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# Chiral Triphenylprolinol Ligands for the Efficient Catalytic Asymmetric Arylation of Aldehydes

**Angélica Venturini Moro,[a] Edward R. T. Tiekink,[b] Julio Zukerman-Schpector,[c] Diogo S. Lüdtke,*[d] and Carlos Roque D. Correia*[a]**

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The synthesis of new chiral amino alcohols by Heck arylation of an enecarbamate is described. These compounds were used as chiral ligands for the catalytic asymmetric arylation of aldehydes and can be easily recovered. Chiral, nonracemic diarylmethanols were obtained in high yields and enantioselectivities.

## Introduction

The asymmetric addition of arylzinc reagents to aromatic aldehydes has received much attention over the past few years, because enantioenriched diarylmethanols are present in a number of biologically and pharmacologically active compounds.[1] For example, this unit can be found in the structure of (*R*)-orphenadrine and (*R*)-neobenodine,[2] which display antihistaminic and anticholinergic activity, and in (*S*)-BMS 184394, which is active against breast cancer and leukemia.[3] In addition to their direct applications, the chiral diarylmethanol nucleus can serve as a precursor for diarylmethane derivatives through $S_N2$ substitution at the CO bond without erosion in enantiomeric purity.[4] Compounds possessing a chiral diarylmethane nucleus behave as antimuscarinics,[5] antidepressants,[6] and endothelin antagonists (Figure 1).[7]

Among the methods available for the generation of reactive arylzinc intermediates, the boron-to-zinc exchange reaction[8] is one of the most interesting, as a number of arylboronic acids are commercially available or can be easily prepared, which allows the synthesis of a number of substituted diarylmethanols.[9,10] Moreover, this methodology allows the synthesis of both enantiomers of a given product by using the same chiral ligand through the appropriate choice of arylboronic acid and aromatic aldehyde reaction partners.

Among the chiral ligands described to catalyze the asymmetric aryl transfer reaction with high enantioselectivity, β-amino alcohols have been the most effective.[11] Considering the proline motif as a privileged framework for the development of asymmetric catalysts,[12] we decided to apply the Heck reaction of arenediazonium salts (Heck–Matsuda reaction) for the synthesis of new chiral arylated amino alcohols and apply them as chiral ligands for the asymmetric arylation of aldehydes (Scheme 1).

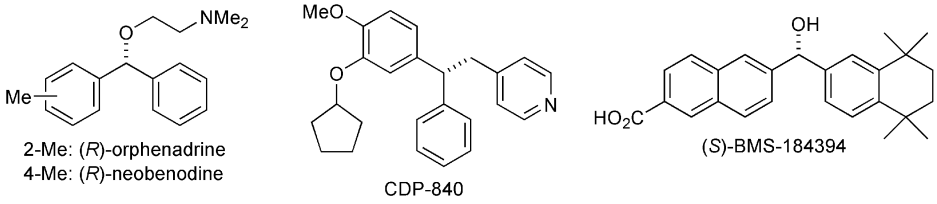


Figure 1. Structure of bioactive diarylmethanol derivatives.

The palladium-catalyzed Heck reaction of arenediazonium salts with electron-rich olefins is an important tool for the synthesis of natural products and biologically important compounds.[13,14] Arenediazonium salts offer several advantages over the more traditionally employed aryl halides; arylations are usually milder, easier to manipulate, faster, and more economic.[15] Even more important is the fact

[a] Instituto de Química, Universidade Estadual de Campinas, UNICAMP,
C.P. 6154, CEP. 13084-917 Campinas, Brazil
E-mail: roque@iqm.unicamp.br
[b] Department of Chemistry, University of Malaya,
Kuala Lumpur 50603, Malaysia
[c] Departamento de Química, Universidade Federal de São Carlos,
São Carlos, Brazil
[d] Faculdade de Ciências Farmacêuticas, Universidade de São Paulo, USP, CEP
05508-900 São Paulo, Brazil
E-mail: dsludtke@usp.br
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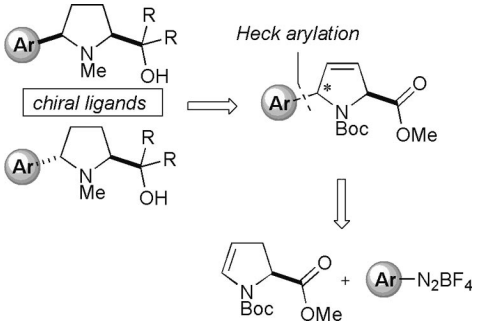
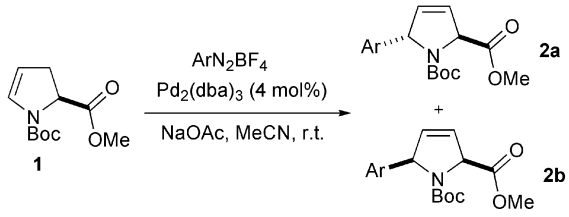



Scheme 1. General structure of the chiral ligands prepared by Heck arylation.

that they undergo extremely facile oxidative addition with $Pd^0$, operating under "ligand-free" conditions to generate a highly reactive cationic $ArPd^{II}$ species.

Table 1. Heck reaction of enecarbamate **1** and arenediazonium salts.




| Entry | Ar | Yield [%] | *trans*/*cis*[a] |
|---|---|---|---|
| 1 | Ph | 85 | 45:55 |
| 2 | 4-$MeOC_6H_4$ | 90 | 85:15 |
| 3 | 4-$FC_6H_4$ | 82 | 44:56 |
| 4 | 2-naphthyl | 70 | 42:58 |

[a] The *trans*/*cis* ratio was determined by GC–MS analysis or by $^1H$ NMR spectroscopy.

## Results and Discussion

The desired chiral ligands were synthesized by a short and efficient synthetic sequence starting from chiral enecarbamate **1**.[16] First, Heck arylation with arenediazonium salts proceeded smoothly in the presence of $Pd_2(dba)_3$ (4 mol-%) as catalyst, delivering the arylated product as a mixture of diastereoisomers in high yields (Table 1). With the exception of the Heck arylation with the 4-methoxybenzenediazonium tetrafluoroborate, the arylation process is unselective and almost equimolar mixtures of the *cis* and *trans* diastereoisomers were obtained. The lack of stereoselectivity in our case is attractive, as it allows the synthesis of a stereochemically diverse set of ligands with modular character. This is an important feature of the synthetic sequence, because it permits fine-tuning of catalytic activity through refinement of the ligand structure.

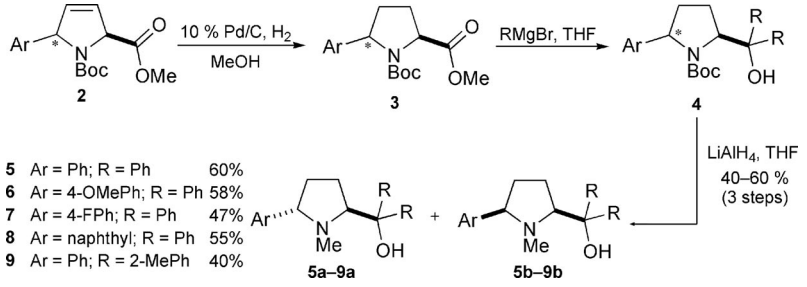
Interestingly, lower stereoselectivity (Table 1, Entries 1, 3, and 4) seems to reflect the stability of the cationic aryl palladium intermediate. We hypothesize that the less-stable cationic aryl palladium intermediates complex rather efficiently with the ester group at C-2, which helps to promote the migratory insertion from the same side of the ester group.

Following our synthetic sequence, the diastereoisomeric mixture of the Heck adduct was then hydrogenated, followed by double Grignard addition, to result in the corresponding amino alcohols **4**. The crude products were then treated with $LiAlH_4$ to reduce the *N*-Boc group to *N*-Me, affording the desired amino alcohols in 40–60% yield over three steps. At this point, diastereoisomeric chiral amino alcohols **5a**–**9a** and **5b**–**9b** were easily separated by flash chromatography (Scheme 2).

Attempts to unequivocally determine the stereochemistry of the chiral *N*-Me amino alcohols by $^1H$ and $^{13}C$ NMR spectroscopy met with problems. To attribute the absolute stereochemistry of the new chiral ligands, the diastereoisomeric mixture of *N*-Boc amino alcohol **4** (Ar = Ph, R = Ph) was separated into the *trans* and *cis* isomers. The *cis* isomer furnished a suitable crystal, which allowed its stereochemistry to be determined by X-ray diffraction analysis (Figure 2). Next, both pure diastereoisomers were converted separately into their corresponding amino alcohols *trans*-**5a** and *cis*-**5b**. Therefore, the stereochemistry of all compounds was attributed. The stereochemistry of remaining ligands **6**–**9** was attributed by comparison of their NMR spectra with those of *trans*-**5a** and *cis*-**5b**.

With the amino alcohols in hands, we turned our attention to evaluate their behavior as chiral ligands for the arylation of *p*-tolualdehyde with phenylboronic acid. The results of these studies are depicted in Table 2.

The transferable aryl group was generated by reaction of phenylboronic acid with $Et_2Zn$ at 60 °C for 12 h.[17] All ligands employed in the catalytic asymmetric arylation reaction furnished the product in good yield and varied levels of enantioselectivity. Initially, the R group was held con-




Scheme 2. Completion of the synthesis of chiral amino alcohols **5**–**9**.

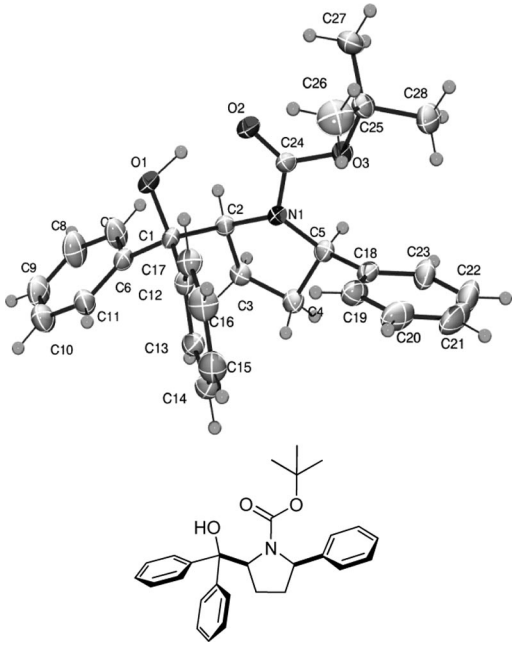
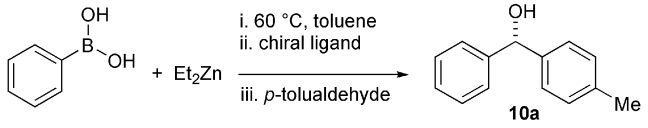



Figure 2. ORTEP drawing of *cis*-*N*-Boc amino alcohol **4b**.

Table 2. Arylation of *p*-tolualdehyde with phenylboronic acid.




| Entry | Ligand (mol-%) | *T* [°C] | Yield [%] | *er* (*S*)[a] |
|---|---|---|---|---|
| 1 | **5a** (10) | 25 | 98 | 88:12 |
| 2 | **5a** (10) | 0 | 98 | 98:2 |
| 3 | **5a** (5) | 0 | 72 | 87:13 |
| 4 | **5a** (10) | –40 | 60 | 99:1 |
| 5 | **5a** (10) | –20 | 99 | 95.5:4.5 |
| 6 | **5b** (10) | 0 | 86 | 97.5:2.5 |
| 7 | **5b** (10) | –20 | 80 | 95:5 |
| 8[b] | **5a** (10) | 0 | 51 | 92:8 |
| 9[b] | **5b** (10) | 0 | 46 | 91:9 |
| 10 | **6a** (10) | 0 | 97 | 93:7 |
| 11 | **6b** (10) | 0 | 99 | 92:8 |
| 12 | **7a** (10) | 0 | 85 | 93:7 |
| 13 | **7b** (10) | 0 | 99 | 89:11 |
| 14 | **8a** (10) | 0 | 99 | 95:5 |
| 15 | **8b** (10) | 0 | 99 | 91:9 |
| 16 | **9a** (10) | 0 | 81 | 91:9 |
| 17 | **9b** (10) | 0 | 81 | 90:10 |

[a] Enantiomeric ratios determined by HPLC with a Chiralcel OD-H column, $\lambda$ = 254 nm, hexanes/*i*PrOH (90:10), 0.5 mL min$^{-1}$. Absolute configuration determined by comparison with literature data. [b] DiMPEG MW 2000 (dimethoxypolyethylene glycol, 10 mol-%) was used as additive.

stant as a phenyl group, and we studied the influence of the substitution pattern at C-5. Thus, ligand **5a** (10 mol-%), which presents the *trans* configuration, was used and the diarylmethanol was obtained in 98% yield with 88:12 *er* (Table 2, Entry 1). A decrease in the reaction temperature proved to be beneficial to the enantioselectivity of the arylation process, as the *er* was greatly improved to 98:2 by conducting the reaction at 0 °C while maintaining the same yield (Table 2, Entry 2). Further decrease in the temperature did not improve the efficiency of the reaction, leading to a decrease in yield or in the *er* (Table 2, Entries 4 and 5). The influence of the stereochemistry at C-5 was then examined. When using ligand **5b** (*cis* relationship), a lower yield of the chiral diarylmethanol was obtained with virtually the same *er*. The addition of DiMPEG, an additive commonly used to improve the enantioselectivity of organozinc additions,[18] resulted in sluggish reactions and erosion in both yield and *er* (Table 2, Entries 8 and 9). The influence of the nature of the Ar group attached to C-5 was further evaluated. Substituted aromatic rings led to diminished *er* values, albeit furnishing the product in high yields in most cases (Table 2, Entries 10–15). Among the ligands possessing a substituted aryl ring, the best results were achieved with **8a** (Ar = naphthyl); chiral secondary alcohol **10a** was obtained in 95:5 *er* in almost quantitative yield (Table 2, Entry 14). Finally, the replacement of the R group from Ph to the more sterically demanding *ortho*-tolyl derivative did not result in any improvement in the reaction outcome (Table 2, Entries 16 and 17).

Importantly, direct comparison of the performance of ligands **5a** and **5b** with known diarylprolinol ligand **11**[19] reveals that smaller amounts of ligand are required to obtain high enantioselectivity in the phenylation of *p*-tolualdehyde (Figure 3). Whereas **11** produced diarylmethanol **10a** in 97:3 *er* with a 20 mol-% loading, a significant decrease in the *er* to 67.5:32.5 was observed with 10 mol-% loading. On the other hand, both ligands **5a** and **5b** provided a highly enantioselective aryl transfer reaction with the use of a ligand loading of only 10 mol-% (up to 98:2 *er*).

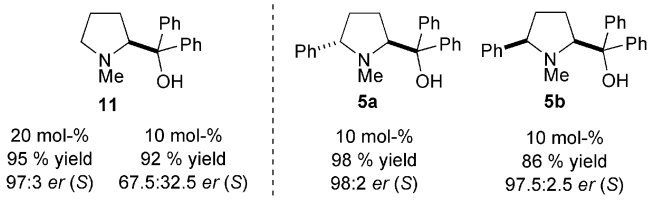
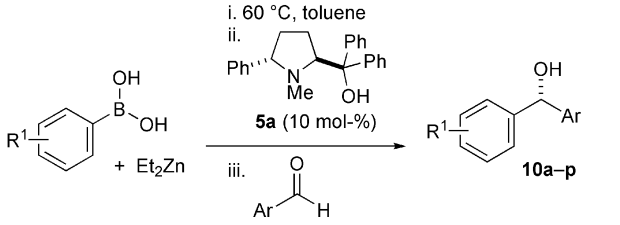



Figure 3. Comparison between proline-based ligands.

With ligand **5a** identified as the most active, we turned our attention to exploit the potential of our system to a broader variety of aldehydes and boronic acids with diverse electronic and steric properties. The results are summarized in Table 3. Reactions of *o*- and *p*-tolualdehyde underwent smooth aryl addition, and the corresponding products were isolated with high *er* values and yields (Table 3, Entries 1 and 2). Phenyl transfer to halogen-substituted aldehydes resulted in good *er* values, albeit in lower levels of enantioselection when compared with *p*-tolualdehyde (Table 3, Entries 3–7). Interestingly, the position of the halogen in the aryl ring did not seem to exert influence in the enantioselectivity of the reaction. The arylation of the heteroaromatic 2-furaldehyde proceeded smoothly, and the corresponding phenyl-heteroarylmethanol was isolated in excellent yield with an *er* of 96:4 (Table 3, Entry 9).

Table 3. Catalytic asymmetric arylation of aldehydes with arylboronic acids.




| Entry | $R^1$ | Ar | Yield [%] | *er*[a] |
|---|---|---|---|---|
| 1 | H | 4-$MeC_6H_4$ | 98 | 98:2 (*S*) |
| 2 | H | 2-$MeC_6H_4$ | 91 | 96:4 (*S*) |
| 3 | H | 4-$ClC_6H_4$ | 94 | 93.5:6.5 (*S*) |
| 4 | H | 2-$ClC_6H_4$ | 93 | 92.5:7.5 (*S*) |
| 5 | H | 4-$BrC_6H_4$ | 94 | 93:7 (*S*) |
| 6 | H | 2-$BrC_6H_4$ | 92 | 93:7 (*S*) |
| 7 | H | 3-$FC_6H_4$ | 75 | 90:10 (*S*) |
| 8 | H | 4-$MeOC_6H_4$ | 91 | 93.5:6.5 (*S*) |
| 9 | H | 2-furyl | 89 | 96:4 (*S*) |
| 10 | 4-Me | $C_6H_5$ | 90 | 92:8 (*R*) |
| 11 | 4-Ph | $C_6H_5$ | 98 | 98:2 (*R*) |
| 12 | 4-MeO | $C_6H_5$ | 83 | 88.5:11.5 (*R*) |
| 13 | 4-Br | $C_6H_5$ | 96 | 96:4 (*R*) |
| 14 | 4-MeO | 4-$ClC_6H_4$ | 71 | 86.5:13.5 (*S*) |
| 15 | 4-Cl | 4-$MeC_6H_4$ | 98 | 96:4 (*R*) |
| 16 | 4-Ph | 2-furyl | 98 | 98.5:1.5 (*S*) |

[a] Enantiomeric ratios determined by HPLC, see Supporting Information for details. Absolute configuration determined by comparison with literature data.

To examine the competence of our catalytic system in the transfer of substituted aryl groups, we examined the reaction of a variety of boronic acids with benzaldehyde under our standard conditions. Gratifyingly, we could observe that the efficiency of the catalytic system was maintained. For example, reaction of 4-biphenylboronic acid and 4-bromophenylboronic acid with benzaldehyde resulted in the corresponding product in very high *er* (Table 3, Entries 11 and 13). Exception to these high levels of selectivity is the reaction with 4-methoxyphenylboronic acid, which resulted in a decrease in the *er* (Table 3, Entry 12; 88.5:11.5 *er*). Another important feature of this methodology is its ability to prepare both enantiomers of a given product by using the same chiral ligand. In fact, this could be accomplished by using our catalytic system. For example, addition of *p*-tolylboronic acid and *p*-bromophenylboronic acid to benzaldehyde proceeded smoothly. The corresponding diarylmethanols were obtained in high yields and high enantioselectivities (Table 3, Entry 1 vs. 10, Entry 5 vs. 13).

Finally, the synthesis of chiral diarylmethanols with substituents other than hydrogen in both aryl rings was pursued. Effectively, this goal was achieved and structural variation was made simultaneously at the boronic acid and at the aldehyde. The arylation reaction occurred uneventfully, and the chiral secondary alcohols were generally obtained in high yields and enantioselectivities. For example, reaction of 4-chlorophenylboronic acid with *p*-tolualdehyde furnished the corresponding product in high *er* (96:4) in essentially quantitative yield (Table 3, Entry 15). Additionally, the reaction between biphenylboronic acid and 2-furaldehyde produced the corresponding chiral secondary alcohol in excellent yield and enantiomeric ratio (98% yield, 98.5:1.5 *er*; Table 3, Entry 16).

Importantly, chiral ligand **5a** could be completely recovered by column chromatography and reused without any loss in the catalytic activity or in the enantioselectivity of the arylation reaction.

## Conclusions

In summary, we have described the synthesis of new and recyclable chiral amino alcohols by using a mild and efficient Heck arylation of an enecarbamate as the key step. Furthermore, these compounds were efficiently used as chiral ligands in the catalytic asymmetric aryl transfer reactions of arylboronic acids to aromatic aldehydes. Chiral, nonracemic diarylmethanols were obtained in high yields and enantioselectivities. Applications of these new chiral amino alcohols as organocatalysts are ongoing and will be reported in due course.

## Experimental Section

**Materials and Methods:** $^1$H NMR spectra were obtained at 250 and 500 MHz. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm and referenced to the solvent peak of residual $CHCl_3$ or tetramethylsilane (TMS). Data are reported as follows: chemical shift ($\delta$), multiplicity, coupling constant ($J$), and integrated intensity. $^{13}$C NMR spectra were obtained at 62.5 and 125 MHz. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm and referenced to the solvent peak $CDCl_3$. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), dd (doublet of doublets), and m (multiplet). Column chromatography was performed by using silica gel (230–400 mesh) following the methods described by Still.[20] Thin-layer chromatography (TLC) was performed by using silica gel $GF_{254}$, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light or treated with phosphomolybdic acid followed by heating. Air- and moisture-sensitive reactions were conducted in flame-dried or oven-dried glassware equipped with tightly fitted rubber septa and under a positive atmosphere of dry argon. Reagents and solvents were handled by using standard syringe techniques. Temperatures above room temperature were maintained by use of a mineral oil bath heated on a hotplate. Enantiomeric excesses were determined by HPLC with a chiral stationary phase. All measurements were performed at a column temperature of 20 °C by using a UV detector at 254 nm, except noted otherwise.

**General Procedure for the Heck Arylation of Enecarbamate 1 with Arenediazonium Salts:** To a round-bottomed flask (or a test tube) was added enecabamate **1** (1.13 g, 5 mmol) and acetonitrile (23 mL). To the resulting suspension was then added $Pd_2(dba)_3$·dba (4 mol-%, 200 mg), sodium acetate (3 equiv., 1.6 g, 15 mmol), and the arenediazonium salt (1.3 equiv., 6.5 mmol). The reaction was stirred at room temperature, and the reaction progress was monitored by the evolution of $N_2$. After the nitrogen bubbling had stopped, the crude reaction mixture was filtered through a plug of silica gel and concentrated under reduced pressure. The product was purified by flash chromatography (hexanes/ethyl acetate) to

provide arylated products **2a** and **2b**, as an inseparable mixture of diastereoisomers, which was directly used in the next step.

**General Procedure for the Synthesis of the Ligands:** To a round-bottomed flask, under a hydrogen atmosphere, was added Heck adduct **2** (3 mmol) and dry methanol (60 mL), followed by the addition of 10% Pd/C (20 wt.-%, 0.18 g). The reaction was stirred at room temperature for 24 h. After this time, the crude reaction mixture was filtered through a plug of Celite and concentrated under reduced pressure. The resulting product was used without further purification. To a round-bottomed flask, under an argon atmosphere, a solution of RMgBr (1 M in THF, 15 mL, 15 mmol, 5 equiv.) was added to a THF (10 mL) solution of ester **3** (3 mmol) at 25 °C, and the mixture was stirred for 4 h before being quenched by careful addition of 2 M NaOH. The heterogeneous mixture was filtered through a pad of Celite and washed with dichloromethane (3 × 50 mL). The combined organic phase was dried with $MgSO_4$, filtered, and concentrated. The resulting product was used without further purification. In a round-bottomed flask, under an argon atmosphere, containing a suspension of lithium aluminum hydride (1.14 g, 30 mmol) in THF (15 mL), cooled to 0 °C, was added a solution of *N*-Boc alcohol **4** in THF (5 mL). The resulting mixture was heated at reflux for 12 h. After this time, the mixture was cooled to 0 °C and 4 M NaOH was added. The mixture was filtered through a pad of Celite and washed with ethyl acetate. The organic layer was separated, and the filtrate was extracted with ethyl acetate (3 × 50 mL). The combined organic phase was dried with $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography (hexanes/ethyl acetate, 95:05).

**[(2*S*,5*S*)-1-Methyl-5-phenylpyrrolidin-2-yl]diphenylmethanol (5a):** Yield: 0.278 g (27%). $[\alpha]_D^{20}$ = +12 (*c* = 1.0, $CHCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.62 (s, 3 H, *N*-$CH_3$), 1.66–1.88 (m, 2 H, $CH_2$), 2.14–2.35 (m, 2 H, $CH_2$), 4.25–4.34 (m, 2 H, 2 CH), 7.06–7.36 (m, 11 H, Ar), 7.61 (dd, *J* = 8.3, 1.5 Hz, 2 H, Ar), 7.69 (dd, *J* = 8.3, 1.5 Hz, 2 H, Ar) ppm. $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ = 29.0, 31.5, 38.4, 70.6, 71.2, 77.3, 125.25, 125.26, 126.1, 126.1, 126.9, 127.8, 128.0, 128.1, 128.3, 142.8, 147.0, 148.3 ppm. IR (film): $\tilde{\nu}$ = 3415, 1490, 705 cm$^{-1}$. MS (ESI): *m*/*z* = 344, 331, 326. HRMS (ESI): calcd. for $C_{24}H_{25}NO$ + H 344.2014; found 344.2012.

**[(2*S*,5*R*)-1-Methyl-5-phenylpyrrolidin-2-yl]diphenylmethanol (5b):** Yield: 0.340 g (33%). $[\alpha]_D^{20}$ = +115 (*c* = 1.02, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 1.66 (s, 3 H, *N*-$CH_3$), 1.68–1.83 (m, 2 H, $CH_2$), 1.92–2.03 (m, 2 H, $CH_2$), 3.54 (dd, *J* = 10.8, 6.0 Hz, 1 H, CH), 3.89 (dd, *J* = 9.8, 4.0 Hz, 1 H, CH), 4.97 (br. s, 1 H, OH), 7.09 (t, *J* = 7.0 Hz, 1 H, Ar), 7.13 (t, *J* = 7.0 Hz, 1 H, Ar), 7.19–7.33 (m, 9 H, Ar), 7.58 (dd, *J* = 8.5, 1.0 Hz, 2 H, Ar), 7.68 (dd, *J* = 8.5, 1.0 Hz, 2 H, Ar) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 28.2, 34.5, 41.0, 72.5, 73.4, 77.8, 125.3, 125.4, 126.1, 126.2, 126.9, 127.2, 128.0, 128.1, 128.4, 142.6, 146.6, 148.0 ppm. IR (film): $\tilde{\nu}$ = 3428, 3263, 1449 cm$^{-1}$. MS (ESI): *m*/*z* = 209, 167. HRMS (ESI): calcd. for $C_{24}H_{25}NO$ + H 344.2014; found 344.2083.

**[(2*S*,5*S*)-5-(4-Methoxyphenyl)-1-methylpyrrolidin-2-yl]diphenylmethanol (6a):** Yield: 0.552 g (49%). $[\alpha]_D^{20}$ = +1 (*c* = 1.0, $CHCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.59 (s, 3 H, *N*-$CH_3$), 1.64–1.89 (m, 2 H, $CH_2$), 2.11–2.31 (m, 2 H, $CH_2$), 3.76 (m, 3 H, $OCH_3$), 4.19–4.28 (m, 2 H, 2 CH), 6.85 (d, *J* = 8.5 Hz, 2 H, Ar), 7.05–7.15 (m, 4 H, Ar), 7.19–7.30 (m, 4 H, Ar), 7.60 (d, *J* = 8.5 Hz, 2 H, Ar), 7.68 (d, *J* = 8.5 Hz, 2 H, Ar) ppm. $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ = 29.0, 31.4, 38.3, 55.1, 70.3, 70.4, 77.2, 113.6, 125.1, 125.2, 126.1, 126.1, 127.9, 128.0, 128.9, 134.5, 147.0, 148.9, 158.4 ppm. IR (film): $\tilde{\nu}$ = 3352, 1511, 1246 cm$^{-1}$. MS (EI): *m*/*z* = 355, 276, 190, 105, 77. HRMS (EI): calcd. for $C_{25}H_{25}NO$ [M – $H_2O$] 355.1936; found 355.1919.

**[(2*S*,5*R*)-5-(4-Methoxyphenyl)-1-methylpyrrolidin-2-yl]diphenylmethanol (6b):** Yield: 0.097 g (9%). $[\alpha]_D^{20}$ = +118 (*c* = 1.0, $CHCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.64 (s, 3 H, *N*-$CH_3$), 1.69–1.84 (m, 2 H, $CH_2$), 1.88–2.04 (m, 2 H, $CH_2$), 3.50 (dd, *J* = 10.3, 5.8 Hz, 1 H, CH), 3.78 (s, 3 H, $OCH_3$), 3.87 (dd, *J* = 9.3, 4.3 Hz, 1 H, CH), 4.99 (br. s, 1 H, OH), 6.86 (d, *J* = 8.8 Hz, 2 H, Ar), 7.07–7.18 (m, 2 H, Ar), 7.23–7.32 (m, 6 H, Ar), 7.56 (d, *J* = 8.5 Hz, 2 H, Ar), 7.67 (d, *J* = 8.5 Hz, 2 H, Ar) ppm. $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ = 28.1, 34.5, 40.8, 55.2, 72.4, 72.8, 77.8, 113.8, 125.3, 125.4, 126.1, 126.2, 127.9, 128.0, 128.1, 134.5, 146.7, 148.1, 158.8 ppm. IR (KBr): $\tilde{\nu}$ = 3371, 3283, 1512, 1248 cm$^{-1}$. MS (EI): *m*/*z* = 355, 190. HRMS (EI): calcd. for $C_{25}H_{25}NO$ [M – $H_2O$] 355.1936; found 355.1935.

**[(2*S*,5*S*)-5-(4-Fluorophenyl)-1-methylpyrrolidin-2-yl]diphenylmethanol (7a):** Yield: 0.224 g (21%). $[\alpha]_D^{20}$ = +9 (*c* = 1.0, $CHCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.59 (s, 3 H, *N*-$CH_3$), 1.63–1.72 (m, 1 H), 1.76–1.88 (m, 1 H), 2.13–2.31 (m, 2 H, $CH_2$), 4.23 (dd, *J* = 8.5, 4.8 Hz, 1 H, CH), 4.29 (d, *J* = 6.8 Hz, 1 H, CH), 6.96–7.06 (m, 2 H, Ar), 7.09–7.17 (m, 4 H, Ar), 7.18–7.31 (m, 4 H, Ar), 7.61 (d, *J* = 8.5 Hz, 2 H, Ar), 7.68 (d, *J* = 8.5 Hz, 2 H, Ar) ppm. $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ = 28.9, 31.5, 38.3, 70.3, 70.5, 77.2, 115.1 (d, *J* = 21.25 Hz), 125.2, 125.2, 126.1, 126.1, 128.0, 128.1, 129.2 (d, *J* = 7.5 Hz), 138.3 (d, *J* = 3.1 Hz), 146.9, 148.2, 161.7 (d, *J* = 243.12 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3292, 1508, 709 cm$^{-1}$. MS (EI): *m*/*z* = 343, 182, 178, 165, 105, 77. HRMS (EI): calcd. for $C_{24}H_{22}FN$ [M – $H_2O$] 343.1736; found 343.1714.

**[(2*S*,5*R*)-5-(4-Fluorophenyl)-1-methylpyrrolidin-2-yl]diphenylmethanol (7b):** Yield: 0.285 g (26%). $[\alpha]_D^{20}$ = +116 (*c* = 1.0, $CHCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.64 (s, 3 H, *N*-$CH_3$), 1.69–1.85 (m, 2 H, $CH_2$), 1.88–2.08 (m, 2 H, $CH_2$), 3.52 (dd, *J* = 10.5, 5.8 Hz, 1 H, CH), 3.89 (dd, *J* = 9.0, 4.3 Hz, 1 H, CH), 4.87 (br. s, 1 H, OH), 6.94–7.03 (m, 2 H, Ar), 7.06–7.19 (m, 2 H, Ar), 7.22–7.31 (m, 6 H, Ar), 7.57 (d, *J* = 8.5 Hz, 2 H, Ar), 7.67 (d, *J* = 8.5 Hz, 2 H, Ar) ppm. $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ = 28.1, 34.6, 40.9, 72.4, 72.7, 77.8, 115.3 (d, *J* = 21.25 Hz), 125.3, 125.4, 126.1, 126.2, 128.0, 128.1, 128.4 (d, *J* = 7.5 Hz), 138.2 (d, *J* = 3.1 Hz), 146.5, 147.9, 162.0 (d, *J* = 243.75 Hz) ppm. IR (film): $\tilde{\nu}$ = 3352, 1508, 1223 cm$^{-1}$. MS (EI): *m*/*z* = 343, 178, 167, 165, 105. HRMS (EI): calcd. for $C_{24}H_{22}FN$ [M – $H_2O$] 343.1736; found 343.1731.

**[(2*S*,5*S*)-1-Methyl-5-(naphthalen-2-yl)pyrrolidin-2-yl]diphenylmethanol (8a):** Yield: 0.272 g (23%). $[\alpha]_D^{20}$ = +1 (*c* = 1.0, $CHCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.67 (s, 3 H, *N*-$CH_3$), 1.75–1.94 (m, 2 H, $CH_2$), 2.23–2.42 (m, 2 H, $CH_2$), 4.38 (dd, *J* = 8.5, 4.3 Hz, 1 H, CH), 4.50 (d, *J* = 5.3 Hz, 1 H, CH), 7.06–7.35 (m, 8 H, Ar), 7.43–7.51 (m, 2 H, Ar), 7.60–7.66 (m, 3 H, Ar), 7.71 (d, *J* = 8.5 Hz, 2 H, Ar), 7.82 (d, *J* = 8.5 Hz, 2 H, Ar) ppm. $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ = 29.1, 31.6, 38.5, 70.9, 71.2, 77.3, 125.3, 125.3, 125.7, 126.0, 126.1, 126.2, 126.2, 126.6, 127.6, 127.8, 128.0, 128.1, 128.2, 132.5, 133.2, 140.4, 147.0, 148.3 ppm. IR (KBr): $\tilde{\nu}$ = 3432, 1449, 746 cm$^{-1}$. MS (EI): *m*/*z* = 375, 210, 182, 105. HRMS (EI): calcd. for $C_{28}H_{25}N$ [M – $H_2O$] 375.1987; found 375.1984.

**[(2*S*,5*R*)-1-Methyl-5-(naphthalen-2-yl)pyrrolidin-2-yl]diphenylmethanol (8b):** Yield: 0.377 g (32%). $[\alpha]_D^{20}$ = +110 (*c* = 1.0, $CHCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.70 (s, 3 H, *N*-$CH_3$), 1.77–1.91 (m, 2 H, $CH_2$), 1.97–2.06 (m, 2 H, $CH_2$), 3.73 (dd, *J* = 9.5, 6.0 Hz, 1 H, CH), 3.96 (dd, *J* = 9.3, 4.5 Hz, 1 H, CH), 5.06 (br. s, 1 H, OH), 7.09–7.19 (m, 2 H, Ar), 7.25–7.34 (m, 4 H, Ar), 7.41–7.52 (m, 3 H, Ar), 7.60 (d, *J* = 8.5 Hz, 2 H, Ar), 7.69–7.73 (m, 3 H, Ar), 7.79–7.85 (m, 3 H, Ar) ppm. $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ = 28.3, 34.4, 41.0, 72.5, 73.5, 77.8, 124.8, 125.3, 125.4, 125.6, 126.0, 126.0, 126.2, 126.2, 127.6, 127.6, 128.0, 128.1, 128.4, 133.0, 133.3, 140.0, 146.7, 148.0 ppm. IR (KBr): $\tilde{\nu}$ = 3424, 1449, 708 cm$^{-1}$.

MS (EI): *m*/*z* = 375, 296, 210. HRMS (EI): calcd. for $C_{28}H_{25}N$ [M – $H_2O$] 375.1987; found 375.1945.

**[(2*S*,5*S*)-1-Methyl-5-phenylpyrrolidin-2-yl]di(*o*-tolyl)methanol (9a):** Yield: 0.200 g (18%). $[\alpha]_D^{20}$ = +154 (*c* = 1.5, $CHCl_3$). $^1H$ NMR (250 MHz, $CDCl_3$): δ = 1.50 (s, 3 H, *N*-$CH_3$), 1.63–1.70 (m, 1 H), 2.02–2.29 (m, 8 H), 2.30–2.46 (m, 1 H), 4.22–4.32 (m, 2 H, 2 CH), 6.88 (d, *J* = 7.0 Hz, 1 H, Ar), 6.93–7.28 (m, 10 H, Ar), 7.50–7.69 (m, 2 H, Ar) ppm. $^{13}C$ NMR (62.5 MHz, $CDCl_3$): δ = 21.7, 22.7, 29.9, 32.4, 38.4, 70.2, 71.1, 77.2, 123.8, 124.9, 126.72, 126.76, 126.82, 127.7, 128.3, 128.3, 129.0, 132.2, 132.5, 136.0, 138.5, 142.0, 143.2, 143.7 ppm. IR (film): ṽ = 3399, 1454, 739 $cm^{-1}$. MS (EI): *m*/*z* = 353, 195, 160. HRMS (EI): calcd. for $C_{26}H_{27}N$ [M – $H_2O$] 353.2144; found 353.2112.

**[(2*S*,5*R*)-1-Methyl-5-phenylpyrrolidin-2-yl]di(*o*-tolyl)methanol (9b):** Yield: 0.245 g (22%). $[\alpha]_D^{20}$ = +87 (*c* = 1.0, $CHCl_3$). $^1H$ NMR (250 MHz, $CDCl_3$): δ = 1.42 (s, 3 H, *N*-$CH_3$), 1.55–1.73 (m, 1 H), 1.90–2.02 (m, 1 H), 2.03–2.26 (m, 8 H), 3.47 (dd, *J* = 11.5, 5.5 Hz, 1 H, CH), 3.81 (dd, *J* = 8.8, 3.8 Hz, 1 H, CH), 4.45 (br. s, 1 H, OH), 6.86 (d, *J* = 7.0 Hz, 1 H, Ar), 6.95–7.30 (m, 11 H, Ar), 7.32–7.42 (m, 1 H, Ar) ppm. $^{13}C$ NMR (62.5 MHz, $CDCl_3$): δ = 21.5, 22.8, 29.6, 35.8, 41.3, 73.5, 73.5, 77.2, 123.8, 125.2, 126.6, 126.8, 126.8, 127.0, 127.2, 128.5, 128.5, 129.1, 132.0, 132.6, 135.4, 139.0, 142.7, 143.5 ppm. IR (film): ṽ = 3422, 1490, 1455 $cm^{-1}$. MS (EI): *m*/*z* = 353, 195, 160. HRMS (EI): calcd. for $C_{26}H_{27}N$ [M – $H_2O$] 353.2144; found 353.2118.

**(2*S*,5*S*)-*tert*-Butyl 2-(Hydroxydiphenylmethyl)-5-phenylpyrrolidine-1-carboxylate (4a):** $[\alpha]_D^{20}$ = –135 (*c* = 0.68, $CHCl_3$). $^1H$ NMR (250 MHz, $CDCl_3$): δ = 0.74–0.97 (m, 1 H), 1.10 (s, 9 H, 3 $CH_3$), 1.14–1.41 (m, 1 H), 1.87–1.95 (m, 1 H), 2.28–2.46 (m, 1 H), 4.50 (d, *J* = 8.3 Hz, 1 H, CH), 5.33 (dd, *J* = 7.8, 1.5 Hz, 1 H, CH), 6.33 (br. s, 1 H, OH), 7.04 (dd, *J* = 6.8, 1.5 Hz, 2 H, Ar), 7.17–7.42 (m, 11 H, Ar), 7.48 (dd, *J* = 8.1, 1.5 Hz, 2 H, Ar) ppm. $^{13}C$ NMR (62.5 MHz, $CDCl_3$): δ = 27.2, 27.8, 32.2, 63.8, 65.9, 80.7, 82.1, 124.8, 124.8, 126.4, 127.1, 127.3, 127.7, 127.8, 128.3, 128.5, 143.8, 146.1, 147.0, 158.4 ppm. IR (film): ṽ = 3503, 1677, 1372, 1346, 1165 $cm^{-1}$. MS (EI): *m*/*z* = 452 [M + Na], 396, 378, 352, 334. HRMS: calcd. for $C_{28}H_{31}NO_3$ + Na 452.2201; found 452.2189.

**(2*S*,5*R*)-*tert*-Butyl 2-(Hydroxydiphenylmethyl)-5-phenylpyrrolidine-1-carboxylate (4b):** $[\alpha]_D^{20}$ = –113 (*c* = 1.0, $CHCl_3$). $^1H$ NMR (250 MHz, $CDCl_3$): δ = 1.14 (s, 9 H, 3 × $CH_3$), 1.19–1.39 (m, 2 H, $CH_2$), 1.96 (dtd, *J* = 12.6, 7.1, 1.8 Hz, 1 H), 2.12–2.37 (m, 1 H), 4.64 (dd, *J* = 10.3, 7.0 Hz, 1 H, CH), 5.09 (dd, *J* = 9.3, 2.5 Hz, 1 H, CH), 6.44 (br. s, 1 H, OH), 6.85–6.89 (m, 2 H, Ar), 7.14–7.35 (m, 9 H, Ar), 7.44–7.48 (m, 2 H, Ar), 7.53–7.57 (m, 2 H, Ar) ppm. $^{13}C$ NMR (62.5 MHz, $CDCl_3$): δ = 27.8, 29.0, 34.1, 64.8, 67.9, 81.2, 81.3, 125.8, 126.3, 126.9, 127.0, 127.5, 127.5, 127.7, 127.8, 128.5, 143.4, 143.7, 147.2, 159.2 ppm. IR (film): ṽ = 3370, 1655, 1350 $cm^{-1}$. MS (EI): *m*/*z* = 357, 356, 313, 312, 216. HRMS: calcd. for $C_{28}H_{31}NO_3$ + H 430.2382; found 430.2340.

**General Procedure for the Asymmetric Arylation of Aldehydes:** In a round-bottomed flask, under an argon atmosphere, diethylzinc (2.1 mmol, toluene solution) was added dropwise to a solution of boronic acid (0.72 mmol) in toluene (1.5 mL) under an argon atmosphere. After stirring for 12 h at 60 °C, the mixture was cooled to room temperature and a toluene solution of chiral amino alcohol (10 mol-%) was introduced. The reaction was stirred for an additional 15 min, cooled to 0 °C, and the aldehyde (0.3 mmol) was subsequently added. After stirring for 6 h at 0 °C, the reaction was quenched with water and saturated $NH_4Cl$. The aqueous layer was extracted with dichloromethane, and the combined organic layer was dried with $MgSO_4$, filtered, and concentrated. Purification by flash chromatography (hexanes/ethyl acetate) afforded the pure diarylmethanols, as well as recovery of the chiral amino alcohol in good yields (>90%). Enantiomeric ratios were measured by HPLC.

**Phenyl(*p*-tolyl)methanol (10a and 10j):** Yield: **10a**, 0.059 g (98%); **10j**, 0.054 g (90%). $^1H$ NMR (250 MHz, $CDCl_3$): δ = 2.27 (br. s, 1 H, OH), 2.31 (s, 3 H, $CH_3$), 5.77 (s, 1 H, CH), 7.12 (d, *J* = 8.0 Hz, 2 H, Ar), 7.22–7.37 (m, 7 H, Ar) ppm. $^{13}C$ NMR (62.5 MHz, $CDCl_3$): δ = 21.1, 76.0, 126.4, 126.5, 127.4, 128.4, 129.1, 137.2, 140.9, 143.9 ppm. HPLC (Chiralcel OD-H; hexane/*i*PrOH, 90:10; 0.5 mL $min^{-1}$): $t_R$ = 16.5 (*S*), 18.2 (*R*) min.

**Phenyl(*o*-tolyl)methanol (10b):** Yield: 0.055 g (91%). $^1H$ NMR (250 MHz, $CDCl_3$): δ = 2.17 (br. s, 1 H, OH), 2.42 (s, 3 H, $CH_3$), 6.00 (s, 1 H, CH), 7.11–7.38 (m, 8 H, Ar), 7.51 (d, *J* = 7.0 Hz, 1 H, Ar) ppm. $^{13}C$ NMR (62.5 MHz, $CDCl_3$): δ = 19.4, 73.4, 126.1, 126.2, 127.1, 127.5, 127.6, 128.5, 130.5, 135.3, 141.4, 142.8 ppm. HPLC (Chiralcel OD-H; hexane/*i*PrOH, 98:02; 0.5 mL $min^{-1}$): $t_R$ = 28.3 (*R*), 30.9 (*S*) min.

**(4-Chlorophenyl)(phenyl)methanol (10c):** Yield: 0.062 g (94%). $^1H$ NMR (250 MHz, $CDCl_3$): δ = 2.51 (br. s, 1 H, OH), 5.74 (s, 1 H, CH), 7.22–7.33 (m, 9 H, Ar) ppm. $^{13}C$ NMR (62.5 MHz, $CDCl_3$): δ = 75.5, 126.5, 127.7, 127.8, 128.5, 128.6, 133.2, 142.1, 143.3 ppm. HPLC (Chiralpak AD-H; hexane/*i*PrOH, 90:10; 1.0 mL $min^{-1}$): $t_R$ = 8.3 (*R*), 9.0 (*S*) min.

**(2-Chlorophenyl)(phenyl)methanol (10d):** Yield: 0.061 g (93%). $^1H$ NMR (500 MHz, $CDCl_3$): δ = 2.35 (d, *J* = 3.5 Hz, 1 H, OH), 6.23 (d, *J* = 3.5 Hz, 1 H, CH), 7.22 (dt, *J* = 7.5, 1.5 Hz, 1 H, Ar), 7.25–7.32 (m, 3 H, Ar), 7.34 (d, *J* = 7.5 Hz, 2 H, Ar), 7.39 (d, *J* = 7.5 Hz, 2 H, Ar), 7.60 (dd, *J* = 8.0, 1.5 Hz, 1 H, Ar) ppm. $^{13}C$ NMR (125 MHz, $CDCl_3$): δ = 72.7, 126.9, 127.1, 127.8, 128.0, 128.5, 128.8, 129.5, 132.5, 141.0, 142.2 ppm. HPLC (Chiralcel OD-H; hexane/*i*PrOH, 95:05; 1.0 mL $min^{-1}$): $t_R$ = 10.2 (*R*), 11.6 (*S*) min.

**(4-Bromophenyl)(phenyl)methanol (10e and 10m):** Yield: **10e**, 0.074 g (94%); **10m**, 0.076 g (96%). $^1H$ NMR (250 MHz, $CDCl_3$): δ = 2.41 (br. s, 1 H, OH), 5.65 (s, 1 H, CH), 7.13 (d, *J* = 8.5 Hz, 2 H, Ar), 7.16–7.26 (m, 5 H, Ar), 7.35 (d, *J* = 8.5 Hz, 2 H, Ar) ppm. $^{13}C$ NMR (62.5 MHz, $CDCl_3$): δ = 75.6, 121.3, 126.5, 127.8, 128.2, 128.6, 131.5, 142.6, 143.3 ppm. HPLC (Chiralcel OB; hexane/*i*PrOH, 90:10; 0.5 mL $min^{-1}$): $t_R$ = 23.4 (*R*), 33.1 (*S*) min.

**(2-Bromophenyl)(phenyl)methanol (10f):** Yield: 0.072 g (92%). $^1H$ NMR (500 MHz, $CDCl_3$): δ = 2.38 (d, *J* = 4.0 Hz, 1 H, OH), 6.19 (d, *J* = 4.0 Hz, 1 H, CH), 7.14 (dt, *J* = 7.5, 1.5 Hz, 1 H, Ar), 7.27 (tt, *J* = 7.5, 1.5 Hz, 1 H, Ar), 7.30–7.36 (m, 3 H, Ar), 7.40 (d, *J* = 7.5 Hz, 2 H, Ar), 7.53 (dd, *J* = 8.0, 1.5 Hz, 1 H, Ar), 7.58 (dd, *J* = 8.0, 2.0 Hz, 1 H, Ar) ppm. $^{13}C$ NMR (125 MHz, $CDCl_3$): δ = 74.8, 122.8, 127.0, 127.7, 127.8, 128.4, 128.5, 129.1, 132.8, 142.1, 142.5 ppm. HPLC (Chiralcel OD-H; hexane/*i*PrOH, 90:10; 1.0 mL $min^{-1}$): $t_R$ = 9.3 (*R*), 10.8 (*S*) min.

**(3-Fluorophenyl)(phenyl)methanol (10g):** Yield: 0.046 g (75%). $^1H$ NMR (250 MHz, $CDCl_3$): δ = 2.30 (s, 1 H, OH), 5.82 (s, 1 H, CH), 6.94 (tdd, *J* = 8.3, 2.5, 0.8 Hz, 1 H, Ar), 7.08–7.17 (m, 2 H, Ar), 7.24–7.37 (m, 6 H, Ar) ppm. $^{13}C$ NMR (62.5 MHz, $CDCl_3$): δ = 75.6 (d, *J* = 1.9 Hz), 113.4 (d, *J* = 21.9 Hz), 114.4 (d, *J* = 21.3 Hz), 122.0 (d, *J* = 2.5 Hz), 126.5, 127.9, 128.6, 129.9 (d, *J* = 8.1 Hz), 143.3, 146.2, 163.0 (d, *J* = 243.7 Hz) ppm. HPLC (Chiralcel OB; hexane/*i*PrOH, 95:05; 0.5 mL $min^{-1}$): $t_R$ = 23.1 (*R*), 24.6 (*S*) min.

**(4-Methoxyphenyl)(phenyl)methanol (10h and 10l):** Yield: **10h**, 0.058 g (91%); **10l**, 0.053 g (83%). $^1H$ NMR (250 MHz, $CDCl_3$): δ = 2.22 (br. s, 1 H, OH), 3.78 (s, 3 H, $OCH_3$), 5.80 (s, 1 H, CH), 6.86 (d, *J* = 8.5 Hz, 2 H, Ar), 7.24–7.39 (m, 7 H, Ar) ppm. $^{13}C$ NMR (62.5 MHz, $CDCl_3$): δ = 55.2, 75.8, 113.8, 126.4, 127.4, 127.9, 128.4, 136.1, 144.0, 159.0 ppm. HPLC (Chiralpak AD-H; hexane/*i*PrOH, 90:10; 1.0 mL $min^{-1}$): $t_R$ = 11.9 (*R*), 12.8 (*S*) min.

**Furan-2-yl(phenyl)methanol (10i):** Yield: 0.047 g (89%). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 2.46 (br. s, 1 H, OH), 5.82 (s, 1 H, CH), 6.11 (dt, $J$ = 3.3, 0.8 Hz, 1 H, C$H_{furyl}$), 6.31 (dd, $J$ = 3.3, 1.8 Hz, 1 H, C$H_{furyl}$), 7.26–7.46 (m, 6 H, Ar and C$H_{furyl}$) ppm. $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ = 70.1, 107.4, 110.2, 126.6, 128.1, 128.5, 140.7, 142.5, 155.9 ppm. HPLC (Chiralcel OD-H; hexane/*i*PrOH, 97:03; 1.0 mL min$^{-1}$): $t_R$ = 21.1 (*S*), 24.8 (*R*) min.

**Biphenyl-4-yl(phenyl)methanol (10k):** Yield: 0.077 g (98%). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 2.41 (br. s, 1 H, OH), 5.74 (s, 1 H, CH), 7.11–7.34 (m, 10 H, Ar), 7.42–7.48 (m, 4 H, Ar) ppm. $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ = 76.0, 126.5, 126.9, 127.0, 127.2, 127.3, 127.6, 128.5, 128.7, 140.4, 140.7, 142.8, 143.7 ppm. HPLC (Chiralcel OB; hexane/*i*PrOH, 95:05; 1.0 mL min$^{-1}$): $t_R$ = 36.3 (*R*), 61.4 (*S*) min.

**(4-Chlorophenyl)(4-methoxyphenyl)methanol (10n):** Yield: 0.053 g (71%). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 2.40 (br. s, 1 H, OH), 3.77 (s, 3 H, $OCH_3$), 5.73 (s, 1 H, CH), 6.85 (d, $J$ = 8.8 Hz, 2 H, $Ar_{OMe}$), 7.22 (d, $J$ = 8.8 Hz, 2 H, $Ar_{OMe}$), 7.28 (s, 4 H, $Ar_{Cl}$) ppm. $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ = 55.2, 75.1, 113.9, 127.7, 127.9, 128.5, 133.0, 135.7, 142.4, 159.1 ppm. HPLC (Chiralcel OD-H; $\lambda$ = 216 nm; hexane/*i*PrOH, 98:02; 0.5 mL min$^{-1}$): $t_R$ = 88.3 (*S*), 95.5 (*R*) min.

**(4-Chlorophenyl)(*p*-tolyl)methanol (10o):** Yield: 0.068 g (98%). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 2.31 (s, 3 H, $CH_3$), 5.70 (s, 1 H, CH), 7.11 (d, $J$ = 8.0 Hz, 2 H, $Ar_{Me}$), 7.18 (d, $J$ = 8.0 Hz, 2 H, $Ar_{Me}$), 7.26 (s, 4 H, $Ar_{Cl}$) ppm. $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ = 21.1, 75.3, 126.4, 127.7, 128.5, 129.2, 133.0, 137.5, 140.5, 142.3 ppm. HPLC (Chiralcel OD-H; hexane/*i*PrOH, 98:02; 0.5 mL min$^{-1}$): $t_R$ = 49.9 (*R*), 52.6 (*S*) min.

**Biphenyl-4-yl(furan-2-yl)methanol (10p):** Yield: 0.074 g (98%). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 2.58 (br. s, 1 H, OH), 5.85 (s, 1 H, CH), 6.16 (d, $J$ = 3.3 Hz, 1 H, C$H_{furyl}$), 6.32 (dd, $J$ = 3.3, 2.0 Hz, 1 H, C$H_{furyl}$), 7.30–7.51 (m, 6 H, Ar), 7.55–7.62 (m, 4 H, Ar) ppm. $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ = 70.0, 107.5, 110.2, 127.0, 127.1, 127.2, 127.3, 128.7, 139.8, 140.7, 140.9, 142.6, 155.8 ppm. HPLC (Chiralcel OB; hexane/*i*PrOH, 95:05; 1.0 mL min$^{-1}$): $t_R$ = 37.3 (*S*), 49.9 (*R*) min.

**Supporting Information** (see footnote on the first page of this article): Copies of the NMR spectra of compounds **5**–**9**; data of X-ray diffraction analysis of *N*-Boc amino alcohol **4b**.

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