4.4. Diisopropyl 2-[(1S,2E)-1,3-diphenyl-2-propen-1-yl]malonate (**10ac**).* Prepared according to the general procedure using (*E*)-1,3-diphenyl-2-propen-1-yl acetate (126 mg, 0.5 mmol) and

diisopropyl malonate (282 mg, 1.5 mmol), while the reaction time was 7 days. The desired product was obtained as colorless oil (30.4 mg, 16% yield). The ee was determined by chiral HPLC with a Daicel ChiralpakIA column (*n*-hexane/2-propanol=90:10, flow rate 0.5 mL/min, detection at 254 nm, minor enantiomer t_R=12.4 min, major enantiomer t_R=14.9 min). $[\alpha]_D^{30}$=−6.5 (*c*=1.0, CH_2Cl_2; 74% ee). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.97 (d, *J*=6.0 Hz, 3H, CH_3), 1.05 (d, *J*=6.0 Hz, 3H, CH_3), 1.16 (d, *J*=6.0 Hz, 3H, CH_3), 1.22 (d, *J*=6.0 Hz, 3H, CH_3), 3.86 (d, *J*=10.8 Hz, 1H, CH), 4.24 (t, *J*=9.6 Hz, 1H, CH), 4.78–4.84 (m, 1H, CH), 4.98–5.06 (m, 1H, CH), 6.33 (dd, *J*=15.6, 8.4 Hz, 1H,=CH), 6.46 (d, *J*=15.6 Hz, 1H,=CH), 7.18–7.31 (m, 10H, ArH) ppm.

*4.4.5. Dibenzyl 2-[(1S,2E)-1,3-diphenyl-2-propen-1-yl]malonate (**10ad**).* Prepared according to the general procedure using (*E*)-1,3-diphenyl-2-propen-1-yl acetate (126 mg, 0.5 mmol) and dibenzyl malonate (426 mg, 1.5 mmol), while the reaction time was 2 days. The desired product was obtained as colorless oil (238 mg, > 99% yield). The ee was determined by chiral HPLC with a Daicel ChiralpakIA column (*n*-hexane/2-propanol=95:5, flow rate 1.0 mL/min, detection at 254 nm, minor enantiomer t_R=21.8 min, major enantiomer t_R=25.2 min). $[\alpha]_D^{30}$=−2.85 (*c*=7.9, CH_2Cl_2; 92% ee). (Ref. 13 $[\alpha]_D^{25}$=−7.1, c=1.0, $CHCl_3$; 95% ee). ^{1}H NMR (300 MHz, $CDCl_3$): δ=4.06 (d, *J*=10.8 Hz, 1H, CH), 4.32 (t, *J*=9.6 Hz, 1H, CH), 4.89 (s, 2H, CH_2), 5.07 (ABq, *J*=12.4 Hz, 2H, CH_2), 6.31 (dd, *J*=15.6, 8.4 Hz, 1H,=CH), 6.40 (d, *J*=15.6 Hz, 1H,=CH), 7.17–7.27 (m, 20H, ArH) ppm.

*4.4.6. Dimethyl 2-[(1S,2E)-1,3-bis(4-chlorophenyl)-2-propen-1-yl] malonate (**10ba**).* Prepared according to the general procedure using (*E*)-1,3-bis(4-chlorophenyl)-2-propen-1-yl acetate (161 mg, 0.5 mmol) and dimethyl malonate (0.17 mL, 1.5 mmol), while the reaction time was 2 days. The desired product was obtained as colorless oil (196 mg, > 99% yield). The ee was determined by chiral HPLC with a Daicel ChiralpakIA column (*n*-hexane/2-propanol=85:15, flow rate 1.0 mL/min, detection at 254 nm, minor enantiomer t_R=10.6 min, major enantiomer t_R=15.7 min). $[\alpha]_D^{30}$=+1.7 (*c*=2.6, CH_2Cl_2; 93% ee). (Ref. 13 $[\alpha]_D^{25}$=−3.1; *c*=1.0, $CHCl_3$; 97% ee). ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.54 (s, 3H, CH_3), 3.70 (s, 3H, CH_3), 3.90 (d, *J*=10.8 Hz, 1H, CH), 4.25 (t, *J*=9.6 Hz, 1H, CH), 6.27 (dd, *J*=15.6, 8.4 Hz, 1H,=CH), 6.41 (d, *J*=16.0 Hz, 1H,=CH), 7.22–7.30 (m, 8H, ArH) ppm.

*4.4.7. Diethyl 2-[(1S,2E)-1,3-bis(4-chlorophenyl)-2-propen-1-yl] malonate (**10bb**).* Prepared according to the general procedure using (*E*)-1,3-bis(4-chlorophenyl)-2-propen-1-yl acetate (161 mg, 0.5 mmol) and diethyl malonate (0.23 mL, 1.5 mmol), while the reaction time was 1 days. The desired product was obtained as white solid (208 mg, 99% yield). The ee was determined by chiral HPLC with a Daicel ChiralpakIA column (*n*-hexane/2-propanol=85:15, flow rate 1.0 mL/min, detection at 254 nm, minor enantiomer t_R=10.5 min, major enantiomer t_R=16.8 min). Mp 80–82 °C, $[\alpha]_D^{30}$=+1.69 (*c*=3.3, CH_2Cl_2; 85% ee). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.05 (t, *J*=5.8 Hz, 3H, CH_3), 1.19 (t, *J*=5.8 Hz, 3H, CH_3), 3.86 (d, *J*=10.8 Hz, 1H, CH), 3.97–4.01 (m, 2H, CH_2), 4.14–4.26 (m, 3H, CH+CH_2), 6.27 (dd, *J*=15.6, 8.4 Hz, 1H,=CH), 6.41 (d, *J*=15.6 Hz, 1H,=CH), 7.22–7.29 (m, 8H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.8, 14.1, 48.4, 57.5, 61.5, 61.7, 127.5, 128.6, 128.8, 129.3, 129.6, 130.8, 132.9, 133.3, 135.1, 138.6, 167.1, 167.5 ppm. IR (KBr): ν 3030, 2984, 2937, 2896, 1760, 1715, 1594, 1493, 1464, 1415, 1388, 1370, 1332, 1254, 1179, 1142, 1095, 1032, 1012, 970, 851, 830, 809, 717, 703 cm^{-1}. HRMS (ESI): calcd for $C_{22}H_{22}Cl_2NaO_4$ $[M+Na]^+$ 443.07874, found: 443.07787.

*4.4.8. Diisopropyl 2-[(1S,2E)-1,3-bis(4-chlorophenyl)-2-propen-1-yl] malonate (**10bc**).* Prepared according to the general procedure using (*E*)-1,3-bis(4-chlorophenyl)-2-propen-1-yl acetate (161 mg, 0.5 mmol) and diisopropyl malonate (282 mg, 1.5 mmol), while the reaction time was 5 days. The desired product was obtained as white solid (164 mg, 73% yield). The ee was determined by chiral HPLC with a Daicel ChiralpakIA column (*n*-hexane/2-propanol=85:15, flow rate 1.0 mL/min, detection at 254 nm, minor enantiomer t_R=9.4 min, major enantiomer t_R=14.0 min). Mp 85–86 °C, $[\alpha]_D^{30}$=+0.66 (*c*=2.4, CH_2Cl_2; 87% ee). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.01 (d, *J*=4.4 Hz, 3H, CH_3), 1.08 (d, *J*=4.0 Hz, 3H, CH_3), 1.16 (d, *J*=4.4 Hz, 3H, CH_3), 1.21 (d, *J*=4.4 Hz, 3H, CH_3), 3.81 (d, *J*=10.8 Hz, 1H, CH), 4.19–4.24 (m, 1H, CH), 4.82–4.87 (m, 1H, CH), 5.00–5.05 (m, 1H, CH), 6.28 (dd, *J*=15.6, 8.4 Hz, 1H,=CH), 6.40 (d, *J*=15.6 Hz, 1H,=CH), 7.22–7.29 (m, 18H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.3, 21.5, 21.6, 48.2, 57.6, 69.0, 69.2, 127.5, 128.6, 128.7, 129.3, 129.6, 130.7, 132.8, 133.2, 135.1, 138.7, 166.6, 167.0 ppm. IR (KBr): ν 3067, 3033, 2982, 2935, 2881, 1740, 1714, 1647, 1593, 1492, 1468, 1456, 1375, 1303, 1259, 1202, 1167, 1102, 1013, 982, 915, 841, 830, 800 cm^{-1}. HRMS (ESI): calcd for $C_{24}H_{26}Cl_2NaO_4$ $[M+Na]^+$ 471.11004, found: 471.10961.

*4.4.9. Dibenzyl 2-[(1S,2E)-1,3-bis(4-chlorophenyl)-2-propen-1-yl] malonate (**10bd**).* Prepared according to the general procedure using (*E*)-1,3-bis(4-chlorophenyl)-2-propen-1-yl acetate (161 mg, 0.5 mmol) and dibenzyl malonate (426 mg, 1.5 mmol), while the reaction time was 1 day. The desired product was obtained as white solid (273 mg, > 99% yield). The ee was determined by chiral HPLC with aDaicel ChiralpakIA column (*n*-hexane/2-isopropanol=80:20, flow rate 1.0 mL/min, detection at 254 nm, minor enantiomer t_R=16.6 min, major enantiomer t_R=23.7 min). Mp 73–74 °C, $[\alpha]_D^{30}$=+2.56 (*c*=8.8, CH_2Cl_2; 95% ee). ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.96 (d, *J*=10.8 Hz, 1H, CH), 4.24 (dd, *J*=10.8, 8.0 Hz, 1H, CH), 4.96 (AB q, *J*=12.4 Hz, 2H, CH_2), 5.11 (AB q, *J*=12.4 Hz, 2H, CH_2), 6.21 (dd, *J*=15.6, 8.0 Hz, 1H,=CH), 6.30 (d, *J*=16.0 Hz, 1H,=CH), 7.04–7.30 (m, 18H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=48.4, 57.5, 67.2, 67.4, 127.6, 128.18, 128.24, 128.29, 128.38, 128.40, 128.49, 128.54, 128.8, 129.0, 129.2, 131.0, 133.0, 133.3, 135.1, 138.2, 166.8, 167.2 ppm. IR (KBr): ν 3065, 3033, 2947, 2890, 1753, 1735, 1587, 1491, 1456, 1410, 1380, 1327, 1265, 1213, 1153, 1093, 1013, 972, 839, 825, 799, 741, 697 cm^{-1}. HRMS (ESI): calcd for $C_{32}H_{26}Cl_2NaO_4$ $[M+Na]^+$ 567.11004, found: 567.11019.

*4.4.10. Dimethyl 2-[(1S,2E)-1,3-bis(4-bromophenyl)-2-propen-1-yl] malonate (**10ca**).* Prepared according to the general procedure using (*E*)-1,3-bis(4-bromophenyl)-2-propen-1-yl acetate (205 mg, 0.5 mmol) and dimethyl malonate (0.17 mL, 1.5 mmol), while the reaction time was 2 days. The desired product was obtained as colorless oil (240 mg, > 99% yield). The ee was determined by chiral HPLC with a Daicel ChiralpakIA column (*n*-hexane/2-propanol 85:15, flow rate 1.0 mL/min, detection at 254 nm, minor enantiomer t_R=12.5 min, major enantiomer t_R=18.4 min). $[\alpha]_D^{30}$=+7.1 (*c*=3.9, CH_2Cl_2; 92% ee). (Ref. 13 $[\alpha]_D^{25}$=+3.1; c=1.0, $CHCl_3$; 97% ee). ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.54 (s, 3H, CH_3), 3.69 (s, 3H, CH_3), 3.91 (d, *J*=10.4 Hz, 1H, CH), 4.23 (t, *J*=9.2 Hz, 1H, CH), 6.28 (dd, *J*=15.6, 8.0 Hz, 1H,=CH), 6.39 (d, *J*=15.6 Hz, 1H,=CH), 7.16 (d, *J*=6.4 Hz, 4H, ArH), 7.38 (d, *J*=7.2 Hz, 2H, ArH), 7.44 (d, *J*=7.2 Hz, 2H, ArH) ppm.

*4.4.11. Diethyl 2-[(1S,2E)-1,3-bis(4-bromophenyl)-2-propen-1-yl] malonate (**10cb**).* Prepared according to the general procedure using (*E*)-1,3-bis(4-bromophenyl)-2-propen-1-yl acetate (205 mg, 0.5 mmol) and diethyl malonate (0.23 mL, 1.5 mmol), while the reaction time was 1 days. The desired product was obtained as white solid (254 mg, > 99% yield). The ee was determined by chiral HPLC with a Daicel ChiralpakIA column (*n*-hexane/2-propanol 85:15, flow rate 1.0 mL/min, detection at 254 nm, monor enantiomer t_R=12.2 min, major enantiomer t_R=19.5 min). Mp 58–60 °C, $[\alpha]_D^{30}$=+4.39 (*c*=5.1, CH_2Cl_2; 81% ee). ^{1}H NMR (400 MHz, $CDCl_3$):

δ=1.05 (t, J=7.0 Hz, 3H, CH_3), 1.20 (t, J=7.0 Hz, 3H, CH_3), 3.86 (d, J=10.8 Hz, 1H, CH), 3.96–4.02 (m, 2H, CH_2), 4.15–4.24 (m, 3H, CH+CH_2), 6.29 (dd, J=16.0, 8.0 Hz, 1H,=CH), 6.40 (d, J=15.6 Hz, 1H,=CH), 7.15–7.19 (m, 4H, ArH), 7.38–7.45 (m, 4H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.8, 14.1, 48.4, 57.3, 61.5, 61.6, 121.0, 121.4, 127.8, 129.4, 129.7, 130.9, 131.6, 131.7, 135.5, 139.1, 167.1, 167.5 ppm. IR (KBr): ν 3029, 2981, 2936, 2901, 2873, 1755, 1726, 1588, 1488, 1464, 1446, 1388, 1369, 1331, 1253, 1174, 1136, 1098, 1072, 1031, 1009, 969, 858, 825, 800, 718 cm^{-1}. HRMS (ESI): calcd for $C_{22}H_{22}Br_2NaO_4$ $[M+Na]^+$ 530.97771 (^{79}Br), found: 530.97774 (^{79}Br), 532.97567 (^{81}Br).

*4.4.12. Diisopropyl 2-[(1S,2E)-1,3-bis(4-bromophenyl)-2-propen-1-yl]malonate (**10cc**).* Prepared according to the general procedure using (*E*)-1,3-bis(4-bromophenyl)-2-propen-1-yl acetate (205 mg, 0.5 mmol) and diisopropyl malonate (282 mg, 1.5 mmol), while the reaction time was 5 days. The desired product was obtained as white solid (191 mg, 71% yield). The ee was determined by chiral HPLC with a Daicel ChiralpakIA column (*n*-hexane/2-propanol 85:15, flow rate 1.0 mL/min, detection at 254 nm, minor enantiomer t_R=10.6 min, major enantiomer t_R=15.8 min). Mp 90–92 °C, $[\alpha]_D^{30}$=+5.8 (c=1.6, CH_2Cl_2; 87% ee). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.01 (d, J=6.0 Hz, 3H, CH_3), 1.07 (d, J=6.0 Hz, 3H, CH_3), 1.16 (d, J=6.0 Hz, 3H, CH_3), 1.21 (d, J=6.0 Hz, 3H, CH_3), 3.79 (d, J=10.8 Hz, 1H, CH), 4.20 (t, J=9.6 Hz, 1H, CH), 4.81–4.86 (m, 1H, CH), 4.99–5.04 (m, 1H, CH), 6.28 (dd, J=15.6, 8.0 Hz, 1H,=CH), 6.38 (d, J=15.6 Hz, 1H,=CH), 7.14–7.18 (m, 4H, ArH), 7.38 (d, J=8.4 Hz, 2H, ArH), 7.43 (d, J=8.0 Hz, 2H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.2, 21.49, 21.54, 48.2, 57.5, 68.9, 69.1, 120.8, 121.2, 127.7, 129.6, 129.7, 130.7, 131.5, 131.6, 135.4, 139.2, 166.5, 166.9 ppm. IR (KBr): ν 3064, 3031, 2979, 2935, 2881, 1738, 1714, 1647, 1589, 1488, 1468, 1456, 1375, 1304, 1259, 1202, 1168, 1102, 1073, 1010, 981, 914, 839, 827, 797 cm^{-1}. HRMS (ESI): calcd for $C_{24}H_{26}Br_2NaO_4$ $[M+Na]^+$ 559.00901 (^{79}Br), found: 559.01034 (^{79}Br), 561.00669 (^{81}Br).

*4.4.13. Dibenzyl 2-[(1S,2E)-1,3-bis(4-bromophenyl)-2-propen-1-yl] malonate (**10cd**).* Prepared according to the general procedure using (*E*)-1,3-bis(4-bromophenyl)-2-propen-1-yl acetate (205 mg, 0.5 mmol) and dibenzyl malonate (426 mg, 1.5 mmol), while the reaction time was 1 days. The desired product was obtained as white solid (316 mg, > 99% yield). The ee was determined by chiral HPLC with a Daicel ChiralpakIA column (*n*-hexane/2-propanol 80:20, flow rate 1.0 mL/min, detection at 254 nm, minor enantiomer t_R=19.3 min, major enantiomer t_R=26.9 min). Mp 80–81 °C, $[\alpha]_D^{30}$=+4.85 (c=6.7, CH_2Cl_2; 95% ee). ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.96 (d, J=10.8 Hz, 1H, CH), 4.23 (dd, J=10.8, 7.6 Hz, 1H, CH), 4.96 (s, 2H, CH_2), 5.11 (ABq, J=12.0 Hz, 2H, CH_2), 6.21 (dd, J=16.0, 7.6 Hz, 1H,=CH), 6.28 (d, J=15.6 Hz, 1H,=CH), 7.02–7.09 (m, 6H, ArH), 7.21–7.28 (m, 8H, ArH), 7.33–7.37 (m, 4H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=48.5, 57.4, 67.3, 67.4, 121.2, 121.4, 127.9, 128.21, 128.26, 128.33, 128.40, 128.44, 128.51, 128.54, 129.1, 129.6, 131.1, 131.5131.8, 135.3, 138.7, 166.8, 167.2 ppm. IR (KBr): ν 3065, 3031, 2959, 1755, 1734, 1587, 1497, 1488, 1455, 1409, 1380, 1324, 1266, 1215, 1169, 1122, 1071, 1009, 976, 907, 824, 797, 748, 730, 697 cm^{-1}. HRMS (ESI): calcd for $C_{32}H_{26}Br_2NaO_4$ $[M+Na]^+$ 655.00901(^{79}Br), found: 655.00966 (^{79}Br), 657.00655 (^{81}Br).

*4.4.14. (E)-Ethyl 2-cyano-3,5-diphenylpent-4-enoate (**12**).*[14] Prepared according to the general procedure using (*E*)-1,3-diphenyl-2-propen-1-yl acetate (126 mg, 0.5 mmol) and ethyl 2-cyanoacetate (170 mg, 1.5 mmol), while the reaction time was 5 days. The desired product was obtained as colorless oil (55 mg, 36% yield). The ee was determined by chiral HPLC on Daicel Chiralpak IB column (*n*-hexane/2-propanol=99:1, flow rate 0.5 mL/min, detection at 254 nm, major diastereomer: minor enantiomer t_R=34.7 min, major enantiomer t_R=38.6 min; minor diastereomer: t_R=112.6 min, t_R=154.3 min). $[\alpha]_D^{30}$=+14.6 (c=1.9, CH_2Cl_2; 80% ee for major diastereomer, 0% ee for minor diastereomer). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.15–1.19 (m, 3H, CH_3), 3.87–3.93 (m, 1H, CH), 4.15–4.17 (m, 2H, CH_2), 4.21–4.25 (m, 1H, CH), 6.41–6.52 (m, 1H, CH), 6.54–6.62 (m, 1H, CH), 7.25–7.38 (m, 10H, ArH) ppm.

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Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2012.02.078.

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