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An efficient route for the allylation of arylaldehydes to give enantiopure homoallylic alcohols

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ABSTRACT

An efficient asymmetric synthesis of homoallylic alcohols is described by the allylation of carbonyl compounds using organocatalysts as chiral directors in the presence of tin metal. The effect of chiral environment is also studied on the allylation reactions. This method allows us to obtain two different enantiomers of homoallylic alcohol in the presence of the corresponding chiral compound. The protocol is applied to various aldehydes to obtain high yields and excellent enantioselectivities for the corresponding homoallylic alcohols.

1. Introduction

Optically active homoallylic alcohols are indispensable scaffolds in the synthesis of natural products[1] and various biologically active compounds.[2] Some enantiopure homoallylic alcohols are used to craft liquid crystal displays.[3] Homoallylic alcohols can be obtained by asymmetric transformations of aldehydes using allyl-transfer reagents. The known synthetic routes to obtain homoallylic alcohols make use of allyl reagents such as allylsilanes,[4,5] allylstannanes,[6] allylindium,[7] allylboranes[8] and allyl bromide,[9] which have been studied to a great extent.

Allylation using allylic organometallic reagents is relatively difficult because they are unstable towards air and moisture. As a result, the reactions have to be carried out under an inert atmosphere and at low temperatures. In recent times many reports have been documented on the Barbier protocols, which involve the generation of an organometallic reagent in situ using organic halides and metals[4] such as In,[10] Sb,[11] Pb,[12] Mn,[13] Fe,[14] Mg,[15] Zn[16] and Sn.[17] After a literature review we noticed that allylation reactions using tin metal have advantages such as simple reaction set up since tin metal does not require strictly dry conditions or an inert atmosphere, and most importantly these compounds are inexpensive and easily available.[18] In the reactions using tin metal, reactive organostannanes are generated in situ from Sn(0/II/IV).[19]

In recent years, the search for more efficient asymmetric stereoselective reactions has led to the combination of organocatalysis with transition metal catalysis.[20] In metal mediated enantioselective catalytic reactions, the metal activates the reagents to form well governed transition states, which transform chiral information. Organocatalysis has experienced great advances; it can be applied in combination with metals for the development of more valuable chemical transformations.

In our previous communications[21] we have reported pyrrolidine based neutral chiral organocatalysts in which enantioselectivities were driven primarily by hydrogen bonding, steric and electronic interactions. High levels of both enantioselectivity and diastereoselectivity were achieved for aldol reactions with catalyst **1** and excellent enantioselectivities were obtained for both the Baylis–Hillman and the Henry reactions with catalyst **2** (Fig. 1).

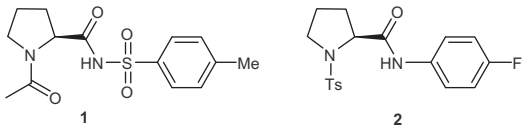

Figure 1. Chiral L-pyrrolidine based organic catalyst.

In metal-complex mediated reactions, the presence of a chiral molecule has a strong influence on the stereo chemical outcome of the product, while a small change in the structure of the chiral organic molecule can alter the geometry of the product.[22]

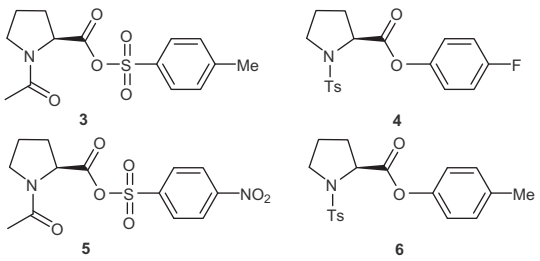

Figure 2. Chiral L-pyrrolidine based organic promoters.

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In connection with this and in continuation of our work on asymmetric reactions,[21,23] we herein report the application of organocatalysts to enantioselective allylations of aldehydes. We have synthesized some new chiral compounds with different substituents at the stereogenic centre of the pyrrolidine ring and its effect on the stereo nature of obtained products was investigated (see Fig. 2).

2. Result and discussion

In order to study the electronic effects and the effect of the chiral substituents of the catalysts, we synthesized some new organic molecules **3–6** and employed these catalysts in allylation reactions. The chiral catalysts were synthesized by known literature methods.

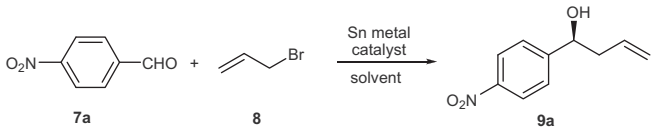
We started our investigation with the model reaction of 4-nitrobenzaldehyde (1 mmol) and allyl bromide (4 mmol) in the presence of tin metal (5 mol %) in *N,N*-dimethylformamide solvent to obtain 1-(4-nitrophenyl) but-3-en-1-ol **9a**. The catalytic efficiencies of chiral catalyst **1–6** were tested using 10 mol % of catalyst at room temperature. As shown in Table 1, compounds **1–6** catalysed the reactions with different behaviours, offering the respective products **9a** with a range of enantioselectivities. Catalysts **2** and **4** displayed lower activity which was due to the bulky tosyl group that caused an overcrowded transient state. Among the N-acylated compounds, catalysts **1** and **3** exhibited better catalytic efficiency. The use of catalysts **1** and **3** provided the corresponding product **9a** in good yields and enantioselectivities. The good catalytic efficiencies of catalysts **1** and **3** can be attributed to the presence of the sulfonamide or sulfanyl group at the stereogenic carbon atom of pyrrolidine. In comparison to catalysts **1** and **3,** both catalysts **5** and **6** gave unproductive yields with lower enantioselectivity for the respective products **9a**. It is worth mentioning here that the *N*-acylated chiral molecules were more efficient than the N-tosylated molecules. Among all six compounds, catalysts **1** and **3** were superior to catalysts **2** and **4–6**. As a result, we opted to use catalysts **1** and **3** for further experimentations.

Various experiments were performed in order to extract and optimize the best reaction conditions for catalysts **1** and **3**. For instance, the reaction was performed using various concentrations of catalysts **1** and **3**. Both catalysts **1** and **3** at a catalytic loading of 15 mol % were able to give higher yields for their respective products **9a** with good ee values. An additional increase in the quantities of compounds **1** and **3** did not lead to an improvement in the results to a significant extent.

In subsequent studies, the reaction was also screened with various solvents in order to examine solvent effect. The reactions were performed using chiral catalysts **1** and **3** at the optimum concentration. In the reaction, we observed that although polar solvents had a positive effect on the reaction with respect to yield of the corresponding product, we also observed that protic solvents diminished the enantioselectivity. Among all of the protic solvents, water showed the deleterious effect on enantioselectivity of the respective product followed by ethanol and methanol. Conversely, using DMSO as the solvent led to good to moderate ee in both catalysts but relatively lower yields for product **9a**. In the non-polar solvent chloroform, the catalysts could not catalyse the reaction efficiently.

Next, we attempted different combinations of *N,N*-dimethylformamide with water to determine the optimum reaction media. The reaction was investigated using 15 mol % of catalyst **1** and the obtained optimum reaction conditions were extended to catalyst **3**.

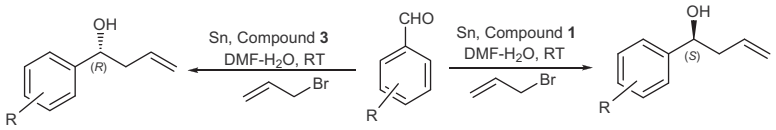
Table 1
Effect of chiral catalyst, catalytic loading and solvent on the synthesis of **9a**[a]

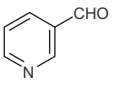
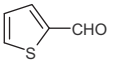
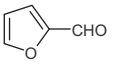


Entry	Catalyst	Catalytic loading	Solvent	Yield[b] (%)	ee[c] (%)	Config.[d]
1	1	10	DMF	69	68	(*S*)
2	2	10	DMF	36	40	(*S*)
3	3	10	DMF	68	64	(*S*)
4	4	10	DMF	29	39	(*S*)
5	5	10	DMF	54	49	(*S*)
6	6	10	DMF	48	41	(*S*)
7	1	15	DMF	79	75	(*S*)
8	3	15	DMF	72	71	(*S*)
9	1	20	DMF	77	68	(*S*)
10	3	20	DMF	73	68	(*S*)
11	1	15	Water	66	44	(*R*)
12	3	15	Water	71	52	(*R*)
13	1	15	Ethanol	54	48	(*R*)
14	3	15	Ethanol	55	46	(*R*)
15	1	15	Methanol	59	49	(*R*)
16	3	15	Methanol	61	50	(*R*)
17	1	15	DMSO	61	67	(*S*)
18	3	15	DMSO	53	59	(*S*)
19	1	15	Chloroform	40	42	(*S*)
20	3	15	Chloroform	43	39	(*S*)
21	1	15	DMF:Water (50:50)	89	84	(*S*)
22	1	15	DMF:Water (60:40)	95	94	(*S*)
23	1	15	DMF:Water (70:30)	73	66	(*S*)
24	3	15	DMF:Water (60:40)	87	91	(*R*)

[a] Conditions: 4-nitrobenzaldehyde (1 mmol), allyl bromide(1.2 mmol), solvent (20 mL) and tin metal (5 mol %) Reaction was stirred at room temperature for 24 h.
[b] Isolated yield.
[c] The enantiomeric excess was determined by chiral HPLC.
[d] The absolute configurations were assigned by comparison of the sign of the specific rotations with the ones reported in the literature.[24]

Table 2
Asymmetric allylation of aromatic aldehydes using optimized conditions[a]



Entry	R	Product	Yield[b] (%)	ee[c] (%)	Confign.[d]
1	4-NO_2	**9a**	95	94	(*S*)
			87	91	(*R*)
2	2-NO_2	**9b**	92	95	(*S*)
			85	90	(*R*)
3	4-Cl	**9c**	88	92	(*S*)
			84	88	(*R*)
4	2-Cl	**9d**	86	90	(*S*)
			80	89	(*R*)
5	4-F	**9e**	91	96	(*S*)
			89	90	(*R*)
6	4-Br	**9f**	93	94	(*S*)
			90	90	(*R*)
7	H	**9g**	89	93	(*S*)
			86	91	(*R*)
8	4-OCH_3	**9h**	85	88	(*S*)
			81	87	(*R*)
9	2-OCH_3	**9i**	87	90	(*S*)
			79	91	(*R*)
10	4-CH_3	**9j**	91	92	(*S*)
			84	89	(*R*)
11	1-Naphthyl	**9k**	72	78	(*S*)
			66	71	(*R*)
12		**9l**	83	88	(*S*)
			80	83	(*R*)
13		**9m**	77	84	(*S*)
			69	87	(*R*)
14		**9n**	79	87	(*S*)
			74	89	(*R*)

[a] Conditions: arylaldehyde (1 mmol), allyl bromide (4.0 mmol), solvent (20 mL) and tin metal (5 mol %) Reaction was stirred at room temperature for 24 h.
[b] Isolated yields.
[c] Determined by chiral-phase HPLC analysis of the product.
[d] The absolute configurations were assigned by comparison of the sign of the specific rotations with the ones reported in the literature.

When both solvents were used in 50:50 compositions, a noteworthy enhancement in the yield and enantioselectivity of the product **9a** was obtained. The best results were obtained using a composition of 60:40. Up to 95% yield was obtained for product **9a** with a maximum enantioselectivity of 94%. The optimum conditions also worked well for chiral catalyst **3**, with product **9a** being obtained in excellent yield and enantioselectivity.

From the results summarized in Table 1, it was noted that protic and aprotic solvents favored the (*R*)- and (*S*)-configuration respectively for the corresponding product. Catalyst **1** at optimum reaction conditions yielded the (*S*)-stereoisomer with excellent yield and ee for 1-(4-nitrophenyl) but-3-en-1-ol; compound **3** under identical reaction conditions gave the (*R*)-stereoisomer for the same product. The above results demonstrate that the chiral nature of the organic catalyst and the solvent have a great influence on the stereoselectivity of obtained products.

The scope of the method was explored to other aromatic aldehydes using both chiral promoters **1** and **3** in the presence of tin metal in DMF–water as the solvent system (Table 2). The reaction proceeded smoothly at room temperature for almost all aldehydes to give high to moderate yields and excellent enantioselectivity. The catalysts showed a broad applicability towards various aldehydes.

3. Conclusion

In conclusion, we have demonstrated a general method for tin mediated enantioselective allylations to obtain both the (*R*)- and (*S*)-enantiomers of homoallylic alcohols using different chiral promoters. We have synthesized different chiral catalysts and utilized them in tin metal mediated allylation reaction. It was found that under the influence of chiral promoters, the reaction gave a range of diverse results. The reaction was found to proceed most efficiently with catalysts **1** and **3** at room temperature to yield the (*R*)- and (*S*)-enantiomer, respectively. Both enantiomers of homoallylic alcohol products were obtained with high enantiomeric excesses and in excellent yields. To the best of our knowledge, this is one of the rare methods that gives both enantiomers of homoallylic alcohols by alteration of chiral promoters under identical reaction conditions.

4. Experimental

4.1. General details

All solvents were used as commercial anhydrous grade without further purification. Aluminium sheets 20 × 20 cm, Silica gel

60 F_{254}, Merck grade was used for thin layer chromatography to determine the progress of reaction. The column chromatography was carried out over silica gel (80–120 mesh). Optical rotations were measured on a Polax-2L digital polarimeter. Melting points were determined in an open capillary tube and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer in $CDCl_3$. Mass spectra were taken on Polaris-Q Thermoscientific GC–MS. The enantiomeric purity was determined on a PerkinElmer Series 200 HPLC Systems with chiral HPLC.

4.2. Typical procedure for preparation of acylation of L-proline

The acylation of L-proline is reported in the literature.[21]

4.3. Typical procedure for preparation of (*S*)-1-tosylpyrrolidine-2-carboxylic acid

The synthesis of the titled compound is reported in the literature.[21]

4.4. General procedure for the synthesis of organocatalysts 3 and 5

A mixture of 4-methylbenzenesulfonic acid/4-nitrobenzenesulfonic acid (1 mmol) and (*S*)-1-acetylpyrrolidine-2-carboxylic acid (1 mmol) acid was added to tetrahydrofuran. The resulting mixture was kept in an ice bath and cooled to 0 °C, followed by the addition of the solution of diethyl azodicarboxylate (1 mmol) and triphenylphosphine (1 mmol) dissolved in THF. The reaction mixture was then stirred for 24 h. After the formation of the product as indicated by chromatography, the reaction mixture was added to ice cold water, stirred and extracted with chloroform. The extracted organic layer was dried over Na_2SO_4 and chloroform was removed under vacuum to obtain a crude product. The crude product was further purified with column chromatography using ethyl acetate: pet ether (4:6) to obtain the pure product.

4.4.1. (*S*)-1-Acetylpyrrolidine-2-carboxylic 4-methylbenzenesulfonic anhydride 3

White solid, (301 mg, 76%), mp 134–136 °C, $[\alpha]_D^{27} = -94.6$ (*c* 0.5, ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47–7.58 (m, 1H), 4.21 (t, *J* = 8.2 Hz, 1H), 3.69 (t, *J* = 8.7 Hz, 2H), 3.31(m, 2H) 2.48 (s, 3H), 2.24–2.30 (m, 2H), 2.14 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.6, 171.2, 145.3, 140.6, 129.8, 127.7, 59.8, 48.5, 31.2, 26.7, 20.9, 20.2; GC–MS: *m*/*z* 311 (M^+); Anal. Calcd for: $C_{14}H_{17}NO_5S$: C, 54.01; H, 5.50; N, 4.50; Found: C, 54.04; H, 5.52; N, 4.53. HPLC: 76% ee. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), Hexane/Ethanol (75/25) + 15 mM Ammonium Acetate, Flow rate 1.5 mL/min, ϰ = 254 nm; t_R (minor) = 12.4 min, t_R (major) = 14.7 min.]

4.4.2. (*S*)-1-Acetylpyrrolidine-2-carboxylic 4-nitrobenzenesulfonic anhydride 5

Light yellowish solid, (309 mg, 71%), mp 117–119 °C, $[\alpha]_D^{27} = -76.4$ (*c* 0.5, ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.34–8.42 (m, 2H), 8.11–8.20 (m, 2H), 4.18 (t, *J* = 7.9 Hz, 1H), 3.72 (t, *J* = 9.1 Hz, 2H), 3.26 (m, 2H) 2.52 (s, 3H), 2.22–2.31 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.2, 173.4, 156.7, 149.9, 128.4, 126.3, 57.6, 47.9, 29.5, 24.3, 21.2; GC–MS: *m*/*z* 342 (M^+); Anal. Calcd for: $C_{13}H_{14}N_2O_7S$: C, 45.61; H, 4.12; N, 8.18; Found: C, 45.64; H, 4.08; N, 8.21. HPLC: 76% ee. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), Hexane/Ethanol (75/25) + 15 mM Ammonium Acetate, Flow rate 1.5 mL/min, ϰ = 254 nm; t_R (minor) = 11.6 min, t_R (major) = 16.8 min.]

4.5. General procedure for the synthesis of organocatalysts 4 and 6

The organocatalysts were prepared by the above procedure using (*S*)-1-tosylpyrrolidine-2-carboxylic acid and *p*-cresol/4-fluorophenol as the starting compounds.

4.5.1. (*S*)-4-Fluorophenyl 1-tosylpyrrolidine-2-carboxylate 4

White solid, (338 mg, 74%), mp 152–154 °C, $[\alpha]_D^{27} = -102.9$ (*c* 0.5, ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69–7.77 (m, 2H), 7.39–7.47 (m, 2H), 7.22–7.34 (m, 4H), 4.17 (t, *J* = 8.6 Hz, 1H), 3.73 (t, *J* = 7.9 Hz, 2H), 3.38 (m, 2H), 2.51 (s, 3H), 2.14–2.19 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.6, 158.4, 144.9, 141.6, 130.6, 128.3, 125.1, 118.2, 56.6, 56.0, 28.6, 21.3, 19.8; GC–MS: *m*/*z* 363 (M^+); Anal. Calcd for: $C_{18}H_{18}FNO_4S$: C, 59.49; H, 4.99; F, 5.23; N, 3.85; Found: C, 59.52; H, 5.03; F, 5.28; N, 3.88. HPLC: 76% ee. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), Hexane/Ethanol (75/25) + 15 mM Ammonium Acetate, Flow rate 1.5 mL/min, ϰ = 254 nm; t_R (minor) = 15.2 min, t_R (major) = 19.0 min.]

4.5.2. (*S*)-*p*-Tolyl 1-tosylpyrrolidine-2-carboxylate 6

White solid, (338 mg, 74%), mp 152–154 °C, $[\alpha]_D^{27} = -119.9$ (*c* 0.5, ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74–7.83 (m, 2H), 7.46–7.54 (m, 2H), 7.14–7.28 (m, 4H), 4.23 (t, *J* = 9.1 Hz, 1H), 3.67 (t, *J* = 8.8 Hz, 2H), 3.32 (m, 2H), 2.46 (s, 6H), 2.19–2.23 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.2, 147.5, 141.3, 139.8, 136.2, 130.1, 129.8, 128.8, 120.9, 56.1, 55.7, 28.1, 22.4, 18.8; GC–MS: *m*/*z* 359 (M^+); Anal. Calcd for: $C_{19}H_{21}NO_4S$: C, 63.49; H, 5.89; N, 3.90; Found: C, 63.49; H, 5.87; N, 3.93. HPLC: 76% ee. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), Hexane/Ethanol (75/25) + 15 mM Ammonium Acetate, Flow rate 1.5 mL/min, ϰ = 254 nm; t_R (minor) = 17.9 min, t_R (major) = 22.5 min.]

4.6. General procedure for the synthesis of 9a–n

To a mixture of the aromatic aldehyde (1 mmol) and organocatalyst **1** or **3** (0.15 mmol) in *N*,*N*-dimethylformamide (14 mL) were added allyl bromide (1.2 mmol) and tin metal (5 mol %) in water (6 mL). The reaction was stirred at room temperature for 24 h (Table 2). The reaction progress was monitored by gas chromatography. After completion of the reaction as indicated by GC, the reaction was quenched with ice cold water (15 mL) and extracted with chloroform (2 × 10 mL). The solvent was evaporated under vacuum to obtain the crude product followed by column chromatography purification using silica gel (100–200 mesh) to afford the pure homoallylic alcohol.

4.6.1. (*S*)-1-(4-Nitrophenyl)but-3-en-1-ol 9a

The product was characterized by comparing the spectroscopic data with those reported in the literature.[24] Pale yellow oil, $[\alpha]_D^{27} = -13.1$ (*c* 3.5, benzene), Lit: +12.9 (*c* 3.5, benzene) for the (*R*)-enantiomer;[24] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27–8.35 (m, 2H), 7.45–7.53 (m, 2H), 5.69–5.76 (m, 1H), 5.19–5.24 (m, 2H), 4.90 (t, *J* = 7.8 Hz, 1H), 2.45–2.56 (m, 2H), 2.08 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.2, 144.28, 134.5, 128.6, 122.7, 117.1, 73.7, 45.3; GC–MS: *m*/*z* 193 (M^+); Anal. Calcd for: $C_{10}H_{11}NO_3$: C, 62.17; H, 5.74; N, 7.25; Found: C, 62.20; H, 5.71; N, 7.22; HPLC: 94% ee. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (minor) = 10.3 min, t_R (major) = 16.7 min.]

4.6.2. (*R*) 1-(4-Nitrophenyl) but-3-en-1-ol

The characterization data of the product are the same as above. Pale yellow oil, $[\alpha]_D^{27} = +13.4$ (*c* 3.5, benzene), Lit: +12.9 (*c* 3.5, benzene);[24] HPLC: 91% ee. [Determined by chiral HPLC with

Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (major) = 10.3 min, t_R (minor) = 16.7 min.]

4.6.3. (*S*)-1-(2-Nitrophenyl)but-3-en-1-ol 9b

The product was characterized by comparing the spectroscopic data with those reported in the literature.[24] Pale yellow oil, $[\alpha]_D^{27} = -36.9$ (*c* 2.9, benzene), Lit: $[\alpha]_D^{27} = -37.1$ (*c* 2.9, benzene);[24] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12–8.17 (m, 1H), 7.71–7.78 (m, 1H), 7.58–7.69 (m, 2H), 5.67–5.74 (m, 1H), 5.22–5.29 (m, 2H), 4.87 (t, *J* = 8.1 Hz, 1H), 2.39–2.45 (m, 2H), 2.04 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.4, 136.1, 134.3, 130.1, 129.8, 127.9, 127.3, 116.9, 72.6, 44.1; GC–MS: *m*/*z* 193 (M^+); Anal. Calcd for: $C_{10}H_{11}NO_3$: C, 62.17; H, 5.74; N, 7.25; Found: C, 62.15; H, 5.77; N, 7.28; HPLC: 95% ee. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (minor) = 12.4 min, t_R (major) = 18.1 min.]

4.6.4. (*R*)-1-(2-Nitrophenyl)but-3-en-1-ol

The characterization data of the product are the same as above. Pale yellow oil, $[\alpha]_D^{27} = +37.4$ (*c* 2.9, benzene), Lit: $[\alpha]_D^{27} = -37.1$ (*c* 2.9, benzene) for the (*S*)-enantiomer;[24] HPLC: 90% ee. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (major) = 12.4 min, t_R (minor) = 18.1 min.]

4.6.5. (*S*)-1-(4-Chlorophenyl)but-3-en-1-ol 9c

The product was characterized by comparing the spectroscopic data with those reported in the literature.[24] Colourless oil, $[\alpha]_D^{27} = -15.6$ (*c* 2.4, benzene), Lit: $[\alpha]_D^{27} = +15.5$ (*c* 2.4, benzene) for the (*R*)-enantiomer;[24] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54–7.63 (m, 2H), 7.39–7.47 (m, 2H), 5.78–5.82 (m, 1H), 5.16–5.21 (m, 2H), 4.85 (t, *J* = 7.9 Hz, 1H), 2.42–2.49 (m, 2H), 2.07 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.3, 134.1, 132.8, 131.9, 128.5, 115.8, 73.8, 42.6; GC–MS: *m*/*z* 182 (M^+); Anal. Calcd for: $C_{10}H_{11}ClO$: C, 65.76; H, 6.07; Found: C, 65.73; H, 6.11; HPLC: 92% ee. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (minor) = 15.2 min, t_R (major) = 19.0 min.]

4.6.6. (*R*)-1-(4-Chlorophenyl)but-3-en-1-ol

The characterization data of the product are the same as above. Colourless oil, $[\alpha]_D^{27} = +15.4$ (*c* 2.4, benzene), Lit: $[\alpha]_D^{27} = +15.5$ (*c* 2.4, benzene);[24] HPLC: 88% ee. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (minor) = 15.2 min, t_R (major) = 19.0 min.]

4.6.7. (*S*)-1-(2-Chlorophenyl)but-3-en-1-ol 9d

The product was characterized by comparing the spectroscopic data with those reported in the literature.[24] Colourless oil, $[\alpha]_D^{27} = -21.3$ (*c* 1.8, $CHCl_3$), $[\alpha]_D^{27} = +21.2$ (*c* 1.8, $CHCl_3$) for the (*R*)-enantiomer;[24] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76–7.81 (m, 1H), 7.42–7.49 (m, 3H), 5.81–5.85 (m, 1H), 5.18–5.24 (m, 2H), 4.87 (t, *J* = 7.8 Hz, 1H), 2.45–2.52 (m, 2H), 2.03 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.5, 135.3, 133.7, 131.9, 130.4, 126.8, 117.02,72.4, 41.8; GC–MS: *m*/*z* 182 (M^+); Anal. Calcd for: $C_{10}H_{11}ClO$: C, 65.76; H, 6.07; Found: C, 65.73; H, 6.11; HPLC: 90% *ee*. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (minor) = 14.6 min, t_R (major) = 20.1 min.]

4.6.8. (*R*)-1-(2-Chlorophenyl)but-3-en-1-ol

The characterization data of the product are the same as above. Colourless oil, $[\alpha]_D^{27} = +20.9$ (*c* 1.8, $CHCl_3$), Lit: $[\alpha]_D^{27} = +21.2$ (*c* 1.8, $CHCl_3$);[24] HPLC: 89% *ee*. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (major) = 14.6 min, t_R (minor) = 20.1 min.]

4.6.9. (*S*)-1-(4-Fluorophenyl)but-3-en-1-ol 9e

The product was characterized by comparing the spectroscopic data with those reported in the literature.[24] colourless oil, $[\alpha]_D^{27} = -21.5$ (*c* 2.0, benzene), Lit: $[\alpha]_D^{27} = +21.5$ (*c* 2.0, benzene) for the (*R*)-enantiomer;[24] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58–7.66 (m, 2H), 7.43–7.49 (m, 2H), 5.75–5.84 (m, 1H), 5.21–5.26 (m, 2H), 4.87 (t, *J* = 8.2 Hz, 1H), 2.52–2.56 (m, 2H), 2.03 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.5, 141.1, 133.6, 127.9, 117.6, 116.7,76.7, 43.9; GC–MS: *m*/*z* 166 (M^+); Anal. Calcd for: $C_{10}H_{11}FO$: C, 72.27; H, 6.67; Found: C, 72.24; H, 6.70; HPLC: 96% ee. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (minor) = 9.5 min, t_R (major) = 13.3 min.]

4.6.10. (*R*)-1-(4-Fluorophenyl)but-3-en-1-ol

The characterization data of the product are the same as above. Colourless oil, $[\alpha]_D^{27} = +21.2$ (*c* 2.0, benzene), Lit: $[\alpha]_D^{27} = +21.5$ (*c* 2.0, benzene)[24]; HPLC: 90% *ee*. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (major) = 9.5 min, t_R (minor) = 13.3 min.]

4.6.11. (*S*)-1-(4-Bromophenyl)but-3-en-1-ol 9f

The product was characterized by comparing the spectroscopic data with those reported in the literature.[24] Colourless oil, $[\alpha]_D^{27} = -12.5$ (*c* 3.5, benzene), Lit: $[\alpha]_D^{27} = +12.6$ (*c* 3.5, benzene) for the (*R*)-enantiomer;[24] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11–8.23 (m, 2H), 7.36–7.47 (m, 2H), 5.81–86 (m, 1H), 5.38–5.44 (m, 2H), 4.73 (t, *J* = 8.0 Hz, 1H), 2.48–2.55 (m, 2H), 2.06 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.6, 134.4, 132.3, 128.4, 123.5, 115.7, 74.5, 45.2; GC–MS: *m*/*z* 225 (M^+); Anal. Calcd for: $C_{10}H_{11}BrO$: C, 52.89; H, 4.88; Found: C, 52.87; H, 4.91; HPLC: 94% ee. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (minor) = 10.8 min, t_R (major) = 14.9 min.]

4.6.12. (*R*)-1-(4-Bromophenyl)but-3-en-1-ol

The characterization data of the product are the same as above. Colourless oil, $[\alpha]_D^{27} = +12.9$ (*c* 3.5, benzene), Lit: $[\alpha]_D^{27} = +12.6$ (*c* 3.5, benzene);[24] HPLC: 90% ee. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (major) = 10.8 min, t_R (minor) = 14.9 min.]

4.6.13. (*S*)-1-Phenylbut-3-en-1-ol 9g

The product was characterized by comparing the spectroscopic data with those reported in the literature.[24] Colourless oil, $[\alpha]_D^{27} = -22.0$ (*c* 2.0, benzene), Lit: $[\alpha]_D^{27} = +22.3$ (*c* 2.0, benzene) for the (*R*)-enantiomer;[24] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54–7.67 (m, 5H), 5.88–5.94 (m, 1H), 5.31–5.39 (m, 2H), 4.79 (t, *J* = 8.3 Hz, 1H), 2.61–2.66 (m, 2H), 2.05 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.1, 134.8, 130.6, 128.5, 127.2, 116.3, 73.8, 43.8; GC–MS: *m*/*z* 148 (M^+); Anal. Calcd for: $C_{10}H_{12}O$: C, 81.04; H, 8.16; Found: C, 81.07; H, 8.19; HPLC: 93% ee. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (minor) = 15.6 min, t_R (major) = 21.9 min.]

4.6.14. (*R*)-1-Phenylbut-3-en-1-ol

The characterization data of the product are the same as above. Colourless oil, $[\alpha]_D^{27} = +22.1$ (*c* 2.0, benzene), Lit: $[\alpha]_D^{27} = +22.3$ (*c* 2.0, benzene);[24] HPLC: 91% ee. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (major) = 15.6 min, t_R (minor) = 21.9 min.]

4.6.15. (*S*)-1-(2-Methoxyphenyl)but-3-en-1-ol 9h

The product was characterized by comparing the spectroscopic data with those reported in the literature.[2a] Colourless oil,

$[\alpha]_D^{27} = -44.6$ (*c* 2.0, benzene);[analogy] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38–7.49 (m, 3H), 7.04–7.13 (m, 3H), 5.78–5.83 (m, 1H), 5.40–5.46 (m, 2H), 4.74 (t, *J* = 7.9 Hz, 1H), 3.79 (s, 3H), 2.46–2.53 (m, 2H), 2.07 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.4, 134.4, 129.7, 128.3, 127.9, 121.7, 116.5, 114.6, 69.7, 57.3, 42.4; GC–MS: *m*/*z* 148 (M^+); Anal. Calcd for: $C_{11}H_{14}O_2$: C, 74.13; H, 7.92; Found: C, 74.17; H, 7.95; HPLC: 84% ee. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (minor) = 13.1 min, t_R (major) = 22.7 min.]

4.6.16. (*R*)-1-(2-Methoxyphenyl)but-3-en-1-ol

The characterization data of the product are the same as above. Colourless oil, $[\alpha]_D^{27} = +44.1$ (*c* 2.0, benzene);[analogy] HPLC: 87% ee. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (major) = 13.1 min, t_R (minor) = 22.7 min.]

4.6.17. (*S*)-1-(4-Methoxyphenyl)but-3-en-1-ol 9i

The product was characterized by comparing the spectroscopic data with those reported in the literature. Colourless oil, $[\alpha]_D^{27}$=−15.6 (*c* 1.6, benzene), Lit: $[\alpha]_D^{27}$ = + 15.4 (*c* 1.6, benzene) for the (*R*)-enantiomer;[24] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47–7.56 (m, 2H), 6.95–7.07 (m, 2H), 5.81–5.85 (m, 1H), 5.33–5.39 (m, 2H), 4.83 (t, *J* = 7.6 Hz, 1H), 3.77 (s, 3H), 2.35–2.41 (m, 2H), 2.03 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.5, 137.4, 134.8, 128.5, 117.1, 115.8, 72.3, 56.2, 40.6; GC–MS: *m*/*z* 148 (M^+); Anal. Calcd for: $C_{11}H_{14}O_2$: C, 74.13; H, 7.92; Found: C, 74.17; H, 7.95; HPLC: 90% *ee*. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (minor) = 10.1 min, t_R (major) = 15.4 min.]

4.6.18. (*R*)-1-(4-Methoxyphenyl)but-3-en-1-ol

The characterization data of the product are the same as above. Colourless oil, $[\alpha]_D^{27}$ = + 15.1 (*c* 1.6, benzene), Lit: $[\alpha]_D^{27}$ = + 15.4 (*c* 1.6, benzene);[24] HPLC: 91% *ee*. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (major) = 10.1 min, t_R (minor) = 15.4 min.]

4.6.19. (*S*)-1-*p*-Tolylbut-3-en-1-ol 9j

The product was characterized by comparing the spectroscopic data with those reported in the literature.[24] Colourless oil, $[\alpha]_D^{27}$=−15.3 (c 2.0, benzene), Lit: $[\alpha]_D^{27}$ = + 15.5 (c 2.0, benzene) for the (*R*)-enantiomer;[24] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37–7.44 (m, 2H), 7.21–7.32 (m, 2H), 5.77–5.82 (m, 1H), 5.41–5.47 (m, 2H), 4.76 (t, *J* = 7.9 Hz, 1H), 2.44–2.50 (m, 2H), 2.38 (s, 3H), 2.04 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.2, 136.4, 134.8, 128.7, 123.6, 116.3, 71.8, 41.4, 21.7; GC–MS: *m*/*z* 162 (M^+); Anal. Calcd for: $C_{11}H_{14}O$: C, 81.44; H, 8.70; Found: C, 81.48; H, 8.73; HPLC: 92% *ee*. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (minor) = 8.9 min, t_R (major) = 13.5 min.]

4.6.20. (*R*)-1-*p*-Tolylbut-3-en-1-ol

The characterization data of the product are the same as above. Colourless oil, $[\alpha]_D^{27}$ = + 15.1 (*c* 2.0, benzene), Lit: $[\alpha]_D^{27}$ = + 15.5 (*c* 2.0, benzene);[24] HPLC: 89% *ee*. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (major) = 8.9 min, t_R (minor) = 13.5 min.]

4.6.21. (*S*)-1-(Naphthalen-1-yl)but-3-en-1-ol 9k

The product was characterized by comparing the spectroscopic data with those reported in the literature.[2a] Colourless oil, $[\alpha]_D^{27}$=−99.0 (*c* 1.0, benzene);[analogy] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91–8.09 (m, 1H), 7.97–8.02 (m, 1H), 7.78–7.82 (m, 1H), 7.60–7.72 (m, 2H), 7.47–7.55 (m, 1H), 7.12–7.19 (m, 1H), 5.86–5.90 (m, 1H), 5.23–5.30 (m, 2H), 4.72 (t, *J* = 7.9 Hz, 1H), 2.37–2.42 (m, 2H), 2.10 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.4, 138.6, 135.7, 134.6, 130.3, 129.9, 127.7, 126.8, 126.0, 125.7, 125.3, 115.8, 75.2, 43.4; GC–MS: *m*/*z* 198 (M^+); Anal. Calcd for: $C_{14}H_{14}O$: C, 84.81; H, 7.12; Found: C, 84.83; H, 7.09; HPLC: 78% *ee*. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (minor) = 18.6 min, t_R (major) = 23.0 min.]

4.6.22. (*R*)-1-(Naphthalen-1-yl)but-3-en-1-ol

The characterization data of the product are the same as above. Colourless oil, $[\alpha]_D^{27}$ = + 98.6 (*c* 1.0, benzene);[analogy] HPLC: 71% *ee*. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (major) = 18.6 min, t_R (minor) = 23.0 min.]

4.6.23. (*S*)-1-(3-Pyridyl)but-3-en-1-ol 9l

The product was characterized by comparing the spectroscopic data with those reported in the literature.[25] brown oil, $[\alpha]_D^{27}$=−40.0 (*c* 0.5, CH_2Cl_2), Lit: $[\alpha]_D^{27}$=−39.9 (*c* 0.5, CH_2Cl_2);[27a] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.61 (s, 1H), 8.47–8.53 (d, *J* = 5.6 Hz, 1H), 7.91–7.96 (m, 1H), 7.43–7.56 (m, 1H), 5.79–5.83 (m, 1H), 5.18–5.23 (m, 2H), 4.69 (t, *J* = 6.4 Hz, 1H), 2.57 (br s, 1H, OH), 2.33–2.39 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.4, 146.5, 140.2, 135.1, 134.3, 124.7, 117.7, 72.4, 43.4; GC–MS: *m*/*z* 149 (M^+); Anal. Calcd for: $C_9H_{11}NO$: C, 72.46; H, 7.43; N, 9.39; Found: C, 72.49; H, 7.41; N, 9.42; HPLC: 88% *ee*. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (minor) = 24.1 min, t_R (major) = 27.5 min.]

4.6.24. (*R*)-1-(3-Pyridyl)but-3-en-1-ol

The characterization data of the product are the same as above. Brown oil, $[\alpha]_D^{27}$ = + 39.8 (*c* 1.15, CH_2Cl_2), Lit: $[\alpha]_D^{27}$=−39.9 (*c* 1.15, CH_2Cl_2) for the (*S*)-enantiomer;[25] HPLC: 83% *ee*. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (major) = 24.1 min, t_R (minor) = 27.5 min.]

4.6.25. (*S*)-1-(Thiophen-2-yl)but-3-en-1-ol 9m

The product was characterized by comparing the spectroscopic data with those reported in the literature.[27a] Colourless oil, $[\alpha]_D^{27}$=−8.3 (*c* 1.20, CH_2Cl_2), Lit: $[\alpha]_D^{27}$=−8.2 (*c* 1.20, CH_2Cl_2);[25] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33–7.37 (m, 1H), 7.10–7.18 (m, 2H), 5.90–5.94 (m, 1H), 5.20–5.26 (m, 2H), 4.89 (t, *J* = 5.3 Hz, 1H), 2.41–2.46 (m, 2H), 2.17 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.8, 134.6, 126.4, 125.3, 123.8, 117.3, 71.3, 42.8; GC–MS: *m*/*z* 154 (M^+); Anal. Calcd for: $C_8H_{10}OS$: C, 62.30; H, 6.54; Found: C, 62.33; H, 6.57; HPLC: 84% *ee*. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (minor) = 19.6 min, t_R (major) = 23.9 min.]

4.6.26. (*R*)-1-(Thiophen-2-yl)but-3-en-1-ol

The characterization data of the product are the same as above. Colourless oil, $[\alpha]_D^{27}$ = + 8.0 (*c* 1.20, CH_2Cl_2), Lit: $[\alpha]_D^{27}$=−8.2 (*c* 1.20, CH_2Cl_2) for the (*S*)-enantiomer;[25] HPLC: 87% *ee*. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (major) = 19.6 min, t_R (minor) = 23.9 min.]

4.6.27. (*S*)-1-(Furan-2-yl)but-3-en-1-ol 9n

The product was characterized by comparing the spectroscopic data with those reported in the literature.[27a] Colourless oil, $[\alpha]_D^{27}$=−32.7 (*c* 0.5, CH_2Cl_2), Lit: $[\alpha]_D^{27}$=−32.6 (*c* 0.5, CH_2Cl_2);[25] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47–7.58 (m, 1H), 6.51–6.62 (m, 2H), 5.86–5.91 (m, 1H), 5.25–5.32 (m, 2H), 4.81 (t, *J* = 5.7 Hz, 1H), 2.27–2.32 (m, 2H), 2.09 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$):

δ 157.6, 142.4, 133.9, 116.9, 112.3, 109.6, 70.1, 43.8; GC–MS: m/z 138 (M^+); Anal. Calcd for: $C_8H_{10}O_2$: C, 69.54; H, 7.30; Found: C, 69.54; H, 7.30; HPLC: 87% *ee*. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (minor) = 20.1 min, t_R (major) = 24.7 min.]

4.6.28. (*R*)-1-(Furan-2-yl)but-3-en-1-ol

The characterization data of the product are the same as above. Colourless oil, $[\alpha]_D^{27} = +32.3$ (*c* 0.5, CH_2Cl_2), Lit: $[\alpha]_D^{27} = -32.3$ (*c* 0.5, CH_2Cl_2) for the (*S*)-enantiomer;[25] HPLC: 86% ee. [Determined by chiral HPLC with Whelk-O1 (25 cm × 4.6 mm), 2% IPA/hexane, Flow rate 1.0 mL/min, λ = 220 nm; t_R (major) = 20.1 min, t_R (minor) = 24.7 min.]

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