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# Synthesis of highly rigid phosphine–oxazoline ligands for palladium-catalyzed asymmetric allylic alkylation†

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A highly rigid spiro phosphine–oxazoline ligand skeleton with a spirocarbon stereogenic center was developed from 7-bromo-1-indanone. The catalytic performance of the ligand was demonstrated in palladium-catalyzed asymmetric allylic alkylation. Under optimized conditions, high yields (up to 99%) and enantioselectivities (up to 99.9% ee) were obtained for reactions of 1,3-diphenylallyl acetates and symmetrical 1,3-dicarbonyl substrates.

## Introduction

Asymmetric catalysis utilizing transition-metal complexes is a powerful tool to prepare enantiopure compounds and is one of the most important frontiers in chemical science.[1] One important and challenging task in the development of asymmetric catalysis is to design and synthesize novel and efficient chiral ligands.[2] The chiral phosphine–oxazoline (PHOX) ligand **1** (Fig. 1) invented by Pfaltz/Helmchen/Williams,[3] coordinates to the metal center with a P and N atom, has proven to be a superior ligand in asymmetric catalysis.[4] For the PHOX skeleton **1**, the R group which is at C-4 of oxazoline is restricted to those found in readily available amino alcohols. Many new phosphine–oxazoline ligands have been developed to improve the asymmetric performance and applicability of the ligands. Burgess developed the phosphine–oxazoline ligand **2** (JM-Phos), which was successfully used in Pd-catalyzed allylic alkylation reactions[5a,b] and Ir-catalyzed hydrogenation of several unfunctionalized olefins.[5c] The R group in the JM-Phos skeleton could be formed from the derivatives of carboxylic acid, giving more scope for diversity. This skeleton is fairly conformationally flexible with an ethylene linker.

Noticeably, the spiro backbone has been recognized as a privileged structure and shown impressive catalytic performance in many cases because the rigid scaffold of the ligands could reduce the conformational obscurity of the catalyst and create an effective asymmetric environment around the central metal.[6] In this context, Zhou[6h] and Ding[6i] have developed SIPHOX (**3**, Fig. 1) and SpinPHOX (**4**, Fig. 1) respectively, which demonstrated excellent asymmetric induction in Ir-catalyzed asymmetric hydrogenation reactions. Despite these elegant contributions, developing a novel and practical backbone of PHOX is still a highly valuable but challenging task.

By taking advantage of the synthetic diversity, the rigid spiro backbone, and the chelating units of the phosphine–oxazoline skeleton, we report a new type of rigid spiro indanyl phosphine–oxazoline ligand (**L**, Fig. 1) synthesized facilely from commercially available 7-bromo-1-indanone. To our knowledge, this is the first phosphine–oxazoline skeleton that bears a spirocarbon stereogenic center. The catalytic performance of the ligand in palladium-catalyzed asymmetric allylic alkylation reactions was investigated.

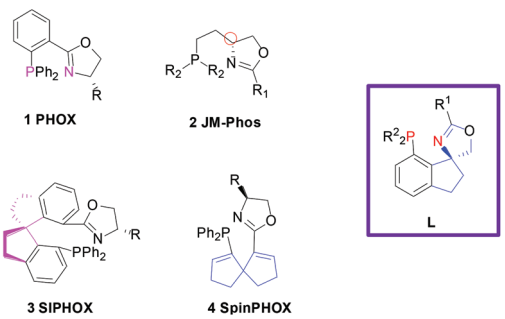


**Fig. 1** Chiral phosphine–oxazoline ligands.

## Results and discussion

The new chiral phosphine–oxazoline ligands **L1–L4** were synthesized from commercially available 7-bromo-1-indanone. The synthetic scheme is outlined in Scheme 1. (*S*)-Amino acid hydrochloride **7** was synthesized by adapting the literature

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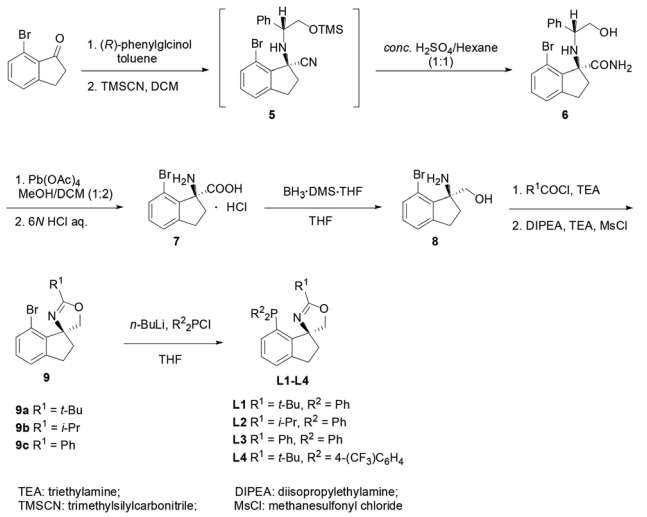



**Scheme 1** Synthesis of spiro phosphine–oxazoline ligands.

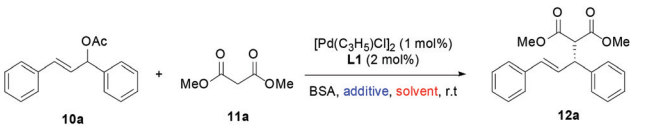
methods.[7] The addition of (*R*)-phenylglycinol to 7-bromo-1-indanone afforded the ketimine intermediate which subsequently reacted with trimethylsilyl carbonitrile to obtain trimethylsilylated aminonitrile **5**. Compound **5** was directly subjected to hydrolysis with sulfuric acid to give hydroxyaminoamide **6**. Compound **6** was treated with lead(IV) acetate and then was hydrolyzed with 6 N hydrochloric acid to afford **7**. Reduction of amino acid hydrochloride **7** by the borane dimethyl sulfide complex gave enantiopure (*S*)-aminoalcohol **8**. The key intermediate **9** was obtained according to the literature methods.[8] Lithium-halogen exchange of **9** with *n*-BuLi followed by the reaction with $R^2{}_2PCl$ afforded the desired ligands **L1–L4**.

The asymmetric allylic alkylation, which is one of the most versatile methods for asymmetric C–C bond-forming reactions,[9] was employed to evaluate the catalytic performance of the new chiral spiro phosphine–oxazoline ligands. The model reaction between 1,3-diphenyl-2-propenyl acetate (**10a**) and dimethyl malonate (**11a**) was initially performed in the presence of $[Pd(C_3H_5)Cl]_2$ (1 mol%), **L1** (2 mol%), *N*,*O*-bis(trimethylsilyl)acetamide (BSA, 3 equiv.) and a catalytic amount of KOAc as the additive in toluene. Excellent enantioselectivity and yield were achieved (98.0% ee and 99% yield) (Table 1, entry 1).

Evaluation of solvents showed that dichloromethane, tetrahydrofuran and acetonitrile all gave good results with high yields and enantioselectivities (Table 1, entries 2–4). Toluene was the best solvent among them (entry 1). Different additives, including NaOAc, CsOAc, $K_2CO_3$ and $Cs_2CO_3$ were tested instead of KOAc to give lower reactivity or enantioselectivity (Table 1, entries 5–8). Herein, KOAc was found to be the best additive; up to 99% yield and 98.0% ee was obtained for the allylic substitution reaction (Table 1, entry 1).

Having these results in hand, the other ligands (**L2–L4**) with different $R^1$ and $R^2$ groups were investigated. To our delight, all the ligands proved to be suitable for the reaction,

**Table 1** Solvent and additive screening[a]

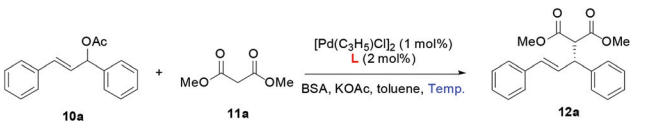



| Entry | Solvent | Additive | Time (h) | Yield[b] (%) | ee[c,d] (%) |
|---|---|---|---|---|---|
| 1 | Toluene | KOAc | 3 | 99 | 98.0 |
| 2 | $CH_2Cl_2$ | KOAc | 12 | 82 | 92.6 |
| 3 | THF | KOAc | 3 | 97 | 91.2 |
| 4 | MeCN | KOAc | 3 | 94 | 92.8 |
| 5 | Toluene | NaOAc | 24 | 90 | 97.8 |
| 6 | Toluene | CsOAc | 3 | 99 | 94.8 |
| 7 | Toluene | $K_2CO_3$ | 24 | 84 | 97.8 |
| 8 | Toluene | $Cs_2CO_3$ | 24 | 92 | 96.0 |

[a] Unless otherwise noted, the reactions were performed with **10a** (0.3 mmol), **11a** (0.9 mmol), $[Pd(C_3H_5)Cl]_2$ (1 mol%), **L1** (2 mol%), BSA (0.9 mmol) and the additive (10 mol%) in a certain solvent (2 mL) at room temperature. [b] Isolated yield. [c] Determined by HPLC using a chiral AD-H column. [d] The absolute configurations were assigned *R via* comparison of specific rotations with the literature data.[10]

giving the desired product **12a** in high yields and enantioselectivities (94–99% yields and 95.2–98.8% ee) (Table 2, entries 1–4), indicating the high efficiency of the new spiro phosphine–oxazoline ligands. Among them, ligand **L2** provided superior results to others and was chosen for further optimization. Subsequent optimization with respect to temperature indicated that the reaction afforded low enantioselectivity at 40 °C and low reactivity at −10 °C. The best result was given at 0 °C (Table 2, entries 7). A decrease of the catalyst loading to 0.5 mol% led to a drop in yield even after extending the reaction time to 24 h, without compromising on the enantioselectivity (78% yield and 98.2% ee) (Table 2, entry 8).

**Table 2** Ligand and temperature screening[a]



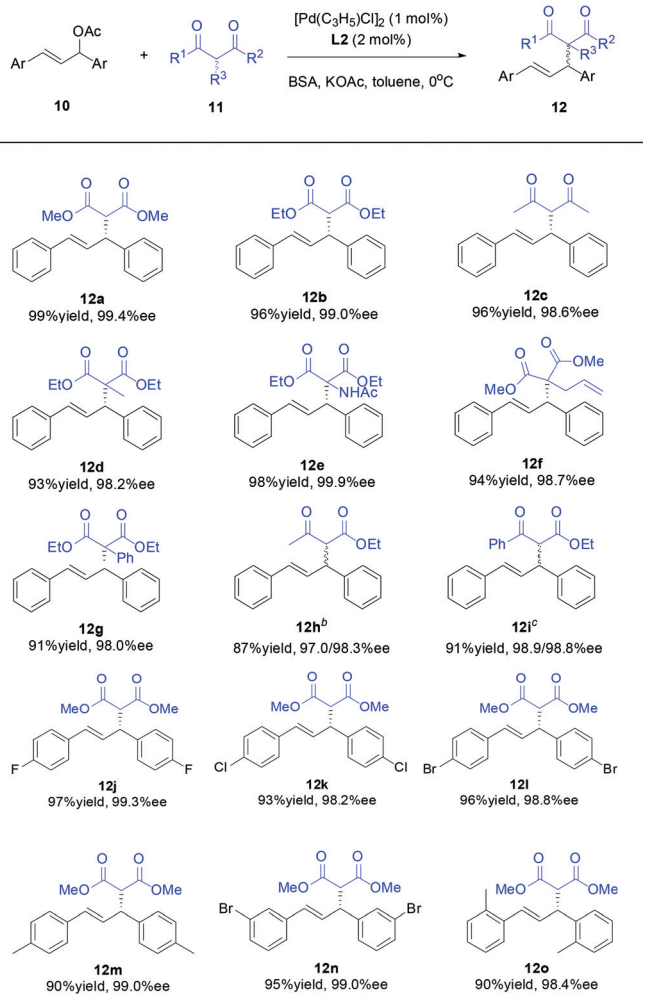

| Entry | Ligand | *T* (°C) | Time (h) | Yield[b] (%) | ee[c,d] (%) |
|---|---|---|---|---|---|
| 1 | **L1** | 25 | 3 | 99 | 98.0 |
| 2 | **L2** | 25 | 3 | 99 | 98.8 |
| 3 | **L3** | 25 | 12 | 94 | 95.2 |
| 4 | **L4** | 25 | 3 | 99 | 97.4 |
| 5 | **L2** | 40 | 1 | 99 | 96.4 |
| 6 | **L2** | 0 | 5 | 99 | 99.4 |
| 7 | **L2** | −10 | 24 | 85 | 99.1 |
| 8[e] | **L2** | 0 | 24 | 78 | 98.2 |

[a] Unless otherwise noted, the reactions were performed with **10a** (0.3 mmol), **11a** (0.9 mmol), $[Pd(C_3H_5)Cl]_2$ (1 mol%), ligand (2 mol%), BSA (0.9 mmol) and KOAc (10 mol%) in toluene (2 mL) at a certain temperature. [b] Isolated yield. [c] Determined by HPLC using a chiral AD-H column. [d] The absolute configurations were assigned *R via* comparison of specific rotations with the literature data.[10] [e] With $[Pd(C_3H_5)Cl]_2$ (0.5 mol%) and **L2** (1 mol%) for 24 h.

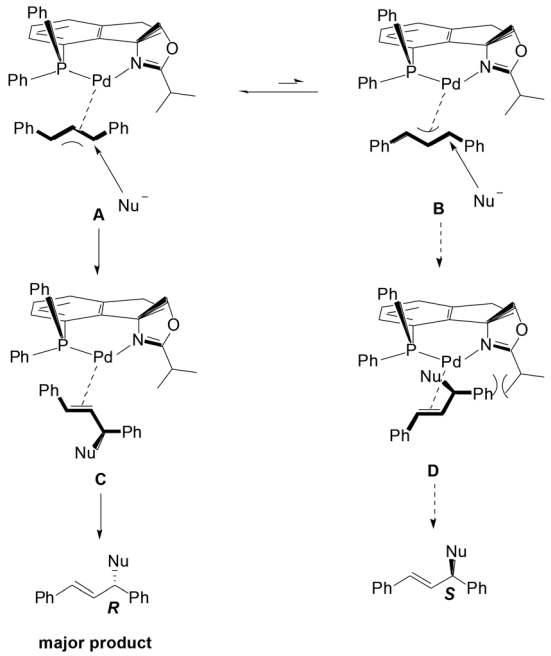
 

Under the optimized conditions, the substrate scope of the reaction was examined using the palladium-**L2** catalyst (Table 3). As shown in Table 3, a wide range of allylic acetates **10** and activated methylene carbonyl compounds **11** were used for the Pd-catalyzed allylic alkylation. For symmetrical 1,3-dicarbonyl substrates **11a–g**, the desired products were obtained in 98.0–99.9% ee (Table 3, **12a–12g**). Notably, the use of methyl, acetylamino, allyl, and phenyl-substituted dialkyl malonates **11d–g** as substrates in this reaction also resulted in the same level of enantioselectivity. Besides, we found that the reaction exhibited high tolerance of the 1,3-diphenylallyl acetate components employing the new ligand. The substrates bearing either electron-donating or electron-withdrawing substituents on the aromatic ring underwent the reaction smoothly to give the corresponding products in good yield with excellent ee values (98.2–99.4%) (Table 3, **12j–12o**).

**Table 3** Substrate scope[a]




[a] Unless otherwise noted, the reactions were performed with **10** (0.3 mmol), **11** (0.9 mmol), $[Pd(C_3H_5)Cl]_2$ (1 mol%), **L2** (2 mol%), BSA (0.9 mmol) and KOAc (10 mol%) in toluene (2 mL) at 0 °C for 5 h. [b] The dr was 51 : 49 as determined using chiral HPLC and $^1$H NMR. [c] The dr was 70 : 30 as determined using chiral HPLC and $^1$H NMR.




**Scheme 2** A plausible reaction mechanism.

Therefore, the ligand **L2** exhibits superior catalytic performance for the allylic alkylation reaction of 1,3-diphenylallyl acetates and symmetric 1,3-dicarbonyl substrates. Unfortunately, for unsymmetrical dicarbonyl compounds **11h–i**, the diastereoselectivity was not good (Table 3, **12h–12i**). The allylic alkylation of unsymmetrical dicarbonyl compounds was still a challenging task.

The stereochemical course of the reaction can be rationalized by means of the model proposed in Scheme 2. It has been reported that the most abundant isomer in the case of 1,3-diphenyl substituted allyl systems corresponds to the *exo-syn–syn* (**A**, W-type), followed by the *endo-syn–syn* one (**B**, M-type) and the two isomers rapidly equilibrate.[11] For the asymmetric alkylation, it is known that, because the *trans* effect directs the nucleophilic attack on the allylic terminus *trans* to the phosphorus atom,[12] **A** is converted into Pd-olefin complex **C** that is less sterically congested compared to complex **D**. As similar steric interactions are already present in the transition states, the reaction leading to **C** is faster than the nucleophilic addition leading to **D**. The *R* configuration of the final product **12a** for the 1,3-diphenyl-substituted starting material **11a** would be in agreement with this assumption.

## Conclusions

In conclusion, we have designed and synthesized a new type of rigid chiral phosphine–oxazoline ligand with a spirocarbon stereogenic center. Notable features of the ligand are the rigid and unique spiro core structure. The ligand exhibited excellent catalytic performance in Pd-catalyzed asymmetric allylic alkylation reactions. High yields (up to 99%) and enantioselectivi-

ties (up to 99.9% ee) were obtained for the reactions of 1,3-diphenylallyl acetates and symmetrical 1,3-dicarbonyl substrates. Further application of these ligands in other asymmetric transformations is currently under development.

## Experimental

### General information

Unless stated otherwise, all reactions were performed under an argon atmosphere using freshly distilled solvents, and the workups were carried out in air. Toluene, DCM, $CH_3CN$ and THF were distilled over dehydrating reagents. Commercially available reagents were used without further purification. The melting points were recorded on a RY-1 microscopic melting apparatus and uncorrected. $^1H$, $^{13}C$ and $^{31}P$ NMR spectra were recorded on a Bruker Avance 500 spectrometer. Chemical shifts were reported in parts per million ($\delta$) relative to tetramethylsilane (TMS). HRMS measurements were performed on an Ultima Global spectrometer or Thermo UltiMate 3000-Q Exactive Focus with an ESI source. High-performance liquid chromatography (HPLC) was performed with a Shimadzu LC-20 Liquid Chromatograph using Chiralcel OD-H, AD-H and IC columns.

**Synthesis of (1*S*,1′*R*)-7-bromo-1-(1-phenyl-2-trimethylsilanyloxy-ethylamino)-indan-1-carbonitrile (5).** To a stirred solution of 7-bromo-1-indanone (12.6 g, 60 mmol) in toluene (240 mL) was added (*R*)-2-phenylglycinol (9.1 g, 66 mmol) and *p*-toluenesulfonic acid (51.6 mg, 0.3 mmol). The resulting mixture was heated to reflux with the azeotropic removal of water until the starting material disappeared (monitored by TLC). After the removal of the solvent at reduced pressure, the residual oil was dissolved in 100 mL of dry $CH_2Cl_2$. The resulting solution was cooled to 0 °C, and to it was added trimethylsiyl cyanide (11.9 g, 120 mmol) dropwise. The reaction mixture was allowed to stir at 0 °C for 2 h and the solution was evaporated *in vacuo* to give aminonitrile **5** as an oil, which was dried *in vacuo* and used for the next procedure without further purification.

**Synthesis of (1*S*,1′*R*)-7-bromo-1-(2-hydroxy-1-phenyl-ethylamino)-indan-1-carboxylic acid amide (6).** Compound **5** was dissolved in *n*-hexane (100 mL) and cooled to −10 °C. Ice-cold conc. $H_2SO_4$ (100 mL) was slowly added to this reaction. The resulting two-phase mixture was allowed to warm gradually to room temperature, and was stirred for 3 days. The *n*-hexane layer was decanted, and the acidic layer was poured onto ice (100 g). This was then cooled in an ice bath, covered with ethyl acetate (150 mL) and basified with $NH_3{\cdot}H_2O$ to pH 9–10. The organic phase was separated and the aqueous phase was extracted with ethyl acetate (3 × 100 mL). The combined organic layers were dried ($MgSO_4$), filtered and evaporated *in vacuo* to give crude hydroxyaminoamide **6**. The residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 1/1) to give a white solid powder hydroxyaminoamide **6** (13.6 g), yield: 61% (two steps), m.p.: 175–177 °C, $[\alpha]_D^{25}$ = 12.98 ($c$ = 0.5, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 7.10–7.04 (m, 5H), 6.98 (s, 1H), 6.95–6.92 (m, 3H), 5.73 (s, 1H), 3.83 (s, 1H), 3.58–3.49 (m, 2H), 3.16 (s, 1H), 2.99 (t, $J$ = 8.0 Hz, 2H), 2.94 (s, 1H), 2.57–2.50 (m, 1H), 2.38–2.33 (m, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ = 178.2, 147.1, 142.7, 141.2, 131.0, 130.0, 128.2, 127.2, 126.4, 124.0, 119.9, 75.3, 67.5, 60.2, 36.7, 31.6. HRMS (ESI): calcd for $C_{18}H_{20}N_2O_2Br$ $[M + H]^+$: 375.0703, found 375.0705.

**Synthesis of (*S*)-1-amino-7-bromo-indan-1-carboxylic acid hydrochloride (7).** A solution of hydroxyaminoamide **6** (3.7 g, 10 mmol) in dry $CH_2Cl_2$ (24 mL) and dry MeOH (12 mL) was cooled to 0 °C under argon. Lead(IV) acetate (5.3 g, 12 mmol) was added. The solution was stirred at 0 °C for 1 h and quenched by the addition of phosphate buffer (0.2 M, pH 7, 100 mL). After stirring at room temperature for 15 min, the solution was diluted with $CH_2Cl_2$ (100 mL) and filtered through Celite. The organic layer was separated and the aqueous layer was extracted with $CH_2Cl_2$ (2 × 100 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated. The remaining yellowish oil was taken up in HCl (6 N, 100 mL) and heated to reflux for 5 h. After cooling to room temperature, the solution was extracted with $CH_2Cl_2$ (3 × 100 mL) and concentrated to leave amino acid hydrochloride **7** as a slightly yellowish solid (2.9 g, 99% yield) without further purification for the next step.

**Synthesis of (*S*)-(1-amino-7-bromo-indan-1-yl)-methanol (8).** To a suspension of amino acid hydrochloride **7** (1.5 g, 5 mmol) in dry THF (10 mL) was added $BH_3$-DMS-THF (2 M, 7.5 mL) at room temperature *via* a syringe. The reaction mixture was then stirred under reflux for 8 h, then cooled to 0 °C and quenched with NaOH (10%, 25 mL) and refluxed for 2 h. The solvent was evaporated, and the remaining aqueous layers were extracted with $CH_2Cl_2$ (3 × 50 mL). The combined organic layers were washed with saturated aqueous solution of $NH_4Cl$, then brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on $SiO_2$ ($CH_2Cl_2$/MeOH = 20/1) to give a white solid powder amino alcohol **8** (0.9 g), yield: 74%. m.p.: 123–125 °C, $[\alpha]_D^{25}$ = −4.62 ($c$ = 0.25, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 7.34 (d, $J$ = 7.8 Hz, 1H), 7.18 (d, $J$ = 7.3 Hz, 1H), 7.09 (t, $J$ = 7.7 Hz, 1H), 3.79 (d, $J$ = 10.7 Hz, 1H), 3.48 (d, $J$ = 10.7 Hz, 1H), 2.89–2.83 (m, 2H), 2.68–2.64 (m, 1H), 2.30 (s, 3H), 1.76 (dd, $J$ = 22.0, 10.0 Hz, 1H); $^{13}C$ NMR (125 MHz, CDCl3): $\delta$ = 147.1, 143.8, 131.5, 129.6, 124.5, 119.0, 68.5, 65.2, 37.3, 29.0. HRMS (ESI): calcd for $C_{10}H_{13}NOBr$ $[M + H]^+$: 242.0175, found 242.0176.

**Synthesis of (*S*)-7-bromo-2′-(*tert*-butyl)-2,3-dihydro-5′*H*-spiro[indene-1,4′-oxazole] (9a).** To a mixture of amino alcohol **8** (533 mg, 2.2 mmol) and triethylamine (1.2 mL, 8.8 mmol) in dry $CH_2Cl_2$ (10 mL) was added a solution of pivaloyl chloride (0.3 mL, 2.3 mmol) in dry $CH_2Cl_2$ (5 mL) at 0 °C. The reaction mixture was stirred for 4 h at room temperature and then cooled to 0 °C, followed by the addition of DIPEA (diisopropylethylamine) (1.5 mL, 8.8 mmol), triethylamine (1.8 mL, 13.2 mmol) and methanesulfonyl chloride (0.4 mL, 4.4 mmol). The resulting mixture was allowed to warm to room temperature and stirred overnight. Compound **9a** was isolated by

column flash chromatography (petroleum ether/ethyl acetate = 30/1) as a yellow oil (583 mg) after the removal of the solvent, the excessive diisopropylethylamine and triethylamine under reduced pressure. Yield: 86%. $[\alpha]_D^{25}$ = −13.7 (*c* = 0.2, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.35 (d, *J* = 7.9 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 4.57 (d, *J* = 8.6 Hz, 1H), 4.19 (d, *J* = 8.7 Hz, 1H), 3.09–3.04 (m, 1H), 2.93–2.87 (m, 1H), 2.43–2.37 (m, 1H), 2.18–2.13 (m, 1H), 1.29 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 173.7, 146.8, 142.6, 131.8, 129.8, 124.0, 120.4, 81.8, 76.7, 41.4, 33.2, 30.0, 27.8. HRMS (ESI): calcd for $C_{15}H_{19}NOBr$ $[M + H]^+$: 308.0645, found 308.0649.

**Synthesis of (*S*)-7-bromo-2′-isopropyl-2,3-dihydro-5′*H*-spiro[indene-1,4′-oxazole] (9b).** Compound **9b** was produced from **8** and isobutyryl chloride by the same method used for **9a** as a yellow oil. Yield: 83%. $[\alpha]_D^{25}$ = −9.6 (*c* = 0.3, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.35 (d, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 7.07 (t, *J* = 7.8 Hz, 1H), 4.65 (d, *J* = 8.8 Hz, 1H), 4.16 (d, *J* = 8.8 Hz, 1H),3.12–3.05 (m, 1H), 2.94–2.87 (m, 1H), 2.68–2.63 (m, 1H), 2.44–2.39 (m, 1H), 2.18–2.12 (m, 1H), 1.26 (d, *J* = 7.0 Hz, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 171.8, 146.8, 142.5, 131.8, 129.8, 124.0, 120.3, 81.7, 76.3, 41.4, 30.0, 28.3, 19.7. HRMS (ESI): calcd for $C_{14}H_{17}NOBr$ $[M + H]^+$: 294.0488, found 294.0492.

**Synthesis of (*S*)-7-bromo-2′-phenyl-2,3-dihydro-5′*H*-spiro[indene-1,4′-oxazole] (9c).** Compound **9c** was produced from **8** and benzoyl chloride by the same method used for **9a** as a colorless oil. Yield: 77%. $[\alpha]_D^{25}$ = −13.3 (*c* = 0.5, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 8.02 (d, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.7 Hz, 1H), 4.83 (d, *J* = 8.7 Hz, 1H), 4.41 (d, *J* = 8.8 Hz, 1H), 3.19–3.13 (m, 1H), 3.01–2.95 (m, 1H), 2.61–2.55 (m, 1H), 2.31–2.26 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 164.1, 146.8, 142.6, 131.9, 131.5, 130.0, 128.6, 128.4, 127.9, 124.0, 120.4, 82.3, 41.4, 30.1. HRMS (ESI): calcd for $C_{17}H_{15}NOBr$ $[M + H]^+$: 328.0332, found 328.0335.

**Synthesis of (*S*)-2′-(*tert*-butyl)-7-(diphenylphosphino)-2,3-dihydro-5′*H*-spiro[indene-1,4′-oxazole] (L1).** To a solution of **9a** (524 mg, 1.7 mmol) in dry THF (4 mL) *n*-BuLi (2.6 mmol, 2.5 M in hexane) was added dropwise at −78 °C. After stirring at the temperature for 1 h, $Ph_2PCl$ (751 mg, 3.4 mmol) was added dropwise at −78 °C. The mixture was stirred at −78 °C for 1 h and room temperature for 1 h. The reaction was terminated with a minimal amount of saturated $NaHCO_3$ (aq.) and extracted with $CH_2Cl_2$ (3 × 10 mL). The combined organic layers were washed with saturated aqueous solution of $NH_4Cl$, then brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on $SiO_2$ (petroleum ether/ethyl acetate = 40/1) to give a white solid **L1** (545 mg), yield: 74%, m.p.: 71–73 °C, $[\alpha]_D^{25}$ = −38.7 (*c* = 0.2, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.30–7.25 (m, 8H), 7.21–7.13 (m, 4H), 6.86 (t, *J* = 5.3 Hz, 1H), 4.68 (s, 1H), 4.32 (s, 1H), 3.05 (s, 1H), 2.95–2.89 (m, 1H), 2.36 (s, 1H), 2.14 (d, *J* = 8.7 Hz, 1H), 1.12 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 173.6, 150.5, 144.3, 138.5, 137.7, 134.6, 134.0, 133.9, 133.6, 133.3, 133.1, 128.4, 128.3, 127.9, 125.6, 81.9, 79.0, 41.5, 33.1, 29.8, 27.4. $^{31}$P NMR (202 MHz, $CDCl_3$): $\delta$ = −21.71. HRMS (ESI): calcd for $C_{27}H_{29}NOP$ $[M + H]^+$: 414.1981, found 414.1988.

**Synthesis of (*S*)-7-(diphenylphosphino)-2′-isopropyl-2,3-dihydro-5′*H*-spiro[indene-1,4′-oxazole] (L2).** Ligand **L2** was produced from **9b** by the same method used for **L1** as a white solid (78%), m.p.: 85–86 °C, $[\alpha]_D^{25}$ = −40.5 (*c* = 0.3, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.30–7.18 (m, 11H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.87 (t, *J* = 5.0 Hz, 1H), 4.75 (dd, *J* = 8.5, 3.0 Hz, 1H), 4.34–4.26 (m, 1H), 3.10–3.04 (m, 1H), 2.96–2.90 (m, 1H), 2.47–2.36 (m, 2H), 2.17–2.12 (m, 1H), 1.11 (d, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 6.9 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 171.5, 150.5, 150.3, 144.2, 138.3, 138.2, 137.6, 137.5, 134.4, 134.0, 133.8, 133.5, 133.3, 133.1, 128.4, 128.0, 125.6, 81.7, 78.8, 41.7, 29.9, 28.3, 19.2. $^{31}$P NMR (202 MHz, $CDCl_3$): $\delta$ = −21.05. HRMS (ESI): calcd for $C_{26}H_{27}NOP$ $[M + H]^+$: 400.1825, found 400.1830.

**Synthesis of (*S*)-7-(diphenylphosphino)-2′-phenyl-2,3-dihydro-5′*H*-spiro[indene-1,4′-oxazole] (L3).** Ligand **L3** was produced from **9c** by the same method used for **L1** as a white solid (81%), m.p.: 125–127 °C, $[\alpha]_D^{25}$ = 45.7 (*c* = 0.2, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.61 (s, 2H), 7.42 (s, 1H), 7.33–7.12 (m, 12H), 7.03 (t, *J* = 7.7 Hz, 2H), 6.85 (dd, *J* = 7.3, 4.8 Hz, 1H), 4.97 (s, 1H), 4.53 (s, 1H), 3.09 (s, 1H), 3.02–2.95 (m, 1H), 2.49 (s, 1H), 2.25 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 164.0, 150.3, 150.1, 144.1, 138.2, 138.1, 136.7, 134.2, 134.0, 133.8, 133.6, 131.0, 128.6, 128.3, 128.1, 128.1, 128.0, 125.6, 82.3, 78.8, 41.6, 30.0. $^{31}$P NMR (202 MHz, $CDCl_3$): $\delta$ = −20.33. HRMS (ESI): calcd for $C_{29}H_{25}NOP$ $[M + H]^+$: 436.1668, found 434.1674.

**Synthesis of (*S*)-7-(bis(4-(trifluoromethyl)phenyl)phosphino)-2′-(*tert*-butyl)-2,3-dihydro-5′*H*-spiro[indene-1,4′-oxazole] (L4).** Ligand **L4** was produced from **9a** and $(4\text{-}CF_3Ph)_2PCl$ by the same method used for **L1** as a white solid (77%), m.p.: 101–103 °C, $[\alpha]_D^{25}$ = 9.4 (*c* = 0.2, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.56 (d, *J* = 7.8 Hz, 4H), 7.35–7.26 (m, 5H), 7.18 (t, *J* = 7.6 Hz, 1H), 6.78 (t, *J* = 6.1 Hz, 1H), 4.61 (d, *J* = 8.3 Hz, 1H), 4.38 (d, *J* = 8.4 Hz, 1H), 3.08–3.03 (m, 1H), 2.98–2.91 (m, 1H), 2.38–2.32 (m, 1H), 2.18–2.14 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 174.0, 150.8, 144.7, 142.7, 142.0, 134.4, 134.1, 133.9, 133.4, 133.2, 131.3, 131.1, 130.9, 130.7, 130.5, 130.2, 129.0, 126.5, 125.2, 123.0, 81.8, 79.2, 41.4, 33.1, 29.6, 27.3. $^{31}$P NMR (202 MHz, $CDCl_3$): $\delta$ = −52.61. HRMS (ESI): calcd for $C_{29}H_{27}NOPF_6$ $[M + H]^+$: 550.1729, found 550.1735.

### General procedure for the Pd-catalyzed asymmetric allylic alkylation

Ligand **L2** (2.4 mg, 2 mol%) and $[Pd(C_3H_5)Cl]_2$ (1.1 mg, 1 mol%) were dissolved in toluene (1.0 mL) in a Schlenk tube under an Ar atmosphere. After 1 h of stirring at room temperature, allylic acetate **10** (0.3 mmol) dissolved in toluene (0.5 mL) was added, followed by malonate **11** (0.9 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (183 mg, 0.9 mmol), and KOAc (2.9 mg, 10 mol%). The mixture was stirred at 0 °C for 5 h and then was diluted with $CH_2Cl_2$ and washed with saturated $NH_4Cl$ (aq). The organic layers were dried over $MgSO_4$ and filtered, and the solvents were evaporated *in vacuo*. The residue was purified by

flash column chromatography, eluting with petroleum ether and ethyl acetate to afford the corresponding product **12**.

### Characterization of the compounds

**(*R*,*E*)-Dimethyl 2-(1,3-diphenylallyl)malonate (12a).** Colorless oil. 99% yield and 99.4% ee, determined by chiral HPLC analysis (Chiralcel AD-H hexane/isopropanol, 90 : 10 v/v, 1.0 mL $min^{-1}$, 25 °C, UV 254 nm), retention times: $t_r$ = 12.358 min for (*R*)-isomer (major), $t_r$ = 17.861 min for (*S*)-isomer (minor). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.32–7.25 (m, 8H), 7.23–7.18 (m, 2H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.32 (dd, *J* = 15.8, 8.7 Hz, 1H), 4.25 (dd, *J* = 10.7, 8.7 Hz, 1H), 3.94 (d, *J* = 10.9 Hz, 1H), 3.69 (s, 3H), 3.51 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ = 168.3, 167.9, 140.3, 136.9, 132.0, 129.2, 128.9, 128.6, 128.0, 127.7, 127.3, 126.5, 57.8, 52.8, 52.6, 49.3.

**(*R*,*E*)-Diethyl 2-(1,3-diphenylallyl)malonate (12b).** Colorless oil. 96% yield and 99.0% ee, determined by chiral HPLC analysis (Chiralcel AD-H hexane/isopropanol, 95 : 5 v/v, 0.7 mL $min^{-1}$, 25 °C, UV 254 nm), retention times: $t_r$ = 23.817 min for (*R*)-isomer (major), $t_r$ = 33.722 min for (*S*)-isomer (minor). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.26–7.24 (m, 6H), 7.23–7.20 (m, 2H), 7.19–7.15 (m, 2H), 6.43 (d, *J* = 16.0 Hz, 1H), 6.29 (dd, *J* = 16.0, 9.0 Hz, 1H), 4.21 (dd, *J* = 11.0, 9.0 Hz, 1H), 4.12 (q, *J* = 7.0 Hz, 2H), 3.95–3.90 (m, 2H), 3.87 (d, *J* = 11.0 Hz, 1H), 1.16 (t, *J* = 7.0 Hz, 3H), 0.96 (t, *J* = 7.0 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 167.9, 167.5, 140.4, 136.9, 131.7, 129.4, 128.7, 128.5, 128.1, 127.6, 127.1, 126.4, 61.6, 61.4, 57.8, 49.3, 14.2, 13.9.

**(*R*,*E*)-3-(1,3-Diphenylallyl)pentane-2,4-dione (12c).** Colorless oil. 96% yield and 98.6% ee, determined by chiral HPLC analysis (Chiralcel AD-H hexane/isopropanol, 95 : 5 v/v, 0.7 mL $min^{-1}$, 25 °C, UV 254 nm), retention times: $t_r$ = 17.200 min for (*R*)-isomer (major), $t_r$ = 18.908 min for (*S*)-isomer (minor). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.32–7.29 (m, 2H), 7.28–7.23 (m, 6H), 7.21–7.17 (m, 2H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.20–6.16 (m, 1H), 4.35–4.32 (m, 2H), 2.24 (s, 3H), 1.91 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 202.9, 202.8, 140.2, 136.6, 131.7, 129.3, 129.1, 128.6, 128.0, 127.8, 127.3, 126.4, 74.6, 49.2, 30.1, 29.8.

**(*S*,*E*)-Diethyl 2-(1,3-diphenylallyl)-2-methylmalonate (12d).** Colorless oil. 93% yield and 98.2% ee, determined by chiral HPLC analysis (Chiralcel AD-H hexane/isopropanol, 95 : 5 v/v, 0.5 mL $min^{-1}$, 25 °C, UV 254 nm), retention times: $t_r$ = 14.188 min for (*S*)-isomer (major), $t_r$ = 13.461 min for (*R*)-isomer (minor). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.35–7.32 (m, 4H), 7.30–7.26 (m, 4H), 7.24–7.16 (m, 2H), 6.70 (dd, *J* = 15.7, 9.0 Hz, 1H), 6.44 (d, *J* = 15.7 Hz, 1H), 4.30 (d, *J* = 8.9 Hz, 1H), 4.20–4.15 (m, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 1.48 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 171.2, 170.9, 139.4, 137.3, 132.5, 129.6, 128.8, 128.4, 128.2, 127.3, 127.1, 126.3, 61.3, 58.8, 53.7, 18.8, 14.0.

**(*S*,*E*)-Diethyl 2-acetoamido-2-(1,3-diphenyl-2-propenyl)malonate (12e).** White powder. 98% yield and 99.9% ee, determined by chiral HPLC analysis (Chiralcel AD-H hexane/isopropanol, 90 : 10 v/v, 1.5 mL $min^{-1}$, 25 °C, UV 254 nm), retention times: $t_r$ = 11.555 min for (*S*)-isomer (major), $t_r$ = 8.282 min for (*R*)-isomer (minor). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.31–7.15 (m, 10H), 6.76 (dd, *J* = 15.9, 7.3 Hz, 1H), 6.58 (s, 1H), 6.30 (d, *J* = 15.9 Hz, 1H), 4.77 (d, *J* = 7.0 Hz, 1H), 4.32–4.24 (m, 2H), 4.17–4.10 (m, 1H), 4.07–4.00 (m, 1H), 1.96 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 169.0, 167.5, 167.1, 138.4, 137.6, 132.4, 129.5, 128.8, 128.4, 128.4, 127.6, 127.2, 126.4, 69.0, 62.7, 62.5, 53.1, 23.2, 14.1, 13.9.

**(*S*,*E*)-Diethyl 2-allyl-2-(1,3-diphenylallyl)malonate (12f).** Colorless oil. 94% yield and 98.7% ee, determined by chiral HPLC analysis (Chiralcel AD-H hexane/isopropanol, 90 : 10 v/v, 0.5 mL $min^{-1}$, 25 °C, UV 254 nm), retention times: $t_r$ = 12.186 min for (*S*)-isomer (major), $t_r$ = 11.248 min for (*R*)-isomer (minor). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.32–7.30 (m, 2H), 7.28–7.24 (m, 4H), 7.23–7.19 (m, 2H), 7.19–7.16 (m, 2H), 6.71 (dd, *J* = 15.7, 8.8 Hz, 1H), 6.35 (d, *J* = 15.7 Hz, 1H), 5.77–5.71 (m, 1H), 5.04–4.99 (m, 2H), 4.15 (d, *J* = 8.8 Hz, 1H), 3.72 (s, 3H), 3.62 (s, 3H), 2.61 (dd, *J* = 14.0, 6.5 Hz, 1H), 2.44 (dd, *J* = 14.5, 8.0 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 170.6, 170.5, 169.3, 139.1, 137.3, 133.9, 133.2, 132.2, 129.3, 129.2, 128.4, 127.3, 126.3, 63.2, 53.7, 52.5, 52.1, 39.4.

**(*S*,*E*)-Diethyl 2-(1,3-diphenylallyl)-2-phenylmalonate (12g).** Colorless oil. 91% yield and 98.0% ee, determined by chiral HPLC analysis (Chiralcel AD-H hexane/isopropanol, 99.2 : 0.8 v/v, 0.5 mL $min^{-1}$, 25 °C, UV 254 nm), retention times: $t_r$ = 37.084 min for (*S*)-isomer (major), $t_r$ = 39.304 min for (*R*)-isomer (minor). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.30–7.25 (m, 9H), 7.19–7.13 (m, 4H), 7.00–6.98 (m, 2H), 6.50–6.40 (m, 2H), 4.64 (d, *J* = 8.8 Hz, 1H), 4.23–4.14 (m, 4H), 1.20 (dt, *J* = 11.9, 7.2 Hz, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 169.7, 169.6, 139.4, 137.4, 135.4, 132.5, 130.1, 129.5, 129.0, 128.4, 127.5, 127.4, 127.2, 126.8, 126.3, 68.0, 61.5, 61.5, 55.2, 53.4, 13.9.

**(*E*)-Ethyl 2-acetyl-3,5-diphenylpent-4-enoate (12h).** Colorless oil. 87% yield, 51 : 49 dr and 97.0%/98.3% ee, determined by chiral HPLC analysis (Chiralcel IC hexane/isopropanol, 98 : 2 v/v, 0.5 mL $min^{-1}$, 25 °C, UV 254 nm), diastereomer A: $t_r$ = 22.813 min (major), $t_r$ = 26.087 min (minor); diastereomer B: $t_r$ = 28.469 min (major), $t_r$ = 33.538 min (minor). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.33–7.25 (m, 16H), 7.24–7.18 (m, 4H), 6.44 (dd, *J* = 18.4, 15.9 Hz, 2H), 6.32–6.22 (m, 2H), 4.31–4.27 (m, 2H), 4.16 (q, *J* = 7.0 Hz, 2H), 4.10 (t, *J* = 11.7 Hz, 2H), 3.94 (q, *J* = 7.5 Hz, 2H), 2.30 (s, 3H), 2.04 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 201.7, 201.5, 167.9, 167.5, 140.3, 140.1, 136.8, 136.6, 131.8, 131.5, 129.5, 129.2, 128.9, 128.6, 128.5, 128.0, 127.9, 127.6, 127.5, 127.1, 127.1, 126.3, 65.5, 65.2, 61.6, 61.4, 48.9, 48.7, 29.8, 14.1, 13.7.

**(*E*)-Ethyl 2-benzoyl-3,5-diphenylpent-4-enoate (12i).** Colorless oil. 91% yield, 70 : 30 dr and 98.9%/98.8% ee, determined by chiral HPLC analysis (Chiralcel AD-H hexane/isopropanol, 98 : 2 v/v, 1.0 mL $min^{-1}$, 25 °C, UV 254 nm), diastereomer A: $t_r$ = 34.726 min (major), $t_r$ = 40.447 min (minor); diastereomer B: $t_r$ = 57.602 min (major), $t_r$ = 45.259 min (minor). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 8.09 (d, *J* = 7.4 Hz, 2H), 7.93 (d, *J* = 7.5 Hz, 4H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.43–7.38 (m, 6H), 7.36–7.33 (m, 6H),

7.31–7.29 (m, 8H), 7.24–7.20 (m, 8H), 7.18–7.11 (m, 6H), 6.53 (d, $J$ = 15.5 Hz, 2H), 6.43–6.35 (m, 3H), 6.26–6.20 (m, 1H), 5.03–4.98 (m, 3H), 4.63–4.55 (m, 3H), 4.16–4.08 (m, 4H), 3.92–3.86 (m, 2H), 1.15 (t, $J$ = 7.1 Hz, 6H), 0.92 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 193.2, 192.7, 168.1, 167.6, 140.9, 140.4, 137.0, 136.6, 133.7, 133.5, 131.8, 131.7, 129.9, 129.8, 128.8, 128.7, 128.5, 128.4, 128.0, 127.5, 127.4, 127.2, 126.9, 126.4, 64.5, 61.8, 61.5, 59.9, 59.7, 49.0, 25.4, 14.2, 13.8.

**(*R*,*E*)-Dimethyl 2-(1,3-bis(4-fluorophenyl)allyl)malonate (12j).** Colorless oil. 97% yield and 99.3% ee, determined by chiral HPLC analysis (Chiralcel AD-H hexane/isopropanol, 80 : 20 v/v, 1.0 mL min$^{-1}$, 25 °C, UV 254 nm), retention times: $t_r$ = 9.629 min for (*R*)-isomer (major), $t_r$ = 14.870 min for (*S*)-isomer (minor). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.29–7.24 (m, 4H), 7.02 (t, $J$ = 8.6 Hz, 2H), 6.97 (t, $J$ = 8.6 Hz, 2H), 6.41 (d, $J$ = 15.8 Hz, 1H), 6.22 (dd, $J$ = 15.7, 8.6 Hz, 1H), 4.24 (t, $J$ = 9.7 Hz, 1H), 3.89 (d, $J$ = 10.8 Hz, 1H), 3.71 (s, 3H), 3.54 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 168.1, 167.7, 163.4, 162.9, 161.5, 161.0, 135.9, 132.9, 130.9, 129.5, 129.5, 128.7, 128.0, 127.9, 115.8, 115.6, 115.4, 57.7, 52.7, 52.6, 48.3.

**(*R*,*E*)-Dimethyl 2-(1,3-bis(4-chlorophenyl)allyl)malonate (12k).** Colorless oil. 93% yield and 98.2% ee, determined by chiral HPLC analysis (Chiralcel AD-H hexane/isopropanol, 80 : 20 v/v, 1.0 mL min$^{-1}$, 25 °C, UV 254 nm), retention times: $t_r$ = 12.863 min for (*R*)-isomer (major), $t_r$ = 19.394 min for (*S*)-isomer (minor). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.25 (d, $J$ = 8.4 Hz, 2H), 7.22–7.17 (m, 6H), 6.35 (d, $J$ = 8.4 Hz, 2H), 6.22 (dd, $J$ = 15.7, 8.5 Hz, 1H), 4.21–4.17 (m, 1H), 3.84 (d, $J$ = 10.8 Hz, 1H), 3.66 (s, 3H), 3.50 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 168.0, 167.6, 138.5, 135.1, 133.5, 133.1, 131.1, 129.3, 129.0, 128.7, 127.6, 57.4, 52.8, 52.7, 48.4.

**(*R*,*E*)-Dimethyl 2-(1,3-bis(4-bromophenyl)allyl)malonate (12l).** Colorless oil. 96% yield and 98.8% ee, determined by chiral HPLC analysis (Chiralcel AD-H hexane/isopropanol, 80 : 20 v/v, 1.0 mL min$^{-1}$, 25 °C, UV 254 nm), retention times: $t_r$ = 16.193 min for (*R*)-isomer (major), $t_r$ = 24.037 min for (*S*)-isomer (minor). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.44 (d, $J$ = 8.3 Hz, 2H), 7.39 (d, $J$ = 8.4 Hz, 2H), 7.17–7.15 (m, 4H), 6.38 (d, $J$ = 15.7 Hz, 1H), 6.27 (dd, $J$ = 15.7, 8.4 Hz, 1H), 4.22 (t, $J$ = 9.6 Hz, 1H), 3.89 (d, $J$ = 10.8 Hz, 1H), 3.70 (s, 3H), 3.55 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 167.9, 167.5, 138.9, 135.4, 131.9, 131.6, 131.1, 129.6, 129.2, 127.9, 121.5, 121.2, 57.2, 52.7, 52.6, 48.4.

**(*R*,*E*)-Dimethyl 2-(1,3-di-*p*-tolylallyl)malonate (12m).** Colorless oil. 90% yield and 99.0% ee, determined by chiral HPLC analysis (Chiralcel AD-H hexane/isopropanol, 80 : 20 v/v, 1.0 mL min$^{-1}$, 25 °C, UV 254 nm), retention times: $t_r$ = 8.439 min for (*R*)-isomer (major), $t_r$ = 11.189 min for (*S*)-isomer (minor). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.16–7.12 (m, 4H), 7.06 (d, $J$ = 8.0 Hz, 2H), 7.02 (d, $J$ = 8.0 Hz, 2H), 6.38 (d, $J$ = 15.8 Hz, 1H), 6.20 (dd, $J$ = 15.7, 8.7 Hz, 1H), 4.16 (t, $J$ = 9.8 Hz, 1H), 3.87 (d, $J$ = 10.9 Hz, 1H), 3.64 (s, 3H), 3.48 (s, 3H), 2.25 (s, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 168.3, 167.8, 137.2, 136.7, 134.1, 131.4, 129.4, 129.1, 128.2, 127.7, 126.3, 57.7, 52.5, 52.4, 48.8, 21.1, 21.0.

**(*R*,*E*)-Dimethyl 2-(1,3-bis(3-bromophenyl)allyl)malonate (12n).** Colorless oil. 95% yield and 99.0% ee, determined by chiral HPLC analysis (Chiralcel AD-H hexane/isopropanol, 95 : 5 v/v, 0.5 mL min$^{-1}$, 25 °C, UV 254 nm), retention times: $t_r$ = 27.531 min for (*R*)-isomer (major), $t_r$ = 40.658 min for (*S*)-isomer (minor). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.46 (s, 1H), 7.42 (s, 1H), 7.38–7.33 (m, 2H), 7.22–7.13 (m, 4H), 6.40 (d, $J$ = 15.8 Hz, 1H), 6.27 (dd, $J$ = 15.7, 8.6 Hz, 1H), 4.21 (t, $J$ = 9.6 Hz, 1H), 3.90 (d, $J$ = 10.8 Hz, 1H), 3.71 (s, 3H), 3.56 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 167.8, 167.4, 142.2, 138.6, 131.0, 130.9, 130.6, 130.4, 130.3, 130.0, 129.8, 129.1, 126.5, 125.1, 122.7, 57.2, 53.4, 52.7, 52.6, 48.6.

**(*R*,*E*)-Dimethyl 2-(1,3-di-*o*-tolylallyl)malonate (12o).** Colorless oil. 90% yield and 98.4% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 95 : 5 v/v, 0.8 mL min$^{-1}$, 25 °C, UV 254 nm), retention times: $t_r$ = 6.428 min for (*R*)-isomer (major), $t_r$ = 7.087 min for (*S*)-isomer (minor). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.30 (d, $J$ = 7.1 Hz, 1H), 7.24–7.16 (m, 3H), 7.14–7.09 (m, 4H), 6.65 (d, $J$ = 15.6 Hz, 1H), 6.01 (dd, $J$ = 15.6, 8.8 Hz, 1H), 4.56 (dd, $J$ = 11.2, 9.1 Hz, 1H), 4.07 (d, $J$ = 11.4 Hz, 1H), 3.74 (s, 3H), 3.52 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 168.4, 167.8, 138.2, 136.4, 136.1, 135.3, 130.8, 130.4, 130.1, 129.7, 127.4, 126.8, 126.3, 126.0, 125.8, 57.1, 53.4, 52.6, 52.4, 44.8, 19.7.

## Conflicts of interest

There are no conflicts to declare.

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