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Enantioselective addition of alkenylzinc reagents to aldehydes with organoboronates as the alkenyl source

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Abstract—Alkenylboronates were used as a vinyl source in the asymmetric addition of an alkenylzinc reagent to aldehydes catalyzed by a dendritic ligand. The resulting allylic alcohol products were obtained in 66–96% ee and 35–64% yields.

1. Introduction

Optically active secondary allylic alcohols represent a very important class of compounds as both versatile synthetic intermediates[1] and key structures commonly found in numerous natural compounds.[2] Recently, great progress has been made in the preparation of this class of compounds by enantioselective addition reactions of in situ generated alkenylzinc reagents to aldehydes in the presence of different types of chiral ligands.[3–5] In general, alkenylzinc reagents are not temperature stable and thus should be used immediately after generation. Presently, two approaches have been extensively applied to prepare the alkenylzinc reagents for asymmetric use:[3] (a) One procedure based on a boron–zinc transmetallation mechanism involving the hydroboration of terminal alkynes followed by an in situ exchange with dialkylzinc was developed by Oppozler et al.;[4] (b) another protocol involving hydrozirconation of alkynes with Schwartz reagent followed by transmetallation with dimethylzinc was established by Wipf et al.[5] In addition, Walsh et al.[6] have also reported the use of tris(vinyl ether) borane as the alkenyl source in the asymmetric alkenylation reactions of aldehydes. Since a stereogenic center and a new carbon–carbon bond are formed concomitantly, this methodology for generating optically active secondary allylic alcohols is attractive, and thus the development of other vinyl sources, remains an intriguing subject in this field.

More recently, Pandya et al.[7] reported that the alkenylation of nitrones could be conducted with an alkenylzinc reagent in situ generated from dialkylzinc and alkenylboronic pinacol esters in DMF. However, disappointing results were obtained when aldehydes and ketones were subjected to similar reaction conditions and no asymmetric attempts were reported. In view of the good stability and easy availability of most alkenyboronic esters, we conceived that the generation of alkenylzinc species with them as the alkenyl source could provide a useful complement to the present methodology for asymmetric synthesis. During the preparation of this manuscript, Bolm et al.[8a] reported a similar protocol using alkenylboronic acids as the alkenyl source, however, the enantioselectivities were not ideal, which would be disadvantageous for further application in asymmetric synthesis. Keeping in mind that the structures of alkenylboronic esters, especially the different alcohol moieties, could have an influence on their reactivities[9] and based on our own experience with the generation of organozinc reagents via boron–zinc transmetallation,[10] we hypothesized that examination of the effects of solvent, temperature and more importantly the structures of the alkenylboronic esters could provide better results. Herein we report our improvement on the use of alkenylboronic esters as the alkenyl source for the asymmetric alkenylation of aldehydes.

2. Results and discussion

In an initial study, (*E*)-styrylboronic acid **1a** was tested for the in situ generation of alkenylzinc reagents. Dendritic ligand **2** (see Table 1), which has been previously successfully applied in the asymmetric arylation of aldehydes,[10a] was used in the following reactions. To our delight, the

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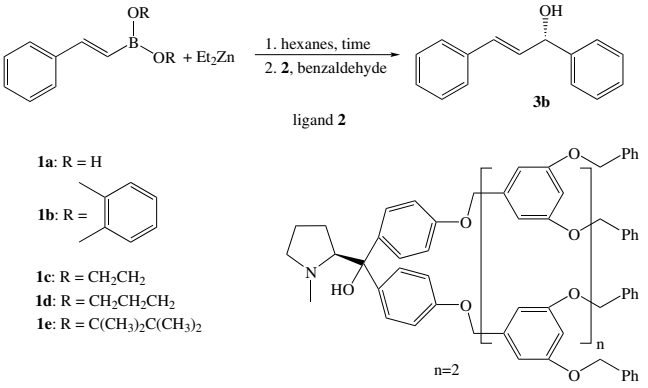
Table 1. Screening of alkenyl source and optimization of reaction conditions for the asymmetric alkenylation of benzaldehyde[a]



Entry	Boronate/acid	Solvent	Time[b] (min)	% Yield[c]	% ee[d,e]
1	**1a**	Various solvents	10	32–71	15–62
2	**1b**	Hexane–toluene	5	77[f]	0
3	**1c**	Hexane–toluene	15	51	70
4	**1d**	Hexane–toluene	40	60	96
5	**1e**	Hexane–toluene	60	5[g]	91
6	**1d**	Hexane–CH_2Cl_2	40	38	93
7	**1d**	Hexane–Et_2O	40	46	92
8	**1d**	Hexane–THF	40	Trace	n.d.
9	**1d**	Hexane–toluene	40	61[h]	96
10	**1d**	Hexane–toluene	40	51[i]	90
11	**1d**	Hexane–toluene	40	17[j]	96
12	**1d**	Hexane–toluene	40	57[k]	93
13	**1d**	Hexane–toluene	40	60[l]	94

[a] Conditions: boronates/Et_2Zn/PhCHO/ligand = 2.0:4.0:1.0:0.05, 0 °C, 8 h.
[b] Time for the mixing of boronates and Et_2Zn.
[c] Yields after silica gel column chromatography.
[d] Determined by HPLC using a chiral OD column (DAICEL).
[e] The absolute configuration was determined to be (*S*) by comparison of the specific rotation value with that of the literature data.
[f] The reaction time was 2 h.
[g] 85% benzaldehyde recovered.
[h] 5 mol % of **2** was used.
[i] 2.5 mol % of **2** was used.
[j] The reaction was performed at −15 °C and 60% benzaldehyde was recovered.
[k] Second reuse of ligand **2**.
[l] Third reuse of ligand **2**.

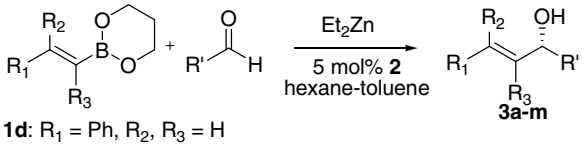
treatment of **1a** with a 3-fold excess of Et_2Zn at 0 °C for 15 min in hexanes followed by the addition of **2** (10 mol %) and benzaldehyde provided the corresponding allylic alcohol **3a** in moderate yield, which indicated the intermediacy of alkenylzinc species generated under the reaction conditions. Unfortunately, the reproducibility of both the yields and ee values remained poor in spite of much effort, including variation of solvents, ligands, and the amount of Et_2Zn[11] (Table 1, entry 1). In addition, using the anhydride of **1a** which has a better chemical homogeneity could provide results of good reproducibility; however, the enantioselectivity was poor (58–60% yield, 31–34% ee). Notably, when the mixture of **1a** and Et_2Zn in hexanes was allowed to stir over 15 min, the white turbid mixture would gradually turn black, which might be due to the coupling of the alkenylzinc species.[12]

We then turned our attention to the use of the corresponding alkenylboronic esters as the alkenyl source. Esters **1b–e** (see Table 1) were easily prepared by condensation with the corresponding diols.[13] Next, when **1b–d** were treated with a 2-fold excess of Et_2Zn in hexanes at 0 °C, the times at which the respective mixtures began to turn black were found to be quite different: 5 min for **1b**, 15 min for **1c** and 40 min for **1d**, which may be explained by the decreasing Lewis acidity of the boron atom in **1b** and **1c** resulting from the different electron back-donating ability of the oxygen atom to the spare *p*-orbital of the boron atom. However, in the case of pinacol ester **1e**, the mixture remained almost unchanged, even at room temperature for 3 h, which may be due to the large steric hinderance around the boron atom. Additionally, the different reactivities of **1b–e** were also reflected in their stabilities: the more reactive **1b** and **1c** underwent facile decomposition upon flash column chromatography, while the less reactive **1d** and **1e** could be purified by flash column chromatography.

Subsequently, the asymmetric alkenylation of benzaldehyde were re-studied with boronates **1b–e** in the presence of ligand **2** using the following procedure: a mixture of boronates (0.4 mmol in 0.4 mL of *n*-hexane) and Et_2Zn (0.8 mmol, 1.0 M in hexanes) was stirred for specified times in hexane at 0 °C before the addition of ligand and benzaldehyde (0.2 mmol) in other specified solvents. The results obtained are shown in Table 1 (entries 2–11). The different reactivities of **1b–e** were well reflected in these results. While the most reactive catechol-derived **1b** provided the highest yield (77%) in racemic form (Table 1, entry 2), extremely low conversion and yield was observed for the most unreactive **1e** (Table 1, entry 5). As shown in entry 9, the best result in terms of both yield (61%) and ee (96%) was obtained with **1d** as the alkenyl source in the presence of 5 mol % of **2**; this result was highly reproducible over several runs. Dendritic ligand **2**, which could be easily recovered by the precipitation method,[10a] could be reused at least twice without significant decreases in yield and ee (Table 1, entries 11 and 12). In addition, we also tested several small molecule ligands under the same reaction conditions, and similarly good results in terms of yields and ees were obtained.[14]

Then, a selected spectrum of aldehydes was examined under the optimum reaction conditions. The results are summarized in Table 2 (entries 1–11). Generally, aromatic aldehydes gave better results than aliphatic ones. The electronic nature of substituents on the benzene ring seemed not to have a significant influence on the enantioselectivities. However, in the case of 2-bromobenzaldehyde (Table 2, entry 7), the ethyl adduct was isolated along with a lower ee, which may be due to the large steric hinderance of the *ortho*-Br atom. Moreover, for the electronic-deficient *para*-CF_3 substituted benzaldehyde, an ethyl adduct product was also observed, which may result from its high reactivity, although no significant reduction in ee was observed (Table 2, entry 4). The enantioselectivity dropped as the steric hinderance decreased in the case of aliphatic aldehydes (Table 2, entries 9–11). As for the structural diversity of the alkenylboronates moiety, both the alkenylboronic ester **1g** (Table 2, entry 12) with the phenyl group connected to

Table 2. Asymmetric alkenylation of various aldehydes[a]



1d: R_1 = Ph, R_2, R_3 = H

1f: R_3 = Ph, R_1, R_2 = H

1g: R_1 = *n*-Butyl, R_2, R_3 = H

Entry	Boronate	R′	Product	% Yield[b]	% ee[c,d]
1	**1d**	Ph	**3a**	61	96
2	**1d**	4-Me–C_6H_4	**3b**	64	92
3	**1d**	4-Cl–C_6H_4	**3c**	57	93
4	**1d**	4-CF_3–C_6H_4	**3d**	50[e]	93
5	**1d**	4-Br–C_6H_4	**3e**	58	84
6	**1d**	3-Br–C_6H_4	**3f**	53	94
7	**1d**	2-Br–C_6H_4	**3g**	40[f]	82
8	**1d**	2-Naph	**3h**	52	91
9	**1d**	*c*-C_6H_{11}	**3i**	46	82
10	**1d**	*i*-Propyl	**3j**	45	76
11	**1d**	*n*-C_4H_9	**3k**	58	66
12	**1f**	Ph	**3l**	35[g]	94
13	**1g**	Ph	**3m**	39[g]	94

[a] Conditions: boronates/Et_2Zn/PhCHO/ligand = 2.0:4.0:1.0:0.05, 0 °C, 8 h.

[b] Yields after silica gel column chromatography.

[c] Determined by HPLC using a chiral OD column (DAICEL).

[d] The absolute configurations of **3a**, **3i**, **3j**, and **3k** were determined by comparison of the specific rotation value with that of the literature data. Otherwise, the stereochemistry was assigned by assuming that a similar reaction pathway was taken.

[e] 20% ethyl adduct was also isolated as a mixture inseparable from **3d** and the ratio was determined by ^{1}H NMR analysis.

[f] 16% ethyl adduct was also isolated as a mixture inseparable from **3g** and the ratio was determined by ^{1}H NMR analysis.

[g] 3 equiv of alkenylboronates were used.

the same carbon with the boron atom and **1f** (Table 2, entry 13) derived from *n*-hexyne with an alkyl chain provided the corresponding allylic alcohol products with benzaldehyde in high enantioselectivity, albeit with lower yields.

3. Conclusion

In conclusion, we have successfully developed a protocol for the asymmetric alkenylation of aldehydes using alkenylboronic esters as the vinyl source. This method provides an alternative method for the synthesis of enantiomerically enriched allylic alcohols. Efforts on further optimization and extension of the scope of this method are currently underway.

4. Experimental

4.1. General

All reactions were carried out under a dry argon atmosphere unless noted otherwise. Analytical TLC was performed on precoated silica gel plates. Column chromatography was conducted with 300–400 mesh silica gel. NMR spectra were recorded at 300 MHz for ^{1}H NMR using $SiMe_4$ as an internal standard in $CDCl_3$ and 282 MHz for ^{19}F NMR using $CFCl_3$ as an internal standard in $CDCl_3$. Enantiomeric excesses were determined by chiral HPLC analysis. Optical rotations were measured on a JASCO 1030 polarimeter. All solvents were dried before use according to standard procedures.

4.2. General procedure for the asymmetric alkenylation of aldehydes

Under an atmosphere of dry argon, to a solution of alkenylboronic ester (0.4 mmol) in 0.4 mL of *n*-hexane was added $ZnEt_2$ (0.8 mmol, 1.0 M in hexanes) 0 °C. After stirring for 40 min at this temperature, ligand **2** in 1 mL toluene was added and solution was again stirred for 10 min followed by the dropwise addition of aldehyde in 0.5 mL toluene over 15 min. The mixture was allowed to stir for 8 h at 0 °C and quenched by the addition of 10 mL of methanol to precipitate the dendritic ligand after which the mixture was filtered and concentrated. To the residue was added 3 mL of 1% aqueous NaOH and the mixture stirred for 2 h at room temperature (this step could facilitate the purification of products by destroying the excess boronic ester), then extracted with ethyl acetate (3×3 mL), and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography (PE/ether = 8:1) to give the desired allylic alcohols. The ee was determined by HPLC analysis using a chiral column.

4.2.1. (*S*)-(*E*)-1,3-Diphenyl-prop-2-en-1-ol 3a.[15] Colorless oil; $[\alpha]_D^{24} = -31.5$ (*c* 0.75, $CHCl_3$) for 96% ee {lit.[12] $[\alpha]_D^{24} = -32.1$ (*c* 0.5, $CHCl_3$) for >99% ee (*s*)}; ^{1}H NMR ($CDCl_3$): δ 7.45–7.21 (m, 10H), 6.70 (d, $J = 15.8$ Hz, 1H), 6.39 (dd, $J = 15.8$, 6.7 Hz, 1H), 5.40 (m, 1H), 2.30 (d, $J = 3.9$ Hz, 1H); HPLC: Daicel CHIRALCEL OD column, hexane/IPA = 4:1, 0.60 mL/min, $\lambda = 254$ nm, $t_R(S) = 23.2$ min, $t_R(R) = 28.7$ min.

4.2.2. (*S*)-(*E*)-3-Phenyl-1-(*p*-tolyl)-2-propenol 3b.[8a] Pale yellow solid; mp 73–75 °C; $[\alpha]_D^{22} = -22.3$ (*c* 0.50, CH_2Cl_2) for 92% ee {lit.[8a] $[\alpha]_D^{20} = +8.0$ (*c* 1.4, CH_2Cl_2) for 34% ee (*R*)}; ^{1}H NMR ($CDCl_3$): δ 7.39–7.16 (m, 9H), 6.68 (d, $J = 15.6$ Hz, 1H), 6.39 (dd, $J = 15.6$, 6.6 Hz, 1H), 5.33 (m, 1H), 2.34 (s, 3H), 2.02 (s, 1H); HPLC: Daicel CHIRALCEL OD column, hexane/IPA = 4:1, 0.60 mL/min, $\lambda = 254$ nm, $t_R(S) = 24.3$ min, $t_R(R) = 36.1$ min.

4.2.3. (*S*)-(*E*)-1-(4-Chlorophenyl)-3-phenylprop-2-en-1-ol 3c.[8a] Pale yellow solid; mp 57–58 °C; $[\alpha]_D^{22} = -16.8$ (*c* 0.65, CH_2Cl_2) for 93% ee {lit.[8a] $[\alpha]_D^{20} = +8.9$ (*c* 1.4, CH_2Cl_2) for 55% ee (*R*)}; ^{1}H NMR ($CDCl_3$): δ 7.39–7.26 (m, 9H), 6.68 (d, $J = 15.7$ Hz, 1H), 6.32 (dd, $J = 15.7$, 6.7 Hz, 1H), 5.36 (d, $J = 6.7$ Hz, 1H), 2.84 (br s, 1H); HPLC: Daicel CHIRALCEL OD column, hexane/IPA = 4:1, 0.60 mL/min, $\lambda = 254$ nm, $t_R(S) = 21.8$ min, $t_R(R) = 31.1$ min.

4.2.4. (*S*)-(*E*)-3-Phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol 3d.[16] Colorless oil; ^{1}H NMR ($CDCl_3$): δ 7.56 (d, $J = 8.3$ Hz, 2H), 7.47 (d, $J = 8.3$ Hz, 2H), 7.35–7.20 (m, 5H), 6.60 (d, $J = 15.8$ Hz, 1H), 6.26 (dd, $J = 15.8$, 6.6 Hz,

1H), 5.34 (d, $J = 6.6$ Hz, 1H), 2.81 (br s, 1H); ^{19}F NMR (282 MHz, $CDCl_3$): δ −62.2; HPLC: Daicel CHIRALCEL OD column, hexane/IPA = 4:1, 0.60 mL/min, $\lambda = 254$ nm, $t_R(S) = 20.3$ min, $t_R(R) = 33.0$ min.

4.2.5. (*S*)-(*E*)-1-(4-Bromophenyl)-3-phenylprop-2-en-1-ol 3e.[17] White solid; mp 65–66 °C; $[\alpha]_D^{22} = -14.9$ (*c* 0.47, $CHCl_3$) for 84% ee; ^{1}H NMR ($CDCl_3$): δ 7.51–7.26 (m, 9H), 6.68 (d, $J = 15.8$ Hz, 1H), 6.32 (dd, $J = 15.8$, 6.5 Hz, 1H), 5.36 (m, 1H), 2.03 (d, $J = 3.2$ Hz, 1H); HPLC: Daicel CHIRALCEL OD column, hexane/IPA = 4:1, 0.60 mL/min, $\lambda = 254$ nm, $t_R(S) = 21.6$ min, $t_R(R) = 30.9$ min.

4.2.6. (*S*)-(*E*)-1-(3-Bromophenyl)-3-phenylprop-2-en-1-ol 3f.[18] Colorless oil; ^{1}H NMR ($CDCl_3$): δ 7.70–7.09 (m, 9H), 6.68 (d, $J = 15.9$ Hz, 1H), 6.32 (dd, $J = 15.9$, 6.0 Hz, 1H), 5.30 (m, 1H), 2.20 (br s, 1H); HPLC: Daicel CHIRALCEL OD column, hexane/IPA = 4:1, 0.60 mL/min, $\lambda = 254$ nm, $t_R(S) = 20.8$ min, $t_R(R) = 30.3$ min.

4.2.7. (*S*)-(*E*)-1-(2-Bromophenyl)-3-phenylprop-2-en-1-ol 3g.[8a] ^{1}H NMR ($CDCl_3$): δ 7.62–7.53 (m, 2H), 7.39–7.12 (m, 7H), 6.74 (d, $J = 15.7$ Hz, 1H), 6.32 (dd, $J = 15.7$, 6.0 Hz, 1H), 5.76 (m, 1H), 2.26 (d, $J = 4.2$ Hz, 1H); HPLC: Daicel CHIRALCEL OD column, hexane/IPA = 4:1, 0.60 mL/min, $\lambda = 254$ nm, $t_R(S) = 18.7$ min, $t_R(R) = 20.2$ min.

4.2.8. (*S*)-(*E*)-1-(Naphthalen-2-yl)-3-phenylprop-2-en-1-ol 3h.[19] White solid; mp 77–78 °C; $[\alpha]_D^{22} = -25.2$ (*c* 0.33, CH_2Cl_2) for 91% ee; ^{1}H NMR ($CDCl_3$): δ 7.85 (m, 4H), 7.56–7.26 (m, 8H), 6.74 (d, $J = 15.8$ Hz, 1H), 6.32 (dd, $J = 15.8$, 6.4 Hz, 1H), 5.56 (d, $J = 5.0$ Hz, 1H), 2.13 (br s, 1H); HPLC: Daicel CHIRALCEL OD column, hexane/IPA = 4:1, 0.60 mL/min, $\lambda = 254$ nm, $t_R(S) = 28.5$ min, $t_R(R) = 43.1$ min.

4.2.9. (*R*)-(*E*)-1-Cyclohexyl-3-phenylprop-2-en-1-ol 3i.[8a] Colorless oil; $[\alpha]_D^{24} = -5.7$ (*c* 0.47, CH_2Cl_2) for 82% ee {lit.[8a] $[\alpha]_D^{20} = +2.5$ (*c* 1.6, CH_2Cl_2) for 33% ee (*S*)}; ^{1}H NMR ($CDCl_3$): δ 7.40–7.23 (m, 5H), 6.54 (d, $J = 15.8$ Hz, 1H), 6.32 (dd, $J = 15.8$, 6.7 Hz, 1H), 4.02 (m, 1H), 1.01–1.93 (m, 12H); HPLC: Daicel CHIRALCEL OD column, hexane/IPA = 4:1, 0.60 mL/min, $\lambda = 254$ nm, $t_R(R) = 13.4$ min, $t_R(S) = 17.5$ min.

4.2.10. (*R*)-(*E*)-4-Methyl-1-phenylpent-1-en-3-ol 3j.[1b] Colorless oil; $[\alpha]_D^{22} = -8.2$ (*c* 0.75, EtOH) for 76% ee {lit.[20] $[\alpha]_D^{20} = -8.0$ (*c* 1.02, EtOH) for 69% ee (*S*)}; ^{1}H NMR ($CDCl_3$): δ 7.41–7.26 (m, 5H), 6.58 (d, $J = 15.8$ Hz, 1H), 6.24 (dd, $J = 15.8$, 6.8 Hz, 1H), 4.03 (m, 1H), 1.84 (m, 1H), 0.99 (d, $J = 5.4$ Hz, 3H), 0.95 (d, $J = 6.7$ Hz, 3H); HPLC: Daicel CHIRALCEL OD column, hexane/IPA = 4:1, 0.60 mL/min, $\lambda = 254$ nm, $t_R(R) = 13.4$ min, $t_R(S) = 17.5$ min.

4.2.11. (*R*)-(*E*)-1-Phenylhept-1-en-3-ol 3k.[21] Colorless oil; $[\alpha]_D^{25} = -2.7$ (*c* 0.47, benzene) for 66% ee; {lit.[21] $[\alpha]_D^{25} = +3.52$ (*c* 3.95, benzene) for 76% ee (*S*)}; ^{1}H NMR ($CDCl_3$): δ 7.41–7.22 (m, 5H), 6.58 (d, $J = 15.8$ Hz, 1H), 6.24 (dd, $J = 15.8$, 6.8 Hz, 1H), 4.28 (m, 1H), 1.60 (m, 3H), 1.38 (m, 4H), 0.92 (m, 3H); HPLC: Daicel CHIRALCEL OD column, hexane/IPA = 4:1, 0.60 mL/min, $\lambda = 254$ nm, $t_R(R) = 14.1$ min, $t_R(S) = 19.4$ min.

4.2.12. (*R*)-1,2-Diphenylprop-2-en-1-ol 3l.[22] Colorless oil; $[\alpha]_D^{22} = -47.6$ (*c* 0.27, $CHCl_3$) for 94% ee ^{1}H NMR ($CDCl_3$): δ 7.41–7.23 (m, 10H), 5.72 (s, 1H), 5.50 (d, $J = 7.6$ Hz, 2H), 2.10 (br s, 1H); HPLC: Daicel CHIRALCEL OD column, hexane/IPA = 4:1, 0.60 mL/min, $\lambda = 254$ nm, $t_R(S) = 13.4$ min, $t_R(R) = 20.9$ min.

4.2.13. (*S*)-(*E*)-4-Methyl-1-phenylpent-1-en-3-ol 3m.[3k] Colorless oil; $[\alpha]_D^{22} = +34.2$ (*c* 0.58, $CHCl_3$) for 94% ee {lit.[3k] $[\alpha]_D^{20} = -37.1$ (*c* 1.34, $CHCl_3$) for 97% ee (*R*)}; ^{1}H NMR ($CDCl_3$): δ 7.38–7.24 (m, 5H), 5.81–5.62 (m, 1H), 5.16 (d, $J = 6.1$ Hz, 1H), 2.05 (m, 2H), 1.88 (s, 1H), 1.43–1.26 (m, 4H); 0.89 (t, $J = 7.0$ Hz, 3H); HPLC: Daicel CHIRALCEL OD column, hexane/IPA = 4:1, 0.60 mL/min, $\lambda = 254$ nm, $t_R(R) = 10.5$ min, $t_R(S) = 12.2$ min.

Acknowledgments

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11. A similar phenomenon was also reported by Bolm et al. (see Ref. 8a) when commercial alkenylboronic acids were used. In our case, the alkenylboronic acid used was prepared from the reaction of the corresponding organomagnesium bromide with $B(OMe)_3$ and purified by column chromatography.
12. A small amount of (1*E*,3*E*)-1,4-diphenylbuta-1,3-diene was isolated from the mixture. Molander et al. have found coupling of alkenylzinc species in the presence of sodium organoboronates: (a) Molander, G. A.; Zinke, P. W. *Organometallics* **1986**, *5*, 2161–2162; For related other studies, see also: (b) Li, H.; Walsh, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 6538–6539; (c) García, C.; Libra, E. R.; Walsh, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 3210–3211; (d) Srebnik, M. *Tetrahedron Lett.* **1991**, *32*, 2449–2452, and Ref. 3f.
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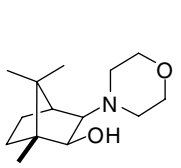
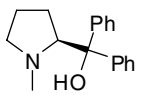
14. Several other small molecule ligands were also tested under the same conditions:



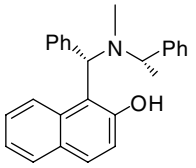
(-)-MIB

51% yield,95% ee



(*S*)-DPMPM

60% yield, 96% ee



61% yield, 96% ee

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