

A Highly Efficient and Practical New Allylboronate Tartramide for the Asymmetric Allylboration of Achiral Aldehydes

Wansuo Chen,^{*,[a]} Yanzhu Liu,^[b] and Zhirong Chen^[a]

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Chiral homoallylic alcohols can be prepared from aldehydes upon reaction with two optically pure allylboronate tartramides. The enantiomeric excess is 10–15 % higher for the allylation of benzaldehyde when using *N,N'*-dibenzyltartramide auxiliary **5b** than when using *N,N'*-diphenyltartramide (**5a**). 2-Allyl-*N,N'*-dibenzyl-1,3,2-dioxaborolane-4,5-dicarbamide (**2b**) affords homoallylic alcohols with 90–

99 % ee upon reaction with some representative aldehydes. The derivatised chiral auxiliaries can be recovered by simple recrystallization, in 85 % yield, without any loss of specific rotation.

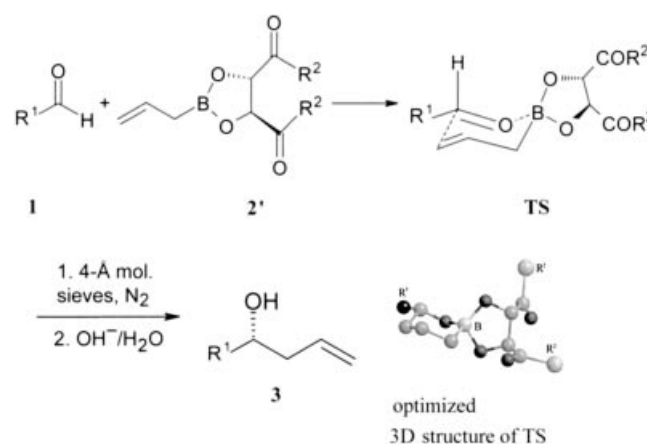
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Introduction

Homoallylic alcohols have been incorporated, usually in a racemic form, into various compounds with interesting biological activity,^[1] such as alkaloids,^[2] micro antibiotics,^[3] (+)-discodermolide^[4] and (+)-negamycin,^[5] etc. Asymmetric allylation of aldehydes to homoallylic alcohols has been comprehensively reviewed,^[6] and the method of stereoselective allylation using optically pure tartrates^[7] and dialkylboranes^[8] has been developed thoroughly by the groups of Roush and Brown, respectively. The chiral tartramide auxiliaries used in this reaction have rarely been reported, with the exception of *N,N'*-dibenzyl-*N,N'*-ethylenetartramide (**6**), which was reported by the Roush group in 1988.^[9a] In this work, the synthesis of chiral homoallylic alcohols in excellent enantioselectivity in the presence of two novel, chiral tartramides auxiliaries (**5a** and **5b**) is described, as well as the comparison with 2-allyl-1,3,2-dioxaborolane-4,5-dicarboxylic acid bis(1'-methylethyl) ester (**9**) and *B*-allylbis(4-isocaranyl)borane (4-^dIcr₂Ball, **10**) in allylboration. The asymmetric allylation of aldehydes with allylboronates (**2'**) gives homoallylic alcohols via a six-membered ring chair-like transition state (TS)^[10] (Scheme 1).

Results and Discussion

Roush has designed the chiral tartramide auxiliary **6**,^[9a] which reacts with aldehydes with high enantioselectivity but just 40–43 % yield. Derived from this restricted auxiliary,



Scheme 1.

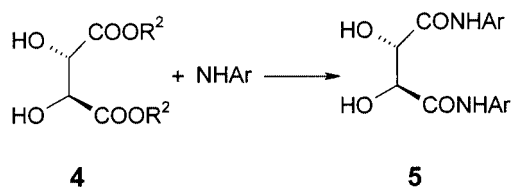
we rationally developed two novel, chiral auxiliaries in two ways from arylamine with chiral tartrate or tartaric acid (Scheme 2). Rotationally pure tartaric acid reacts with aniline directly in the presence of K₂CO₃ or BF₃·OEt₂ to give **5a** in 90 % yield; compound **5b** was prepared by the amidation of diethyl tartrate with benzylamine in 94 % yield. The two tartramides were purified by recrystallization from AcOH/H₂O in high yield.

In general, aniline hardly reacts with organic acids because of the conjugation between the lone electron pair of the nitrogen atom and the π electrons of the benzene ring. Because of this we unexpectedly obtained imide **7** as the main product when using benzylamine. Thus, optically pure tartrates have to be chosen to avoid imide formation during the preparation of **5b** (Scheme 2).

Allylboronate tartramides **2** were synthesized by two routes: the reaction of triallylborane with aryl tartramide **5** or monoallylboron difluoride with **8** (Scheme 3).

[a] Department of Chemical Engineering and the Unilab Research Center of Chemical Reaction Engineering, Zhejiang University, Hangzhou 310027, P. R. China

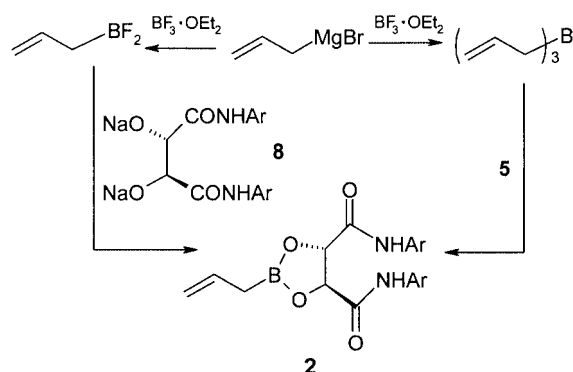
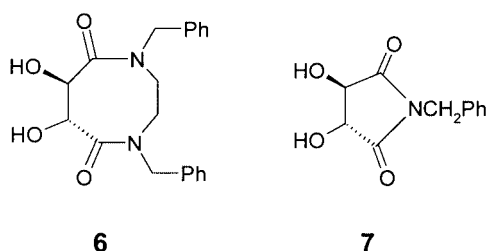
[b] Department of Chemistry, Nanchang University, Nanchang 330047, P.R. China
Fax: +86-571-8795-1227
E-mail: wansuochen@yahoo.com.cn



a $R^2 = \text{H}$, $\text{Ar} = \text{Ph}$

b $R^2 = \text{Et}$, $\text{Ar} = \text{CH}_2\text{Ph}$

Scheme 2.



Scheme 3.

As can be seen from Scheme 3, we prefer the second one because of the high yield for the preparation of **2**. However, it must be noted that the sodium hydride used to prepare **8** is very sensitive to moisture, so the reagents and solvents used must be dried prior to use. Fortunately, the unreacted sodium hydride does not affect the following allylboration reaction. For analytical purposes, benzaldehyde was selected to react with **2** under various conditions and the results are listed in Table 1.

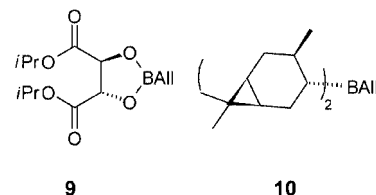
Table 1. Asymmetric allylation of benzaldehyde with **2**.

Entry	Reactants	T [°C]	t [h]	Solvent	Yield ^[a] [%]	ee ^[b] [%]
1	(<i>S,S</i>)- 2a	23	18	diethyl ether	62.5	6.4 (<i>R</i>)
2	(<i>R,R</i>)- 2b	0	14	toluene	77.7	34 (<i>S</i>)
3	(<i>R,R</i>)- 2b	−20	14	toluene	80.5	46 (<i>S</i>)
4	(<i>S,S</i>)- 2b	−40	16	THF	79.6	61 (<i>R</i>)
5	(<i>S,S</i>)- 2b	−60	16	toluene	83.5	85 (<i>R</i>)
6	(<i>S,S</i>)- 2a	−78	14	THF	76.2	72 (<i>R</i>)
7	(<i>S,S</i>)- 2a	−78	18	toluene	82.3	80 (<i>R</i>)
8	(<i>R,R</i>)- 2b	−78	18	diethyl ether	87.0	83 (<i>S</i>)
9	(<i>R,R</i>)- 2b	−78	14	toluene	87.8	90 (<i>S</i>)

[a] Yield of isolated product. [b] Determined by chiral HPLC analysis on a Daicel chiralcel OD-H column (C18, 250 × 4.6 mm, 5 μm) with 2% IPA/hexane (v/v) as mobile phase with UV/Vis detection ($\lambda = 220$ nm, SPD-M10A). The single-enantiomer structures were assigned by comparison of HPLC traces and optical rotation values with known compounds and based on the assumption of a single reaction pathway for all substrates.

As shown, the yields and optical purities are up to 87.8% and 90%, respectively (Table 1, entry 9), and the aprotic solvent toluene is better than diethyl ether because protic solvents break the bond between the boron atom and carbonyl group in the tartramide auxiliaries. The enantioselectivity benefits from a lower temperature, whereas the time scarcely affects yield and enantioselectivity because the reaction is fast in the first two hours, but then slows down according to HPLC monitoring. More importantly, the enantioselectivity is better when using benzyl amide auxiliary **2b** than aniline auxiliary **2a** in the allylboration (Table 1, entries 7 and 9).

Some other representative achiral aldehydes were also selected to react with **2b** at −78 °C. The experimental data are summarized in Table 2 and compared with the reagents used by the Roush (reagent **9**) and Brown (reagent **10**) groups.



As shown, we prefer **2b** to the widely used DIPT auxiliary **9** and 4- dIcr_2Ball because of its high enantioselectivity (Table 2, entries 2–4), and the derivatised chiral auxiliary **5b**

Table 2. Comparison of the enantioselectivities achieved in the allylboration of representative aldehydes with **2b** (−78 °C in toluene), **9** (Roush reagent, −78 °C) and 4- dIcr_2Ball (**10**, Brown reagent, −100 °C).

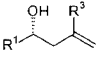
	Aldehydes	Products	ee [%]		
			9 ^[a]	10 ^[b]	2b
1	benzaldehyde (1a)	(<i>R</i>)- 3a	71	98	90
2	<i>n</i> -butyraldehyde (1b)	(<i>S</i>)- 3b	79 ^[c]	98	95 ^[d]
3	pivaldehyde (1c)	(<i>R</i>)- 3c	82	≥99	98 ^[d]
4	cyclohexanecarboxaldehyde (1d)	(<i>R</i>)- 3d	87		99 ^[d]

[a] See ref.^[9a] [b] At −100 °C, essentially instantaneous.^[7c] [c] Value for 1-decanal.^[9b] [d] At −78 °C [16 h, determined by the same chiral column with a Refractive Index detector (RID-10A)].

can easily be recovered by recrystallisation, in 85% yield, without any loss of specific rotation.

We also explored the allylboration of **2b** [or *N,N'*-dibenzyl-2-methylallyl-1,3,2-dioxaborolane-4,5-dicarbamide (**2b'**)] with several other achiral aldehydes. To the best of our knowledge, this is the first time that 2-methylallylborolane has been found to react with this novel auxiliary with satisfactory yields and enantioselectivities (Table 3, entry 2).

Table 3. Reactions of (*S,S*)-**2b** and (*S,S*)-**2b'** with some other achiral aldehydes.

Entry	Aldehydes (R'CHO)		<i>T</i>		<i>t</i>		% Yield ^[a] ee ^[b]	
			[°C]	[h]	[h]			
1	4-bromobutyraldehyde (1e)	(<i>R</i>)- 3e , R ³ = H	-78	18		89	97	
2	2-chlorobenzaldehyde (1f)	(<i>R</i>)- 3f , R ³ = Me	-78	18		87	92	
3	pyridine-2-carboxaldehyde (1g)	(<i>S</i>)- 3g , R ³ = H	-78	18		92	94	

[a] Yield of isolated product after purification by column chromatography. [b] Determined on a Chiralcel OD-H Column (C18, 250×4.6 mm, 5 μm) with 2% IPA/hexane (v/v) as mobile phase with a UV/Vis Detector (SPD-M10A) or a Refractive Index Detector (RID-10A).

In summary, we have described a highly convenient procedure for the asymmetric allylboration of a variety of representative aldehydes controlled by an efficient and practical chiral auxiliary **5b**, which affords homoallylic alcohols in 90–99% *ee*. This novel chiral auxiliary can be recovered by recrystallisation, in high yield, without any decrease in enantioselectivity. Consequently, we believe that this novel auxiliary will become even more valuable for stereoselective synthesis of natural products and new chiral drugs.

Experimental Section

General: ¹H and ¹³C NMR spectra were measured at 500 MHz and 125 MHz, respectively, on an Avance DMX500 instrument. Chemical shifts are reported in δ units relative to internal CHCl₃ (δ = 7.24 or 77.0 ppm) or DMSO (δ = 2.43 ppm) as the internal standard.

All reactions were conducted in oven-dried (120 °C) glassware under an atmosphere of nitrogen. All solvents were freshly distilled before use. Et₂O and THF were distilled from sodium benzophenone ketyl and toluene was distilled from sodium metal.

Analytical TLC was performed with 2.5×10 cm plates coated with a 0.25 mm layer of silica gel containing PF254 indicator. Analytical HPLC was performed with a UV/Vis or refractive index detector connected to a reversed phase HPLC system (C18 column, 250×4.6 mm, 5 μm) on a Shimadzu instrument. Preparative HPLC was conducted with a C18 column (250×40 mm, 20 μm) on a Lab-Alliance instrument. All chromatograph solvents were distilled prior to use.

The enantiomeric excess was determined with a Daicel chiralcel OD-H column (C18, 250×4.6 mm, 5 μm) with 2% IPA/hexane (v/v) as mobile phase and a UV/Vis detector (λ = 220 nm, SPD-M10A) or a Refractive Index Detector (RID-10A).

Amidation of Optically Pure Tartaric Acid to *N,N'*-Diphenyltartramide [(*S,S*)-5a**]:** A mixture of xylene (25 mL), aniline (5 g, 70 mmol) and L-(+)-tartaric acid (2.25 g, 15 mmol) was refluxed for 2 h.

DMF (2.5 mL, 33 mmol) was added and refluxed for an additional 3 h. The mixture was then cooled to room temperature to afford a white solid, which was isolated by filtration, washed with water and 95% EtOH in water, and recrystallised from 90% acetic acid in water to obtain **5a** as white crystals. Yield: 4.1 g (90%). M.p. 261.1–263.0 °C. [α]_D²⁰ = +139 (*c* = 1.0, DMF). ¹H NMR ([D₆]DMSO, 500 MHz): δ = 9.62 (s, 2 H), 7.76–7.74 (d, 4 H), 7.34–7.30 (t, 4 H), 7.10–7.05 (t, 2 H), 6.05–6.00 (d, 2 H), 4.51–4.48 (d, 2 H) ppm. ¹³C NMR ([D₆]DMSO, 125.7 MHz): δ = 172.00, 138.54, 129.00, 124.42, 121.63, 73.41 ppm. IR: ν̄ = 3410, 3300, 1670 cm⁻¹. C₁₆H₁₆N₂O₄ (300.3): calcd. C 63.99, H 5.37, N 9.33; found C 63.03, H 5.14, N 10.52.

Amidation of Chiral Diethyl Tartrate to *N,N'*-Dibenzyltartramide [(*S,S*)-5b**]:** A mixture of methanol (20 mL), benzylamine (6.0 g, 56 mmol), K₂CO₃ (0.1 g, 0.72 mmol) and D-(–)-diethyl tartrate (5.2 g, 25 mmol) was refluxed for 8 h. It was then cooled to room temperature to afford a white solid, which was filtered, washed with water, and recrystallised from 50% ethanol in water to obtain **5b** as white crystals. Yield: 7.8 g (94%). M.p. 202.0–204.0 °C. [α]_D²⁰ = –75.08 (*c* = 2.0, DMF). ¹H NMR ([D₆]DMSO, 500 MHz): δ = 7.22–7.35 (m, 10 H), 5.74–5.75 (d, 2 H), 4.30–4.42 (m, 4 H) ppm. ¹³C NMR ([D₆]DMSO, 125.7 MHz): δ = 173.15, 141.70, 128.62, 127.00, 126.85, 73.81, 44.48 ppm. IR: ν̄ = 3360, 3300, 1650 cm⁻¹. C₁₈H₂₀N₂O₄ (328.4): calcd. C 65.84, H 6.14, N 8.53; found C 65.62, H 6.48, N 8.41.

Preparation of Triallylborane:^[11] Mg turnings (3.0 g, 125 mmol), a crystal of iodine, BF₃·Et₂O (4.7 g, 33 mmol) and dry diethyl ether (80 mL) were placed in the reaction flask, and the reaction was initiated by a dropwise addition of 1.0 mL of neat allyl bromide, while vigorously stirring the reaction mixture. A further portion of allyl bromide (7.36 mL, 100 mmol) dissolved in anhydrous diethyl ether (50 mL) was added slowly over a period of 1 h, and the solvent was allowed to reflux smoothly. The reaction mixture was stirred for an additional 2 h. The clear ethereal layer was transferred into a distillation flask and the solvent was removed at atmospheric pressure. Distillation under vacuum in a short-path distillation assembly afforded triallylborane (3.7 g, 84%), b.p. 65 °C at 20 Torr. ¹H NMR (CDCl₃, 500 MHz): δ = 5.96–5.83 (m, 2 H), 5.05 (d, 2 H), 1.92 (d, 2 H) ppm. C₉H₁₅B (134.0): calcd. C 80.65, H 11.28, B 8.07; found C 80.12, H 11.07, B 8.81.

Preparation of Monoallylboron Difluoride:^[11] The procedure is similar to the synthesis of triallylborane except that the ratio of BF₃ to allyl bromide used in the reaction is 1:1. C₃H₅BF₂ (89.9): calcd. C 40.09, H 5.61, B 12.03, F 42.27; found C 40.16, H 5.07, B 12.85, F 41.92.

Preparation of **8:** Optically pure *N,N'*-diaryltartramide (20 mmol, **5a** or **5b**) was added to a solution of 80% sodium hydride (1.3 g, 40 mmol) in 50 mL of dry diethyl ether in three portions under an atmosphere of nitrogen, and then stirred for 1 h. The mixture was not purified and was used directly in the subsequent reaction with monoallylboron difluoride.

Preparation of 2-Allyl-*N,N'*-dibenzyl-1,3,2-dioxaborolane-4,5-dicarbamide [(*S,S*)-2**] from **5**:** A suspension of **5** (20 mmol) in 60 mL of dry diethyl ether was treated with triallylborane (2.68 g, 20 mmol) at 23 °C. The suspension became a clear solution within a few minutes and was stirred for 3 h before being concentrated in vacuo with exclusion of moisture. The resulting white foam was stripped overnight at 0.1 mmHg to give reagent **2** in 86% yield, which was used directly in the next experiments.

2a: ¹H NMR ([D₆]DMSO, 500 MHz): δ = 8.26–8.24 (t, 2 H), 7.75–7.07 (m, 10 H), 5.93–5.87 (m, 2 H), 5.22 (d, 2 H), 4.86 (d, 2 H),

3.93 (d, 2 H) ppm. ^{13}C NMR ($[\text{D}_6]\text{DMSO}$, 125.7 MHz): δ = 173.11, 141.72, 135.54, 128.60, 126.80, 117.26, 78.72, 29.30 ppm.

2b: ^1H NMR ($[\text{D}_6]\text{DMSO}$, 500 MHz): δ = 8.26–8.24 (t, 2 H), 7.75–7.07 (m, 10 H), 5.93–5.87 (m, 2 H), 5.20 (d, 2 H), 4.85 (d, 2 H), 4.40–4.29 (m, 4 H), 3.93 (d, 2 H) ppm. ^{13}C NMR ($[\text{D}_6]\text{DMSO}$, 125.7 MHz): δ = 173.12, 141.71, 135.54, 128.60, 126.80, 117.26, 78.74, 44.42, 29.31 ppm.

Preparation of 2 from 8: A solution of monoallylboron difluoride in anhydrous diethyl ether was added dropwise to the mixture of **8** obtained above at room temperature under an atmosphere of nitrogen. The solution was stirred for 3 h before being concentrated in vacuo with exclusion of moisture. The resulting white foam was stripped at 0.1 mmHg to give **2a** or **2b** in 98% yield.

General Preparation of Chiral Homoallyl Alcohols 3a–g: A solution of freshly distilled aldehyde in dry toluene was added dropwise to a solution of **2a** or **2b** in toluene at -78°C containing 4-Å molecular sieves. The resulting mixture was kept at -78°C until the reaction was judged complete by TLC analysis (about 16 h), and was then terminated by addition of an excess of NaHCO_3 in H_2O . This two-phase mixture was stirred for 2 h, and then separated. The organic phase was extracted with Et_2O . The upper phase was dried with anhydrous Na_2SO_4 , and then concentrated in vacuo to obtain the product homoallylic alcohols, which were purified by preparative HPLC with methanol as the mobile phase.

(R)-Phenylbut-3-en-1-ol (3a): $[\alpha]_{\text{D}}^{20}$ = +30.9 (c = 2.0, benzene). IR (NaCl): $\tilde{\nu}$ = 3383, 3075, 1641 cm^{-1} . ^1H NMR (CDCl_3 , 500 MHz): δ = 7.65–7.29 (m, 5 H), 5.70–5.65 (m, 1 H), 5.11–5.00 (m, 2 H), 4.74 (t, 1 H), 2.90–2.40 (m, 2 H) ppm. ^{13}C NMR (CDCl_3 , 125.7 MHz): δ = 143.99, 134.55, 128.30, 127.41, 125.92, 117.94, 73.40, 43.64 ppm. MS: m/z (%) = 148 [M^+]. $\text{C}_{10}\text{H}_{12}\text{O}$ (148.2): calcd. C 81.04, H 10.81; found C 80.78, H 11.07.

(S)-Hept-4-en-1-ol (3b): $[\alpha]_{\text{D}}^{20}$ = -12.5 (c = 10.2, benzene). ^1H NMR (CDCl_3 , 500 MHz): δ = 5.75–5.65 (m, 1 H), 5.05–4.95 (d, 2 H), 3.30–3.20 (m, 1 H), 2.25–2.20 (m, 1 H), 2.02–1.95 (d, 1 H), 1.50–1.42 (d, 2 H), 1.33 (m, 2 H), 0.96 (m, 3 H) ppm. ^{13}C NMR (CDCl_3 , 125.7 MHz): δ = 137.71, 115.75, 72.18, 42.34, 40.23, 16.72, 14.45 ppm. MS: m/z (%) = 115 [M^+]. $\text{C}_7\text{H}_{14}\text{O}$ (114.2): calcd. C 73.63, H 12.36; found C 73.22, H 12.77.

(R)-2,2-Dimethylhex-5-en-3-ol (3c): $[\alpha]_{\text{D}}^{20}$ = +3.9 (c = 1.5, benzene). ^1H NMR (CDCl_3 , 500 MHz): δ = 5.74 (m, 1 H), 5.20–5.10 (m, 2 H), 3.25 (d, J = 11.1 Hz 1 H), 2.40–2.32 (m, 1 H), 2.05–1.95 (m, 1 H), 0.88 (s, 9 H) ppm. ^{13}C NMR (CDCl_3 , 125.7 MHz): δ = 137.72, 115.76, 80.38, 38.41, 37.05, 23.73 ppm. MS: m/z (%) = 138 [M^+]. $\text{C}_8\text{H}_{16}\text{O}$ (128.2): calcd. C 74.94, H 12.58; found C 75.11, H 12.41.

(S)-1-Cyclohexylbut-3-en-1-ol (3d): $[\alpha]_{\text{D}}^{20}$ = -8.9 (c = 0.54, EtOH). ^1H NMR (CDCl_3 , 500 MHz): δ = 5.90–5.72 (m, 1 H), 5.18–5.11 (m, 2 H), 3.35 (m, 1 H), 2.40–2.24 (m, 1 H), 2.20–2.05 (m, 1 H), 1.92–1.50 (m, 6 H), 1.45–0.90 (m, 6 H) ppm. ^{13}C NMR (CDCl_3 , 125.7 MHz): δ = 137.72, 115.76, 73.34, 44.93, 40.12, 28.31, 27.54, 26.15 ppm. MS: m/z (%) = 154 [M^+]. $\text{C}_{10}\text{H}_{18}\text{O}$ (154.3): calcd. C 77.87, H 11.76; found C 77.26, H 12.37.

(R)-1-Bromohex-5-en-3-ol (3e): $[\alpha]_{\text{D}}^{20}$ = +7.4 (c = 1.0, EtOH). ^1H NMR (CDCl_3 , 500 MHz): δ = 5.70–5.65 (m, 1 H), 5.10–4.96 (d, 2 H), 3.30–3.25 (m, 3 H), 2.25–2.20 (m, 1 H), 2.05–1.90 (m, 3 H) ppm. ^{13}C NMR (CDCl_3 , 125.7 MHz): δ = 137.71, 115.75, 70.82, 41.34, 39.76, 27.65 ppm. MS: m/z (%) = 194 [M^+]. $\text{C}_7\text{H}_{13}\text{BrO}$ (193.1): calcd. C 43.54, H 6.79, Br 41.38; found C 43.68, H 6.82, Br 41.21.

(R)-1-(2-Chlorobenzyl)-3-methylbut-3-en-1-ol (3f): $[\alpha]_{\text{D}}^{20}$ = +18.5 (c = 1.0, EtOH). ^1H NMR (CDCl_3 , 500 MHz): δ = 7.45–7.00 (m, 4

H), 5.10–4.95 (d, 2 H), 4.65 (m, 1 H), 2.65–2.30 (m, 2 H), 1.76–1.72 (m, 3 H) ppm. ^{13}C NMR (CDCl_3 , 125.7 MHz): δ = 142.62, 137.44, 132.57, 129.13, 128.66, 127.11, 111.33, 64.22, 47.84, 23.95 ppm. MS: m/z (%) = 197 [M^+]. $\text{C}_{11}\text{H}_{13}\text{ClO}$ (196.7): calcd. C 67.18, H 6.66, Cl 18.03; found C 67.06, H 6.52, Cl 18.29.

(R)-1-Pyridin-3-ylbut-3-en-1-ol (3g): $[\alpha]_{\text{D}}^{20}$ = +28.0 (c = 1.0, EtOH). ^1H NMR (CDCl_3 , 500 MHz): δ = 8.70–8.64 (d, 1 H), 8.60 (d, 1 H), 7.98 (d, 1 H), 7.53 (m, 1 H), 5.83–5.63 (m, 1 H), 5.10–5.01 (m, 2 H), 4.87 (t, 1 H), 3.51 (s, 1 H), 2.47 (m, 2 H) ppm. ^{13}C NMR (CDCl_3 , 125.7 MHz): δ = 147.12, 146.30, 141.82, 137.93, 132.84, 125.22, 119.20, 70.00, 43.16 ppm. MS: m/z (%) = 150 [M^+]. $\text{C}_9\text{H}_{11}\text{NO}$ (149.2): calcd. C 72.46, H 7.43, N 9.39; found C 71.92, H 7.32, N 10.04.

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