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A highly enantioselective synthesis of chiral allylic alcohols by asymmetric addition of novel mixed reagents of trialkenylbismuthines/dialkylzincs to aldehydes

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Abstract—A novel mixture of reagents of trialkenylbismuthines/dialkylzincs was developed and applied toward the synthesis of chiral allylic alcohols. The chiral β-amino alcohols catalyzed addition of the mixed reagents of trialkenylbismuthines/dialkylzincs to aldehydes gave enantiomerically enriched allylic alcohols with up to 97% ee.

1. Introduction

Chiral allylic alcohols are extremely versatile and useful synthetic intermediates. These chiral building blocks are typically synthesized by the selective 1,2-reduction of α,β-unsaturated carbonyl compounds,[1] kinetic resolution of the corresponding racemic compounds,[2] or the addition of vinyl groups to aldehydes.[3–7] In the latter methodology, the addition of dialkenylzinc reagents to aldehydes provides a convenient and promising way to obtain chiral allylic alcohols.[3,8] Oppolzer[4] and Wipf[5] have also reported the addition of in situ generated alkylalkenylzincs, made from terminal alkynes by hydroboration[4] or hydrozirconation,[5] followed by subsequent metal exchange reaction. Meanwhile, the chemistry of organobismuth reagents has attracted much interest.[9] Bismuth is the heaviest element of group 15 and, similar to nitrogen and phosphorus, has a pair of electrons in its highest s orbital. Therefore, organobismuth reagents act not only as organometallic reagents, but also as basic reagents.[9a] The control of this reactivity is still a challenge. Previously, we showed that novel mixed reagents of triarylbismuthines/dimethylzinc (Me_2Zn) could be used as an effective aryl source for highly enantioselective aryl transfer reactions to aldehydes catalyzed by a β-aminoalcohol.[10] Herein, we report the highly enantioselective addition of mixed reagents of trialkenylbismuthines/dialkylzincs to aldehydes. The reaction provides enantiomerically enriched allylic alcohols with up to 97% ee.

2. Results and discussion

First, the enantioselective addition of a mixed reagent of trivinylbismuthine/Me_2Zn to aldehydes was examined. To a diethyl ether solution of trivinylbismuthine[11] was added 3 mol equiv of Me_2Zn in hexane. The mixture was refluxed for 1 h and then cooled to 0 °C to provide a solution of the alkenylating reagent. The chiral catalyst, (*R*)-diphenyl(1-pyrrolidin-2-yl)methanol (DPMPM),[12] and aldehyde were subsequently added and reacted at this temperature. The results are shown in Table 1. When benzaldehyde **1a** was reacted with a mixed reagent of trivinylbismuthine/Me_2Zn, 1-phenylprop-2-en-1-ol **2a** with 90% ee was obtained (entry 1). When we mixed trivinylbismuthine and Me_2Zn at room temperature, the vinylation product was obtained with an obvious decrease in conversion efficiency. These results suggest that transmetallation at room temperature proceeds slowly. Presumably, it does not reach an equilibrium within 1 h. The addition of the reagent to 4-chlorobenzaldehyde **1b** gave allylic alcohol **2b** with 97% ee (entry 2). Reaction with 4-bromobenzaldehyde **1c** gave allylic alcohol **2c** with 97% ee in 81% yield (entry 3). When *p*-tolaldehyde **1d** and *p*-anisaldehyde **1e** were used as substrates, the ee values of the

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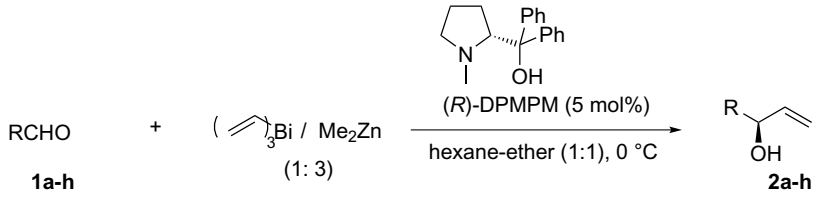
Table 1. Enantioselective vinylation of aldehydes **1** using a mixed reagent of $(C_2H_3)_3Bi/Me_2Zn$



Entry[a]	Aldehyde **1**		Allyl alcohol **2**[b]			
	R			Yield (%)	ee (%)	Config.
1	C_6H_5	**1a**	**2a**	51	90	(*R*)
2	4-ClC_6H_4	**1b**	**2b**	64	97	(*R*)
3	4-BrC_6H_4	**1c**	**2c**	81	97	(*R*)
4	4-$CH_3C_6H_4$	**1d**	**2d**	55	92	(*R*)
5	4-$CH_3OC_6H_4$	**1e**	**2e**	57	92	(*R*)
6	2-Naphthyl	**1f**	**2f**	74	95	(*R*)
7	$C_6H_5CH_2CH_2$	**1g**	**2g**	50	80	(*R*)
8	(*E*)-$C_6H_5CH{=}CH$	**1h**	**2h**	61	89	(*R*)

[a] Reaction were carried out in diethyl ether/hexane = 1:1 at 0 °C. Molar ratio. Chiral catalyst/Aldehyde **1**/Trivinylbismuthine/Me_2Zn = 0.05:1:3:9. For detailed conditions, see Ref. 13.

[b] Isolated yield. The ee value was determined by HPLC analysis on a column fitted with a chiral stationary phase. The configurations of **2a**,**b**,**d**–**f**,**h** were determined by comparison of the sign of the specific rotation with known compounds. The configuration of **2g** was determined by comparison of the retention time in HPLC analysis with reported values. The configuration of **2c** was tentatively assigned by configuration of the chiral catalyst used.

obtained allylic alcohols **2d** and **2e** were estimated to be 92%, respectively (entries 4 and 5). Addition to 2-naphthaldehyde **1f** and aliphatic 3-phenylpropanal **1g** also proceeded enantioselectively (95% and 80% ee, entries 6 and 7). Reaction with α,β-unsaturated aldehydes was also examined (entry 8): reaction of cinnamaldehyde **1h** provided diallylic alcohol in 61% yield with 89% ee.

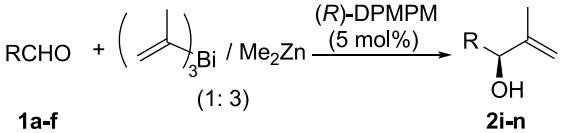
Next, the introduction of an isopropenyl group, that is, an α-branched alkenyl group was examined (Table 2). When a mixed reagent of triisopropenylbismuthine[13]/Me_2Zn was added to benzaldehyde **1a**, the corresponding (*R*)-2-methyl-1-phenylprop-2-en-1-ol **2i** with 91% ee was obtained (entry 1). Addition to aldehydes **1b** and **1c** gave chiral allylic alcohols **2j** and **2k** with 90% and 94% ee in 80 and 62% yield, respectively (entries 2 and 3). Reaction with *p*-tolaldehyde, 4-anisaldehyde, and 2-naphthaldehyde gave chiral allylic alcohols **2l**–**n** in 91–93% ee's (entries 4–6).

Finally, the enantioselective alkenylation with a mixed reagent of tris(2-methylprop-1-enyl)bismuthine[14]/Me_2Zn was examined (Scheme 1). In the presence of (1*R*,2*S*)-1-phenyl-2-(1-pyrrolidinyl)-1-propanol (PPP)[15] as a chiral catalyst, the asymmetric addition of a 2-methyl-1-propenyl group to 4-bromobenzaldehyde **1c** proceeded smoothly and gave enantiomerically enriched 1-(4-bromophenyl)-3-methylbut-2-en-1-ol **2o** with 80% ee.

3. Conclusion

In conclusion, we have developed a novel mixture of reagents of trialkenylbismuthines and dialkylzincs. The addition of an alkenyl group to aromatic aldehydes in the presence of chiral β-amino alcohol catalysts gave highly enantiomerically enriched allylic alcohols. With this novel mixed reagent, not only were terminal alkenyl groups,

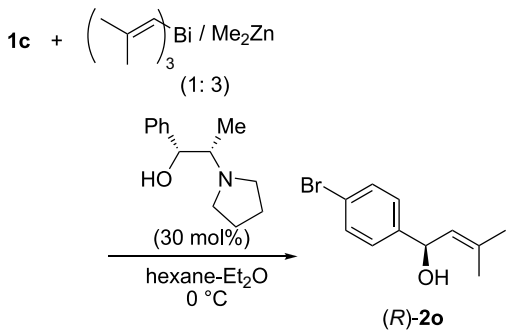
Table 2. Enantioselective isopropenylation of aldehydes **1** using a mixed reagent of $(C_3H_5)_3Bi/Me_2Zn$



Entry[a]	Aldehyde **1**	Allyl alcohol **2**[b]			
			Yield (%)	ee (%)	Config.
1	**1a**	**2i**	67	91	*R*
2	**1b**	**2j**	80	90	*R*
3	**1c**	**2k**	62	94	*R*
4	**1d**	**2l**	70	93	*R*
5	**1e**	**2m**	63	91	*R*
6	**1f**	**2n**	61	92	*R*

[a] Reaction were carried out in diethyl ether/hexane = 1:1 at 0 °C. Molar ratio. Chiral catalyst/aldehyde **1**/trialkenylbismuthine/Me_2Zn = 0.05:1:2.5:7.5.

[b] The configurations of **2i**,**j**,**l**,**m** were determined by comparison of sign of the specific rotation with known compounds. The configurations of **2k**,**n** were tentatively assigned by configuration of the chiral catalyst used.



Scheme 1.

but also an α-branched alkenyl group and a *cis*-substituted alkenyl group were introduced. These various alkenyl groups were easily introduced as substituents of relatively stable triorganobismuthines. Thus, this system provides a complementary way to known routes for synthesizing chiral allylic alcohols.

4. Experimental

4.1. General procedure for the catalytic and asymmetric alkenylation of aldehydes using mixed reagents of trialkenylbismuthines and dimethylzinc

Under an inert atmosphere of nitrogen, in a well-dried reaction vessel, dimethylzinc (1.0 M in hexane; 4.5 mmol) was added to a solution of trialkenylbismuthine (1.5 mmol) in fleshly distilled diethyl ether (4.5 mL) at room temperature. The mixture was heated at reflux for 1 h, then cooled to 0 °C. A hexane (4.5 mL) solution of (*R*)-DPMPM (5 mol %) and aldehyde (0.5 mmol) was added to the reaction mixture, after which the mixture was stirred for 12 h at 0 °C. After treatment with an adequate amount of 1 M aq HCl, the mixture was neutralized with satd aq $NaHCO_3$. The resulting mixture was filtered through Celite, and extracted with AcOEt. The combined organic extracts were dried over $MgSO_4$, and concentrated under the reduced pressure. The residue was purified by a preparative silica gel TLC (developing solvent: hexane/diethyl ether/acetone = 7:2:1) to give the optically active allyl alcohol. The ee value was determined by HPLC using a chiral stationary phase.

4.1.1. (*R*)-1-Phenylprop-2-en-1-ol 2a.[16] Yield 51%. 90% ee. Colorless oil; $[\alpha]_D^{22} = +1.0$ (*c* 0.9, $CHCl_3$) {lit.[16] $[\alpha]_D^{25} = -1.3$ (*c* 1.74, $CHCl_3$, >95%) for (*S*)-**2a** with >95% ee}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.96 (1H, br d, $J = 3.1$ Hz,), 5.1–5.3 (2H, m), 5.36 (1H, ddd, $J = 16.9$, 1.4, 1.4 Hz,), 6.06 (1H, ddd, $J = 16.9$, 10.3, 5.9 Hz,), 7.3–7.4 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 75.4, 115.1, 126.3, 127.8, 128.6, 140.3, 142.5; FT-IR (neat) *v* 3343, 3067, 3032, 1665, 1453, 1208, 1022, 739, 700 cm^{-1}; HRMS (ESI) calcd for $C_9H_{10}O$ ($[M+Na]^+$) 157.0629, found 157.0634. HPLC conditions: Daicel Chiralcel OD-H; eluent: 5% 2-propanol in hexane, flow rate, 1.0 mL/min, rt, retention time (min): 9.5 (*S*)-isomer, 11.6. (*R*)-isomer.

4.1.2. (*R*)-1-(4-Chlorophenyl)prop-2-en-1-ol 2b.[17] Yield 64%. 97% ee. Colorless oil; $[\alpha]_D^{22} = +15.2$ (*c* 1.1, $CHCl_3$) {lit.[17] $[\alpha]_D^{25} = -13.2$ (*c* 0.6, $CHCl_3$) for (*S*)-**2b** with 82% ee}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.01 (1H, br s), 5.1–5.3 (2H, m), 5.34 (1H, ddd, $J = 16.9$, 1.4, 1.4 Hz), 6.00 (1H, ddd, $J = 16.9$, 10.3, 6.2 Hz), 7.3–7.4 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 74.8, 115.8, 127.8, 128.8, 133.5, 140.0, 141.1; FT-IR (neat) *v* 3353, 2924, 2876, 1597, 1491, 1408, 1092, 1015, 801 cm^{-1}; HRMS (ESI) calcd for C_9H_9OCl 191.0240 ($[M+H]^+$), found 191.0248. HPLC conditions: Daicel Chiralcel OB-H; eluent: 0.5% 2-propanol in hexane, flow rate, 1.0 mL/min, rt, retention time (min): 33.4 (*R*)-isomer, 40.5 (*S*)-isomer.

4.1.3. (*R*)-1-(4-Bromophenyl)prop-2-en-1-ol 2c.[18] Yield 81%. 97% ee. Colorless oil; $[\alpha]_D^{22} = -16.8$ (*c* 1.2, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.98 (1H, br s), 5.1–5.3 (2H, m), 5.34 (1H, br d, $J = 17.2$ Hz), 6.00 (1H, ddd, $J = 17.2$, 10.3, 6.2 Hz), 7.2–7.3 (2H, m), 7.4–7.6 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 74.7, 115.7, 121.6, 128.0, 131.6, 139.8, 141.5; FT-IR (neat) *v* 3436, 3017, 2982, 1593, 1487, 1404, 1011, 990, 928, 818 cm^{-1}. HPLC conditions: Daicel Chiralpak AD-H; eluent: 4% 2-propanol in hexane, flow rate, 0.5 mL/min, rt, retention time (min): 24.6 (*R*)-isomer, 26.4 (*S*)-isomer.

4.1.4. (*R*)-1-*p*-Tolylprop-2-en-1-ol 2d.[17] Yield 55%. 92% ee. Colorless oil; $[\alpha]_D^{22} = +3.5$ (*c* 0.4, $CHCl_3$) for the sample with 95% ee. {lit.[17] $[\alpha]_D = -3.8$ (*c* 0.8, $CHCl_3$) for (*S*)-**2d** with 99% ee}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.95 (1H, br s), 2.35 (3H, s), 5.1–5.2 (2H, m), 5.34 (1H, br d, $J = 16.7$ Hz), 6.05 (1H, ddd, $J = 16.7$, 10.0, 6.2 Hz), 7.17 (2H, d, $J = 7.9$ Hz), 7.27 (2H, d, $J = 7.9$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 21.1, 75.1, 114.9, 126.3, 129.2, 137.5, 139.7, 140.3; FT-IR (neat) *v* 3360, 3275, 2922, 1512, 1422, 1034, 990, 926, 816 cm^{-1}. HPLC conditions: Daicel Chiralcel OJ-H; eluent: 5% 2-propanol in hexane, flow rate, 1.0 mL/min, rt, retention time (min): 15.7 (*R*)-isomer, 16.9 (*S*)-isomer.

4.1.5. (*R*)-1-(4-Methoxyphenyl)prop-2-en-1-ol 2e.[19] Yield 57%. 92% ee. Colorless oil; $[\alpha]_D^{22} = +3.7$ (*c* 1.5, $CHCl_3$) {lit.[19] $[\alpha]_D^{26} = +4.2$ (*c* 1.11, $CHCl_3$) for (*R*)-**2e** with 95%}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.89 (1H, br s), 3.81 (3H, s), 5.1–5.2 (2H, m), 5.34 (1H, ddd, $J = 16.7$, 1.4, 1.4 Hz), 6.05 (1H, ddd, $J = 16.7$, 10.2, 5.9 Hz), 6.8–7.0 (2H, m), 7.2–7.4 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 55.4, 75.0, 114.0, 114.9, 127.8, 134.9, 140.4, 159.3; FT-IR (neat) *v* 3409, 2838, 1611, 1512, 1248, 1175, 1034, 992, 926, 831 cm^{-1}. HPLC conditions: Daicel Chiralcel OD-H; eluent: 3% 2-propanol in hexane, flow rate, 1.0 mL/min, rt, retention time (min): 16.7 (*R*)-isomer, 20.3 (*S*)-isomer.

4.1.6. (*R*)-1-(Naphthalene-2-yl)prop-2-en-1-ol 2f.[20] Yield 74%. 95% ee. Colorless oil; $[\alpha]_D^{25} = -4.9$ (*c* 0.7, $CHCl_3$) {lit.[20] (*R*) $[\alpha]_D^{18} = -9.1$ (*c* 1, $CHCl_3$) for (*R*)-**2f** with 98% ee}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.05 (1H, br d, $J = 3.5$ Hz), 5.26 (1H, br d, $J = 10.0$ Hz,), 5.3–5.5 (2H, m), 6.13 (1H, ddd, $J = 16.9$, 10.0, 6.2 Hz), 7.4–7.5 (3H, m), 7.8–7.9 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 75.5, 115.4, 124.5, 124.9, 126.0, 126.2, 127.6, 128.0, 128.4, 133.3, 134.5, 139.9, 140.1; FT-IR (neat) *v* 3426, 3358,

3057, 1638, 1601, 1125, 1038, 990, 928, 820, 747 cm^{-1}. HPLC conditions: Daicel Chiralpak AS-H; eluent: 4% 2-propanol in hexane, flow rate, 0.7 mL/min, rt, retention time (min): 17.0 (*R*)-isomer, 20.3 (*S*)-isomer.

4.1.7. (*R*)-5-Phenylpent-1-en-3-ol 2g.[21] Yield 50%. 80% ee. Colorless oil; $[\alpha]_D^{21} = -5.8$ (*c* 1.3, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.55 (1H, br s), 1.8–1.9 (2H, m), 2.6–2.8 (2H, m), 4.13 (1H, br d, $J = 5.9$ Hz), 5.14 (1H, ddd, $J = 10.3$, 1.4, 1.4 Hz), 5.25 (1H, ddd, $J = 16.9$, 1.4, 1.4 Hz), 5.91 (1H, ddd, $J = 16.9$, 10.3, 5.9 Hz), 7.1–7.4 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 31.6, 38.5, 72.5, 114.9, 125.8, 128.4, 128.4, 141.0, 141.8; FT-IR (neat) *v* 3434, 2930, 2857, 1454, 1036, 992, 698 cm^{-1}. HPLC conditions: Daicel Chiralcel OD-H; eluent: 3% 2-propanol in hexane, flow rate, 1.0 mL/min, rt, retention time (min): 17.1 (*R*)-isomer, 26.0 (*S*)-isomer.

4.1.8. (4*E*,3*R*)-1-Phenylpenta-1,4-dien-3-ol 2h.[16] Yield 61%. 89% ee. Colorless oil; $[\alpha]_D^{22} = -33.9$ (*c* 1.0, $CHCl_3$) {lit.[16] $[\alpha]_D^{25} = +38.5$ (*c* 1.90, $CHCl_3$) for (*S*)-**2h** with >95% ee}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.61 (1H, br s), 4.82 (1H, br t, $J = 6.1$ Hz), 5.20 (1H, ddd, $J = 10.5$, 1.3, 1.3 Hz), 5.34 (1H, ddd, $J = 17.2$, 1.3, 1.3 Hz), 5.97 (1H, ddd, $J = 17.2$, 10.5, 6.1), 6.23 (1H, dd, $J = 16.0$, 6.1 Hz), 6.62 (1H, d, $J = 16.0$ Hz), 7.2–7.5 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 73.8, 115.4, 126.5, 127.8, 128.6, 130.3, 130.8, 136.5, 139.2; FT-IR (neat) *v* 3505, 1451, 990, 966, 928, 752, 693 cm^{-1}. HPLC conditions: Daicel Chiralpak AS-H; eluent: 3% 2-propanol in hexane, flow rate, 1.0 mL/min, rt, retention time (min): 13.4 (*R*)-isomer, 15.9 (*S*)-isomer.

4.1.9. (*R*)-2-Methyl-1-phenylprop-2-en-1-ol 2i.[3d] Yield 67%. 91% ee. Colorless oil; $[\alpha]_D^{22} = +26.6$ (*c* 0.6, $CHCl_3$) {lit.[3d] $[\alpha]_D^{23} = -27.4$ (*c* 4.5, $CHCl_3$) for (*S*)-**2i** with 89% ee}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.61 (3H, s), 1.96 (1H, br s), 4.96 (1H, br s), 5.14 (1H, br s), 5.21 (1H, br s), 7.2–7.4 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 18.2, 77.9, 111.1, 126.4, 127.6, 128.4, 141.9, 146.8; FT-IR (neat) *v* 3406, 1655, 1493, 1450, 1375, 900, 839 cm^{-1}. HPLC conditions: Daicel Chiralpak AS-H; eluent: 3% 2-propanol in hexane, flow rate, 0.7 mL/min, rt, retention time (min): 11.0 (*R*)-isomer, 12.2 (*S*)-isomer.

4.1.10. (*R*)-1-(4-Chlorophenyl)-2-methylprop-2-en-1-ol 2j.[3e] Yield 80%. 90% ee. Colorless oil; $[\alpha]_D^{22} = +6.7$ (*c* 0.4, $CHCl_3$) {lit.[3e] $[\alpha]_D^{24} = -7.4$ (*c* 1.6, $CHCl_3$) for (*S*)-**2j** with 89% ee}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.59 (3H, s), 1.98 (1H, br d, $J = 3.1$ Hz), 4.96 (1H, br s), 5.12 (1H, br s), 5.19 (1H, br s), 7.3–7.4 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 17.9, 77.2, 111.7, 127.8, 128.5, 133.3, 140.3, 146.5; FT-IR (neat) *v* 3391, 1655, 1491, 1439, 1406, 1375, 1091, 1041, 904, 844, 819, 790 cm^{-1}. HPLC conditions: Daicel Chiralcel OB-H; eluent: 3% 2-propanol in hexane, flow rate, 0.9 mL/min, rt, retention time (min): 10.1 (*R*-isomer), 13.0 (*S*-isomer).

4.1.11. (*R*)-1-(4-Bromophenyl)-2-methylprop-2-en-1-ol 2k Yield 62%. 94% ee. Colorless oil; $[\alpha]_D^{22} = +13.9$ (*c* 1.8, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.59 (3H, s), 1.98 (1H, br d, $J = 3.1$ Hz,), 4.96 (1H, br s), 5.10 (1H, br s), 5.18 (1H, br s), 7.2–7.3 (2H, m), 7.4–7.45 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 17.9, 77.3, 111.8, 121.4, 128.1, 131.4, 140.9, 146.4; FT-IR (neat) *v* 3370, 2920, 2855, 1651, 1485, 1071, 1011, 907 cm^{-1}; HRMS (ESI) calcd for $C_{10}H_{10}OBr$ ($[M-H]^-$) 226.9895, found 226.9888. HPLC conditions: Daicel Chiralpak AS-H; eluent: 1% ethanol in hexane, flow rate, 1.0 mL/min, rt, retention time (min): 14.8 (*R*)-isomer, 16.9 (*S*)-isomer.

4.1.12. (*R*)-2-Methyl-1-*p*-tolylprop-2-en-1-ol 2l.[3e] Yield 70%. 93% ee. Colorless oil; $[\alpha]_D^{22} = +12.1$ (*c* 0.2, $CHCl_3$) for (*R*)-**2l** with 86% ee {lit.[3e] $[\alpha]_D^{20} = -12.1$ (*c* 0.131, $CHCl_3$) for (*S*)-**2l** with 96% ee}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.61 (3H, s), 1.88 (1H, br s), 2.34 (3H, s), 4.95 (1H, br s), 5.10 (1H, br s), 5.20 (1H, br s), 7.15 (2H, d, $J = 7.9$ Hz), 7.26 (2H, d, $J = 7.9$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 18.4, 21.1, 77.7, 110.8, 126.4, 129.1, 139.0, 142.8, 146.9; FT-IR (neat) *v* 3387, 2971, 2922, 2863, 1655, 1512, 1449, 1375, 1047, 901 cm^{-1}. HPLC conditions: Daicel Chiralpak AS-H; eluent: 1.5% ethanol in hexane, flow rate, 1.0 mL/min, rt, retention time (min): 9.0 (*R*)-isomer, 11.1 (*S*)-isomer.

4.1.13. (*R*)-1-(4-Methoxyphenyl)-2-methylprop-2-en-1-ol 2m.[3d] Yield 63%. 91% ee. Colorless oil; $[\alpha]_D^{22} = +56.7$ (*c* 0.2, $CHCl_3$) {lit.[3d] $[\alpha]_D^{22} = -51.5$ (*c* 1.6, $CHCl_3$) for (*S*)-**2m** with 92% ee}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.61 (3H, s), 1.89 (1H, br d, $J = 2.7$ Hz), 3.80 (3H, s), 4.94 (1H, br s), 5.08 (1H, br s), 5.20 (1H, br s), 6.8–6.9 (2H, m), 7.2–7.3 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.5, 55.3, 77.4, 110.6, 113.8, 127.8, 134.1, 147.0, 159.1; FT-IR (neat) *v* 3424, 2838, 1611, 1512, 1248, 1173, 1036, 901, 825 cm^{-1}. HPLC conditions: Daicel Chiralcel OB-H; eluent: 3% 2-propanol in hexane, flow rate, 1.0 mL/min, rt, retention time (min): 19.4 (*R*)-isomer, 32.5 (*S*)-isomer.

4.1.14. (*R*)-2-Methyl-1-(naphthalen-2-yl)prop-2-en-1-ol 2n.[22] Yield 61%. 92% ee. Colorless oil; $[\alpha]_D^{22} = +17.6$ (*c* 2.2, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.64 (3H, s), 2.05 (1H, br d, $J = 3.4$ Hz), 5.01 (1H, br s), 5.28 (1H, br s), 5.31 (1H, br s), 7.4–7.5 (3H, m), 7.7–7.9 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 18.3, 78.0, 111.5, 124.4, 125.2, 125.9, 126.1, 127.7, 128.0, 128.2, 133.0, 133.3, 139.3, 146.7; FT-IR (neat) *v* 3426, 3056, 2973, 2920, 1653, 1601, 1508, 1049, 901, 816, 745 cm^{-1}. HPLC conditions: Daicel Chiralpak AD-H; eluent: 4% 2-propanol in hexane, flow rate, 0.7 mL/min, rt, retention time (min): 21.8 (*R*)-isomer, 25.6 (*S*)-isomer.

4.2. Synthesis of (*R*)-1-(4-bromophenyl)-3-methylbut-2-en-1-ol 2o

Under a nitrogen atmosphere, dimethylzinc (1.0 M in hexane; 1.5 mL, 1.5 mmol) was added to a solution of tris(2-methylprop-1-enyl)bismuthine (188.0 mg, 0.50 mmol) in Et_2O (1.5 mL) at room temperature. The mixture was heated at reflux for 1 h, then cooled to 0 °C. A solution of (1*R*,2*S*)-PPP (13.1 mg, 0.06 mmol) in hexane (1.0 mL) was added to the reaction mixture. A solution of *p*-bromobenzaldehyde (37.0 mg, 0.20 mmol) in hexane (1.5 mL) was added to the mixture and the mixture was stirred for 12 h at 0 °C. The reaction was quenched by adding aq

hydrochloric acid. After the mixture was neutralized by the addition of satd aq $NaHCO_3$, the mixture was filtered through Celite, extracted with AcOEt, and dried over $MgSO_4$. Concentration and purification by preparative silica gel TLC (hexane/diethyl ether/acetone = 7:2:1) gave 1-(4-bromophenyl)-3-methylbut-2-en-1-ol (31.5 mg, 0.13 mmol). The ee value was estimated to be 80% by HPLC analysis (Chiralcel OJ-H). Colorless amorphous; $[\alpha]_D^{22} = -89.4$ (c 1.3, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.75 (3H, d, $J = 1.1$ Hz), 1.79 (3H, d, $J = 1.1$ Hz), 1.83 (1H, br s), 5.34 (1H, br d, $J = 9.2$ Hz), 5.42 (1H, br d, $J = 9.2$ Hz), 7.2–7.3 (2H, m), 7.4–7.5 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.3, 25.8, 70.1, 121.0, 127.3, 127.6, 131.5, 135.9, 143.1; FT-IR (KBr) ν 3301, 2982, 1487, 1377, 1149, 1073, 1009, 862, 810 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{12}OBr$ ($[M-H]^+$) 241.0052, found. 241.0044. HPLC conditions: Daicel Chiralcel OJ-H; eluent: 1% 2-propanol in hexane, flow rate, 0.5 mL/min, rt, retention time (min): 33.0 (*S*)-isomer, 34.4 (*R*)-isomer.

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