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PAPER

Asymmetric additive-free aryl addition to aldehydes using perhydrobenzoxazines as ligands and boroxins as aryl source†‡

Rebeca Infante, Javier Nieto* and Celia Andrés*

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A highly efficient enantioselective aryl addition to aldehydes using boroxins as aryl source and conformationally restricted perhydro-1,3-benzoxazines as ligands is reported. Both enantiomeric forms of chiral arylphenylmethanols and 1,1′-disubstituted diarylmethanols are afforded with excellent yields and enantioselectivities using the same ligand by means of an appropriate combination of boroxin and aromatic aldehyde. The enantiocontrol is not significantly influenced by electronic effects or steric hindrance, even with substituted boroxins. Very homogeneous ee's are reached when substituted arylboroxins are employed, without the use of any class of additive or pre-treatment.

Introduction

The enantioselective synthesis of diarylmethanols has been the focus of many catalytic studies, due to the value of these compounds as useful precursors of numerous molecules with important pharmacological properties, such as antihistaminic, antiarrhythmic, diuretic, laxative, antidepressive, local-anesthetic and anticholinergic.[1] So far, one of the most efficient and simple approaches to their preparation is the asymmetric arylzinc addition to aromatic aldehydes in the presence of a chiral ligand to form the C–C bond and the stereocenter. In this context, the *in situ* generation of arylzinc reagents through a boron-to-zinc transmetallation process constitutes an important advance.[2]

In 2002, Bolm *et al.* reported a general protocol for the *in situ* synthesis of arylzinc species from arylboronic acids and diethylzinc.[3] One important advantage of this methodology is that many aryl boronic acids are commercially available at a convenient price or can be easily prepared.[4] However, a significant drawback of this method is the large amount of diethylzinc necessary for the transmetallation step due to the acidity of boronic acids. More recently, the introduction of triarylboroxins, which can be easily prepared by heating of the corresponding aryl boronic acid, has permitted a significant reduction of the amount of zinc reagent.[5] In addition, boroxins represent the most atom-economical source of aryl groups, and they could also been applied in an industrial process.[6] Theoretical and experimental studies performed by Pericàs have demonstrated that the boron-to-zinc transmetallation step is a fast process, in contrast to the long reaction times described in previous reports.[5d]

The most important feature of this methodology is that the synthesis of either enantiomer of a diarylmethanol is feasible with the same chiral ligand by means of an appropriate combination of arylboronic acid or triarylboroxin and aromatic aldehyde. Nevertheless, the efficiency and enantioselectivity of these complementary processes usually differ significantly, especially when neither additives nor pre-treatments are employed.[7] Subsequently, we thought that it was necessary to explore new ligands in order to overcome this weakness. Considering the excellent and homogeneous results obtained with conformationally restricted perhydro-1,3-benzoxazines as ligands for the enantioselective ethylation of aldehydes,[8] we decided that these compounds could also catalyze the asymmetric addition of arylboroxins to aryl aldehydes and keep high levels of efficiency and selectivity for both enantiomeric diarylmethanols.

Results and discussion

The asymmetric arylation of 2-naphthaldehyde by means of diethylzinc and phenylboroxin as the aryl source in the presence of catalytic amounts of perhydrobenzoxazines **1a–f** derived from (–)-8-aminomenthol was chosen as a reaction model to examine both the reaction conditions and the efficiency of these ligands, previously synthesized in our laboratory (Fig. 1).[8–10]

This reaction is known to occur in two steps, which involve a boron-to-zinc transmetallation and the addition of the *in situ* generated zinc reagent to the carbonyl component. For the formation of the zinc reagent we initially employed Pericàs' protocol, which requires the heating of a 1 : 4 mixture of triphenylboroxin and diethylzinc in toluene at 60 °C for 30 min,[5d] although the influence of the aryl source and the diethylzinc solvent was also studied. Concerning the addition step, several reaction parameters, such

Instituto CINQUIMA and Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Valladolid, Dr Mergelinas/n, 47011 Valladolid, Spain. E-mail: javiernr@qo.uva.es

† Dedicated to the memory of Prof. Rafael Suau.

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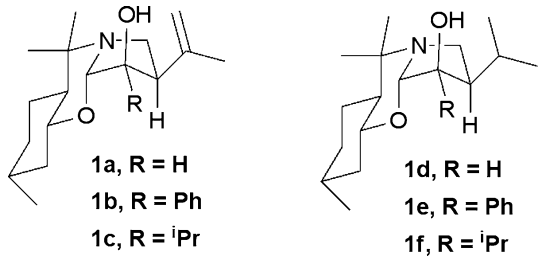
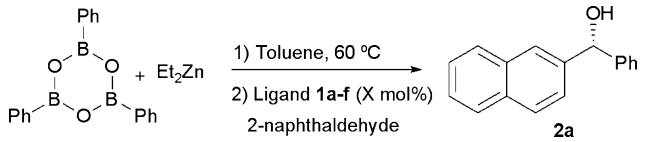


Fig. 1 Perhydrobenzoxazines **1a–f**.

Table 1 Some representative results from screening of reaction conditions for the asymmetric phenyl addition to 2-naphthaldehyde catalyzed by **1a–1f**



Entry[a]	Ligand (mol%)	T/°C	Time (min)	Yield (%)[b]	ee (%)[c,d]
1[e]	**1e** (10)	0	60	90	92
2[f]	**1e** (10)	0	60	91	91
3	**1e** (10)	0	60	98	94
4	**1e** (10)	0	30	97	94
5	**1e** (10)	25	60	97	87
6	**1e** (10)	–20	60	89	91
7	**1e** (5)	0	60	88	92
8	**1e** (1)	0	60	70	83
9	**1a** (10)	0	60	82	42
10	**1b** (10)	0	60	81	68
11	**1c** (10)	0	60	89	70
12	**1d** (10)	0	60	95	60
13	**1f** (10)	0	60	87	11

[a] $(PhBO)_3/ZnEt_2$/aldehyde = 0.6 : 2.4 : 1. [b] Yield of product after purification by flash chromatography. [c] Determined by HPLC analysis using a chiral Chiralpak AS-H column. [d] Configuration of the predominant enantiomer of the product was determined by comparison with the literature data. [e] Phenylboronic acid was employed instead of triphenylboroxin. $PhB(OH)_2/ZnEt_2$/aldehyde = 1.2 : 3.8 : 1. [f] A mixture toluene/hexane 1 : 1 was used as solvent.

as temperature, reaction time, catalyst loading and catalyst, were examined. The results are collected in Table 1.

When phenylboronic acid was used as the aryl source and the addition step was carried out at 0 °C, employing 10 mol% of ligand **1e**, the product **2a** was obtained in good yield and enantioselectivity (entry 1). Although good enantioselectivities had been previously found for the addition of arylboroxins to aldehydes, those values were usually slightly lower and less uniform than those obtained with the corresponding arylboronic acids.[5e,7a] Nevertheless, the opposite behavior was shown by our ligand, and triphenylboroxin led under the same conditions to the product in higher yield and improved enantioselection (entry 3). Besides, a substantial reduction of the amount of diethylzinc (2.4 equiv for the boroxin *vs.* 3.8 equiv for the boronic acid) was possible as previously reported,[5a] so triarylboroxins were chosen as optimal aryl sources. With regard to the solvent, toluene was found to be superior to hexane in terms of yield and selectivity (entries 2, 3).

It can also be observed that the results were not affected by the reduction of the reaction time for the addition step, and the product could be isolated almost quantitatively after 30 min with an excellent enantiocontrol (entry 4). Temperature variations indicated a maximal enantioselectivity in the reactions performed at 0 °C. In this context, when the reaction was run at room temperature, the chemical yield remained in the same level, but lower enantiomeric excess was observed (entry 5). Conversely, a lower temperature, such as –20 °C, resulted in a decrease of both enantioselectivity and yield (entry 6).

No detrimental effect on enantioselectivity was perceived when the amount of ligand was reduced to 5 mol% (entry 7). Even at lower catalyst loading, diarylmethanol **2a** was obtained with good yield and substantial enantioselection (83% ee, entry 8). It is remarkable that only the most efficient ligands keep the enantioselectivity at 5 mol%, but very few of them are able to reach good levels of selectivity at 1 mol%, especially without any class of additive.[11] Additionally, that reduction is usually more noteworthy in the cases where the aryl source is a boroxin.[5a,c,e]

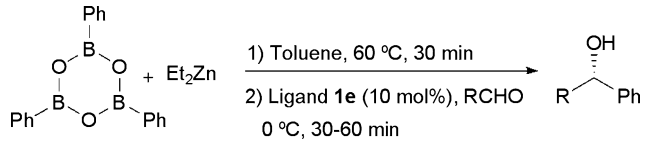
Next, the effect of the substituent on the stereogenic center which supports the hydroxyl group in the ligand structure was studied (entries 3, 12 and 13). The use of the secondary alcohol **1d** led to the product with a moderate selectivity (entry 12). Interestingly, the replacement of the phenyl group in **1e** by an isopropyl substituent (**1f**) had a dramatic effect on the enantiocontrol of the process (entries 3, 13). On the other hand, the unsaturated analogs bearing an isopropenyl group (**1a–1c**), instead of an isopropyl group, were also explored as ligands (entries 9–11). In these cases, the chemical yields were also good, but the enantioselectivity was not improved with respect to **1e**. In summary, these results demonstrate that a tertiary alcohol is necessary on the perhydrobenzoxazine structure in order to obtain good enantioselectivities and they also showed that the stereocenter substitution is critical, so the optimal ligand was **1e**.

Once we had established the optimal reaction conditions, our attention was turned to exploit the possibility to vary the structure of the aldehyde and study the asymmetric phenyl addition to a series of substrates with different steric and electronic properties. These results are summarized in Table 2.

To our delight, steric effects did not play an important role in the enantioselection. For instance, *ortho*-substituted benzaldehydes underwent the phenyl addition with excellent ee values as well as their *para* analogs (entries 2, 3 *vs.* 7 and 8). Besides, very interesting was the uniformly high enantiocontrol achieved with *p*-tolualdehyde, *o*-tolualdehyde and *p*-chlorobenzaldehyde (93–97% ee; entries 2, 7 and 9), because the corresponding addition products are high-value building blocks for the medically useful antihistaminics neobenodine, phenadrine and clemastine. The highest ee was obtained by using *o*-tolualdehyde, which furnished the desired (*R*)-(phenyl)(*o*-tolyl)methanol **2b** with 97% ee in 88% yield (entry 2). Phenylation of electron-deficient aldehydes, such as *p*-chloro and the highly reactive *p*-trifluoromethylbenzaldehydes, provided the corresponding alcohols **2i** and **2j** in high yields with very high levels of enantioselection, 93% and 91% ee respectively (entries 9 and 10). Further investigations into heteroaromatic aldehydes, such as 2-furfural and 2-thienal, and α,β-unsaturated aldehydes were carried out, and the corresponding products were delivered with good to high ee's (81–91% ee, entries 11–15) and excellent yields in all cases.

As we commended in the introduction, both enantiomers became accessible with a single catalyst, although it is known that the efficiency of these complementary approaches can differ

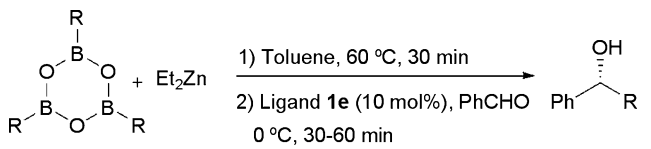
Table 2 Catalytic asymmetric phenyl transfer to several aldehydes in the presence of **1e**



Entry[a]	R	Product	Yield (%)[b]	ee (%)[c,d]
1	2-naphthyl	**2a**	98	94
2	*o*-$CH_3C_6H_4$	**2b**	88	97
3	*o*-$OCH_3C_6H_4$	**2c**	97	93
4	*o*-ClC_6H_4	**2d**	92	88
5	*o*-BrC_6H_4	**2e**	83	90
6	*m*-ClC_6H_4	**2f**	96	91
7	*p*-$CH_3C_6H_4$	**2g**	86	95
8	*p*-$OCH_3C_6H_4$	**2h**	93	96
9	*p*-ClC_6H_4	**2i**	98	93
10	*p*-$CF_3C_6H_4$	**2j**	93	91
11	2-furyl	**2k**	82	85
12	2-thienyl	**2l**	85	91
13	(*E*)-$C_6H_5CH{=}CH$	**2m**	94	82
14	(*E*)-*p*-$OCH_3C_6H_4CH{=}CH$	**2n**	83	81
15	(*E*)-2-(2-furyl)vinyl	**2o**	92	87

[a] **1e**/$(PhBO)_3$/$ZnEt_2$/aldehyde = 0.1 : 0.6 : 2.4 : 1. [b] Yield of product after purification by flash chromatography. [c] Determined by chiral HPLC analysis, see experimental for full details. [d] Configuration of the predominant enantiomer of the product was determined by comparison with the literature data.

Table 3 Catalytic asymmetric aryl transfer to benzaldehyde in the presence of **1e**



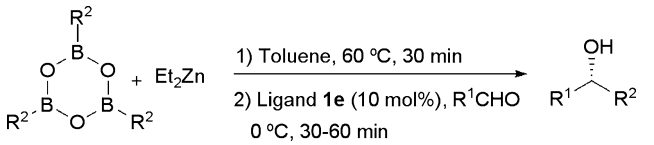
Entry[a]	R	Product	Yield (%)[b]	ee (%)[c,d]
1	2-naphthyl	*ent*-**2a**	89	95
2	*o*-$CH_3C_6H_4$	*ent*-**2b**	97	94
3	*p*-$CH_3C_6H_4$	*ent*-**2g**	93	97
4	*p*-$OCH_3C_6H_4$	*ent*-**2h**	95	94
5	*p*-ClC_6H_4	*ent*-**2i**	94	88

[a] **1e**/$(ArBO)_3$/$ZnEt_2$/aldehyde = 0.1 : 0.6 : 2.4 : 1. [b] Yield of product isolated after purification by flash chromatography. [c] Determined by chiral HPLC analysis, see experimental for full details. [d] Configuration of the predominant enantiomer of the product was determined by comparison with the literature data.

considerably.[4a,4d,7] In order to examine whether different aryl groups could be transferred to aldehydes with the same stereoselectivity, the asymmetric aryl transfer reactions of some substituted triarylboroxins to benzaldehyde were examined (Table 3).

Surprisingly, we could observe that the efficiency of the catalytic system was maintained very high in all cases, independent of the electronic and steric effects. For example, benzaldehyde underwent smooth *p*-methoxyphenyl addition with 94% ee (entry 4), and the aryl transfer from tri(*p*-chloropheny)lboroxin to benzaldehyde afforded the product with 94% yield and 88% ee (entry 5). In contrast to previously published results,[12] an *ortho*-substituted arylboroxin was perfectly tolerated and the corresponding alcohol was isolated with as high enantioselectivity as other substrates.

Table 4 Catalytic asymmetric aryl transfer to several substituted aldehydes in the presence of **1e**



Entry[a]	R^1	R^2	Product	Yield (%)[b]	ee (%)[c,d]
1	*p*-ClC_6H_4	*o*-$CH_3C_6H_4$	**2p**	81	89
2	*o*-$CH_3C_6H_4$	*p*-ClC_6H_4	*ent*-**2p**	99	94
3	*p*-ClC_6H_4	*p*-$CH_3C_6H_4$	**2q**	98	97
4	*p*-$CH_3C_6H_4$	*p*-ClC_6H_4	*ent*-**2q**	99	84
5	*p*-$CH_3C_6H_4$	2-naphthyl	**2r**	99	98
6	2-naphthyl	*p*-$CH_3C_6H_4$	*ent*-**2r**	90	95
7	*p*-$OCH_3C_6H_4$	2-naphthyl	**2s**	84	92
8	2-naphthyl	*p*-$OCH_3C_6H_4$	*ent*-**2s**	90	94
9	*p*-ClC_6H_4	2-naphthyl	**2t**	99	93
10	2-naphthyl	*p*-ClC_6H_4	*ent*-**2t**	94	88
11	*p*-$CF_3C_6H_4$	2-naphthyl	**2u**	88	90
12	*p*-$CF_3C_6H_4$	*o*-$CH_3C_6H_4$	**2v**	95	89
13	*p*-$CF_3C_6H_4$	*p*-$CH_3C_6H_4$	**2w**	91	89
14[e]	*p*-$CH_3C_6H_4$	*p*-$CF_3C_6H_4$	*ent*-**2w**	34	95
15	*p*-$CF_3C_6H_4$	*p*-ClC_6H_4	**2x**	96	96

[a] **1e**/$(ArBO)_3$/$ZnEt_2$/aldehyde = 0.1 : 0.6 : 2.4 : 1. [b] Yield of product isolated after purification by flash chromatography. [c] Determined by chiral HPLC analysis, see experimental for full details. [d] Configuration of the predominant enantiomer of the product was determined by comparison with the literature data. [e] 10 mol% of DiMPEG (MW 2000) was used as additive. The product was isolated as a racemic mixture without any class of additive.

In this way, (*S*)-(phenyl)(*o*-tolyl)methanol *ent*-**2b** was readily obtained in 97% yield with 94% ee (entry 2). Even the bulky tri(2-naphthyl)lboroxin allowed the desired alcohol *ent*-**2a** to be obtained with good yield and very high enantioselection (95% ee, entry 1). An excellent result was reached for the reaction between tri(*p*-tolyl)boroxin and benzaldehyde, obtaining 97% ee (entry 3).

With this gratifying ligand in our hands and the excellent results achieved, we were wondering about the flexibility of this methodology with the goal to investigate the preparation of more functionalized molecules, like 1,1′-disubstituted diarylmethanols. To this aim, a series of reverse combinations of both substituted boroxins and aldehydes was explored, and the results are summarized in Table 4.

In general, both enantiomers of a given product could be easily obtained in good yields and high enantioselectivities by means of the same ligand **1e**, independently of the substitution on the triarylboroxin or the aldehyde employed (entries 1–10). For example, the reaction between *p*-tolualdehyde and tri(2-naphthyl)lboroxin yielded the corresponding product **2r** quantitatively with 98% ee (entry 5). Complementarily, when the reverse combination of substrates was employed (*i.e.*, 2-naphthaldehyde and tri(*p*-tolyl)lboroxin, entry 6), the enantiomeric product *ent*-**2r** was also afforded in good yield with no significant reduction in the enantioselectivity. In a similar way, the enantiomeric partners **2p** - *ent*-**2p**, **2q** - *ent*-**2q**, **2s** - *ent*-**2s** and **2t** - *ent*-**2t** were isolated with good or excellent yields and selectivities, observing only minor differences in terms of ee between the couples (entries 1–2, 7–10), with the only exception of *p*-chlorophenyl-*p*-tolyl-methanol (entries 3–4).

In order to study the effect of the triarylboroxin in the arylation of the challenging electron-poor *p*-trifluoromethylbenzaldehyde, a set of experiments was carried out (entries 11–13, 15). To our surprise, the results in terms of chemical yield and enantioselectivity were excellent as well, even with boroxins bearing electron-withdrawing groups, such as a chlorine atom (entry 15) or an *ortho* substituent (entry 12). Even more challenging was the use of the electronically deficient tri(*p*-trifluoromethylphenyl)boroxin as the aryl source, as in the only previous report[5d] the product was obtained in a racemic way. In fact, the alcohol *ent*-**2w** was isolated as a racemate when ligand **1e** was employed under the standard conditions (entry 14). Nevertheless, although a modest yield of product *ent*-**2w** was also obtained, an unprecedented extraordinary enantioselectivity was achieved when 10 mol% of DiMPEG [dimethoxypoly-(ethylene glycol), MW 2000] was used (95% ee, entry 14).[13]

Conclusions

In summary, we have developed a new catalytic system for the enantioselective arylation of aromatic aldehydes using chiral perhydro-1,3-benzoxazines as ligands. The reactions occur in very good yields and with excellent enantiocontrol without any pretreatment or additive for a wide variety of aromatic, heteroaromatic and α,β-unsaturated aldehydes. Furthermore, the high efficiency is virtually independent of the electronic and steric characteristics when different substituted triarylboroxins are transferred to the same aldehyde, allowing the use of *ortho*-substituted triarylboroxins and bulky triarylboroxins.

In addition, the appropriate choice of the two reaction partners, boroxin and aldehyde, gives access to both enantiomers of the 1,1′-diarylmethanols with the same catalyst and similarly high enantioselectivity.

Experimental

All reactions were carried out in anhydrous solvents under argon atmosphere in flame-dried glassware by means of Schlenk techniques. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75 MHz) spectra were recorded in $CDCl_3$. Chemical shifts for protons are reported in ppm from tetramethylsilane with the residual $CHCl_3$ resonance as internal reference. Chemical shifts for carbons are reported in ppm from tetramethylsilane and are referenced to the carbon resonance of the solvent. Data are reported as follows: chemical shift, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; sp, septet; m, multiplet; br, broad), coupling constants in Hertz, and integration. Specific rotations were measured using a 5 mL cell with a 1 dm path length, and a sodium lamp, and concentration is given in g per 100 mL. Flash chromatography was carried out using silica gel (230–240 mesh). Chemical yields refer to pure isolated substances. TLC analysis was performed on glass-backed plates coated with silica gel 60 and an F_{254} indicator, and visualized by either UV irradiation or by staining with I_2 or ethanolic phosphomolybdic acid solution. Chiral HPLC analysis was performed using a Daicel Chiralcel OD Column, Chiralpak AD-H or Chiralpak AS-H. UV detection was monitored at 220 nm or at 254 nm. High resolution mass spectrometry analyses (HRMS) were performed by a quadrupole spectrometer with TOF analyzer.

Unless otherwise indicated, all compounds were purchased from commercial sources and used as received. All boronic acids used are commercially available or can be easily prepared.[14] Racemic samples were prepared by addition of Grignard reagents to the corresponding aldehydes. Triarylboroxins were freshly prepared by heating the corresponding arylboronic acid for 8 h at 110 °C in a conventional oven and used without further purification.

Ligands **1a–1f** were prepared according reported procedures.[8–10]

Typical procedure for enantioselective addition of aryls to aldehydes

To a suspension of triarylboroxin (0.3 mmol) in anhydrous toluene (0.5 mL) under argon atmosphere was added dropwise a 1.1 M solution of Et_2Zn in toluene (1.1 mL, 1.2 mmol). The resulting mixture was heated at 60 °C in a pre-heated bath for 30 min to give a clear solution. Once this solution was cooled to room temperature, a solution of ligand **1e** (18 mg, 0.05 mmol) in toluene (0.5 mL) was added. The resulting mixture was then cooled to 0 °C in an ice bath and after 15 min of stirring at that temperature, the aldehyde (0.5 mmol) was added. After 30–60 min, the reaction mixture was quenched with aqueous saturated NH_4Cl, extracted with CH_2Cl_2 (3 × 15 mL), dried over $MgSO_4$, filtered off, and the solvents were evaporated. Purification by silica gel column chromatography with different mixtures of ethyl acetate/hexane gave the pure alcohols. Enantiomeric excess was determined by chiral HPLC.

(*S*)-2-Naphthyl(phenyl)methanol (2a). This compound was obtained from benzaldehyde (51 μl, 0.5 mmol) and tri(2-naphthyl)boroxin (138.6 mg, 0.3 mmol) and purified by flash chromatography (ethyl acetate/hexane = 1 : 20). White solid ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.50 (br s, 1H, OH), 6.00 (s, 1H), 7.27–7.54 (m, 8H), 7.80–7.88 (m, 3H), 7.91 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 76.3 (CH), 124.7 (CH), 125.0 (CH), 125.9 (CH), 126.2 (CH), 126.7 (2CH), 127.6 (2CH), 128.0 (CH), 128.3 (CH), 128.5 (2CH), 132.8 (C), 133.2 (C), 141.0 (C), 143.6 (C). IR (KCl) ν 3398, 3058, 1602, 1508, 1493, 1452, 1023, 1266, 814, 738, 701 cm^{-1}. HPLC (Chiralpak AS-H, hexane : isopropanol = 90 : 10, 1 mL min^{-1}, λ = 254 nm) t_R = 8.2 min for enantiomer *R*, t_R = 9.3 min for enantiomer *S*. Configuration was assigned by comparing HPLC elution order with that of the literature data.[5a]

(*R*)-2-Naphthyl(phenyl)methanol (*ent*-2a). This compound is the enantiomer of **2a** and was obtained from 2-naphthaldehyde (78.2 mg, 0.5 mmol) and triphenylboroxin (93.6 mg, 0.3 mmol).

(*R*)-Phenyl(*o*-tolyl)methanol (2b). This compound was obtained from *o*-tolualdehyde (60 μl, 0.5 mmol) and triphenylboroxin (93.6 mg, 0.3 mmol). Both were purified by flash chromatography (ethylacetate/hexane = 1 : 20). White solid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.28 (s, 3H), 2.73 (br s, 1H, OH), 6.00 (s, 1H), 7.19–7.41 (m, 8H), 7.55 –7.57 (m, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.3 (CH_3), 73.2 (CH), 126.0 (CH), 126.2 (CH), 127.0 (2CH), 127.4 (CH), 127.5 (CH), 128.4 (2CH), 130.4 (CH), 135.3 (C), 141.3 (C), 142.7 (C). IR (Nujol) ν 3196, 2022, 1899, 1809, 1602, 1302, 1014, 765, 698 cm^{-1}. HPLC (Chiralpak AD-H, hexane : isopropanol = 99 : 1, 1 mL min^{-1}, λ = 220 nm) t_R = 28.0 min for enantiomer *R*, t_R = 31.0 min for enantiomer *S*. Configuration was assigned by comparing HPLC elution order with that of the literature data.[4f]

(*S*)-Phenyl(*o*-tolyl)methanol (*ent*-2b). This compound is enantiomer of **2b** and was obtained from benzaldehyde (51 µl, 0.5 mmol) and tri(*o*-tolyl)boroxin (106.3 mg, 0.3 mmol).

(*R*)-(*o*-Methoxyphenyl)(phenyl)methanol (2c). This compound was obtained from *o*-methoxybenzaldehyde (62 µl, 0.5 mmol) and triphenylboroxin (93.6 mg, 0.3 mmol) and purified by flash chromatography (ethylacetate/hexane = 1 : 10). White solid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.67 (br s, 1H, OH), 3.87 (s, 3H), 6.25 (s, 1H), 7.02 (d, J = 8.2 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 7.41–7.54 (m, 5H), 7.58–7.62 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 55.0 (CH_3), 71.4 (CH), 110.4 (CH), 120.5 (CH), 126.3 (2CH), 126.8 (CH), 127.4 (CH), 127.8 (2CH), 128.3 (CH), 131.8 (C), 143.2 (C), 156.3 (C). IR (Nujol) ν 3422, 3062, 3030, 2028, 1948, 1902, 1601, 1490, 1243, 1113, 1184, 1027, 856, 755, 699, 652 cm^{-1}. HPLC (Chiralcel OD, hexane : isopropanol = 98 : 2, 1 mL min^{-1}, λ = 220 nm) t_R = 42.3 min for enantiomer *S*, t_R = 53.5 min for enantiomer *R*. Configuration was assigned by comparing HPLC elution order with that of the literature data.[7b]

(*R*)-(*o*-Chlorophenyl)(phenyl)methanol (2d). This compound was obtained from *o*-chlorobenzaldehyde (56 µl, 0.5 mmol) and triphenylboroxin (93.6 mg, 0.3 mmol) and purified by flash chromatography (ethylacetate/hexane = 1 : 15). White solid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.29 (br s, 1H, OH), 6.19 (s, 1H), 7.22–7.44 (m, 8H), 7.64 (dd, J_1 = 7.7 Hz, J_2 = 1.8 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 72.3 (CH), 126.8 (2CH), 126.9 (CH), 127.6 (CH), 127.8 (CH), 128.3 (2CH), 128.5 (CH), 129.3 (CH), 132.2 (C), 140.8 (C), 142.1 (C).). IR (Nujol) ν 3338, 2019, 1491, 1308, 1183, 1055, 1020, 752, 698 cm^{-1}. HPLC (Chiralcel OD, hexane : isopropanol = 98 : 2, 1 mL min^{-1}, λ = 220 nm) t_R = 26.5 min for enantiomer *R*, t_R = 34.9 min for enantiomer *S*. Configuration was assigned by comparing HPLC elution order with that of the literature data.[15]

(*R*)-(*o*-Bromophenyl)(phenyl)methanol (2e). This compound was obtained from *o*-bromobenzaldehyde (92.2 mg, 0.5 mmol) and triphenylboroxin (93.6 mg, 0.3 mmol) and purified by flash chromatography (ethylacetate/hexane = 1 : 20). Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.61 (d, J = 3.7 Hz, 1H, OH), 6.19 (d, J = 3.5 Hz, 1H), 7.17 (td, J_1 = 7.7 Hz, J_2 = 1.8 Hz, 1H), 7.27–7.44 (m, 6H), 7.56 (dd, J_1 = 7.9 Hz, J_2 = 1.3 Hz, 1H), 7.60 (dd, J_1 = 7.7 Hz, J_2 = 1.8 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 74.7 (CH), 122.7 (C), 127.0 (2CH), 127.7 (2CH), 128.4 (3CH), 129.0 (CH), 132.8 (CH), 142.1 (C), 142.4 (C). IR (Film) ν 3347, 3064, 3031, 1654, 1569, 1494, 1466, 1452, 1438, 1184, 1016, 751, 720, 699 cm^{-1}. HPLC (Chiralcel OD, hexane : isopropanol = 98 : 2, 1 mL min^{-1}, λ = 220 nm) t_R = 29.0 min for enantiomer *R*, t_R = 42.2 min for enantiomer *S*. Configuration was assigned by comparing HPLC elution order with that of the literature data.[5a]

(*R*)-(*m*-Chlorophenyl)(phenyl)methanol (2f). This compound was obtained from *m*-chlorobenzaldehyde (58 µl, 0.5 mmol) and triphenylboroxin (93.6 mg, 0.3 mmol) and purified by flash chromatography (ethylacetate/hexane = 1 : 15). White solid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.11 (ps d, J = 3.3 Hz, 1H, OH), 5.70 (ps d, J = 2.8 Hz, 1H), 7.20–7.38 (m, 8H), 7.40 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 75.4 (CH), 124.5 (CH), 126.5 (3CH), 127.5 (CH), 127.8 (CH), 128.5 (2CH), 129.6 (CH) 134.2 (C), 143.0 (C), 145.6 (C). IR (Nujol) ν 3356, 3063, 3029, 2019, 1950, 1890, 1596, 1575, 1493, 1472, 1432, 1185, 1079, 1036, 1022, 888, 781, 765, 701 cm^{-1}. HPLC (Chiralcel OD, hexane : isopropanol = 98 : 2, 1 mL min^{-1}, λ = 220 nm) t_R = 41.5 min for enantiomer *S*, t_R = 45.9 min for enantiomer *R*. Configuration was assigned by comparing HPLC elution order with that of the literature data.[5a]

(*R*)-Phenyl(*p*-tolyl)methanol (2g). This compound was obtained from *p*-tolualdehyde (56 µl, 0.5 mmol) and triphenylboroxin (93.6 mg, 0.3 mmol) and purified by flash chromatography (ethylacetate/hexane = 1 : 20). White solid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.56 (s, 3H), 3.65 (br s, 1H, OH), 5.84 (s, 1H), 7.34 (ps d, J = 7.9 Hz, 2H), 7.43 (ps d, J = 8.1 Hz, 2H), 7.46–7.55 (m, 5H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 20.9 (CH_3), 75.5 (CH), 126.3 (2CH), 126.4 (2CH), 127.0 (CH), 128.1 (2CH), 128.8 (2CH), 136.7 (C), 140.8 (C), 143.8 (C). IR (Nujol) ν 3270, 3081, 2022, 1941, 1897, 1489, 1309, 1171, 1037, 1019, 795, 775, 692 cm^{-1}. HPLC (Chiralcel OD, hexane : isopropanol = 90 : 10, 0.8 mL min^{-1}, λ = 254 nm) t_R = 13.3 min for enantiomer *S*, t_R = 14.9 min for enantiomer *R*. (Chiralpak AS-H, hexane : isopropanol = 95 : 5, 1 mL min^{-1}, λ = 254 nm) t_R = 8.8 min for enantiomer *R*, t_R = 9.7 min for enantiomer *S*. Configuration was assigned by comparing HPLC elution order with that of the literature data.[5a]

(*S*)-Phenyl(*p*-tolyl)methanol (*ent*-2g). This compound is the enantiomer of **2g** and was obtained from benzaldehyde (51 µl, 0.5 mmol) and tri(*p*-tolyl)boroxin (106.3 mg, 0.3 mmol).

(*R*)-(*p*-Methoxyphenyl)(phenyl)methanol (2h). This compound was obtained from *p*-methoxybenzaldehyde (61 µl, 0.5 mmol) and triphenylboroxin (93.6 mg, 0.3 mmol) and purified by flash chromatography (ethylacetate/hexane = 1 : 15–1 : 10). White solid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.40 (br s, 1H, OH), 3.80 (s, 3H), 5.80 (s, 1H), 6.88 (ps d, J = 9.0 Hz, 2H), 7.27–7.41 (m, 7H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 55.0 (CH_3), 75.4 (CH), 113.6 (2CH), 126.3 (2CH), 127.1 (CH), 127.8 (2CH), 128.2 (2CH), 136.1 (C), 143.9 (C), 158.7 (C). IR (KBr) ν 3406, 3065, 2952, 2837, 1896, 1612, 1511, 1494, 1449, 1304, 1266, 1173, 1111, 1035, 810, 780, 729, 699 cm^{-1}. HPLC (Chiralpak AD-H, hexane : isopropanol = 90 : 10, 1 mL min^{-1}, λ = 220 nm) t_R = 14.2 min for enantiomer *R*, t_R = 15.3 min for enantiomer *S*. Configuration was assigned by comparing HPLC elution order with that of the literature data.[4h]

(*S*)-(*p*-Methoxyphenyl)(phenyl)methanol (*ent*-2h). This compound is the enantiomer of **2h** and was obtained from benzaldehyde (51 µl, 0.5 mmol) and tri(*p*-methoxyphenyl)boroxin (120.6 mg, 0.3 mmol).

(*R*)-(*p*-Chlorophenyl)(phenyl)methanol (2i). This compound was obtained from *p*-chlorobenzaldehyde (72.8 mg, 0.5 mmol) and triphenylboroxin (93.6 mg, 0.3 mmol) and purified by flash chromatography (ethylacetate/hexane = 1 : 15). White solid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.00 (ps d, J = 3.3 Hz, 1H, OH), 5.64 (ps d, J = 3.1 Hz, 1H), 7.26 (ps d, J = 8.3 Hz, 2H), 7.33–7.45 (m, 7H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 75.1 (CH), 126.3 (2CH), 127.5 (CH), 127.7 (2CH), 128.3 (4CH), 132.8 (C), 141.9 (C), 143.1 (C).). IR (Nujol) ν 3337, 3086, 3064, 1958, 1911, 1491, 1271, 1181, 1092, 1034, 1013, 791, 760, 742, 720, 702 cm^{-1}. HPLC (Chiralpak AD-H, hexane : isopropanol = 90 : 10, 1 mL min^{-1}, λ = 220 nm) t_R = 8.6 min for enantiomer *R*, t_R = 9.3 min for enantiomer *S*. Configuration was assigned by comparing HPLC elution order with that of the literature data.[4h]

(*S*)-(*p*-Chlorophenyl)(phenyl)methanol (*ent*-2i). This compound is the enantiomer of **2i** and was obtained from benzaldehyde (51 µl, 0.5 mmol) and tri(*p*-chlorophenyl)boroxin (124.2 mg, 0.3 mmol).

(*R*)-Phenyl(*p*-(trifluoromethyl)phenyl)methanol (2j). This compound was obtained from *p*-(trifluromethyl)benzaldehyde (69 µl, 0.5 mmol) and triphenylboroxin (93.6 mg, 0.3 mmol) and purified by flash chromatography (ethylacetate/hexane = 1 : 10). White solid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.53 (br s, 1H, OH), 5.74 (br s, 1H), 7.31–7.42 (m, 5H), 7.46 (ps d, J = 8.1 Hz, 2H), 7.61 (ps d, J = 8.1 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 75.5 (CH), 124.1 (q, $J_{C\text{-}F}$ = 272 Hz, 1C), 125.2 (CH), 125.3 (CH), 126.6 (4CH), 128.0 (CH), 128.6 (2CH), 129.5 (q, $J_{C\text{-}CF}$ = 32 Hz, 1C), 143.0 (C), 147.4 (C). ^{19}F-NMR (282 MHz, $CDCl_3$) δ –62.76 (s, 3F). IR (KBr) ν 3371, 3068, 3029, 2637, 1932, 1618, 1493, 1450, 1419, 1329, 1163, 1125, 1112, 1068, 1016, 731, 698 cm^{-1}. HPLC (Chiralcel OD, hexane : isopropanol = 90 : 10, 1 mL min^{-1}, λ = 220 nm) t_R = 11.1 min for enantiomer *R*, t_R = 12.3 min for enantiomer *S*. Configuration was assigned by comparing HPLC elution order with that of the literature data.[16]

(*R*)-2-Furyl(phenyl)methanol (2k). This compound was obtained from 2-furfural (42 µl, 0.5 mmol) and triphenylboroxin (93.6 mg, 0.3 mmol) and purified by flash chromatography (ethylacetate/hexane = 1 : 10). White solid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.41 (br s, 1H, OH), 5.78 (br s, 1H), 6.14 (ps d, J = 3.3 Hz, 1H), 6.35 (dd, J_1 = 3.3 Hz, J_2 = 2.0 Hz, 1H), 7.33–7.48 (m, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 69.7 (CH), 107.2 (CH), 110.0 (CH), 126.5 (2CH), 127.7 (CH), 128.2 (2CH), 140.7 (C), 142.2 (CH), 155.8 (C). IR (KBr) ν 3368, 3102, 3064, 3032, 2881, 1603, 1492, 1452, 1198, 1142, 1011, 940, 9276, 815, 737, 700 cm^{-1}. HPLC (Chiralcel OD, hexane : isopropanol = 98 : 2, 1 mL min^{-1}, λ = 220 nm) t_R = 34.5 min for enantiomer *S*, t_R = 43.5 min for enantiomer *R*. Configuration was assigned by comparing HPLC elution order with that of the literature data.[7a]

(*R*)-2-Thienyl(phenyl)methanol (2l). This compound was obtained from 2-thiophenecarboxaldehyde (47 µl, 0.5 mmol) and triphenylboroxin (93.6 mg, 0.3 mmol) and purified by flash chromatography (ethylacetate/hexane = 1 : 15). White solid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.87 (ps d, J = 3.7 Hz, 1H, OH), 6.01 (ps d, J = 3.3 Hz, 1H), 6.90 (ps d, J = 3.5 Hz, 1H), 6.97 (dd, J_1 = 5.0 Hz, J_2 = 3.5 Hz, 1H), 7.28 (ddd, J_1 = 5.0 Hz, J_2 = 1.3 Hz, J_3 = 0.5 Hz, 1H), 7.32–7.48 (m, 5H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 72.2 (CH), 124.8 (CH), 125.3 (CH), 126.2 (2CH), 126.5 (CH), 127.9 (CH), 128.4 (2CH), 143.0 (C), 148.0 (C). IR (Nujol) ν 3256, 3090, 3033, 1961, 1895, 1655, 1560, 1492, 1280, 1264, 1198, 1144, 1031, 1011, 919, 853, 742, 724, 700 cm^{-1}. HPLC (Chiralcel OD, hexane : isopropanol = 98 : 2, 1 mL min^{-1}, λ = 220 nm) t_R = 37.0 min for enantiomer *S*, t_R = 40.9 min for enantiomer *R*. Configuration was assigned by comparing HPLC elution order with that of the literature data.[17]

(*S*,*E*)-1,3-Diphenylprop-2-en-1-ol (2m). This compound was obtained from (*E*)-cinnamaldehyde (64 µl, 0.5 mmol) and triphenylboroxin (93.6 mg, 0.3 mmol) and purified by flash chromatography (ethylacetate/hexane = 1 : 15–1 : 10). White solid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.62 (br s, 1H, OH), 5.39 (d, J = 6.4 Hz, 1H), 6.42 (dd, J_1 = 15.8 Hz, J_2 = 6.6 Hz, 1H), 6.71 (d, J = 15.8 Hz, 1H), 7.26–7.50 (m, 10H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 74.7 (CH), 126.2 (2CH), 126.5 (2CH), 127.5 (CH), 127.6 (CH), 128.4 (4CH), 130.2 (CH), 131.4 (CH), 136.4 (C), 142.6 (C). IR (Nujol) ν 3351, 3084, 3058, 3027, 2019, 1954, 1883, 1654, 1599, 1492, 1472, 1013, 966, 744, 694 cm^{-1}. HPLC (Chiralcel OD, hexane : isopropanol = 90 : 10, 1 mL min^{-1}, λ = 254 nm) t_R = 17.3 min for enantiomer *S*, t_R = 22.9 min for enantiomer *R*. (Chiralpak AS-H, hexane : isopropanol = 95 : 5, 1 mL min^{-1}, λ = 254 nm) t_R = 10.9 min for enantiomer *S*, t_R = 12.5 min for enantiomer *R*. Configuration was assigned by comparing HPLC elution order with that of the literature data.[5b]

(*S*,*E*)-3-(*p*-Methoxyphenyl)-1-phenylprop-2-en-1-ol (2n)[18]. This compound was obtained from (*E*)-*p*-methoxycinnamaldehyde (82.6 mg, 0.5 mmol) and triphenylboroxin (93.6 mg, 0.3 mmol) and purified by flash chromatography (ethylacetate/hexane = 1 : 10). Yellow oil. $[\alpha]_D$ –28.7 (*c* 1.7, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.56 (br s, 1H, OH), 3.82 (s, 3H), 5.35 (d, J = 6.6 Hz, 1H), 6.27 (dd, J_1 = 15.8 Hz, J_2 = 6.8 Hz, 1H), 6.63 (d, J = 15.8 Hz, 1H), 6.87 (ps d, J = 8.8 Hz, 2H), 7.34 (ps d, J = 8.8 Hz, 2H), 7.36–7.48 (m, 5H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 55.2 (CH_3), 75.1 (CH), 113.9 (2CH), 126.2 (2CH), 127.6 (CH), 127.7 (2CH), 128.5 (2CH), 129.2 (C), 129.3 (CH), 130.0 (CH), 142.9 (C), 159.2 (C). IR (film) ν 3349, 3031, 2837, 1891, 1654, 1608, 1511, 1451, 1301, 1251, 1175, 1093, 1034, 968, 832, 761, 701 cm^{-1}. HPLC (Chiralcel OD, hexane : isopropanol = 90 : 10, 1 mL min^{-1}, λ = 254 nm) t_R = 18.2 min for enantiomer *R*, t_R = 20.5 min for enantiomer *S*. Configuration was assigned by assuming an analogous mechanism for the aryl transfer.

(*S*,*E*)-3-(2-Furyl)-1-phenylprop-2-en-1-ol (2o)[19]. This compound was obtained from (*E*)-3-(2-furyl)acrylaldehyde (63.0 mg, 0.5 mmol) and triphenylboroxin (93.6 mg, 0.3 mmol) and purified by flash chromatography (ethylacetate/hexane = 1 : 10–1 : 8). Red oil. $[\alpha]_D$ –44.1 (*c* 1.6, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.70 (br s, 1H, OH), 5.33 (d, J = 5.9 Hz, 1H), 6.28 (d, J = 3.3 Hz, 1H), 6.63–6.41 (m, 2H), 6.53 (d, J = 15.8 Hz, 1H), 7.30–7.44 (m, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 74.4 (CH), 108.3 (CH), 111.2 (CH), 118.5 (CH), 126.3 (2CH), 127.6 (CH), 128.5 (2CH), 130.0 (CH), 141.9 (CH), 142.5 (C), 152.1 (C). IR (Film) ν 3368, 3030, 2871, 1654, 1602, 1560, 1492, 1453, 1256, 1152, 1068, 1013, 962, 884, 862, 737, 700 cm^{-1}. HPLC (Chiralpak AS-H, hexane : isopropanol = 95 : 5, 1 mL min^{-1}, λ = 254 nm) t_R = 12.8 min for enantiomer *S*, t_R = 16.2 min for enantiomer *R*. Configuration was assigned by assuming an analogous mechanism for the aryl transfer.

(*S*)-(*p*-Chlorophenyl)(*o*-tolyl)methanol (2p). This compound was obtained from *p*-chlorobenzaldehyde (72.8 mg, 0.5 mmol) and tri(*o*-tolyl)boroxin (106.3 mg, 0.3 mmol) and purified by flash chromatography (ethylacetate/hexane = 1 : 15). White solid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.23 (s, 3H), 2.85 (br s, 1H, OH), 5.87 (s, 1H), 7.15–7.32 (m, 3H), 7.22 (ps d, J = 8.6 Hz, 2H), 7.30 (ps d, J = 8.6 Hz, 2H), 7.42–7.45 (m, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.2 (CH_3), 72.4 (CH), 126.1 (CH), 126.2 (CH), 127.6 (CH), 128.3 (2CH), 128.4 (2CH), 130.5 (CH), 133.1 (C), 135.2 (C), 140.9 (C), 141.2 (C). IR (Nujol) ν 3256, 3059, 1969, 1901, 1953, 1488, 1406, 1176, 1088, 1015, 864, 817, 752, 730 cm^{-1}. HPLC (Chiralcel OD, hexane : isopropanol = 99 : 1, 1 mL min^{-1}, λ = 254 nm) t_R = 74.3 min for enantiomer *R*, t_R = 81.4 min for enantiomer *S*. (Chiralpak AD-H, hexane : isopropanol = 95 : 5, 1 mL min^{-1}, λ = 254 nm) t_R = 12.0 min for enantiomer *S*, t_R = 13.0 min for enantiomer *R*.

Configuration was assigned by comparing HPLC elution order with that of the literature data.[12c]

(*R*)-(*p*-Chlorophenyl)(*o*-tolyl)methanol (*ent*-2p). This compound is the enantiomer of **2p** and was obtained from *o*-tolualdehyde (60 µl, 0.5 mmol) and tri(*p*-chlorophenyl)boroxin (124.2 mg, 0.3 mmol).

(*R*)-(*p*-Chlorophenyl)(*p*-tolyl)methanol (2q). This compound was obtained from *p*-chlorobenzaldehyde (72.8 mg, 0.5 mmol) and tri(*p*-tolyl)boroxin (106.3 mg, 0.3 mmol) and purified by flash chromatography (ethylacetate/hexane = 1 : 15). White solid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.35 (s, 3H), 2.32–2.41 (br s, 1H, OH), 5.77 (br s, 1H), 7.14–7.18 (m, 2H), 7.22–7.27 (m, 2H), 7.31 (s, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 21.1 (CH_3), 75.4 (CH), 126.5 (2CH), 127.7 (2CH), 128.5 (2CH), 129.3 (2CH), 133.1 (C), 137.6 (C), 140.5 (C), 142.3 (C). IR (Nujol) ν 3283, 2019, 1900, 1511, 1190, 1179, 1087, 1038, 1012, 799, 766 cm^{-1}. HPLC (Chiralcel OD, hexane : isopropanol = 95 : 5, 1 mL min^{-1}, λ = 220 nm) t_R = 14.4 min for enantiomer *R*, t_R = 15.7 min for enantiomer *S*. Configuration was assigned by comparing HPLC elution order with that of the literature data.[12c]

(*S*)-(*p*-Chlorophenyl)(*p*-tolyl)methanol (*ent*-2q). This compound is the enantiomer of **2q** and was obtained from *p*-tolualdehyde (56 µl, 0.5 mmol) and tri(*p*-chlorophenyl)boroxin (124.2 mg, 0.3 mmol).

(*S*)-2-Naphthyl(*p*-tolyl)methanol (2r)[20]. This compound was obtained from *p*-tolualdehyde (56 µl, 0.5 mmol) and tri(2-naphthyl)boroxin (138.6 mg, 0.3 mmol) and purified by flash chromatography (ethylacetate/hexane = 1 : 20). White solid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.10 (s, 1H, OH), 5.93 (s, 1H), 7.22 (ps d, *J* = 7.9 Hz, 2H), 7.35 (ps d, *J* = 7.9 Hz, 2H), 7.47 (ps d, *J* = 8.3 Hz, 1H), 7.55–7.58 (m, 2H), 7.83–7.93 (m, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 21.0 (CH_3), 75.9 (CH), 124.7 (CH), 124.8 (CH), 125.7 (CH), 126.0 (CH), 126.6 (2CH), 127.5 (CH), 128.0 (CH), 128.1 (CH), 129.0 (2CH), 132.7 (C), 133.1 (C), 137.1 (C), 140.6 (C), 141.2 (C). IR (Nujol) ν 3294, 1601, 1508, 1332, 1243, 1166, 1122, 1026, 1016, 868, 822, 778, 763, 745 cm^{-1}. HPLC (Chiralcel OD, hexane : isopropanol = 95 : 5, 1 mL min^{-1}, λ = 254 nm) t_R = 27.2 min for enantiomer *S*, t_R = 30.7 min for enantiomer *R*. Configuration was assigned by assuming an analogous mechanism for the aryl transfer.

(*R*)-2-Naphthyl(*p*-tolyl)methanol (*ent*-2r). This compound is enantiomer of **2r** and was obtained from 2-naphthaldehyde (78.2 mg, 0.5 mmol) and tri(*p*-tolyl)boroxin (106.3 mg, 0.3 mmol). $[\alpha]_D$ −30.5 (*c* 1.9, $CHCl_3$).

(*S*)-(*p*-Methoxyphenyl)(2-naphthyl)methanol (2s). This compound was obtained from *p*-methoxybenzaldehyde (61 µl, 0.5 mmol) and tri(2-naphthyl)boroxin (138.6 mg, 0.3 mmol) and purified by flash chromatography (ethylacetate/hexane = 1 : 10–1 : 8). White solid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.73 (br s, 1H, OH), 3.79 (s, 3H), 5.93 (s, 1H), 6.88 (ps d, *J* = 8.8 Hz, 2H), 7.32 (ps d, *J* = 8.3 Hz, 2H), 7.42 (dd, J_1 = 8.6 Hz, J_2 = 1.8 Hz, 1H), 7.48–7.54 (m, 2H), 7.79–7.90 (m, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 55.2 (CH_3), 75.7 (CH), 113.8 (2CH), 124.6 (CH), 124.7 (CH), 125.8 (CH), 126.1 (CH), 127.6 (CH), 128.0 (3CH), 128.1 (CH), 132.7 (C), 133.1 (C), 135.9 (C), 141.3 (C), 158.9 (C). IR (KBr) ν 3368, 3056, 2837, 1896, 1610, 1585, 1509, 1463, 1441, 1249, 1175, 1121, 1033, 865, 818, 780, 762, 738, 703 cm^{-1}. HPLC (Chiralcel OD, hexane : isopropanol = 90 : 10, 1 mL min^{-1}, λ = 254 nm) t_R = 21.0 min for enantiomer *S*, t_R = 25.1 min for enantiomer *R*. Configuration was assigned by comparing HPLC elution order with that of the literature data.[21]

(*R*)-(*p*-Methoxyphenyl)(2-naphthyl)methanol (*ent*-2s). This compound is the enantiomer of **2s** and was obtained from 2-naphthaldehyde (78.2 mg, 0.5 mmol) and tri(*p*-methoxyphenyl)boroxin (120.6 mg, 0.3 mmol).

(*S*)-(*p*-Chlorophenyl)(2-naphthyl)methanol (2t). This compound was obtained from *p*-chlorobenzaldehyde (72.8 mg, 0.5 mmol) and tri(2-naphthyl)boroxin (138.6 mg, 0.3 mmol) and purified by flash chromatography (ethylacetate/hexane = 1 : 15). White solid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.50 (ps d, *J* = 3.3 Hz, 1H), 5.80 (ps d, *J* = 2.6 Hz, 1H), 7.26–7.33 (m, 4H), 7.36 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.54–7.59 (m, 2H), 7.79 (s, 1H), 7.82–7.89 (m, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 75.4 (CH), 124.4 (CH), 125.0 (CH), 126.0 (CH), 126.2 (CH), 127.6 (CH), 127.8 (2CH), 127.9 (CH), 128.3 (CH), 128.4 (2CH), 132.7 (C), 133.0 (C), 133.1 (C), 140.4 (C), 141.7 (C). IR (Nujol) ν 3339, 3055, 1952, 1906, 1601, 1508, 1489, 1166, 1122, 1092, 1013, 953, 867, 810, 775, 764, 748 cm^{-1}. HPLC (Chiralcel OD, hexane : isopropanol = 90 : 10, 1 mL min^{-1}, λ = 254 nm) t_R = 19.7 min for enantiomer *S*, t_R = 22.4 min for enantiomer *R*. Configuration was assigned by comparing HPLC elution order with that of the literature data.[21]

(*R*)-(*p*-Chlorophenyl)(2-naphthyl)methanol (*ent*-2t). This compound is the enantiomer of **2t** and was obtained from 2-naphthaldehyde (78.2 mg, 0.5 mmol) and tri(*p*-chlorophenyl)boroxin (124.2 mg, 0.3 mmol).

(*S*)-2-Naphthyl(*p*-(trifluoromethyl)phenyl)methanol (2u). This compound was obtained from *p*-(trifluoromethyl)benzaldehyde (69 µl, 0.5 mmol) and tri(2-naphthyl)boroxin (138.6 mg, 0.3 mmol) and purified by flash chromatography (ethylacetate/hexane = 1 : 15). White solid. $[\alpha]_D$ −45.3 (*c* 2.2, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.87 (br s, 1H, OH), 5.95 (s, 1H), 7.38 (dd, J_1 = 8.6 Hz, J_2 = 1.8 Hz, 1H), 7.49–7.57 (m, 2H), 7.51 (ps d, *J* = 7.3 Hz, 2H), 7.60 (ps d, *J* = 8.3 Hz, 2H), 7.70–7.80 (m, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 75.7 (CH), 124.1 (q, $J_{C\text{-}F}$ = 272 Hz, 1C), 124.4 (CH), 125.4 (3CH), 126.3 (CH), 126.4 (CH), 126.7 (2CH), 127.7 (CH), 128.0 (CH), 128.7 (CH), 129.6 (q, $J_{C\text{-}CF}$ = 32 Hz, 1C), 133.0 (C), 133.1 (C), 140.3 (C), 147.2 (C). ^{19}F-NMR (282 MHz, $CDCl_3$) δ −62.81 (s, 3F). IR (Nujol) ν 3369, 2019, 1924, 1618, 1499, 1336, 1168, 1157, 1127, 1108, 1069, 1016, 846, 822, 814, 776, 762, 744 cm^{-1}. HRMS calcd for $C_{18}H_{13}F_3O + Na^+$, 325,0816; found, 325,0822. HPLC (Chiralcel OD, hexane : isopropanol = 90 : 10, 1 mL min^{-1}, λ = 220 nm) t_R = 19.8 min for enantiomer *S*, t_R = 22.5 min for enantiomer *R*. Configuration was assigned by assuming an analogous mechanism for the aryl transfer.

(*S*)-*o*-Tolyl(*p*-(trifluoromethyl)phenyl)methanol (2v). This compound was obtained from *p*-(trifluoromethyl)benzaldehyde (69 µl, 0.5 mmol) and tri(*o*-tolyl)boroxin (106.3 mg, 0.3 mmol) and purified by flash chromatography (ethylacetate/hexane = 1 : 15). White solid. $[\alpha]_D$ −34.5 (*c* 2.3, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.26 (s, 3H), 3.68 (s, 1H, OH), 5.88 (s, 1H), 7.20–7.24 (m, 1H), 7.26–7.31 (m, 2H), 7.35–7.40 (m, 1H), 7.40

(ps d, J = 8.1 Hz, 2H), 7.61 (ps d, J = 8.1 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.1 (CH_3), 72.4 (CH), 124.1 (q, $J_{C\text{-}F}$ = 272 Hz, 1C), 125.2 (2CH), 126.2 (CH), 126.5 (CH), 127.1 (2CH), 127.9 (CH), 129.7 (q, $J_{C\text{-}CF}$ = 32 Hz, 1C), 130.7 (CH), 135.4 (C), 140.6 (C), 146.6 (C). ^{19}F-NMR (282 MHz, $CDCl_3$) δ −62.81 (s, 3F). IR (Nujol) ν 3325, 3069, 3024, 2645, 2019, 1924, 1619, 1490, 1417, 1327, 1166, 1126, 1058, 1017, 863, 840, 816, 787, 752 cm^{-1}. HRMS calcd for $C_{15}H_{13}F_3O$ + Na^+, 289.0816; found, 289.0806. HPLC (Chiralcel OD, hexane : isopropanol = 90 : 10, 1 mL min^{-1}, λ = 220 nm) t_R = 10.9 min for enantiomer *R*, t_R = 12.2 min for enantiomer *S*. Configuration was assigned by assuming an analogous mechanism for the aryl transfer.

(*R*)-*p*-Tolyl(*p*-(trifluoromethyl)phenyl)methanol (2w). This compound was obtained from *p*-(trifluoromethyl)benzaldehyde (69 µl, 0.5 mmol) and tri(*p*-tolyl)boroxin (106.3 mg, 0.3 mmol) and purified by flash chromatography (ethylacetate/hexane = 1 : 15). White solid. $[\alpha]_D$ −44.3 (*c* 1.8, C_6H_6), ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.28–2.35 (br s, 1H, OH), 2.35 (s, 3H), 5.86 (s, 1H), 7.17 (ps d, J = 7.9 Hz, 2H), 7.25 (ps d, J = 8.1 Hz, 2H), 7.51 (ps d, J = 8.1 Hz, 2H), 7.60 (ps d, J = 8.3 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 21.1 (CH_3), 75.5 (CH), 124.3 (q, $J_{C\text{-}F}$ = 272 Hz, 1C), 125.3 (CH), 125.4 (CH), 126.5 (2CH), 126.6 (2CH), 129.4 (2CH), 129.6 (q, $J_{C\text{-}CF}$ = 32 Hz, 1C), 137.9 (C), 140.3 (C), 147.7 (C). ^{19}F-NMR (282 MHz, $CDCl_3$) δ −62.82 (s, 3F). IR (Nujol) ν 3326, 2666, 2019, 1924, 1618, 1509, 1338, 1162, 1128, 1110, 1069, 1017, 873, 833, 800, 762 cm^{-1}. HPLC (Chiralcel OD, hexane : isopropanol = 90 : 10, 1 mL min^{-1}, λ = 220 nm) t_R = 9.1 min for enantiomer *R*, t_R = 10.7 min for enantiomer *S*. Configuration was assigned by comparing the sign of optical rotation with that of the literature data.[22]

(*S*)-*p*-Tolyl(*p*-(trifluoromethyl)phenyl)methanol (*ent*-2w). This compound is enantiomer of **2w** and was obtained from *p*-tolualdehyde (56 µl, 0.5 mmol) and tri(*p*-(trifluoromethyl)phenyl)boroxin (154.7 mg, 0.3 mmol). $[\alpha]_D$ = +40.6 (c 0.4, C_6H_6).

(*S*) - (*p* - Chlorophenyl)(*p* - (trifluoromethyl) phenyl) methanol (2x). This compound was obtained from *p*-(trifluoromethyl)-benzaldehyde (69 µl, 0.5 mmol) and tri(*p*-chlorophenyl)boroxin (124.2 mg, 0.3 mmol) and purified by flash chromatography (ethylacetate/hexane = 1 : 15). White solid. $[\alpha]_D$ −27.1 (*c* 2.3, C_6H_6). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.48 (ps d, J = 3.3 Hz, 1H, OH), 5.85 (br s, 1H), 7.27–7.35 (m, 4H), 7.48 (ps d, J = 8.1 Hz, 2H), 7.61 (ps d, J = 8.1 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 75.0 (CH), 124.0 (q, $J_{C\text{-}F}$ = 272 Hz, 1C), 125.5 (CH), 125.6 (CH), 126.6 (2CH), 127.9 (2CH), 128.9 (2CH), 129.9 (q, $J_{C\text{-}CF}$ = 33 Hz, 1C), 133.8 (C), 141.5 (C), 147.0 (C). ^{19}F-NMR (282 MHz, $CDCl_3$) δ −62.93 (s, 3F). IR (Nujol) ν 3260, 3055, 1929, 1618, 1491, 1331, 1169, 1156, 1109, 1092, 1070, 1040, 1014, 872, 854, 834, 792, 764 cm^{-1}. HPLC (Chiralcel OD, hexane : isopropanol = 95 : 5, 1 mL min^{-1}, λ = 220 nm) t_R = 15.2 min for enantiomer *S*, t_R = 16.7 min for enantiomer *R*. Configuration was assigned by comparing the sign of optical rotation with that of the literature data.[23]

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