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A chiral spirocyclic borate ligand as a catalyst for the enantioselective Nozaki–Hiyama–Kishi allylation of arylaldehydes

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ABSTRACT

A chiral spirocyclic borate catalyst was used in the enantioselective Nozaki–Hiyama–Kishi allylation of arylaldehydes to determine the relationship between enantioselectivity and the Hammet constant for the production of homoallyl alcohols.

1. Introduction

As an area of asymmetric synthesis, the enantioselective formation of C–C bonds through the addition of carbon nucleophiles to carbonyl compounds has been extensively explored. The asymmetric version of the Nozaki–Hiyama–Kishi (NHK) reaction is a notable protocol for this kind of transformation that allows for the addition of organochromium fragments to aldehydes and ketones with high enantioselectivity.[1] Some interesting features of the NHK reaction are its mild reaction conditions compatible to a variety of functional groups and the formation with versatile synthetic intermediates.[2] In particular, the asymmetric addition of allylchromiums to aldehydes and ketones is accomplished with higher enantioselectivity[3,4] when compared to that obtained with other allylation procedures employing allyltin,[5] allyborane,[6] or allylsilanes.[7] Recently, we demonstrated the NHK allylation of ketones with good yields and high enantioselectivities (up to 97%) with the new chiral spirocyclic borate ligand **2**.[8] The high degree of asymmetric induction observed with more difficult NHK reaction substrates (ketones) encouraged us to examine the application of the ligand **2** for various aldehydes.

The electronic effects of substrates on enantioselectivity in various asymmetric transformations have been explored to provide insight into their mechanism.[9] Earlier, our group explored similar correlations for the asymmetric dialkylzinc addition to substituted benzaldehydes, asymmetric Strecker reaction and asymmetric ring opening of epoxides with thiols[10] using chiral bipyridyl ligand **1**. Herein, the relationship between enantioselectivity and the Hammett constants in the asymmetric NHK reaction of aromatic aldehydes in the presence of Cr(II)–**2** complex is investigated (Fig. 1).

2. Results and discussion

Chiral spirocyclic borate ligand **2** can be readily assembled from various aminoalcohols and pinene derived bipyridyl ketone in a 30–35% overall yield.[8] The diastereomer of **2**, optimized for ketone allylation, was used as such for the present investigation and no further stereochemical diversity of **2** was explored. A series of four chiral ligands **2**–**5**, varying at the alkyl group of the aminoalcohol moiety, were used in the study. For comparison, bipyridyl ligand **1** was synthesized as reported.[10a] With a full set of chiral ligands in hand, we set out to examine their application in the NHK allylation of benzaldehyde. The active catalyst was formed in situ by reacting the chiral ligand with a catalytic amount of Cr(III) and a base in a degassed and anhydrous solvent in the presence of an excess of Mn(0) as co-reductant and TMSCl.[1b] The addition of allyl reagents, followed by benzaldehyde, produced homoallylic alcohol **6** in good to moderate yield and enantioselectivity. The results obtained for screening ligands **1–5** are given in Table 1.

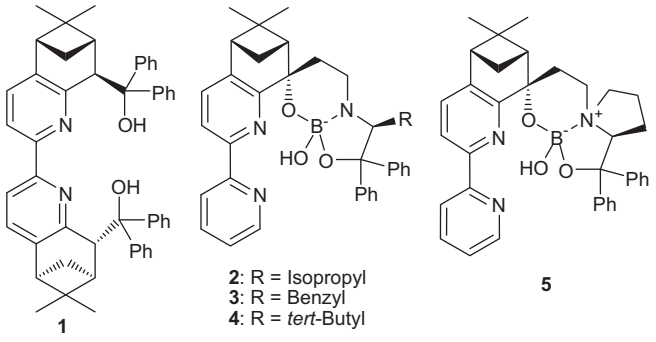

Figure 1. Chiral bipyridyl and chiral spirocyclic borate ligands used for aldehyde allylation.

The enantioselective outcome of the reaction was moderate in the case of bipyridyl ligand **1** (Table 1, entry 1). On the other hand, the enantioselectivity of reactions in the presence of spirocyclic borate ligands **2–5** was strongly dependant on the nature of the ligand's aminoalcohol moiety and followed a similar trend, as observed for ketone allylation. The best result was obtained with **2** (Table 1, entry 2), with the isopropyl group at the aminoalcohol

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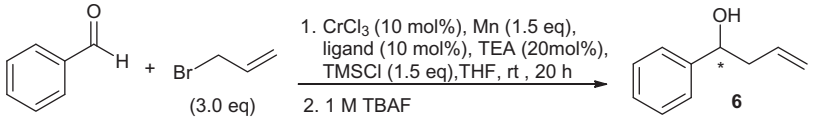
unit producing **6** in 81% ee and was, therefore, used for further optimization studies.

Allylation of benzaldehyde, in the presence of a Cr–**2** catalyst, was further optimized with respect to the nature of the solvents and bases employed, catalyst loading, and allyl counterparts. The optimization results are listed in Table 2. Of all solvents employed, THF afforded the highest yield and enantioselectivity of **6** (Table 2, entries 1–5). The reaction of benzaldehyde at lower temperatures in the presence of TEA or replacing TEA with Hunig's base or potassium carbonate failed to produce any encouraging results (Table 2, entries 6–8). The use of other allyl reagents was not as enantioselective as allyl bromide. Allyl iodide produced similar activity with a little loss in yield and asymmetric induction (Table 2, entry 10). Low or no enantioselectivity was observed respectively for allyl chloride and allylstannane (tetraallyl tin) (Table 2, entries 9 and 11). Reducing the catalyst loading to one-half with the optimized condition was equally effective but required a slightly longer reaction time (Table 2, entry 12). The lower catalyst loading was further used as an optimized catalyst loading for the substrate screening. When $CrBr_3$ was used in this reaction, the enantioselectivity was 77%ee.

Substituted benzaldehydes with electron releasing and electron withdrawing substituents were reacted in the presence of Cr–**2** complexes under the optimized conditions and the results are shown in Table 3. All of the positional isomers were employed to study the electronic effects of the substituent on the enantioselective outcome of the reaction. Substrates with electron-donating groups at the 2- and 4-positions afforded a high degree of enantioselection compared to the same substituents at the 3-position. Conversely, electron withdrawing groups at the 2-position of benzaldehyde afforded poor selectivity in comparison to the 3- and 4-positions. The correlations of ln([*R*]/[*S*]) with the Hammett constants of both *ortho*-substituents (σ_{ortho}) and *para*-substituents (σ_{para}) were performed using the Hammett equation ln([*R*]/[*S*]) = $\sigma\rho$. The corresponding Hammett plots for *para*- and *ortho*-substituents are shown on Figure 3a and b, respectively. A concave downward deviated Hammett plot with relatively large negative σ values (−0.17 and −0.27) observed for *para*-substituted substrates suggests that the coordination of the chromium complex with aldehyde should be involved at least in the enantio-determination step. The electron releasing groups increase the electron density of the aryl moiety leading to enhanced π–π interaction between the bipyridyl ring of the ligand and the benzaldehyde ring (Fig. 2).[11] The aromatic plane of bipyridine and benzaldehyde in an edge-on arrangement (around 90°) generally leads to attraction. Therefore, the benzaldehydes' aromatic ring may be fixed tightly to the bipyridine group of ligand **2** and the *Re*-face of carbonyl group may favor allylation and thus increase enantioselectivity. This is evident from the similar enantioselectivity observed for *p*-chlorobenzaldehyde and benzaldehyde substituted with an electron-donating substituent. A similar effect is observed in the case of alkylation of substituted benzaldehydes using diethylzinc,[10a] and the asymmetric trimethylsilylcyanation of substituted benzaldehydes using trimethylsilylcyanide.[10b] *ortho*-Substitution shows a similar trend in the variation of enantiomeric excesses, with a linear Hammett plot.

Table 1
Nozaki–Hiyama–Kishi allylation of benzaldehyde catalyzed by a Cr(II) complex formed from chiral ligands **1**–**5**



Entry	Ligand	Yield[a] (%)	ee[b] (%)
1	**1**	75	69
2	**2**	83	81
3	**3**	80	25
4	**4**	81	39
5	**5**	77	25

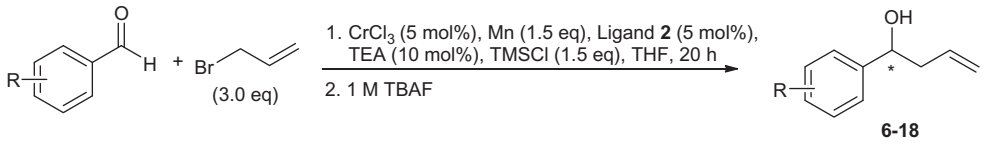
[a] Isolated yields after column chromatography.
[b] Determined by chiral HPLC using Chiralcel OD-H column.

Table 2
Nozaki–Hiyama–Kishi allylation reactions of benzaldehyde catalyzed by Cr(II)–**2** under various conditions[c]

Entry	Solvent	*T* (°C)	Base	Allyl halide	Ligand (mol %)	Yield[a] (%)	ee[b] (%)
1	CH_3CN	rt	TEA	Allyl bromide	10	39	55
2	Ether	rt	TEA	Allyl bromide	10	—	—
3	CH_2Cl_2	rt	TEA	Allyl bromide	10	70	35
4	Toluene	rt	TEA	Allyl bromide	10	55	13
5	THF	rt	TEA	Allyl bromide	10	83	81
6	THF	5	TEA	Allyl bromide	10	65	71
7	THF	rt	K_2CO_3	Allyl bromide	10	75	62
8	THF	rt	DIPEA	Allyl bromide	10	78	67
9	THF	rt	TEA	Allyl chloride	10	61	19
10	THF	rt	TEA	Allyl iodide	10	76	75
11	THF	rt	TEA	Tetraallyl tin	10	70	0
12	THF	rt	TEA	Allyl bromide	5	82	81

[a] Isolated yields after column chromatography.
[b] Determination by chiral HPLC (Chiralcel OD-H column).
[c] Reaction conditions: $CrCl_3$ (5 mol %), Mn (1.5 equiv), solvent (2 mL), ligand **2** (5 mol %), base (10 mol %), allyl halide (3.0 equiv) and TMSCl (1.5 equiv) at room temperature.

Table 3
Nozaki–Hiyama–Kishi allylation reactions of substituted benzaldehydes catalyzed by Cr(II)–**2**



Entry	R	Products	Yield[a] (%)	ee[b] (%)	Hammett constants[12]	$[\alpha]_D^T$ (T °C, c) CH_2Cl_2	Configuration
1	H	6	83	81	σ, 0	+44.5 (25, 1.13)	(*R*)
2	*o*-OMe	7	77	74	σ_o,+0.12	+57.5 (26, 1.25)	(*R*)
3	*m*-OMe	8	72	46[d]	σ_m, +0.12	+35.7 (26.4, 1.50)	(*R*)
4	*p*-OMe	9	68	80	σ_p, −0.27	+44.6 (26.8, 1.63)	(*R*)
5	*o*-Me	10	80	61[c]	σ_o, +0.29	+41.9 (25, 2.49)	(*R*)
6	*m*-Me	11	70	56	σ_m, −0.07	+29.4 (25.4, 1.10)	(*R*)
7	*p*-Me	12	73	77[c]	σ_p, −0.17	+39.1 (26, 1.73)	(*R*)
8	*o*-Cl	13	70	9[c]	σ_o, +1.28	+61.6 (25, 0.70)	(*R*)
9	*m*-Cl	14	78	78	σ_m, +0.37	+39.2 (24.5, 1.10)	(*R*)
10	*p*-Cl	15	75	79[c]	σ_p, +0.23	+43.6 (23.7, 1.00)	(*R*)
11	*o*-CN	16	54	9	σ_o, +1.06	+9.2 (25, 0.85)	na
12	*m*-CN	17	45	45	σ_m, +0.56	+15.3 (25.2, 0.40)	na
13	*p*-CN	18	60	47[c]	σ_p, +0.66	+20.9 (26, 1.20)	na

[a] Isolated yields after column chromatography.
[b] Determination by chiral HPLC (Chiralcel OD-H column).
[c] The enantiometric excesses were determined from their benzoates.
[d] The enantiometric excesses were determined by 1-(3-methoxy-phenyl)-butan-1-ol.

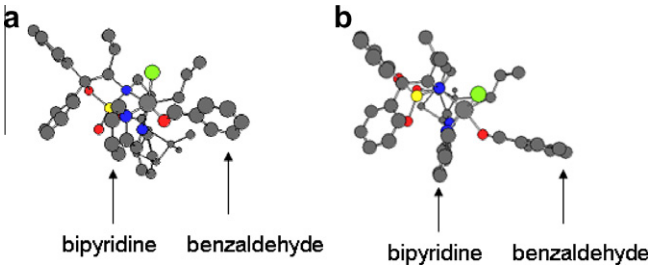


Figure 2. The aromatic plane of bipyridine and benzaldehyde in an edge-on arrangement (around 90°) generally leads to attraction.

3. Conclusion

A class of bipyridine-containing ligands **2–5** were prepared. The ligands were adopted in the chromium-catalyzed enantioselective allylation of benzaldehyde with excellent conversion and good enantioselectivity values of up to 81% ee. Again, the results reveal the significant effect of the moieties in the amino acid derivative on the sense of asymmetric induction. The Hammett substituent constants were correlated with the enantiomeric excesses of homoallyl alcohols from the NHK allylation of *ortho*- and *para*-substituted benzaldehydes using allyl bromide.

4. Experimental

4.1. General

All reactions were carried out in anhydrous solvents. THF and diethyl ether were distilled from sodium-benzophenone under argon. Toluene, CH_3CN, CH_2Cl_2, and hexane were distilled from CaH_2. ^1H NMR spectra were obtained at 300 or 400 MHz (as indicated), and ^{13}C NMR spectra were obtained at 75.5 or 100.6 MHz NMR spectrometer. Chemical shifts (δ) are reported in ppm relative to $CDCl_3$ (7.26 and 77.0 ppm). Mass spectra (MS) and high resolution mass spectra (HRMS) were determined on a mass spectrometer. Infrared spectra were recorded using a FT/IR spectrometer. All asymmetric reactions were conducted in dry glassware under nitrogen using a standard glovebox. Enantiomeric excesses were determined using high performance liquid chromatography (HPLC) with a Chiracel OD-H chiral column. Optical rotations were measured using a polarimeter at the indicated temperature using a sodium lamp (D line, 589 nm). Flash column chromatography was performed using silica gel 60 (70–230 mesh).

4.2. Representative procedure for the Nozaki–Hiyama–Kishi reaction

A mixture of $CrCl_3$ (4.0 mg, 5 mol %) and Mn (83.0 mg, 0.75 mmol) in THF (2.00 mL) was stirred at room temperature for

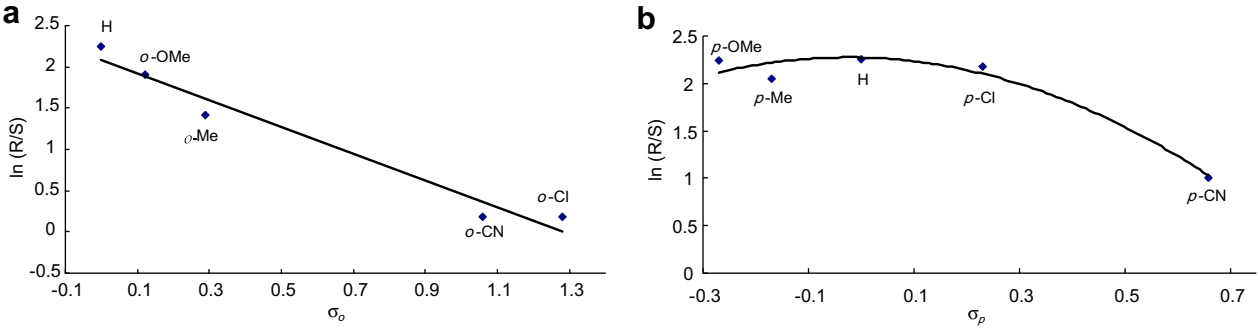


Figure 3. (a) The correlation of the Hammett constants (σ_o) and the enantiomeric excesses (ln(R/S)) and (b) the Hammett constants (σ_p) and the enantiomeric excesses of the NHK allylation reaction of substituted benzaldehydes in the presence of a Cr(III)–**2** complex.

1 h, at which point ligand **2** (13.5 mg, 5 mol %) and TEA (7 μL, 10 mol %) were added. After 1 h stirring at room temperature, allyl bromide (65 μL, 1.5 mmol) was added and the solution was stirred for another 1 h; benzaldehyde (50 μL, 0.5 mmol) and TMSCl (93 μL, 0.75 mmol) were added and stirred at room temperature for 20 h. The reaction was quenched by adding a saturated sodium bicarbonate solution (5 mL), and the solid residue was removed by filtration through a plug of Celite. The filtrate was extracted with dichloromethane (10 mL × 3), and the combined extracts were dried over sodium sulfate. After the organic phase was filtered and concentrated, the residue was dissolved in THF (2 mL), TBAF (1.5 mL, 1.5 mmol) was added slowly, and the solution was stirred for 30 min. The reaction was quenched by adding a saturated sodium bicarbonate solution (3 mL), and the aqueous phase was extracted with dichloromethane (5 mL × 3). The combined extracts were dried over sodium sulfate. Following the filtration and concentration of the organic phase, the residue was purified by flash column chromatography using silica gel as the stationary phase and ethyl acetate–hexane as the mobile phase to obtain 1-phenyl-but-3-en-1-ol **6** (61 mg, 83%). $[\alpha]_D^{25} = +44.5$ (*c* 1.13, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36–7.26 (m, 5H), 5.86–5.77 (m, 1H), 5.19–5.13 (m, 2H), 4.75–4.70 (m, 1H), 2.56–2.49 (m, 2H), 2.17 (s, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 143.9, 134.5, 128.4, 127.5, 125.8, 118.4, 73.3, 43.8. IR (KBr): 3389, 3082, 3028, 2983, 2929, 2902, 1641, 1596, 1492, 1454, 757, 700 cm^{-1}. MS (EI) m/z: $[M]^+$ 148 (0.2), 107 (100), 79 (88), 77 (48), 51 (12). HRMS-EI (m/z): $[M]^+$ calcd for $C_{10}H_{12}O$, 148.0888; found, 148.0882. The enantioselectivity was measured by HPLC (Chiralcel OD-H, 2-propanol/hexanes, 1:9, 0.25 mL/min) to be 81% ee.

4.2.1. 1-(2-Methoxy-phenyl)-but-3-en-1-ol 7

Yield: 77.0%. $[\alpha]_D^{26.0} = +57.5$ (*c* 1.25, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35–7.22 (m, 2H), 6.98–6.86 (m, 2H), 5.87–5.81 (m, 1H), 5.17–5.09 (m, 2H), 4.98–4.94 (m, 1H), 3.85 (s, 3H), 2.64–2.48 (m, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$,): δ 156.3, 135.2, 131.8, 128.3, 126.8, 120.7, 117.5, 110.4, 69.6, 55.2, 41.9. IR (KBr): 3417, 3073, 3002, 2937, 2836, 1639, 1601, 1588, 1490, 1463, 1287, 1240, 1048, 781, 754 cm^{-1}. MS (EI) *m/z*: $[M]^+$ 178 (0.6), 160 (10), 137 (100), 109 (40), 94 (31), 77 (27). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{11}H_{14}O_2$, 178.0994; found, 178.0995. The enantioselectivity was measured by HPLC (Chiralcel OD-H, 2-propanol/hexanes, 1:9, 0.25 mL/min) to be 74% ee.

4.2.2. 1-(3-Methoxy-phenyl)-but-3-en-1-ol 8

Yield: 72.0%. $[\alpha]_D^{26.4} = +35.7$ (*c* 1.50, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29–7.26 (t, *J* = 4.5 Hz, 1H), 6.93–6.92 (t, *J* = 1.5 Hz, 2H), 6.83–6.80 (m, 1H), 5.85–5.76 (m, 1H), 5.19–5.12 (m, 2H), 4.71 (s, 1H), 3.81 (s, 3H), 2.56–2.45 (m, 2H), 2.07 (s, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 159.7, 145.6, 134.4, 129.4, 118.4, 118.1, 113.0, 111.3, 73.2, 68.3, 55.2, 43.8. IR (KBr): 3417, 3073, 3010, 2937, 2836, 1641, 1601, 1587, 1487, 1461, 1263, 1155, 1043, 785, 754, 700 cm^{-1}. MS (EI) *m/z*: $[M]^+$ 178 (3.5), 137 (91), 109 (100), 94 (42), 77 (42), 66 (19). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{11}H_{14}O_2$, 178.0994; found, 178.0990.

4.2.3. 1-(3-Methoxy-phenyl)-butan-1-ol 8a

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.27 (t, *J* = 4.0 Hz, 1H), 7.25–6.93 (m, 2H), 6.83–6.81 (m, 1H), 4.69–4.65 (t, *J* = 8.0 Hz, 1H), 1.81 (s, 1H), 1.81–1.66 (m, 2H), 1.47–1.32 (m, 2H), 0.97–0.93 (t, *J* = 4.0 Hz, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 159.7, 146.7, 129.4, 118.2, 112.9, 111.4, 74.3, 55.2, 41.2, 19.0, 13.9. IR (KBr): 3360, 3064, 2959, 2929, 2866, 1600, 1573, 1470, 1432, 1384, 1198, 1028, 785, 746, 698 cm^{-1}. MS (EI) *m/z*: $[M]^+$ 180 (32), 137 (100), 109 (58), 94 (34), 77 (35). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{11}H_{16}O_2$, 180.1150; found, 180.1152. The enantioselectivity was measured by HPLC (Chiralcel OD-H, 2-propanol/hexanes, 1:9, 0.25 mL/min) to be 46% ee.

4.2.4. 1-(4-Methoxy-phenyl)-but-3-en-1-ol 9

Yield: 68%. $[\alpha]_D^{26.8} = +44.6$ (*c* 1.63, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29–7.25 (m, 2H), 6.91–6.87 (m, 2H), 5.87–5.73 (m, 1H), 5.18–5.11 (m, 2H), 4.70–4.67 (t, *J* = 4.5 Hz, 1H), 3.80 (s, 3H), 2.52–2.47 (t, *J* = 7.5 Hz, 2H), 2.04 (s, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 159.0, 136.0, 134.6, 127.0, 118.2, 113.8, 73.0, 55.9, 43.7. IR (KBr): 3417, 3082, 2934, 2830, 1641, 1612, 1587, 1513, 1470, 1434, 1299, 1247, 1175, 1035, 916, 872, 832 cm^{-1}. MS (EI) *m/z*: $[M]^+$ 178 (0.4), 137 (100), 109 (38), 94 (29), 77 (31). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{11}H_{14}O_2$, 178.0990; found, 178.0995. The enantioselectivity was measured by HPLC (Chiralcel OD-H, 2-propanol/hexanes, 1:9, 0.25 mL/min) to be 80% ee.

4.2.5. 1-*o*-Tolyl-but-3-en-1-ol 10

Yield: 80%. $[\alpha]_D^{25.0} = +41.9$ (*c* 2.49, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50–7.47 (m, 1H), 7.47–7.15 (m, 3H), 5.87–5.73 (m, 1H), 5.22–5.14 (m, 2H), 5.00–4.96 (m, 1H), 2.52–2.42 (m, 2H), 2.34 (s, 3H), 1.86 (s, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 141.9, 134.7, 134.3, 130.3, 127.2, 126.2, 125.1, 118.2, 69.7, 42.6, 19.0. IR (KBr): 3379, 3073, 3023, 2976, 2932, 1640, 1605, 1486, 1460, 1434, 1380, 1287, 1215, 1179, 1049, 999, 915, 870, 756, 726 cm^{-1}. MS (EI) *m/z*: $[M]^+$ 162 (1.4), 121 (100), 93 (25), 91 (14), 77 (7). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{11}H_{14}O$, 162.1045; found, 162.1052.

4.2.6. Benzoic acid 1-*o*-tolyl-but-3-enyl ester 10a

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11–8.09 (m, 2H), 7.58–7.54 (m, 1H), 7.48–7.43 (m, 3H), 7.22–7.18 (m, 3H), 6.29–6.26 (m, 1H), 5.83–5.79 (m, 1H), 5.18–5.08 (m, 2H), 2.80–2.69 (m, 2H), 2.49 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 165.7, 138.7, 135.0, 133.4, 132.9, 130.4, 129.6, 128.3, 127.7, 126.2, 125.8, 118.1, 72.6, 40.3, 19.3. IR (KBr): 3082, 3019, 2974, 2929, 2857, 1715, 1641, 1600, 1492, 1451, 1313, 1273, 1070, 1021, 970, 921, 764, 710 cm^{-1}. MS (EI) *m/z*: $[M]^+$ 266 (0.1), 225 (19), 129 (12), 105 (100), 77 (30). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{18}H_{18}O_2$, 266.1307; found, 266.1311. The enantioselectivity was measured by HPLC (Chiralcel OD-H, 2-propanol/hexanes, 1:9, 0.25 mL/min) to be 61% ee.

4.2.7. 1-*m*-Tolyl-but-3-en-1-ol 11

Yield: 70%. $[\alpha]_D^{25.4} = +29.4$ (*c* 1.10, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24–7.22 (d, *J* = 8.0 Hz, 1H), 7.18–7.14 (t, *J* = 8.0 Hz, 2H), 7.10–7.08 (d, *J* = 8.0 Hz, 1H), 5.87–5.76 (m, 1H), 5.19–5.13 (m, 2H), 4.72–4.69 (m, 1H), 2.55–2.47 (m, 2H), 2.36 (s, 3H), 1.56 (s, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 143.8, 138.0, 134.5, 128.32, 128.30, 126.4, 122.8, 118.3, 73.3, 43.8, 21.4. IR (KBr): 3388, 3074, 3023, 2977, 2920, 2866, 1641, 1608, 1590, 1487, 1432, 1156, 1049, 997, 915, 786, 703 cm^{-1}. MS (EI) *m/z*: $[M]^+$ 162 (0.3), 121 (100), 93 (80), 91 (48), 77 (34). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{11}H_{14}O$, 162.1045; found, 162.1050. The enantioselectivity was measured by HPLC (Chiralcel OD-H, 2-propanol/hexanes, 1:9, 0.25 mL/min) to be 56% ee.

4.2.8. 1-*p*-Tolyl-but-3-en-1-ol 12

Yield: 73%. $[\alpha]_D^{26.0} = +39.1$ (*c* 1.73, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.24 (d, *J* = 8.0 Hz, 2H), 7.17–7.15 (d, *J* = 8.0 Hz, 2H), 5.86–5.76 (m, 1H), 5.19–5.12 (m, 2H), 4.71–4.68 (m, 1H), 2.52–2.49 (m, 2H), 2.35 (s, 3H), 2.07 (s, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 140.9, 137.1, 134.6, 129.1, 125.8, 118.19, 73.2, 43.7, 21.1. IR (KBr): 3390, 3075, 3009, 2977, 2922, 1902, 1640, 1615, 1513, 1432, 1309, 1198, 1179, 1106, 1044, 998, 914, 871, 816, 537 cm^{-1}. MS (EI) *m/z*: $[M]^+$ 162 (0.3), 121 (100), 93

(35), 91 (30), 77 (25). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{11}H_{14}O$, 162.1045; found, 162.1046.

4.2.9. Benzoic acid 1-*p*-tolyl-but-3-enyl ester 12a

^1H NMR (400 MHz, $CDCl_3$): δ 8.10–8.08 (m, 2H), 7.58–7.54 (m, 1H), 7.46–7.42 (m, 2H), 7.35–7.33 (d, J = 8.0 Hz, 2H), 7.19–7.17 (d, J = 8.0 Hz, 2H), 6.06–6.04 (t, J = 4.0 Hz, 1H), 5.84–5.77 (m, 1H), 5.17–5.06 (m, 2H), 2.84–2.70 (m, 2H), 2.37 (s, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 165.7, 137.7, 137.2, 133.4, 132.8, 130.5, 129.6, 129.1, 128.3, 126.5, 118.0, 75.7, 40.8, 21.1. IR (KBr): 3064, 3028, 2938, 2866, 1715, 1645, 1605, 1583, 1515, 1443, 1345, 1313, 1270, 1178, 1109, 1070, 1029, 975, 921, 814, 710, 683 cm^{-1}. MS (EI) *m/z*: $[M]^+$ 266 (0.1), 225 (22), 105 (100), 77 (21). HRMS (EI): $[M]^+$ calcd for $C_{18}H_{18}O_2$, 266.1307; found, 266.1313. The enantioselectivity was measured by HPLC (Chiralcel OD-H, 2-propanol/hexanes, 1:9, 0.25 mL/min) to be 77% ee.

4.2.10. 1-(2-Chloro-phenyl)-but-3-en-1-ol 13

Yield: 70%. $[\alpha]_D^{25.0} = +61.6$ (*c* 0.70, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ 7.58–7.55 (t, J = 4.5 Hz, 1H), 7.34–7.18 (m, 3H), 5.88–5.83 (m, 1H), 5.22–5.14 (m, 3H), 2.66–2.59 (m, 1H), 2.43–2.36 (m, 1H), 2.06 (s, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 141.1, 134.2, 131.7, 129.4, 128.4, 127.1, 118.7, 69.6, 42.0. IR (KBr): 3389, 3073, 2983, 2920, 2857, 1637, 1600, 1573, 1470, 1434, 1200, 1129, 1033, 994, 921, 754, 701 cm^{-1}. MS (EI) *m/z*: $[M]^+$ 182 (0.8), 143 (24), 141 (100), 113 (37), 78 (9). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{10}H_{11}ClO$, 182.0498; found, 182.0502.

4.2.11. Benzoic acid 1-(2-chloro-phenyl)-but-3-enyl ester 13a

^1H NMR (400 MHz, $CDCl_3$): δ 8.12–8.10 (t, J = 4.0 Hz, 2H), 7.60–7.56 (t, J = 4.0 Hz, 1H), 7.50–7.44 (m, 3H), 7.39–7.37 (t, J = 4.0 Hz, 1H), 7.26–7.21 (m, 2H), 6.47–6.43 (m, 1H), 5.87–5.82 (m, 1H), 5.16–5.08 (m, 2H), 2.78–2.73 (m, 2H); ^{13}C NMR (100.6 MHz, CDCl3): δ 165.4, 138.1, 133.0, 132.9, 132.1, 130.2, 129.6, 128.8, 128.4, 127.1, 126.9, 118.3, 72.5, 39.5. IR (KBr): 3073, 2929, 2857, 1724, 1641, 1605, 1451, 1358, 1335, 1318, 1267, 1178, 1107, 1070, 1024, 984, 926, 755, 710 cm^{-1}. MS (EI) *m/z*: $[M]^+$ 286 (0.03), 139 (18), 128 (18), 105 (100), 77 (73), 51 (22). HRMS-EI (m/z): $[M]^+$ calcd for C17H15ClO2, 286.0761; found, 286.0755. The enantioselectivity was measured by HPLC (Chiralcel OD-H, 2-propanol/hexanes, 1:9, 0.25 mL/min) to be 9% ee.

4.2.12. 1-(3-Chloro-phenyl)-but-3-en-1-ol 14

Yield: 78%. $[\alpha]_D^{24.5} = +39.2$ (*c* 1.10, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ 7.64 (s, 1H), 7.37–7.21 (m, 3H), 5.83–5.72 (m, 1H), 5.20–5.15 (m, 2H), 4.74–4.69 (m, 1H), 2.55–2.42 (m, 2H), 2.04 (s, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 145.9, 134.3, 133.8, 129.6, 127.6, 126.0, 123.9, 118.9, 72.5, 43.8. IR (KBr): 3389, 3082, 3010, 2974, 2938, 2911, 1642, 1600, 1574, 1475, 1432, 1345, 1299, 1196, 1092, 1078, 1051, 918, 881, 785, 741, 695 cm^{-1}. MS (EI) *m/z*: $[M]^+$ 182 (0.7), 143 (29), 141 (89), 113 (45), 77 (100), 51 (18). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{10}H_{11}ClO$, 182.0498; found, 182.0495. The enantioselectivity was measured by HPLC (Chiralcel OD-H, 2-propanol/hexanes, 1:9, 0.25 mL/min) to be 78% ee.

4.2.13. 1-(4-Chloro-phenyl)-but-3-en-1-ol 15

Yield: 75%. $[\alpha]_D^{23.7} = +43.6$ (*c* 1.00, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.31–7.25 (m, 4H), 5.81–5.70 (m, 1H), 5.16–5.11 (m, 2H), 4.70–4.66 (m, 1H), 2.48–2.42 (m, 2H), 2.25 (s, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 142.3, 133.9, 133.1, 128.5, 127.2, 118.7, 72.5, 43.8. IR (KBr): 3389, 3077, 2992, 2907, 1641, 1596, 1492, 1410, 1304, 1191, 1091, 1051, 1013, 918, 870, 830, 781, 647, 624, 535 cm^{-1}. MS (EI) *m/z*: $[M]^+$ 182 (0.7), 143 (31), 141 (100), 113 (19), 77 (69). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{10}H_{11}ClO$, 182.0498; found, 182.0491.

4.2.14. Benzoic acid 1-(4-chloro-phenyl)-but-3-enyl ester 15a

^1H NMR (300 MHz, $CDCl_3$): δ 8.09–8.06 (d, J = 6.0 Hz, 2H), 7.59–7.54 (t, J = 7.5 Hz, 1H), 7.47–7.42 (t, J = 7.5 Hz, 2H), 7.38–7.31 (m, 4H), 6.04–5.99 (t, J = 7.5 Hz, 1H), 5.82–5.73, (m, 1H), 5.15–5.07 (m, 1H), 2.82–2.65 (m, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 165.6, 138.7, 133.7, 133.1, 132.8, 130.2, 129.6, 128.7, 128.4, 127.9, 118.6, 75.1, 40.8. IR (KBr): 3066, 2924, 2844, 1720, 1640, 1604, 1582, 1488, 1449, 1413, 1342, 1320, 1268, 1177, 1102, 1071, 1026, 982, 919, 822, 711, 529 cm^{-1}. MS (EI) *m/z*: $[M]^+$ 286 (0.05), 245 (7), 139 (10), 129 (15), 105 (100), 77 (62), 51 (19). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{17}H_{15}ClO_2$, 286.0761; found, 286.0752. The enantioselectivity was measured by HPLC (Chiralcel OD-H, 2-propanol/hexanes, 1:9, 0.25 mL/min) to be 79% ee.

4.2.15. 2-(1-Hydroxy-but-3-enyl)-benzonitrile 16

Yield: 54%. $[\alpha]_D^{25.0} = +9.2$ (*c* 0.85, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.85–7.83 (d, J = 8.0 Hz, 1H), 7.56–7.52 (m, 1H), 7.52–7.44 (m, 1H), 7.36–7.34 (d, J = 8.0 Hz, 1H), 5.83–5.73 (m, 1H), 5.51–5.48 (t, J = 6.0 Hz, 1H), 5.19–5.12 (m, 2H), 2.73–2.55 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 167.9, 146.7, 131.9, 129.4, 128.8, 123.8, 121.6, 119.0, 82.1, 39.3; IR (KBr): 3293, 3077, 2978, 2910, 2222, 1940, 1840, 1763, 1681, 1614, 1468, 1431, 1368, 1305, 1264, 1238, 1206, 1153, 1101, 1047, 921, 836, 780, 741, 711, 663, 565 cm^{-1}; MS (EI) *m/z*: $[M+1]^+$ 174 (3.2), 133 (100), 105 (40), 77 (40), 51 (17). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{11}H_{11}NO$, 173.0841; found, 173.0834. The enantioselectivity was measured by HPLC (Chiralcel OD-H, 2-propanol/hexanes, 1:9, 0.25 mL/min) to be 9% ee.

4.2.16. 3-(1-Hydroxy-but-3-enyl)-benzonitrile 17

Yield: 45%. $[\alpha]_D^{25.2} = +15.3$ (*c* 0.40, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (s, 1H), 7.60–7.54 (m, 2H), 7.46–7.43 (t, J = 6.0 Hz, 1H), 5.82–5.72 (m, 1H), 5.19–5.14 (m, 2H), 4.79–4.76 (m, 1H), 2.56–2.43 (m, 2H), 2.42 (s, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 145.31, 133.3, 131.1, 130.2, 129.5, 129.1, 119.4, 118.8, 112.4, 72.1, 43.8. IR (KBr): 3443, 3073, 3010, 2983, 2924, 2230, 1642, 1605, 1587, 1479, 1433, 1308, 1227, 1156, 1056, 994, 919, 867, 801, 741, 694, 489 cm^{-1}. MS (EI) *m/z*: $[M]^+$ 173 (0.8), 132 (100), 104 (6). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{11}H_{11}NO$, 173.0841; found, 173.0833. The enantioselectivity was measured by HPLC (Chiralcel OD-H, 2-propanol/hexanes, 1:9, 0.25 mL/min) to be 45% ee.

4.2.17. 4-(1-Hydroxy-but-3-enyl)-benzonitrile 18

Yield: 60%. $[\alpha]_D^{26.0} = +20.9$ (*c* 1.20, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.65–7.62 (t, J = 6.0 Hz, 2H), 7.48–7.46 (d, J = 4.0 Hz, 2H), 5.82–5.72 (m, 1H), 5.20–5.15 (m, 2H), 4.81–4.79 (t, J = 4.0 Hz, 1H), 2.57–2.41 (m, 2H), 2.39 (s, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 149.0, 133.3, 132.2, 126.4, 119.5, 118.8, 111.2, 72.3, 43.8. IR (KBr): 3834, 3442, 3076, 2979, 2908, 2348, 2229, 1928, 1840, 1642, 1609, 1572, 1504, 1415, 1303, 1056, 919, 872, 839, 759, 566 cm^{-1}. MS (EI) *m/z*: $[M]^+$ 173 (0.8), 132 (100), 104 (43), 77 (20). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{11}H_{11}NO$, 173.0841; found, 173.0836.

4.2.18. Benzoic acid 1-(4-cyano-phenyl)-but-3-enyl ester 18a

^1H NMR (400 MHz, $CDCl_3$): δ 8.08–8.06 (m, 2H), 7.67–7.64 (m, 2H), 7.61–7.57 (m, 1H), 7.52–7.44 (m, 4H), 6.06–6.03 (m, 1H), 5.76–5.72 (m, 1H), 5.14–5.09 (m, 2H), 2.78–2.70 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 165.5, 145.4, 133.3, 132.3, 132.1, 129.8, 129.6, 128.5, 127.0, 119.0, 118.5, 111.8, 74.9, 40.6. IR (KBr): 3063, 2925, 2857, 2345, 2229, 1974, 1924, 1714, 1645, 1601, 1451, 1335, 1318, 1269, 1173, 1108, 1065, 989, 921, 835, 712, 633, 563 cm^{-1}. MS (EI) *m/z*: $[M]^+$ 277 (0.4), 236 (8), 105 (100), 77 (23). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{18}H_{15}NO_2$, 277.1103; found, 277.1109. The enantioselectivity was measured

by HPLC (Chiralcel OD-H, 2-propanol/hexanes, 1:9, 0.25 mL/min) to be 47% ee.

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