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Chiral *N*-(*tert*-butyl)-*N*-methylaniline type ligands: synthesis and application to palladium-catalyzed asymmetric allylic alkylation

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ABSTRACT

We found that *N*-(*tert*-butyl)-*N*-methylanilines **1** have C(aryl)–N(amine) bond axial chirality and succeeded the optical resolution of C–N bond atropisomers of amines **1** by a chiral palladium resolving agent and/or a chiral HPLC method. Finally, we demonstrated the ability of chiral amines **1** as a ligand in palladium-catalyzed asymmetric allylic alkylation of allylic esters with malonates (up to 95% ee).

1. Introduction

C(aryl)–C(aryl) bond axially chiral biaryls[1] including BINAP[2] are important molecules that affect asymmetric inductions as ligands for transition metal catalysts. For nonbiaryl C–C bond axially chiral ligands, Clayden et al. reported the synthesis and optical resolution of C(aryl)–C(carbonyl) bond axially chiral *N*,*N*-diisopropyl-2-ethyl-6-diphenylphosphinylbenzamide.[3] The half-life times of racemization of this compound and its palladium complex from $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ at 25 °C were 2 days and 5 min, respectively. So, this compound was not used as chiral ligand for transition metal catalysts. On the other hand, C–N bond axially chiral cyclic amine compounds[4] have been reported, including the indoline-type ligands **L1**[5] (Fig. 1) and the indole-type ligands **L2**[6] (Fig. 1) for palladium-catalyzed asymmetric reactions. Recently, we prepared C(aryl)–N(amine) bond atropisomers of acyclic 1-adamantylamine derivatives **L3**[7] (Fig. 1) using an approach similar to the synthesis of ligands **L1** and **L2**. The 1-adamantyl group is one of the most bulky and rigid substituents. Thus, C–N bond axial chirality of **L3** was stable for use of chiral ligand in transition metal catalytic reactions.

Then, we were interested in the C(aryl)–N(amine) bond axial chirality of aniline derivatives with a *tert*-butyl group, which has a smaller substituent than the 1-adamantyl group. Herein, we report the synthesis and optical resolution of *N*-(*tert*-butyl)-*N*-

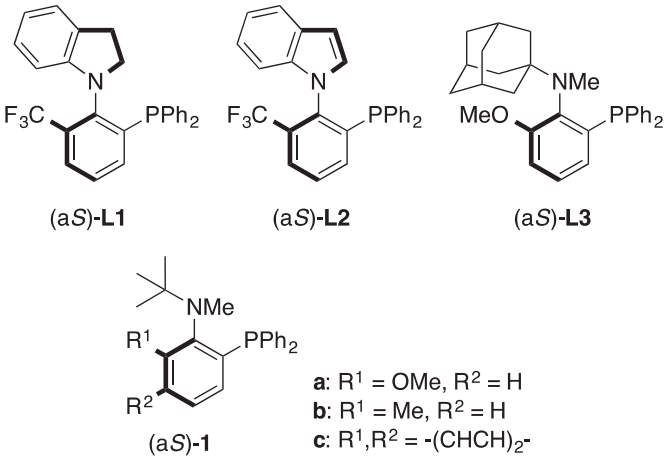

Fig. 1. C–N bond axially chiral ligands **L1**–**L3** and **1**.

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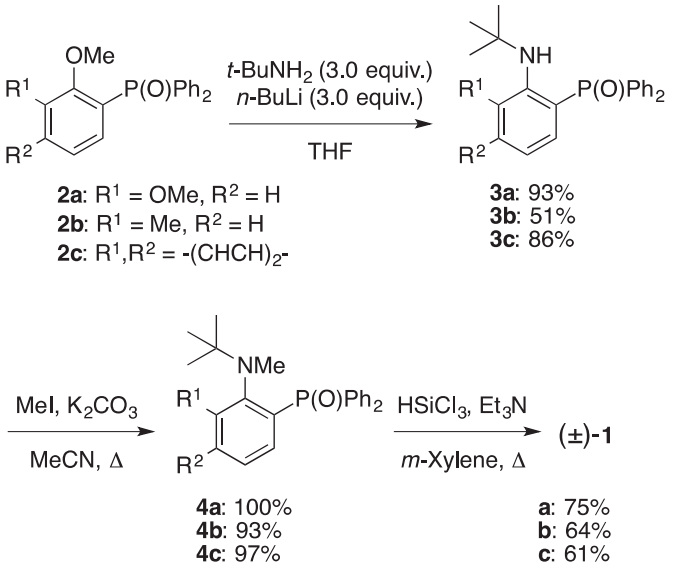
methylanilines **1** (Fig. 1) with C(aryl)–N(amine) bond axial chirality by a chiral palladium resolving agent and/or a chiral HPLC method, the investigation of a rotation barrier for C–N bond axial stability, and an application in a palladium-catalyzed asymmetric allylic alkylation of allylic esters with malonates.

2. Results and discussion

Racemic amines (±)-**1** were easily prepared in three steps. A nucleophilic aromatic substitution (S_NAr) reaction of the corresponding phosphine oxides such as 2,3-dimethoxyphenyldiphenylphosphine oxide (**2a**)[7] with lithium salt of *tert*-butylamine gave the corresponding aminophosphine oxide **3a**. N-methylation of **3a** occurred using MeI in the presence of K_2CO_3. This aminophosphine oxide **4a** was converted into the desired racemic amine (±)-**1a** using trichlorosilane–triethylamine in good yield (Scheme 1). Racemic amines (±)-**1b** and (±)-**1c** were also easily prepared from **2b**[8] and **2c**[9] in the same manner. To investigate whether C(aryl)–N(amine) bond axial chirality exists in amines (±)-**1**, we analytically separated these isomers using HPLC with a chiral stationary phase column. As a result, we obtained nearly resolved UV plots for amines (±)-**1** in addition to a pair of clear positive (+) and negative (−) CD trace signals of HPLC run at 254 nm.



Scheme 1. Preparation of racemic amines (±)-**1**.

We firstly attempted the optical resolution of (±)-**1a** into each atropisomer using a chiral HPLC. Although we tried optical resolution using a semi-preparative HPLC with a chiral stationary phase column (Daicel CHIRALCEL® OD), we obtained only moderate optical purities of (a*S*)-(+)-**1a** and (a*R*)-(−)-**1a** with low yields. So, we attempted the optical resolution of (±)-**1a** using (*S*)-(+)-di-μ-chloro-bis[1-[(dimethylamino)ethyl]-2-naphthyl-*C*,*N*]dipalladium(II) ((*S*)-**5**)[10] as a chiral resolving agent (Scheme 2). The resulting diastereomeric palladium complex mixtures (a*S*)-**1a**·(*S*)-**5** and (a*R*)-**1a**·(*S*)-**5** were separable by silica gel column chromatography. The individual diastereomers were treated with ethylenediamine (EDA) to release optically active (a*S*)-(+)-**1a** and (a*R*)-(−)-**1a**. After the optical purification using a semi-preparative chiral HPLC (Daicel CHIRALCEL® OD), the optical purity of (a*S*)-(+)-**1a** was more than 99% ee from chiral HPLC analyses. We also obtained the optical purity of (a*S*)-(+)-**1b** with more than 99% ee under a similar method (Scheme 2). On the other hand, we could not obtain chiral **1c** by optical resolution using a chiral resolving agent. The optical resolution of (±)-**1c** was achieved using a semi-preparative chiral HPLC (Daicel CHIRALCEL® OJ) (Scheme 3). The optical purities of (a*S*)-(+)-**1c** and (a*R*)-(−)-**1c** were more than 99% ee from chiral HPLC analyses.

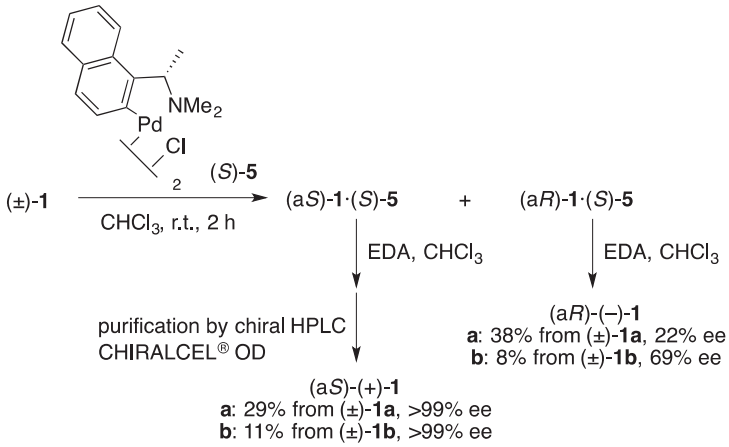
We found that the palladium complex (±)-**1a**·(*S*)-**5** was easily epimerizated to (a*S*)-**1a**·(*S*)-**5** (ca. 30% de) in $CHCl_3$. We also tried the optical resolution of (±)-**1a** using a chiral resolving agent with epimerization at 50 °C in $CHCl_3$ (Scheme 4). In this case, (a*S*)-(+)-**1a** (>99% ee) was obtained 50% yield from (±)-**1a** after chiral HPLC purification.

The determination of the absolute configurations of **1** was made by single-crystal X-ray analysis of (a*S*)-(+)-**1a** (CCDC 1036778), (a*S*)-**1b**·(*S*)-**5** (CCDC 1036779), and (a*R*)-(−)-**1c** (CCDC 1036780) (Figs. 2–4).

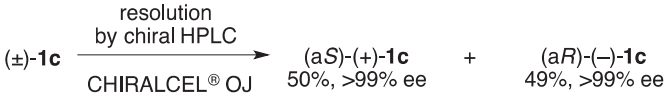
Barriers to the racemization of amines **1** in nonane for the stability of the C–N bond axial chirality were also determined. A small portion of the solution of optically active **1** in nonane was removed at regular intervals and subsequently analyzed for enantiomeric excesses by chiral HPLC analysis. We repeated the experiment at four temperatures and determined the rate constants (k_{rac}) of **1** at each temperature. For example, the rotational barrier ($\Delta G^{\ddagger}_{rac}$) of **1a** was found to be 27.7 kcal/mol in nonane at 25 °C based on the Arrhenius and Eyring equations.[11] This result corresponds to a half-life of approximately 4 months in nonane at 25 °C (Table 1).

To investigate the nature of the palladium complex's structure, amine (±)-**1c** was treated with $PdCl_2(MeCN)_2$ to produce palladium complex (±)-**6** and a suitable crystal was obtained from hexane–$CHCl_3$. X-ray analysis of (±)-**6** (CCDC 1036781) was carried out (Fig. 5). The solid-state structure shows that amine **1c** is coordinated to palladium with a five-membered chelate ring by phosphorus and nitrogen atom. The *trans* influence of the P,N-ligand is reflected in the lengthening of the Pd–Cl bond in *trans* disposition to the phosphorus to the Pd–Cl distance the *trans* to the nitrogen [2.4118(11) versus 2.2975(11) Å].

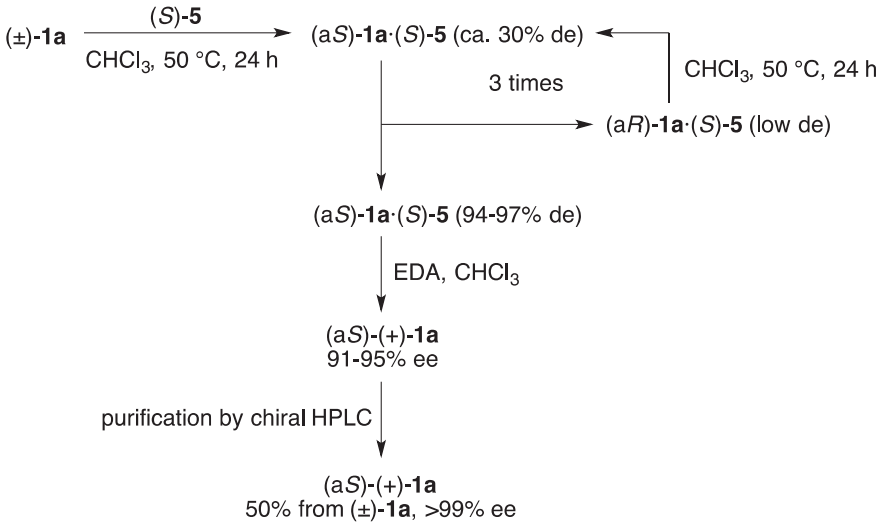
Finally, we investigated the ability of chiral amines **1** as ligands for the palladium-catalyzed asymmetric allylic alkylation.[12] This reaction was carried out in the presence of 2 mol % of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, 4 mol % of **1**, 3 equiv of *N*,*O*-bis(trimethylsilyl)acetamide (BSA), and 10 mol % of base (Table 2). Although the reaction using adamantylamine-type ligand **L3** acquired 10 mol % of palladium and ligand for a long reaction time such as 48 h,[7] chiral ligands **1** can induce 71–88% yield and 77–83% ee in dichloromethane at 0 °C using 1,3-diphenyl-2-propenyl acetate (**7a**) with dimethyl malonate (**8a**) using 4 mol % of palladium and ligand for 24 h (entries 1–3). When the reaction was carried out using (a*S*)-**1a** as a ligand, the enantioselectivity of product (*S*)-**9a** obtained was higher than the case of chiral amines (a*S*)-**1b** and (a*S*)-**1c** with good yields (entry 1 vs entries 2 and 3). We examined the effect of the reaction solvents and bases using chiral ligand (a*S*)-**1a**. When the reaction was carried out in ether, (*S*)-**9a** was obtained in good yield with good enantioselectivity (90.2% ee) (entry 5). With NaOAc instead of LiOAc, the enantioselectivity was decreased (entry 5 vs entry 10). When the reaction under −10 °C was also carried out, the enantioselectivity of (*S*)-**9a** was slightly decreased to 89.9% ee (entry 11). We next investigated the asymmetric allylic alkylation of similar malonates and allylic esters. The reaction with diethyl malonate (**8b**) instead of **8a** gave corresponding product in good yield with 95% ee (entry 12). The reaction with dibenzyl or di-*t*-butyl malonates (**8c** or **8d**) gave corresponding products in 78% with 92% ee and 77% yield with 88% ee, respectively (entries 13 and 14). The reaction with diethyl methylmalonate (**8e**) also gave the corresponding product in good yield with good enantioselectivity (entry 15). When 1,3-diphenyl-2-propenyl pivalate (**7b**) was used instead of **7a**, the reaction with a diethyl malonate



Scheme 2. Optical resolution and purification of (±)-**1a** and (±)-**1b**.



Scheme 3. Optical resolution of (±)-**1c** by chiral HPLC.



Scheme 4. Optical resolution of (±)-**1a** with epimerization.

(**8b**) gave product (*S*)-**9b** in good yield with high enantioselectivity (entry 16). When 1,3-di-(4-chlorophenyl)-2-propenyl acetate (**7c**) was used instead of **7a**, the reaction with a diethyl malonate (**8b**) gave product (*S*)-**9f** in good yield with moderate enantioselectivity (entry 17).

3. Conclusion

We found that *N*-(*tert*-butyl)-*N*-methylanilines (±)-**1** were easily prepared in three steps and have C(aryl)–N(amine) bond axial chirality. We succeeded the optical resolution of C–N bond atropisomers of amines **1** by a chiral palladium resolving agent and/or a semi-preparative chiral HPLC method. We also found that chiral amines **1** are effective ligands for palladium-catalyzed asymmetric allylic alkylation of allylic esters with malonates (up to 95% ee).

4. Experimental section

4.1. General experimental

^{1}H NMR and ^{13}C NMR spectra were measured with a Bruker DPX-300 spectrometer (300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR). The chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. The Mass spectra (MS) of the compounds were recorded using a Shimadzu GCMS-QP 5050 (EI-MS) spectrometer. The high-resolution Mass spectra (HRMS) of the compounds were recorded using a Thermo Fisher Sci. Exactive (ESI-MS) spectrometer. Optical rotations were recorded on a Jasco P-2100 polarimeter. Chiral HPLC was performed on Jasco HPLC systems consisting of the following: Pump, PU-980, PU-1580, or PU-2089; detector, UV-970 or UV-2075 and CD-2095.

4.2. Preparation of aminophosphine oxide 3a

To the solution of *tert*-butylamine (1.60 mL, 15.1 mmol) in THF (4.0 mL) at −80 °C was added slowly *n*-BuLi in hexane (9.5 mL, 15.2 mmol, 1.60 M). The reaction mixture was stirred for 60 min at −80 °C and for 135 min at room temperature. After phosphine oxide **2a** (1.692 g, 5.0 mmol) in THF (3.0 mL) was added, and the

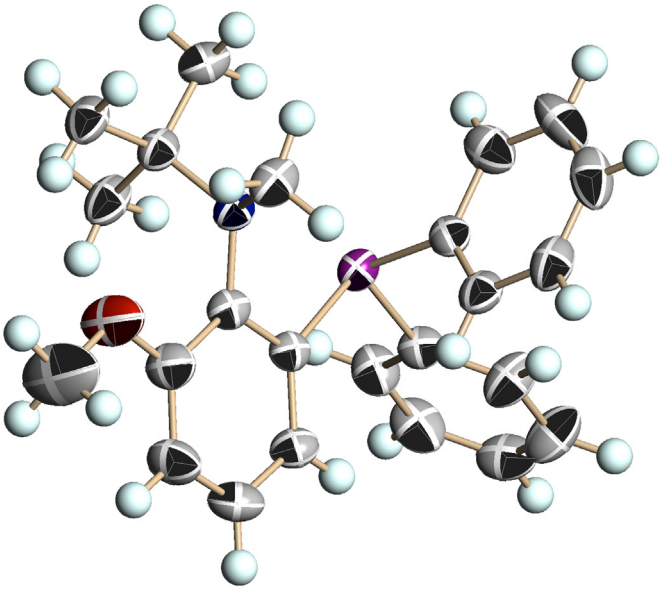


Fig. 2. ORTEP drawing of (a*S*)-(+)-**1a**.

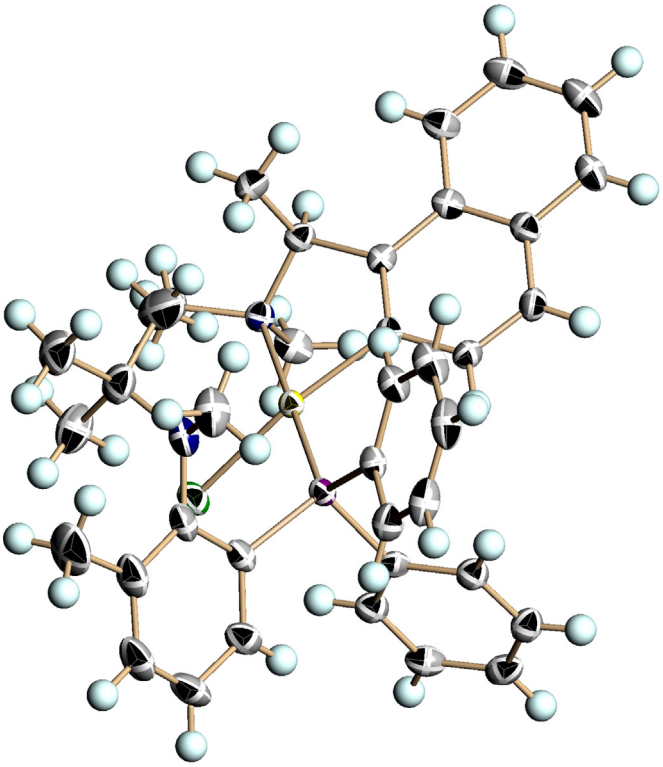


Fig. 3. ORTEP drawing of (a*S*)-**1b**·(*S*)-**5**.

stirring was continued for 16 h at room temperature. The mixture was diluted with ether and quenched with satd NH_4Cl aq. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane–EtOAc=2:1): 1.772 g, 4.67 mmol, 93%; mp 140–142 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.05 (s, 9H), 3.81 (s, 3H), 6.30 (br s, 1H), 6.41 (ddd, J=1.3, 7.7 and 14.2 Hz, 1H), 6.70 (td, J=7.8 and 3.5 Hz, 1H), 6.95 (d, J=7.9 Hz, 1H), 7.43–7.66 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.6×3, 53.5, 54.9, 115.2 (d, J_{cp}=2.1 Hz), 118.8 (d, J_{cp}=15.6 Hz), 120.4 (d, J_{cp}=103.8 Hz), 125.7 (d,

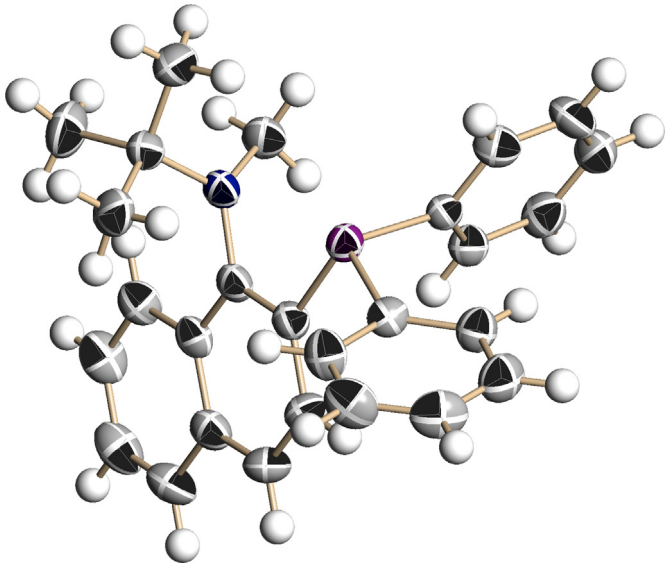


Fig. 4. ORTEP drawing of (a*R*)-(−)-**1c**.

Table 1
Racemization parameter of **1**

Thermodynamic parameter at 25 °C	**1a**	**1b**	**1c**
Half-life (year)	3.5×10^{-1}	2.7×10^{3}	2.7×10^{3}
K_{rac}	3.16×10^{-8}	4.09×10^{-12}	4.09×10^{-12}
ΔH (kcal/mol)	27.9	39.5	46.8
ΔS (cal/mol K)	0.844	22.0	46.5
ΔG (kcal/mol)	27.7	33.0	33.0

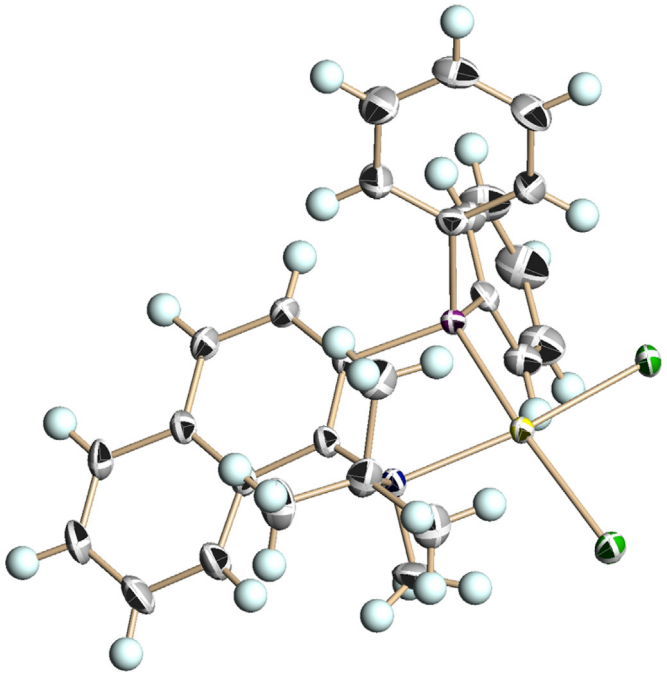
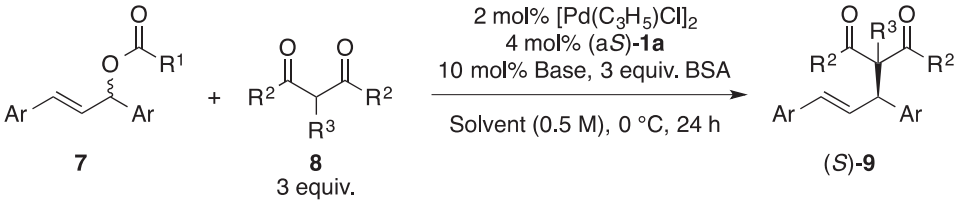


Fig. 5. X-ray structure of palladium complex (±)-**6** (Solvent molecules ($CHCl_3$) are omitted for clarity).

J_{cp}=11.8 Hz), 128.3×4 (d, J_{cp}=12.1 Hz), 131.7×2 (d, J_{cp}=2.7 Hz), 132.0×4 (d, J_{cp}=9.9 Hz), 133.0×2 (d, J_{cp}=103.4 Hz), 143.7 (d, J_{cp}=5.5 Hz), 152.5 (d, J_{cp}=11.8 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 35.8; EI-MS m/z (rel intensity) 379 (M^+, 20); HRMS (ESI-orbitrap) m/z calcd for $C_{23}H_{26}O_2NP$+Na 402.1593, found 402.1582.

Table 2
Palladium-catalyzed asymmetric allylic alkylation using (a*S*)-**1**[a]



Entry	Ar	R^1	R^2	R^3	Solvent	Base	Yield (%)[b]	Ee (%)[c]
1	Ph	Me	OMe	H	DCM	LiOAc	88(**9a**)	83
2[d]	Ph	Me	OMe	H	DCM	LiOAc	71(**9a**)	80
3[e]	Ph	Me	OMe	H	DCM	LiOAc	82(**9a**)	77
4	Ph	Me	OMe	H	THF	LiOAc	85(**9a**)	87
5	Ph	Me	OMe	H	Et_2O	LiOAc	96(**9a**)	90.2
6	Ph	Me	OMe	H	1,4-dioxane	LiOAc	90(**9a**)	89
7	Ph	Me	OMe	H	PhMe	LiOAc	89(**9a**)	87
8	Ph	Me	OMe	H	$PhCF_3$	LiOAc	90(**9a**)	87
9	Ph	Me	OMe	H	MeCN	LiOAc	71(**9a**)	89.7
10	Ph	Me	OMe	H	Et_2O	NaOAc	73(**9a**)	88
11[f]	Ph	Me	OMe	H	Et_2O	LiOAc	76(**9a**)	89.9
12	Ph	Me	OEt	H	Et_2O	LiOAc	89(**9b**)	95
13	Ph	Me	OCH_2Ph	H	Et_2O	LiOAc	78(**9c**)	92
14[g]	Ph	Me	O*t*-Bu	H	Et_2O	LiOAc	77(**9d**)	88
15	Ph	Me	OEt	Me	Et_2O	LiOAc	88(**9e**)	93
16	Ph	*t*-Bu	OEt	H	Et_2O	LiOAc	80(**9b**)	94
17	*p*-ClC_6H_4	Me	OEt	H	Et_2O	LiOAc	64(**9f**)	84

[a] The reactions were carried out on 0.2 mmol scale of **7** in various solvent (0.4 mL) at various temperature with 3.0 equiv of **8** and BSA, in the presence of LiOAc (10 mol %), (a*S*)-**1** (4 mol %) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2 mol %; Pd=4 mol %).
[b] Isolated yields.
[c] Determined by HPLC analysis using a chiral column.
[d] This reaction was carried out using (a*S*)-**1b** instead of (a*S*)-**1a**.
[e] This reaction was carried out using (a*S*)-**1c** instead of (a*S*)-**1a**.
[f] This reaction was carried out at −10 °C.
[g] This reaction was carried out for 48 h.

4.3. Preparation of aminophosphine oxide 3b

To the solution of *tert*-butylamine (1.60 mL, 15.1 mmol) in THF (2.0 mL) at −80 °C was added slowly *n*-BuLi in hexane (9.4 mL, 15.1 mmol, 1.60 M). The reaction mixture was stirred for 30 min at −80 °C and for 2 h at room temperature. After phosphine oxide **2b** (1.612 g, 5.0 mmol) in THF (10.0 mL) was added, and the stirring was continued for 18 h at room temperature. The mixture was diluted with ether and quenched with satd NH_4Cl aq. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane−EtOAc=2:1): 0.919 g, 2.53 mmol, 51%; mp 129–130 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.03 (s, 9H), 2.40 (s, 3H), 6.21 (br s, 1H), 6.69–6.81 (m, 2H), 7.29 (d, J=6.8 Hz, 1H), 7.42–7.48 (m, 4H), 7.51–7.56 (m, 2H), 7.59–7.65 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.1 (d, J_{cp}=1.5 Hz), 31.0×3, 54.6, 120.1 (d, J_{cp}=14.4 Hz), 122.8 (d, J_{cp}=102.4 Hz), 128.4×4 (d, J_{cp}=12.1 Hz), 131.7×2 (d, J_{cp}=1.0 Hz), 131.8 (d, J_{cp}=11.4 Hz), 132.0×4 (d, J_{cp}=9.6 Hz), 133.7×2 (d, J_{cp}=102.8 Hz), 135.1 (d, J_{cp}=8.4 Hz), 135.6 (d, J_{cp}=2.3 Hz), 153.2 (d, J_{cp}=4.4 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 36.8; EI-MS *m*/*z* (rel intensity) 363 (M^+, 12); HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{23}H_{26}ONP$+H 364.1825, found 364.1808.

4.4. Preparation of aminophosphine oxide 3c

To the solution of *tert*-butylamine (4.74 mL, 45.0 mmol) in THF (10.0 mL) at −80 °C was added slowly *n*-BuLi in hexane (27.0 mL, 45.1 mmol, 1.67 M). The reaction mixture was stirred for 15 min at −80 °C and for 4 h at room temperature. After phosphine oxide **2c** (5.376 g, 15.0 mmol) in THF (20.0 mL) was added, and the stirring was continued for 16 h at room temperature. The mixture was diluted with ether and quenched with satd NH_4Cl aq. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane−EtOAc=2:1): 5.149 g, 12.89 mmol, 86%; mp 132–133 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.11 (s, 9H), 6.84 (br s, 1H), 6.94 (q, J=4.4 and 8.5 Hz, 1H), 7.31 (dd, J=2.3 and 8.5 Hz 1H), 7.41–7.56 (m, 8H), 7.64–7.72 (m, 5H), 8.53 (d, J=8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.7×3, 56.4, 116.5 (d, J_{cp}=103.9 Hz), 120.6 (d, J_{cp}=13.2 Hz), 124.4, 127.2, 127.9, 128.1, 128.39 (d, J_{cp}=12.6 Hz), 128.43×4 (d, J_{cp}=11.9 Hz), 131.8×2 (d, J_{cp}=2.7 Hz), 132.0×4 (d, J_{cp}=9.6 Hz), 132.5 (d, J_{cp}=9.9 Hz), 133.8×2 (d, J_{cp}=103.3 Hz), 136.1 (d, J_{cp}=2.1 Hz), 154.8 (d, J_{cp}=4.4 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 36.4; EI-MS *m*/*z* (rel intensity) 399 (M^+, 27); HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{26}H_{26}ONP$+H 400.1825, found 400.1814.

4.5. Preparation of aminophosphine oxide 4a

To the solution of phosphine oxide **3a** (1.518 g, 4.0 mmol) in MeCN (15.0 mL) was added K_2CO_3 (1.106 g, 8.0 mmol) and MeI (5.0 mL, 80.0 mmol) at room temperature. The reaction mixture was stirred for 16 h at room temperature. The reaction mixture was filtered and evaporated under reduced pressure. The residue was purified by silica gel chromatography (hexane−EtOAc=2:1): 1.568 g, 3.99 mmol, 100%; mp 163–165 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.18 (s, 9H), 1.83 (s, 3H), 3.79 (s, 3H), 6.64 (ddd, J=1.7, 7.3 and 13.6 Hz, 1H), 7.01–7.12 (m, 2H), 7.38–7.50 (m, 6H), 7.63–7.70 (m, 2H), 7.82–7.88 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.8×3, 33.1, 54.8, 56.3, 115.3 (d, J_{cp}=2.4 Hz), 125.8 (d, J_{cp}=12.8 Hz), 126.0 (d, J_{cp}=15.5 Hz), 127.7×2 (d, J_{cp}=12.8 Hz), 128.0×2 (d, J_{cp}=11.9 Hz), 130.3 (d, J_{cp}=2.4 Hz), 130.8 (d, J_{cp}=2.7 Hz), 130.9×2 (d, J_{cp}=9.5 Hz), 132.3×2 (d, J_{cp}=8.4 Hz), 134.2 (d, J_{cp}=17.9 Hz), 135.1 (d,

J_{cp}=25.0 Hz), 137.3 (d, J_{cp}=107.3 Hz), 144.1 (d, J_{cp}=3.9 Hz), 160.7 (d, J_{cp}=10.7 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.9; EI-MS *m*/*z* (rel intensity) 393 (M^+, 3); HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{24}H_{28}O_2NP$+Na 416.1750, found 416.1740.

4.6. Preparation of aminophosphine oxide 4b

To the solution of phosphine oxide **3b** (0.759 g, 2.09 mmol) in $CHCl_3$ (2.0 mL) was added K_2CO_3 (0.553 g, 4.0 mmol), MeI (2.5 mL, 40.0 mmol) and MeCN (8.0 mL) at room temperature. The reaction mixture was stirred at 50 °C. After 24 h and 48 h, MeI (2.5 mL, 40.0 mmol) was added. After 72 h, the reaction mixture was filtered and evaporated under reduced pressure. The residue was purified by silica gel chromatography (hexane–EtOAc=4:1): 0.731 g, 1.94 mmol, 93%; mp 172–173 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (s, 9H), 1.86 (s, 3H), 2.33 (s, 3H), 6.89–7.04 (m, 2H), 7.31 (d, *J*=7.3 Hz, 1H), 7.37–7.49 (m, 6H), 7.57–7.64 (m, 2H), 7.79–7.86 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.8 (d, J_{cp}=1.4 Hz), 28.1×3, 33.9, 56.7, 124.7 (d, J_{cp}=14.7 Hz), 127.7, 127.9, 128.0×2 (d, J_{cp}=11.1 Hz), 130.4 (d, J_{cp}=2.6 Hz), 130.7 (d, J_{cp}=2.6 Hz), 130.9×2 (d, J_{cp}=9.5 Hz), 132.3×2 (d, J_{cp}=8.1 Hz), 132.7 (d, J_{cp}=13.7 Hz), 134.2 (d, J_{cp}=9.9 Hz), 135.6 (d, J_{cp}=16.5 Hz), 136.2 (d, J_{cp}=2.2 Hz), 137.3 (d, J_{cp}=107.8 Hz), 140.7 (d, J_{cp}=7.7 Hz), 153.7 (d, J_{cp}=4.3 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.5; EI-MS *m*/*z* (rel intensity) 377 (M^+, 5); HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{24}H_{28}ONP$+H 378.1981, found 378.1968.

4.7. Preparation of aminophosphine oxide 4c

To the solution of phosphine oxide **3c** (3.995 g, 10.0 mmol) in MeCN (40.0 mL) was added K_2CO_3 (2.764 g, 20.0 mmol) and MeI (12.5 mL, 200 mmol) at room temperature. The reaction mixture was stirred at 50 °C. After 24 h, MeI (12.5 mL, 200 mmol) was added. After 48 h, the reaction mixture was filtered and evaporated under reduced pressure. The residue was purified by silica gel chromatography (hexane–EtOAc=2:1): 4.003 g, 9.68 mmol, 97%; mp 194–195 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (s, 9H), 2.15 (s, 3H), 7.15 (q, *J*=4.2 and 8.5 Hz, 1H), 7.37–7.40 (m, 3H), 7.45–7.55 (m, 5H), 7.58–7.66 (m, 3H), 7.85–7.91 (m, 3H), 8.10 (d, *J*=8.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.7×3, 35.6, 57.1, 125.6, 125.7 (d, J_{cp}=13.1 Hz), 126.8, 127.3, 127.8×2 (d, J_{cp}=11.9 Hz), 128.2×2 (d, J_{cp}=10.7 Hz), 128.7, 129.6 (d, J_{cp}=14.3 Hz), 130.5 (d, J_{cp}=3.3 Hz), 130.9 (d, J_{cp}=2.4 Hz) 131.0×2 (d, J_{cp}=9.5 Hz), 132.3×2 (d, J_{cp}=7.8 Hz), 133.6 (d, J_{cp}=108.5 Hz), 134.6 (d, J_{cp}=58.7 Hz), 135.2 (d, J_{cp}=3.6 Hz), 135.5 (d, J_{cp}=54.9 Hz), 137.0, 154.9 (d, J_{cp}=3.6 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.7; EI-MS *m*/*z* (rel intensity) 413 (M^+, 2); HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{27}H_{28}ONP$+H 414.1981, found 414.1968.

4.8. Preparation of aminophosphine (±)-1a

To a mixture of phosphine oxide **4a** (0.394 g, 1.04 mmol) and triethylamine (3.0 mL, 21.5 mmol) in *m*-xylene (4.0 mL) was added trichlorosilane (2.0 mL, 19.8 mmol) at 0 °C under an Ar atmosphere. The reaction mixture was stirred at 120 °C for 8 h. After being cooled to room temperature, the mixture was diluted with Et_2O and quenched with 2 M aqueous NaOH solution. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane–EtOAc=40:1): 0.295 g, 0.781 mmol, 75%; mp 119–121 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (s, 9H), 2.01 (s, 3H), 3.76 (s, 3H), 6.39 (ddd, *J*=1.4 and 2.5 and 7.6 Hz, 1H), 6.82 (d, *J*=8.0 Hz, 1H), 7.04 (ddd, *J*=1.0 and 7.7 and 8.0 Hz, 1H), 7.20–7.36 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.3×3 (d, J_{cp}=4.8 Hz), 33.5, 54.7, 55.9, 111.7, 124.5, 126.4, 127.8, 128.1×2 (d, J_{cp}=7.2 Hz), 128.2×2 (d, J_{cp}=6.0 Hz), 128.4, 133.8×2 (d, J_{cp}=20.3 Hz), 134.7×2 (d, J_{cp}=22.1 Hz), 138.0 (d, J_{cp}=11.6 Hz), 139.7 (d, J_{cp}=16.7 Hz), 142.3 (d, J_{cp}=21.5 Hz), 144.7, 159.5 (d, J_{cp}=3.6 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ −13.2; EI-MS *m*/*z* (rel intensity) 377 (M^+, 23); HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{24}H_{28}ONP$+Na 400.1801, found 400.1796; HPLC (Daicel CHIRALCEL® OD-H, 0.46 ϕ×25 cm, UV 254 nm), hexane=100, 0.5 mL/min: t_R=14.7 min (CD: λ_{ext} ($\Delta\varepsilon$) 254 (+)) and 16.6 min (CD: λ_{ext} ($\Delta\varepsilon$) 254 (−)).

4.9. Preparation of aminophosphine (±)-1b

To a mixture of phosphine oxide **4b** (0.189 g, 0.5 mmol) and triethylamine (1.5 mL, 10.8 mmol) in *m*-xylene (2.0 mL) was added trichlorosilane (1.0 mL, 9.91 mmol) at 0 °C under an Ar atmosphere. The reaction mixture was stirred at 130 °C for 24 h. After being cooled to room temperature, the mixture was diluted with Et_2O and quenched with 2 M aqueous NaOH solution. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane–EtOAc=80:1): 0.115 g, 0.318 mmol, 64%; mp 108–110 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (s, 9H), 2.18 (s, 3H), 2.30 (s, 3H), 6.68 (dt, *J*=2.1 and 7.5 Hz, 1H), 6.97 (t, *J*=7.4 Hz, 1H), 7.12 (d, *J*=6.9 Hz, 1H), 7.19–7.31 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.6 (d, J_{cp}=2.1 Hz), 28.5×3 (d, J_{cp}=6.6 Hz), 34.3 (d, J_{cp}=1.5 Hz), 55.8, 125.5, 127.8, 128.1×2 (d, J_{cp}=7.7 Hz), 128.3×2 (d, J_{cp}=5.6 Hz), 128.4, 131.8, 132.2, 133.7×2 (d, J_{cp}=20.0 Hz), 134.5×2 (d, J_{cp}=21.1 Hz), 138.4 (d, J_{cp}=13.0 Hz), 139.4 (d, J_{cp}=1.4 Hz), 139.7 (d, J_{cp}=16.1 Hz), 144.0, 152.9 (d, J_{cp}=22.5 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ −12.0; EI-MS *m*/*z* (rel intensity) 361 (M^+, 33); HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{24}H_{28}NP$+H 362.2032, found 362.2021; HPLC (Daicel CHIRALCEL® OD-H, 0.46 ϕ×25 cm, UV 254 nm), hexane=100, 0.3 mL/min: t_R=11.6 min (CD: λ_{ext} ($\Delta\varepsilon$) 254 (+)) and 12.7 min (CD: λ_{ext} ($\Delta\varepsilon$) 254 (−)).

4.10. Preparation of aminophosphine (±)-1c

To a mixture of phosphine oxide **4c** (0.414 g, 1.0 mmol) and triethylamine (3.0 mL, 21.6 mmol) in *m*-xylene (10.0 mL) was added trichlorosilane (2.0 mL, 19.8 mmol) at 0 °C under an Ar atmosphere. The reaction mixture was stirred at 100 °C for 1 h and 120 °C for 6 h. After being cooled to room temperature, the mixture was diluted with Et_2O and quenched with 2 M aqueous NaOH solution. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane–EtOAc=40:1): 0.244 g, 0.613 mmol, 61%; mp 111–112 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (s, 9H), 2.52 (s, 3H), 7.03 (dd, *J*=8.5 and 2.6 Hz, 1H), 7.25–7.35 (m, 10H), 7.43–7.47 (m, 2H), 7.57 (d, *J*=8.5 Hz, 1H), 7.79–7.82 (m, 1H), 8.07–8.10 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.8×3 (d, J_{cp}=6.3 Hz), 36.0 (d, J_{cp}=3.3 Hz), 56.0, 125.4, 125.9, 125.98, 126.01, 126.1, 127.9, 128.2 (d, J_{cp}=7.3 Hz), 128.37×2 (d, J_{cp}=1.5 Hz), 128.42×2 (d, J_{cp}=1.0 Hz), 130.2, 133.5×2 (d, J_{cp}=19.8 Hz), 134.3×2 (d, J_{cp}=21.3 Hz), 134.9 (d, J_{cp}=2.5 Hz), 135.4, 138.6 (d, J_{cp}=13.9 Hz), 139.4 (d, J_{cp}=16.3 Hz), 139.7 (d, J_{cp}=3.3 Hz), 152.4 (d, J_{cp}=24.0 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ −12.2; EI-MS *m*/*z* (rel intensity) 397 (M^+, 35), 154 (100); HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{27}H_{28}NP$+H 398.2032, found 398.2029; HPLC (Daicel CHIRALCEL® OJ, 0.46 ϕ×25 cm, UV 254 nm), hexane–EtOH=80:20, 0.3 mL/min: t_R=11.6 min (CD: λ_{ext} ($\Delta\varepsilon$) 254 (−)) and 15.9 min (CD: λ_{ext} ($\Delta\varepsilon$) 254 (+)).

4.11. Optical resolution of (±)-1a (Scheme 2)

A mixture of (±)-**1a** (0.113 g, 0.30 mmol) and (*S*)-(+)-di-μ-chloro-bis[1-[(dimethylamino)ethyl]-2-naphthyl-*C*,*N*]dipalladium(II) ((*S*)-**5**) (0.103 g, 0.15 mmol) in $CHCl_3$ (2.0 mL) was stirred at room temperature for 2 h. The mixture was concentrated under reduced pressure, and the residue was purified by silica gel column

chromatography ($CHCl_3$–EtOAc=3:1) to separate the diastereomeric mixture. 0.1 M solution of ethylenediamine (0.5 mmol) in chloroform (5.0 mL) was added to an individual diastereomer at room temperature and stirred for 20 min. The mixture was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (hexane–EtOAc=100:1) (and semi-preparative chiral HPLC (Daicel CHIRALCEL® OD) for (a*S*)-(+)-**1a**) to afford optically active (a*S*)-(+)-**1a** or (a*R*)-(−)-**1a**.

(a*S*)-(+)-**1a**: 33.3 mg, 0.088 mmol, 29%, >99% ee; mp 98–99 °C; $[\alpha]_D^{20}$ +90.4 (*c* 0.51, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (s, 9H), 2.01 (s, 3H), 3.76 (s, 3H), 6.39 (ddd, *J*=1.4 and 2.4 and 7.7 Hz, 1H), 6.83 (d, *J*=7.5 Hz, 1H), 7.04 (ddd, *J*=0.9 and 7.1 and 8.5 Hz, 1H), 7.20–7.33 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.3×3 (d, J_{cp}=4.8 Hz), 33.5, 54.7, 55.9, 111.7, 124.5, 126.3 (d, J_{cp}=1.1 Hz), 127.8, 128.1×2 (d, J_{cp}=8.1 Hz), 128.2×2 (d, J_{cp}=6.2 Hz), 128.4, 133.8×2 (d, J_{cp}=20.0 Hz), 134.7×2 (d, J_{cp}=21.4 Hz), 138.0 (d, J_{cp}=11.7 Hz), 139.7 (d, J_{cp}=16.1 Hz), 142.3 (d, J_{cp}=21.2 Hz), 144.7, 159.5 (d, J_{cp}=3.0 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ −13.2; EI-MS *m*/*z* (rel intensity) 377 (M^+, 22); HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{24}H_{28}ONP$+H 378.1981, found 378.1974; HPLC (Daicel CHIRALCEL® OD-H, 0.46 ϕ×25 cm×2, UV 254 nm), hexane=100, 0.1 mL/min: t_R=90.9 min (major) and 97.1 min (minor).

(a*R*)-(−)-**1a**: 42.7 mg, 0.113 mmol, 38%, 22% ee; mp 104–105 °C; $[\alpha]_D^{20}$ −20.6 (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (s, 9H), 2.01 (s, 3H), 3.76 (s, 3H), 6.39 (ddd, *J*=1.4 and 2.4 and 7.6 Hz, 1H), 6.83 (d, *J*=7.7 Hz, 1H), 7.04 (ddd, *J*=0.7 and 7.5 and 8.2 Hz, 1H), 7.20–7.33 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.3×3 (d, J_{cp}=4.8 Hz), 33.5, 54.7, 55.9, 111.7, 124.5, 126.3 (d, J_{cp}=1.2 Hz), 127.8, 128.1×2 (d, J_{cp}=8.1 Hz), 128.2×2 (d, J_{cp}=6.2 Hz), 128.4, 133.8×2 (d, J_{cp}=20.0 Hz), 134.7×2 (d, J_{cp}=21.4 Hz), 138.0 (d, J_{cp}=11.7 Hz), 139.7 (d, J_{cp}=16.1 Hz), 142.3 (d, J_{cp}=21.2 Hz), 144.7, 159.5 (d, J_{cp}=3.0 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ −13.1; EI-MS *m*/*z* (rel intensity) 377 (M^+, 22); HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{24}H_{28}ONP$+H 378.1981, found 378.1974; HPLC (Daicel CHIRALCEL® OD-H, 0.46 ϕ×25 cm×2, UV 254 nm), hexane=100, 0.2 mL/min: t_R=47.0 min (minor) and 51.2 min (major).

4.12. Optical resolution of (±)-1a with epimerization (Scheme 4)

A mixture of (±)-**1a** (0.394 g, 1.0 mmol) and (*S*)-(+)-di-μ-chloro-bis[1-[(dimethylamino)ethyl]-2-naphthyl-*C*,*N*]dipalladium(II) ((*S*)-**5**) (0.340 g, 0.50 mmol) in $CHCl_3$ (5.0 mL) was stirred at 50 °C for 24 h. The mixture was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography ($CHCl_3$–EtOAc=3:1) to separate the diastereomeric mixture. 0.1 M solution of ethylendiamine (0.5 mmol) in chloroform (5.0 mL) was added to (a*S*)-**1a**·(*S*)-**5** (94–97% de: Determined by ^{1}H NMR analysis) at room temperature and stirred for 20 min. The mixture was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (hexane–EtOAc=100:1). On the other hand, low de of (a*R*)-**1a**·(*S*)-**5** was dissolved in $CHCl_3$ (4.0 mL) and stirred at 50 °C for 24 h. The solution was concentrated again under reduced pressure, and the residue was separate the diastereomeric mixture by silica gel column chromatography (hexane–EtOAc=4:1). After three times of epimerization and separation, (a*S*)-(+)-**1a** (91–95% ee: Determined by HPLC analysis) was purified by semi-preparative chiral HPLC (Daicel CHIRALCEL® OD) to afford optically pure (a*S*)-(+)-**1a**.

(a*S*)-(+)-**1a**: 188 mg, 0.50 mmol, 50%, >99% ee; mp 97–98 °C; $[\alpha]_D^{20}$ +98.8 (*c* 0.50, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (s, 9H), 2.01 (s, 3H), 3.76 (s, 3H), 6.39 (ddd, *J*=1.4 and 2.4 and 7.6 Hz, 1H), 6.83 (d, *J*=7.6 Hz, 1H), 7.04 (ddd, *J*=0.8 and 7.6 and 8.1 Hz, 1H), 7.20–7.34 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.3×3 (d, J_{cp}=4.9 Hz), 33.5, 54.7, 55.9, 111.7, 124.5, 126.3 (d, J_{cp}=1.1 Hz), 127.8, 128.1×2 (d, J_{cp}=8.1 Hz), 128.2×2 (d, J_{cp}=6.2 Hz), 128.4, 133.8×2 (d, J_{cp}=19.8 Hz), 134.7×2 (d, J_{cp}=21.6 Hz), 138.0 (d, J_{cp}=11.7 Hz), 139.7 (d, J_{cp}=16.1 Hz), 142.3 (d, J_{cp}=21.2 Hz), 144.7, 159.5 (d, J_{cp}=3.0 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ −13.2; EI-MS *m*/*z* (rel intensity) 377 (M^+, 19); HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{24}H_{28}ONP$+H 378.1981, found 378.1975; HPLC (Daicel CHIRALCEL® OD-H, 0.46 ϕ×25 cm×2, UV 254 nm), hexane=100, 0.1 mL/min: t_R=100.8 min (major) and 108.8 min (minor); X-ray diffraction analysis data: Colorless Plate crystals from hexane–$CHCl_3$, orthorhombic space group $P2_12_12_1$, *a*=10.5224(2) Å, *b*=11.5963(3) Å, *c*=17.9011(4) Å, α=90°, β=90°, γ=90°, *V*=2184.31(9) Å^3, *Z*=4, ρ=1.148 g/cm^3, μ(Cu*K*α)=1.196 mm^{-1}. The structure was solved by the direct method of full-matrix least–squares, where the final *R* and *Rw* were 0.0413 and 0.1043 for 3558 reflections.

4.13. Optical resolution of (±)-1b (Scheme 2)

A mixture of (±)-**1b** (0.181 g, 0.50 mmol) and (*S*)-(+)-di-μ-chloro-bis[1-[(dimethylamino)ethyl]-2-naphthyl-*C*,*N*]dipalladium(II) ((*S*)-**5**) (0.170 g, 0.25 mmol) in $CHCl_3$ (2.0 mL) was stirred at room temperature for 2 h. The mixture was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (hexane–EtOAc=4:1) to separate the diastereomeric mixture. 0.1 M solution of ethylendiamine (0.5 mmol) in chloroform (5.0 mL) was added to an individual diastereomer at room temperature and stirred for 20 min. The mixture was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (hexane–EtOAc=100:1) (and semi-preparative chiral HPLC (Daicel CHIRALCEL® OD) for (a*S*)-(+)-**1b**) to afford optically active (a*S*)-(+)-**1b** or (a*R*)-(−)-**1b**.

(a*S*)-(+)-**1b**: 19.5 mg, 0.054 mmol, 11%, >99% ee; $[\alpha]_D^{20}$ +110.3 (*c* 0.50, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (s, 9H), 2.18 (s, 3H), 2.30 (s, 3H), 6.68 (dt, *J*=1.9 and 7.6 Hz, 1H), 6.97 (t, *J*=7.5 Hz, 1H), 7.12 (d, *J*=7.3 Hz, 1H), 7.19–7.31 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.6 (d, J_{cp}=2.2 Hz), 28.5×3 (d, J_{cp}=6.5 Hz), 34.3 (d, J_{cp}=1.5 Hz), 55.8, 125.5, 127.8, 128.1×2 (d, J_{cp}=7.7 Hz), 128.3×2 (d, J_{cp}=5.6 Hz), 128.4, 131.8, 132.2, 133.7×2 (d, J_{cp}=20.0 Hz), 134.5×2 (d, J_{cp}=21.1 Hz), 138.4 (d, J_{cp}=13.0 Hz), 139.4 (d, J_{cp}=1.4 Hz), 139.7 (d, J_{cp}=16.1 Hz), 144.0, 152.9 (d, J_{cp}=22.5 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ −12.0; EI-MS *m*/*z* (rel intensity) 361 (M^+, 35); HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{24}H_{28}NP$+H 362.2032, found 362.2025; HPLC (Daicel CHIRALCEL® OD-H, 0.46 ϕ×25 cm×2, UV 254 nm), hexane=100, 0.1 mL/min at 0 °C: t_R=103.0 min (major) and 109.4 min (minor).

(a*R*)-(−)-**1b**: 15.1 mg, 0.042 mmol, 8%, 69% ee; mp 81–83 °C; $[\alpha]_D^{20}$ −78.5 (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (s, 9H), 2.18 (s, 3H), 2.30 (s, 3H), 6.68 (dt, *J*=1.9 and 7.6 Hz, 1H), 6.97 (t, *J*=7.5 Hz, 1H), 7.12 (d, *J*=6.8 Hz, 1H), 7.19–7.31 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.6 (d, J_{cp}=2.1 Hz), 28.5×3 (d, J_{cp}=6.6 Hz), 34.3 (d, J_{cp}=1.5 Hz), 55.8, 125.5, 127.8, 128.1×2 (d, J_{cp}=7.7 Hz), 128.3×2 (d, J_{cp}=5.6 Hz), 128.4, 131.8, 132.2, 133.7×2 (d, J_{cp}=20.0 Hz), 134.5×2 (d, J_{cp}=21.1 Hz), 138.4 (d, J_{cp}=13.0 Hz), 139.4 (d, J_{cp}=1.4 Hz), 139.7 (d, J_{cp}=16.1 Hz), 144.0, 152.9 (d, J_{cp}=22.5 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ −12.0; EI-MS *m*/*z* (rel intensity) 361 (M^+, 43); HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{24}H_{28}NP$+H 362.2032, found 362.2024; HPLC (Daicel CHIRALCEL® OD-H, 0.46 ϕ×25 cm×2, UV 254 nm), hexane=100, 0.2 mL/min: t_R=50.6 min (minor) and 54.5 min (major).

4.14. Preparation of palladium complex (aS)-1b·(S)-5

A mixture of (±)-**1b** (0.072 g, 0.20 mmol) and (*S*)-(+)-di-μ-chloro-bis[1-[(dimethylamino)ethyl]-2-naphthyl-*C*,*N*]dipalladium(II) ((*S*)-**5**) (0.068 g, 0.10 mmol) in $CHCl_3$ (4.0 mL) was stirred at room temperature for 2 h. The mixture was concentrated under reduced pressure, and the residue was purified by silica gel column

chromatography (hexane–EtOAc=4:1) to separate the diastereomeric mixture and recrystallization from hexane–$CHCl_3$ to afford (a*S*)-**1b**·(*S*)-**5**: 23.0 mg, 0.033 mmol, 16%, 94% de; mp 114–116 °C; $[\alpha]_D^{20}$ −68.6 (*c* 0.51, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 3H), 1.54 (s, 9H), 2.00 (d, *J*=6.5 Hz, 3H), 2.28 (s, 3H), 2.78 (d, *J*=1.3 Hz, 3H), 2.97 (d, *J*=3.5 Hz, 3H), 4.33 (quin, *J*=6.4 Hz, 1H), 6.58 (dd, *J*=6.2 and 8.6 Hz, 1H), 6.87 (d, *J*=8.6 Hz, 1H), 7.01 (dt, *J*=1.8 and 7.7 Hz, 1H), 7.16–7.46 (m, 11H), 7.59–7.72 (m, 4H), 8.58 (br-s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4, 22.0, 30.8×3, 33.4, 48.0, 51.3 (d, J_{cp}=2.4 Hz), 57.7, 73.5 (d, J_{cp}=3.3 Hz), 123.3×2, 123.5 (d, J_{cp}=6.0 Hz), 123.9×2, 124.4 (d, J_{cp}=10.7 Hz), 125.5, 127.2×2 (d, J_{cp}=10.4 Hz), 128.3 (d, J_{cp}=9.5 Hz), 128.6×2, 128.8, 129.0, 129.9 (d, J_{cp}=2.4 Hz), 130.1 (d, J_{cp}=2.1 Hz), 131.1, 132.0 (d, J_{cp}=40.6 Hz), 133.6 (d, J_{cp}=41.7 Hz), 134.3×2 (d, J_{cp}=2.1 Hz), 134.4 (d, J_{cp}=8.4 Hz), 137.3 (d, J_{cp}=10.7 Hz), 138.5 (d, J_{cp}=56.3 Hz), 140.7 (d, J_{cp}=6.0 Hz), 147.9, 149.9 (d, J_{cp}=2.1 Hz), 151.9 (d, J_{cp}=7.2 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 39.2; HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{38}H_{44}N_2ClPPd$–Cl 665.2271, found 665.2272; X-ray diffraction analysis data: Yellow Prismatic crystals from hexane–$CHCl_3$, hexagonal space group $P6_5$, *a*=13.1253(4) Å, *b*=13.1253(4) Å, *c*=33.8217(11) Å, α=90°, β=90°, γ=120°, *V*=5046.0(3) Å^3, *Z*=6, ρ=1.385 g/cm^3, μ (Mo*K*α)=0.708 mm^{-1}. The structure was solved by the direct method of full-matrix least–squares, where the final *R* and *Rw* were 0.0225 and 0.0540 for 6828 reflections.

4.15. Optical resolution of (±)-1c (Scheme 3)

HPLC resolution of (±)-**1c** (20.0 mg, 0.050 mmol) dissolved in hexane (4 mL) was carried out by successive injections of 1 mL on a CHIRALCEL® OJ (1.0 ϕ×25 cm). A hexane was used as the eluent working at a flow rate of 0.5 mL/min and with UV monitoring at 254 nm. Enantiomerically pure (*S*)-(+)-**1c** and (*R*)-(−)-**1c** were, respectively, obtained by evaporation of fractions.

(a*S*)-(+)-**1c**: 10.0 mg, 0.025 mmol, 50%, >99% ee; mp 133–135 °C; $[\alpha]_D^{20}$ +245.2 (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (s, 9H), 2.52 (s, 3H), 7.03 (dd, *J*=8.5 and 2.5 Hz, 1H), 7.25–7.33 (m, 10H), 7.42–7.49 (m, 2H), 7.57 (d, *J*=8.5 Hz, 1H), 7.79–7.83 (m, 1H), 8.07–8.10 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.8×3 (d, J_{cp}=6.3 Hz), 36.0 (d, J_{cp}=3.3 Hz), 56.0, 125.4, 125.9, 125.98, 126.01, 126.1, 127.9, 128.2 (d, J_{cp}=7.3 Hz), 128.37×2 (d, J_{cp}=1.5 Hz), 128.42×2 (d, J_{cp}=1.0 Hz), 130.2, 133.5×2 (d, J_{cp}=19.8 Hz), 134.3×2 (d, J_{cp}=21.3 Hz), 134.9 (d, J_{cp}=2.5 Hz), 135.4, 138.6 (d, J_{cp}=13.9 Hz), 139.4 (d, J_{cp}=16.3 Hz), 139.7 (d, J_{cp}=3.3 Hz), 152.4 (d, J_{cp}=24.0 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ −12.2; EI-MS *m*/*z* (rel intensity) 397 (M^+, 43); HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{27}H_{28}NP$+H 398.2032, found 398.2026; HPLC (Daicel CHIRALCEL® OJ 0.46 ϕ×25×2, UV 254 nm), hexane–EtOH=95:5, 0.5 mL/min: t_R=17.1 min (minor) and 24.8 min (major).

(a*R*)-(−)-**1c**: 9.7 mg, 0.025 mmol, 49%, >99% ee; mp 109–110 °C; $[\alpha]_D^{20}$ −242.2 (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (s, 9H), 2.51 (s, 3H), 7.03 (dd, *J*=8.4 and 2.6 Hz, 1H), 7.24–7.33 (m, 10H), 7.42–7.48 (m, 2H), 7.57 (d, *J*=8.5 Hz, 1H), 7.79–7.83 (m, 1H), 8.07–8.10 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.8×3 (d, J_{cp}=6.3 Hz), 36.0 (d, J_{cp}=3.3 Hz), 56.0, 125.4, 125.9, 125.98, 126.01, 126.1, 127.9, 128.2 (d, J_{cp}=7.3 Hz), 128.37×2 (d, J_{cp}=1.5 Hz), 128.42×2 (d, J_{cp}=1.0 Hz), 130.2, 133.5×2 (d, J_{cp}=19.8 Hz), 134.3×2 (d, J_{cp}=21.3 Hz), 134.9 (d, J_{cp}=2.5 Hz), 135.4, 138.6 (d, J_{cp}=13.9 Hz), 139.4 (d, J_{cp}=16.3 Hz), 139.7 (d, J_{cp}=3.3 Hz), 152.4 (d, J_{cp}=24.0 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ −12.2; EI-MS *m*/*z* (rel intensity) 397 (M^+, 30); HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{27}H_{28}NP$+H 398.2032, found 398.2025; HPLC (Daicel CHIRALCEL® OJ 0.46 ϕ×25×2, UV 254 nm), hexane–EtOH=95:5, 0.5 mL/min: t_R=12.4 min (major) and 17.8 min (minor); X-ray diffraction analysis data: Colorless Plate crystals from hexane–$CHCl_3$, orthorhombic space group $P2_12_12_1$, *a*=10.5342(6) Å, *b*=11.9064(7) Å, *c*=17.7165(9) Å, α=90°, β=90°, γ=90°, *V*=2222.1(2) Å^3, *Z*=4, ρ=1.188 Mg/m^3, μ (Cu*K*α)=1.170 mm^{-1}. The structure was solved by the direct method of full-matrix least–squares, where the final *R* and *Rw* were 0.0419 and 0.0900 for 3101 reflections.

4.16. Elucidation of the thermal racemization of optically active 1

A small amount of optically active (a*S*)-**1** or (a*R*)-**1** was dissolved in nonane at room temperature. The solution was kept at a constant temperature in a thermostat oil bath, a small portion removed every passage of times, and the transitions of enantiomeric excess were measured by chiral HPLC analysis.

4.17. Preparation of palladium complex (±)-6

To a solution of $PdCl_2(MeCN)_2$ (18.1 mg, 0.05 mmol) in a $CHCl_3$ (4.0 mL) was added (±)-**1c** (19.7 mg, 0.05 mmol) at room temperature and stirred for 24 h. The reaction mixture was filtered and evaporated under reduced pressure. The residue was purified by recrystallization from hexane–$CHCl_3$ to afford palladium complex (±)-**6**: 25.4 mg, 0.044 mmol, 88%; mp 174–176 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.65 (s, 9H), 4.64 (s, 3H), 7.21–7.67 (m, 11H), 7.83 (d, *J*=8.3 Hz, 1H), 7.93–7.97 (m, 1H), 8.18 (dd, *J*=4.9 and 12.0 Hz, 2H), 8.49–8.52 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.8, 51.2×3, 71.3, 125.9 (d, J_{cp}=58.6 Hz), 127.0, 127.7, 128.2, 128.4 (d, J_{cp}=3.0 Hz), 128.7, 128.8, 129.3×2 (d, J_{cp}=11.5 Hz), 130.0, 130.1, 130.4 (d, J_{cp}=20.6 Hz), 131.0, 131.3 (d, J_{cp}=7.3 Hz), 131.8 (d, J_{cp}=3.0 Hz), 132.4 (d, J_{cp}=3.0 Hz), 133.7×2 (d, J_{cp}=8.9 Hz), 133.8, 133.9, 137.7, 155.1 (d, J_{cp}=14.3 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 37.6; HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{27}H_{28}NCl_2PPd$–Cl 538.0677, found 538.0679; X-ray diffraction analysis data: Yellow Prismatic crystals from hexane–$CHCl_3$, Triclinic space group *P*-1, *a*=9.1121(4) Å, *b*=11.5775(5) Å, *c*=17.0169(7) Å, α=81.1510(10)°, β=89.4900(10)°, γ=70.9870(10)°, *V*=1675.43(12) Å^3, *Z*=2, ρ=1.613 Mg/m^3, μ (Mo*K*α)=10.958 mm^{-1}. The structure was solved by the direct method of full-matrix least–squares, where the final *R* and *Rw* were 0.0604 and 0.1670 for 25,498 reflections.

4.18. General procedure for the palladium-catalyzed allylic alkylation

To a mixture of [Pd(η^3-C_3H_5)Cl]$_2$ (1.47 mg, 4.0 μmol), chiral aminophosphine ligand **1** (8.0 μmol), and LiOAc (1.3 mg, 20 μmol) in a solvent (0.4 mL) was added BSA (0.15 mL, 0.60 mmol) and racemic allylic ester **7** (0.20 mmol) at room temperature under an Ar atmosphere. After 10 min, malonate **8** (0.6 mmol) was added at 0 or −10 °C. After 24 or 48 h, the reaction mixture was diluted with ether and water. The organic layer was washed with brine and dried over $MgSO_4$. The filtrate was concentrated with a rotary evaporator and the residue was purified by column chromatography.

*4.18.1. (S)-**9a** (Table 1, entry 5).*[13] 62.0 mg, 0.191 mmol, 96%, 90.2% ee; $[\alpha]_D^{20}$ −19.3 (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.52 (s, 3H), 3.71 (s, 3H), 3.96 (d, *J*=10.9 Hz, 1H), 4.27 (dd, *J*=8.5 and 10.9 Hz, 1H), 6.33 (dd, *J*=8.5 and 15.7 Hz, 1H), 6.48 (d, *J*=15.8 Hz, 1H), 7.20–7.33 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 49.1, 52.4, 52.6, 57.6, 126.4, 127.1, 127.5, 127.8, 128.4, 128.7, 129.0, 131.8, 136.8, 140.1, 167.8, 168.2; EI-MS *m*/*z* (rel intensity) 324 (M^+, 18); HPLC (Daicel CHIRALPAK® AD-H, 0.46 ϕ×25 cm, UV 254 nm), hexane–2-propanol=90:10, 0.5 mL/min: t_R=31.2 min (minor) and 35.3 min (major).

*4.18.2. (S)-**9b** (Table 1, entry 12).*[13] 62.8 mg, 0.178 mmol, 89%, 95% ee; $[\alpha]_D^{20}$ −19.2 (*c* 0.51, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.01 (t, *J*=7.1 Hz, 3H), 1.21 (t, *J*=7.1 Hz, 3H), 3.90–4.02 (m, 3H), 4.17 (q, *J*=7.2 Hz, 2H), 4.26 (dd, *J*=8.4 and 11.0 Hz, 1H), 6.33 (dd, *J*=8.4 and

15.7 Hz, 1H), 6.48 (d, *J*=15.8 Hz, 1H), 7.17–7.32 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 14.2, 49.2, 57.7, 61.3, 61.6, 126.3, 127.1, 127.5, 128.0, 128.4, 128.6, 129.3, 131.6, 136.8, 140.3, 167.4, 167.8; EI-MS *m*/*z* (rel intensity) 352 (M^+, 20); HPLC (Daicel CHIRALPAK® AD-H, 0.46 ϕ×25 cm, UV 254 nm), hexane–2-propanol=85:15, 1.0 mL/min: t_R=8.0 min (minor) and 10.1 min (major).

*4.18.3. (S)-**9c** (Table 1, entry 13).*[13] 74.6 mg, 0.157 mmol, 78%, 92% ee; mp 53–55 °C; $[\alpha]_D^{20}$ −6.7 (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.04 (d, *J*=10.9 Hz, 1H), 4.30 (dd, *J*=8.2 and 10.9 Hz, 1H), 4.93 (dd, *J*=12.3 and 14.2 Hz, 2H), 5.10 (dd, *J*=12.2 and 14.0 Hz, 2H), 6.30 (dd, *J*=8.2 and 15.8 Hz, 1H), 6.42 (d, *J*=15.8 Hz, 1H), 7.03–7.06 (m, 2H), 7.17–7.34 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 49.2, 57.8, 67.1×2, 67.3×2, 126.4×2, 127.1, 127.5, 127.9×2, 128.1×2, 128.2, 128.3, 128.36, 128.40×3, 128.5, 128.7×2, 129.0, 131.9×2, 135.07, 135.10, 136.7, 140.1, 167.1, 167.5; HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{32}H_{28}O_4$+Na 499.1880, found 499.1873; HPLC (Daicel CHIRALPAK® AD-H, 0.46 ϕ×25 cm, UV 254 nm), hexane–2-propanol=85:15, 1.0 mL/min: t_R=18.9 min (minor) and 23.0 min (major).

*4.18.4. (S)-**9d** (Table 1, entry 14).*[13] 62.9 mg, 0.154 mmol, 77%, 88% ee; mp 63–65 °C; $[\alpha]_D^{20}$ −8.7 (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (s, 9H), 1.42 (s, 9H), 3.73 (d, *J*=10.9 Hz, 1H), 4.16 (dd, *J*=8.1 and 11.0 Hz, 1H), 6.33 (dd, *J*=8.1 and 15.8 Hz, 1H), 6.45 (d, *J*=15.8 Hz, 1H), 7.18–7.32 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.6, 27.9, 49.0, 59.3, 81.5, 81.8, 126.3, 126.8, 127.3, 128.2, 128.4, 128.5, 130.1, 131.2, 137.0, 140.8, 166.7, 167.2; HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{26}H_{32}O_4$+Na 431.2193, found 431.2182; HPLC (Daicel CHIRALPAK® AD-H, 0.46 ϕ×25 cm, UV 254 nm), hexane–2-propanol=97:3, 0.3 mL/min: t_R=35.5 min (minor) and 51.4 min (major).

*4.18.5. (S)-**9e** (Table 1, entry 15).*[13] 64.2 mg, 0.175 mmol, 88%, 93% ee; $[\alpha]_D^{20}$ +32.7 (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (t, *J*=7.1 Hz, 3H), 1.23 (t, *J*=7.1 Hz, 3H), 1.47 (s, 3H), 4.08 (q, *J*=7.1 Hz, 2H), 4.17 (dq, *J*=1.3 and 7.1 Hz, 2H), 4.29 (d, *J*=8.9 Hz, 1H), 6.44 (d, *J*=15.7 Hz, 1H), 6.70 (dd, *J*=8.9 and 15.7 Hz, 1H), 7.17–7.35 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 14.0, 18.8, 53.7, 58.8, 61.3, 126.3, 127.1, 127.3, 128.2, 128.4, 128.8, 129.6, 132.6, 137.3, 139.4, 170.9, 171.2; EI-MS *m*/*z* (rel intensity) 366 (M^+, 5); HPLC (Daicel CHIRALPAK® AD-H, 0.46 ϕ×25 cm, UV 254 nm), hexane–2-propanol=199:1, 0.3 mL/min: t_R=44.2 min (minor) and 52.6 min (major).

*4.18.6. (S)-**9f** (Table 1, entry 17).*[14] 67.6 mg, 0.160 mmol, 64%, 84% ee; mp 78–80 °C; $[\alpha]_D^{20}$ −3.0 (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.05 (t, *J*=7.1 Hz, 3H), 1.20 (t, *J*=7.1 Hz, 3H), 3.86 (d, *J*=10.9 Hz, 1H), 4.00 (dq, *J*=1.3 and 7.1 Hz, 2H), 4.2 (m, 3H), 6.27 (dd, *J*=9.0 and 15.0 Hz, 1H), 6.41 (d, *J*=15.0 Hz, 1H), 7.3 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 14.1,48.4, 57.5,61.6, 61.7, 127.5, 128.7, 128.9, 129.3, 129.4, 130.9, 133.0, 133.3, 135.0, 138.6, 167.1, 167.5; EI-MS *m*/*z* (rel intensity) 422 (M^+, 29); HPLC (Daicel CHIRALPAK® IA, 0.46 ϕ×25 cm, UV 254 nm), hexane–2-propanol=85:15, 1.0 mL/min: t_R=6.2 min (minor) and 7.5 min (major).

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Supplementary data

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