Chinese Journal of Chemistry, **2004**, *22*, 310—314 **Article**

Dramatic Substituent Effect on the CCL-catalyzed Kinetic Resolution of 1-Aryl-2,3-allenols

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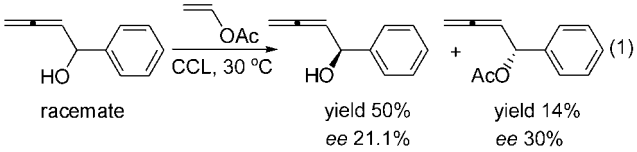
Optically active 1-aryl-2,3-allenols were obtained via CCL-mediated kinetic resolution of the racemic allenols. The substitution pattern of the aromatic ring, regarding to both the type of the substituent and its position on the aromatic ring, was found to be critical for the kinetic resolution of 1-aryl-2,3-allenols.

Keywords allenol, enzyme, kinetic resolution

Introduction

Allenes are a class of compounds with unique reactivities due to the existence of the two orthogonal π-bonds and have been found to be very useful intermediates in organic synthesis.[1] During the study of allenes, we and others have developed some allenol-based methodologies for the preparation of oxiranes,[2] 2,5-dihydrofuran,[3] α-methylenelactone,[4] α- or γ-amino alcohol,[5] and α,β-unsaturated ketones.[6] So it is desired for us to develop a facial route for the preparation of optically active allenols. Biocatalytic methods are now well-established routes to enantiomerically pure or enriched alcohols with the advantages of easy availability of starting materials and the biocatalyst, providing that high stereoselectivity can be realized for both products. However, due to the notion that many allenes are harmful to the biocatalyst,[7] the reports on the kinetic resolution of allenes using enzyme or microorganism as the catalyst are very limited.[8] During the course of our systematic studying of allenes, it was found that Novozym-435 (a form of *candida antarctica lipase B*) is an efficient biocatalyst for the kinetic resolution of a series of racemic 2,3-allenols affording highly optical active (*S*)-2,3-allenols and (*R*)-2,3-allenyl acetates in high yields and excellent *ee* values.[9] However, when it was applied for the resolution of 1-phenylbuta-2,3-dien-1-ol, the result was rather disappointing [Eq. (1)].



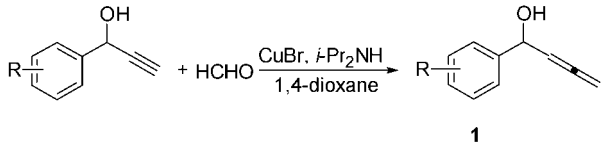
In an attempt to develop a facile route to optically active 1-aryl-2,3-allenols, we decided to study the kinetic resolution of racemic 1-aryl-2,3-allenols. In this paper, we wish to report our recent work on the CCL-catalyzed kinetic resolution of racemic 1-aryl-2,3-allenols.

Results and discussion

Synthesis of starting racemic 2,3-allenols

Racemic 2,3-allenols can be synthesized very conveniently via CuBr-mediated reaction of corresponding propargylic alcohols with paraformaldehyde (Scheme 1).[10]

Scheme 1 Synthesis of racemic 2,3-allenols



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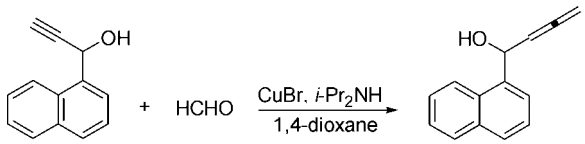
1a: R = 3,4-2Cl; **1b**: R = 4-Et; **1c**: R = 4-CN; **1d**: R = 2-Cl; **1e**: R = 4-Cl; **1f**: R = 4-*i*-Pr; **1g**: R = H; **1h**: R = 4-F; **1i**: R = 2-CF_3; **1j**: R = 4-CH_3; **1k**: R = 2,6-2Cl



1l

Kinetic resolution of racemic 2,3-allenols

The resolution of 1-(3',4'-dichlorophenyl)buta-2,3-dien-1-ol (**1a**) with vinyl acetate was studied using dif-

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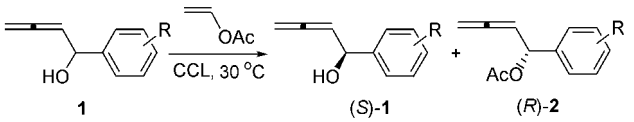
ferent enzymes. With lipases such as PPL, lipase G, lipolase and Novozym 871, the reaction did not occur. When we used CCL as the catalyst, the reaction proceeded to afford optically active **2a** in 22% yield and 90% *ee*. With these results in hand, we went on optimizing the reaction conditions. However, no better results were obtained. Then, a series of racemic 2,3-allenols were synthesized to investigate if the substituents on the aromatic ring would affect the stereoselectivity of the reaction. Some typical results were listed in Table 1. As shown in Table 1, the substituent of the benzene moiety has a dramatic effect on the CCL-catalyzed kinetic resolution of racemic 1-aryl-2,3-allenols. With the *para*-substituent on the aromatic ring being ethyl, cyano, chloro, *i*-propyl, H, F and methyl, the results were very different (Entries 2, 3, 5—8 and 10, Table 1): with 1-(4'-ethylphenyl)buta-2,3-dien-1-ol (**1b**), optically active allenyl acetate (**2b**) could be obtained in 24% yield and 93% *ee* together with **1b** in 42% yield and 65% *ee* (Entry 2, Table 1); while with 1-phenylbuta-2,3-dien-1-ol (**1g**) and 1-(4'-*i*-propylphenyl)buta-2,3-dien-1-ol (**1f**), the results were very disappointing (Entries 6 and 7, Table 1); the reaction of 1-(4'-methylphenyl)buta-2,3-dien-1-ol and 1-(4'-fluorophenyl)buta-2,3-dien-1-ol did not occur (Entries 8 and 10, Table 1). The position of the substituent on the aromatic ring also affects the stereoselectivity of the kinetic resolution of racemic 1-aryl-2,3-allenols. The result of 1-(2'-chlorophenyl)-buta-2,3-dien-1-ol is better than that of 1-(4'-chlorophenyl)buta-2,3-dien-1-ol. With 1-(3',4'-dichloro-phenyl)-buta-2,3-dien-1-ol, optically active **2a** could be obtained in 90% *ee*. However, the reaction did not occur

Table 1 CCL-Catalyzed kinetic resolution of racemic1-aryl-2, 3-allenols[a]



1 (*S*)-**1** (*R*)-**2**

Entry	R	Time/d	(*S*)-**1**		(*R*)-**2**	
			Yield[b]/%	*ee*[c]/%	Yield[b]/%	*ee*[c]/%
1	3,4-2Cl (**1a**)	4	57 (**1a**)	22	22 (**2a**)	90
2	4-CH_2CH_3 (**1b**)	7	42 (**1b**)	65	24 (**2b**)	93
3	4-CN (**1c**)	4	53 (**1c**)	36	24 (**2c**)	93
4	2-Cl (**1d**)	4	45 (**1d**)	43	43 (**2d**)	80
5	4-Cl (**1e**)	4	37 (**1e**)	57	44 (**2e**)	49
6	4-*i*-Pr (**1f**)	4	63 (**1f**)	9	17 (**2f**)	14
7	H (**1g**)	4	55 (**1g**)	20	20 (**2g**)	62
8	4-F (**1h**)	4	No reaction[d]			
9	2-CF_3 (**1i**)	4	No reaction[d]			
10	4-CH_3 (**1j**)	4	No reaction[d]			
11	2,6-2Cl (**1k**)	4	No reaction[d]			

[a] The reaction was carried out at 30 ℃ using alcohol (*ca*. 100 mg) and CCL (70 mg) in vinyl acetate (5 mL). [b] Isolated yield based on alcohol. [c] Enantiomeric excess determined via HPLC. [d] No reaction was observed.

when the substrate was 1-(2',6'-dichlorophenyl)buta-2,3-dien-1-ol. When we turned to 1-(1'-naphthyl)buta-2,3-dien-1-ol, optically active **2l** could be afforded in 22% yield with 93% *ee* [Eq. (2)]. The absolute configurations of **1** and **2** were tentatively determined to be *S* by comparison of the sign of the specific rotation of the obtained (+)-1-phenyl-prop-2-yn-1-ol (**1g**) with the known (*R*)-(−)-**1g**.[10b] From the above results, we can also conclude that aryl moiety is the large substituent at the hydroxymethine center as allenyl group is the medium group (Figure 1). The result is in accordance with Kazlauskas rule.[11]

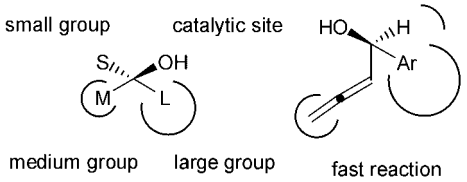
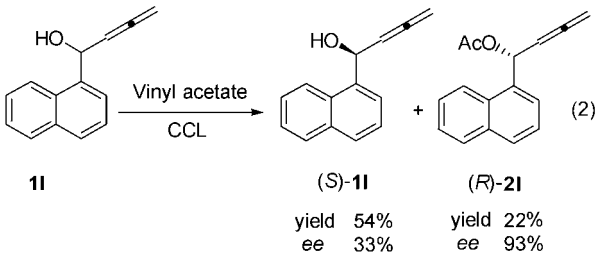


Figure 1 Kazlauskas rule.



In conclusion, it was found that CCL could be used for the kinetic resolution of 1-aryl-2,3-allenols. The substitution pattern is critical to the stereoselectivity of the reaction. Minor change of the substitutent on the aromatic ring can lead to dramatic change of the stereoselectivity of the reaction. Further studies on this reaction are being carried out in our laboratory.

Experimental

Synthesis of the starting racemic 1-aryl-2,3-allenols[10]

Synthesis of (±)-1-(3',4'-dichlorophenyl)buta-2, 3-dien-1-ol (1a) Typical procedure: To a reaction flask containing CuBr (1.45 g, 10 mmol) and paraformaldehyde (1.48 g, 49 mmol) were added subsequently *i*-Pr_2NH (5 mL, 38.2 mmol), 1-(3',4'-dichlorophenyl)-prop-2-yn-1-ol (4.02 g, 20 mmol) and 1,4-dioxane (30 mL). The mixture was heated at 120 ℃ for 1.5 h as monitored by TLC. After cooling, filtration and evaporation, H_2O (10 mL) and ethyl ether (40 mL) were added. After filtration, extraction with ethyl ether (40 mL×3) and drying over anhydride Na_2SO_4, the resulting crude product was submitted to chromatography on silica gel (petroleum ether-diethyl ether, 10∶1, *V*∶*V*) to afford **1a** (2.37 g, 55%).

Synthesis of (±)-1-(4'-ethylphenyl)buta-2,3-dien-1-ol (1b) The reaction of 1-(4'-ethylphenyl)prop-2-yn-1-ol (8.00 g, 50 mmol), paraformaldehyde (3.70 g, 123 mmol), CuBr (3.60 g, 25 mmol) and *i*-Pr_2NH (9.27 g, 92 mmol) in 1,4-dioxane (77 mL) afforded **1b** (4.52 g,

52%).

Synthesis of (±)-1-(4'-cyanophenyl)buta-2,3-dien-1-ol (1c)[12] The reaction of 1-(4'-cyanophenyl)-prop-2-yn-1-ol (1.90 g, 12 mmol), paraformaldehyde (0.90 g, 30 mmol), CuBr (0.87 g, 6 mmol) and *i*-Pr_2NH (2.22 g, 22 mmol) in 1,4-dioxane (18.5 mL) afforded **1c** (1.27 g, 62%).

Synthesis of (±)-1-(2'-chlorophenyl)buta-2,3-dien-1-ol (1d)[13] The reaction of 1-(2'-chlorophenyl)-prop-2-yn-1-ol (16.60 g, 100 mmol), paraformaldehyde (7.40 g, 246 mmol), CuBr (7.24 g, 50 mmol) and *i*-Pr_2NH (18.54 g, 184 mmol) in 1,4-dioxane (154 mL) afforded **1d** (8.20 g, 41%).

Synthesis of (±)-1-(4'-chlorophenyl)buta-2,3-dien-1-ol (1e)[14] The reaction of 1-(4'-chlorophenyl)-prop-2-yn-1-ol (9.20 g, 55 mmol), paraformaldehyde (4.10 g, 137 mmol), CuBr (4.00 g, 27.8 mmol) and *i*-Pr_2NH (10.20 g, 100 mmol) in 1,4-dioxane (85 mL) afforded **1e** (6.18 g, 62%).

Synthesis of (±)-1-(4'-*i*-propylphenyl)buta-2,3-dien-1-ol (1f) The reaction of 1-(4'-*i*-propylphenyl)prop-2-yn-1-ol (3.48 g, 20 mmol), paraformaldehyde (1.48 g, 49 mmol), CuBr (1.45 g, 10 mmol) and *i*-Pr_2NH (5.0 mL, 38.2 mmol) in 1,4-dioxane (30 mL) afforded **1f** (1.58 g, 42%).

Synthesis of (±)-1-phenylbuta-2,3-dien-1-ol (1g)[10a] The reaction of 1-phenylprop-2-yn-1-ol (13.2 g, 100 mmol), paraformaldehyde (7.40 g, 246 mmol), CuBr (7.24 g, 50 mmol) and *i*-Pr_2NH (18.54 g, 184 mmol) in 1,4-dioxane (154 mL) afforded **1g** (7.59 g, 52%).

Synthesis of (±)-1-(4'-fluorophenyl)buta-2,3-dien-1- ol (1h)[16] The reaction of 1-(4'-fluorophenyl)-prop-2-yn-1-ol (7.50 g, 50 mmol), paraformaldehyde (3.70 g, 123 mmol), CuBr (3.62 g, 25.2 mmol) and *i*-Pr_2NH (9.27 g, 92 mmol) in 1,4-dioxane (77 mL) afforded **1h** (4.29 g, 52%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.36 (dd, J=6.6, 1.8 Hz, 2H), 7.03 (t, J=6.6 Hz, 2H), 5.40 (q, J=6.3 Hz, 1H), 5.30—5.20 (m, 1H), 5.00—4.80 (m, 2H), 2.50 (bs, 1H).

Synthesis of (±)-1-(2'-trifluoromethylphenyl)-buta-2,3-dien-1-ol (1i) The reaction of 1-(2'-trifluoromethylphenyl)prop-2-yn-1-ol (8.85 g, 44.3 mmol), paraformaldehyde (3.70 g, 123 mmol), CuBr (3.62 g, 25.2 mmol) and *i*-Pr_2NH (13 mL, 92 mmol) in 1,4-dioxane (77 mL) afforded **1i** (5.87 g, 55%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.90—7.80 (m, 1H), 7.80—7.56 (m, 2H), 7.46—7.38 (m, 1H), 5.80—5.72 (m, 1H), 5.45 (q, J=6.1 Hz, 1H), 5.08—4.84 (m, 2H), 2.33 (s, 1H); IR (neat) ν: 3365, 1949 cm^{-1}; MS (70 eV) *m/z* (%): 214 (M^+, 1.86), 57 (100).

Synthesis of (±)-1-(4'-methylphenyl)buta-2,3-dien-1- ol (1j)[14] The reaction of 1-(4'-methylphenyl)-prop-2-yn-1-ol (5.84 g, 40 mmol), paraformaldehyde (2.96 g, 99 mmol), CuBr (2.89 g, 20 mmol) and *i*-Pr_2NH (10.0 mL, 76.4 mmol) in 1,4-dioxane (62.8 mL) afforded **1j** (3.36 g, 53%). liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.20 (d, J=8.1 Hz, 2H), 7.08 (d, J=8.1 Hz, 2H), 5.34 (q, J=6.3 Hz, 1H), 5.20—5.08 (m, 1H), 4.86—4.81 (m, 2H), 2.25 (s, 3H), 2.02 (bs, 1H); MS (70 eV) *m/z* (%): 160 (M^+, 3.70), 121 (100).

Synthesis of (±)-1-(2',6'-dichlorophenyl)buta-2,3-dien-1-ol (1k) The reaction of 1-(2',6'-dichlorophenyl)prop-2-yn-1-ol (11 g, 55 mmol), paraformaldehyde (4.44 g, 148 mmol), CuBr (4.34 g, 30 mmol) and *i*-Pr_2NH (11.12 g, 111 mmol) in 1,4-dioxane (92.4 mL) afforded **1k** (4.50 g, 39%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.22 (d, J=7.8 Hz, 2H), 7.08 (t, J=7.8 Hz, 1H), 6.00—5.90 (m, 1H), 5.50 (q, J=7.5 Hz, 1H), 4.84 (d, J=3.4 Hz, 1H), 4.82 (d, J=3.4 Hz, 1H), 3.16 (d, J=11.7 Hz, 1H); IR (neat) ν: 3421, 1946 cm^{-1}; MS (70 eV) *m/z* (%): 215 [M^+($2\times^{35}$Cl)+1, 1.55], 217 [M^+(^{35}Cl^{37}Cl)+1, 1.07], 219 [M^+($2\times^{37}$Cl)+1, 0.43], 197 (100); HRMS calcd for $C_{10}H_8Cl_2O$ [M^+($2\times^{35}$Cl)]: 213.9952, found 213.9965.

Synthesis of (±)-1-(1'-naphthyl)buta-2,3-dien-1-ol (1l)[16] The reaction of 1-(1'-naphthyl)prop-2-yn-1-ol (3.64 g, 20 mmol), paraformaldehyde (1.48 g, 49 mmol), CuBr (1.45 g, 10 mmol) and *i*-Pr_2NH (5 mL, 38.2 mmol) in 1,4-dioxane (30 mL) afforded **1l** (1.99 g, 51%).

Kinetic resolution of racemic allenols (1a—1h and 1l)

Synthesis of (*S*)-1-(3',4'-dichlorophenyl)buta-2,3-dien-1-ol [(*S*)-1a] and (*R*)-(−)-1-(3',4'-dichlorophenyl)buta-2,3-dien-1-ol acetate [(*R*)-(−)-2a] Typical Procedure: To a racemic mixture of (±)-1-(3',4'-dichlorophenyl)buta-2,3-dien-1-ol (l00 mg) and vinyl acetate (5 mL) was added CCL (70 mg). The mixture was stirred at 30 ℃ for 96 h as monitored by TLC. Filtration, evaporation and purification by flash chromatography on silica gel (eluent: petroleum ether∶ether= 40∶1—10∶1) afforded (*S*)-**1a** (57 mg, 57%) and (*R*)-**2a** (27 mg, 22%).

(*S*)-**1a**: 22% *ee* [HPLC conditions: ChiralPak AD column (0.46 cmϕ×25 cm); λ: 254 nm; rate: 0.7 mL/min; eluent: hexane∶*i*-PrOH=97∶3], liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.44 (d, J=2.1 Hz, 1H), 7.35 (d, J=8.3 Hz, 1H), 7.15 (dd, J=2.1, 8.3 Hz, 1H), 5.32 (q, J=6.5 Hz, 1H), 5.20—5.08 (m, 1H), 4.90 (d, J=2.2 Hz, 1H), 4.88 (d, J=2.2 Hz, 1H), 2.11 (d, J=3.8 Hz, 1H); IR (neat) ν: 3346, 1953 cm^{-1}; MS (70 eV) *m/z* (%): 218 [M^+($2\times^{37}$Cl), 0.27], 216 [M^+(^{35}Cl^{37}Cl)], 1.44), 214 [M^+($2\times^{35}$Cl), 2.32], 175 (100); HRMS calcd for $C_{10}H_8Cl_2O$ [M^+($2\times^{35}$Cl)]: 213.9952, found 213.9950.

(*R*)-**2a**: 90% *ee* [HPLC conditions: ChiralPak AS column (0.46 cmϕ×25 cm); λ: 254 nm; rate: 0.7 mL/min; eluent: hexane∶*i*-PrOH=100∶2.5], liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.47 (d, J=2.1 Hz, 1H), 7.43 (d, J=8.2 Hz, 1H), 7.20 (dd, J=2.1, 8.2 Hz, 1H), 6.24—6.18 (m, 1H), 5.38 (q, J=6.4 Hz, 1H), 5.00—4.80 (m, 2H), 2.13 (s, 3H); IR (neat) ν: 1953, 1739 cm^{-1}; MS (70 eV) *m/z*: 260 [M^+($2\times^{37}$Cl), 0.62], 258 [M^+(^{37}Cl ^{35}Cl), 2.93], 256 [M^+($2\times^{35}$Cl), 4.30], 179 (100); HRMS calcd for $C_{12}H_{10}Cl_2O_2$ [M^+($2\times^{35}$Cl)]: 256.0058, found 256.0040.

Synthesis of (*S*)-1-(4'-ethylphenyl)buta-2,3-dien-1-ol [(*S*)-1b] and (*R*)-1-(4'-ethylphenyl)buta-2,3-dien-1-ol acetate [(*R*)-2b] The reaction of racemic 1-(4'-ethylphenyl)buta-2,3-dien-1-ol (100 mg), vinyl acetate (5 mL) and CCL (70 mg) afforded (*S*)-**1b** (42 mg, 42%) and (*R*)-**2b** (30 mg, 24%).

(*S*)-**1b**: 65% *ee* [GC condition: RT-βDEXcst column: (30 meters, 0.25 m ID, 0.25 μm DF); carrier: N_2, 7.3 psi; injector: 250 ℃; detector (FID, H_2, 0.218 MPa): 250 ℃; oven temperature: 130 ℃ (10 min) then 1 ℃/min to 180 ℃ (2 min)], liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.32 (d, J=7.8 Hz, 2H), 7.20 (d, J=7.8 Hz, 2H), 5.47 (q, J=6.6 Hz, 1H), 5.40—5.10 (m, 1H), 5.06—4.80 (m, 2H), 2.65 (q, J=7.5 Hz, 2 H), 2.21 (bs, 1H), 1.24 (t, J=7.5 Hz, 3H); IR (neat) v: 3376, 1955 cm^{-1}; MS (70 eV) *m/z* (%): 174 (M^+, 16.03), 145 (100); HRMS calcd for $C_{12}H_{14}O$ (M^+): 174.1045, found 174.1031.

(*R*)-**2b**: 93% *ee* [HPLC conditions: ChiralPak AS column (0.46 cmϕ×25 cm); λ: 254 nm; rate: 0.7 mL/min; eluent: hexane∶*i*-PrOH=100∶1], liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.35 (d, J=8.1 Hz, 2H), 7.24 (d, J=8.1 Hz, 2H), 6.40—6.25 (m, 1H), 5.17 (q, J=6.6 Hz, 1H), 5.20—4.90 (m, 2H), 2.69 (q, J=7.6 Hz, 2H), 2.14 (s, 3H), 1.28 (t, J=7.6 Hz, 3H); IR (neat) v: 1956, 1738 cm^{-1}; MS (70 eV) *m/z* (%): 216 (M^+, 7.05), 174 (M^++1−$COCH_3$, 11.20), 145 (100); HRMS calcd for $C_{14}H_{16}O_2$ (M^+): 216.1150, found 216.1133.

Synthesis of (S)-1-(4'-cyanophenyl)buta-2,3-dien-1-ol [(*S*)-1c][12] and (*R*)-(−)-1-(4'-cyanophenyl)buta-2,3-dien-1-ol acetate [(*R*)-(−)-2c] The reaction of racemic 1-(4'-cyanophenyl)buta-2,3- dien-1-ol (100 mg), vinyl acetate (5 mL) and CCL (70 mg) afforded (*S*)-**1c** (53 mg, 53%) and (*R*)-**2c** (30 mg, 24%).

(*S*)-**1c**: 36% *ee* [HPLC conditions: ChiralPak AS column (0.46 cmϕ×25 cm); λ: 254 nm; rate: 0.7 mL/min; eluent: hexane∶*i*-PrOH=90∶10], liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.58 (d, J=8.1 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 5.40—5.24 (m, 2H), 4.90—4.78 (m, 2H), 2.22 (d, J=2.3 Hz, 1H); IR(neat) v: 3447, 2227, 1947 cm^{-1}; MS (70 eV) *m/z* (%): 171 (M^+, 6.57), 153 (100).

(*R*)-**2c**: 93% *ee* [HPLC conditions: ChiralPak AS column (0.46 cmϕ×25 cm); λ: 254 nm; rate: 0.7 mL/min; eluent: hexane∶*i*-PrOH=90∶10], liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.56 (d, J=6.7 Hz, 2H), 7.39 (d, J=6.7 Hz, 2H), 6.24—6.18 (m, 1H), 5.31 (q, J=6.7 Hz, 1H), 4.78—4.65 (m, 2H), 2.05 (s, 3H); IR (neat) v: 2229, 1955, 1738 cm^{-1}; MS (70 eV) *m/z* (%): 171 (M^++1−$COCH_3$, 77.99), 170 (M^+−$COCH_3$, 42.00), 43 (100.0); HRMS calcd for $C_{11}H_9NO$ (M^++1−$COCH_3$): 171.0684, found 171.0665.

Synthesis of (*S*)-1-(2'-chlorophenyl)buta-2,3-dien-1-ol [(*S*)-1d][13] and (*R*)-1-(2'-chlorophenyl)buta-2,3-dien-1-ol acetate [(*R*)-2d] The reaction of racemic 1-(2'-chlorophenyl)buta-2,3-dien-1-ol (97 mg), vinyl acetate (5 mL) and CCL (70 mg) afforded (*S*)-**1d** (44 mg, 45%) and (*R*)-**2d** (52 mg, 43%).

(*S*)-**1d**: 43% *ee* [HPLC conditions: Chiralcel OD Column (0.46 cmϕ×25 cm); λ: 254 nm; rate: 0.7 mL/min; eluent: hexane∶*i*-PrOH=97∶3], liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.34 (d, J=8.0 Hz, 1H), 7.40—7.10 (m, 3H), 5.67 (s, 1H), 5.60—5.40 (m, 1H), 5.04—4.84 (m, 2H), 2.35 (s, 1H); IR (neat) v: 3172, 1948 cm^{-1}; MS (70 eV) *m/z* (%): 180 (M^+, 0.25), 163 (100).

(*R*)-**2d**: 80% *ee* [HPLC conditions: ChiralPak AS column (0.46 cmϕ×25 cm); λ: 254 nm; rate: 0.7 mL/min; eluent: hexane∶*i*-PrOH=100∶1.5], liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.70—7.10 (m, 4H), 6.70 — 6.55 (m, 1H), 5.45 (q, J = 6.4 Hz, 1H), 5.10—4.80 (m, 2H), 2.14 (s, 3H); IR (neat) v: 1955, 1742 cm^{-1}; MS (70 eV) *m/z* (%): 224 [M^+(^{37}Cl), 1.18], 222 [M^+(^{35}Cl), 3.44], 182 [M^+ (^{37}Cl)+1−$COCH_2$, 11.85], 180 [M^+(^{35}Cl)+1−$CCOH_3$, 36.30], 145 (100); HRMS calcd for $C_{10}H_9ClO$ [M^+(^{35}Cl)+1−$CCOH_3$]: 180.0342, found 180.0335.

Synthesis of (*S*)-1-(4'-chlorophenyl)buta-2,3-dien-1-ol [(*S*)-1e][14] and (*R*)-1-(4'-chlorophenyl)buta-2,3-dien-1-ol acetate [(*R*)-2e] The reaction of racemic 1-(4'-chlorophenyl)buta-2,3-dien-1-ol (95 mg), vinyl acetate (5 mL) and CCL (70 mg) afforded (*S*)-**1e** (34 mg, 37%) and (*R*)-**2e** (51 mg, 44%).

(*S*)-**1e**: 57% *ee* [HPLC conditions: ChiralPak AD column (0.46 cmϕ×25 cm); λ: 254 nm; rate: 0.7 mL/min; eluent: hexane∶*i*-PrOH=95∶5], liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.33 (s, 4H), 5.37 (q, J=6.4 Hz, 1H), 5.30—5.18 (m, 1H), 4.94 (d, J=2.1 Hz, 1H), 4.92 (d, J=2.1 Hz, 1H), 2.30 (bs, 1H); IR (neat) v: 3309, 1948, 1595 cm^{-1}; MS (70 eV) *m/z* (%): 182 [M^+(^{37}Cl), 6.20], 180 [M^+(^{35}Cl), 18.08], 141 (100).

(*R*)-**2e**: 49% *ee* [HPLC conditions: ChiralPak AS column (0.46 cmϕ×25 cm); λ: 254 nm; rate: 0.7 mL/min; eluent: hexane∶*i*-PrOH=70∶30], liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.34 (s, 4H), 6.40—6.20 (m, 1H), 5.44 (q, J=6.6 Hz, 1H), 5.10—4.85 (m, 2H), 2.14 (s, 3H); IR (neat) v: 1956, 1737 cm^{-1}; MS (70 eV) *m/ z*: 224 [M^+(^{37}Cl), 2.09], 222 [M^+(^{35}Cl), 3.44], 182 [M^+ (^{37}Cl) + 1 − $COCH_3$, 11.85], 180 [M^+(^{35}Cl) + 1 − $COCH_3$, 180], 145 (100.0); HRMS calcd for $C_{10}H_9ClO$ [M^+(^{35}Cl)+1−$COCH_3$]: 180.0342, found 180.0324.

Synthesis of (*S*)-1-(4'-*i*-propylphenyl)buta-2,3-dien-1-ol [(*S*)-1f] and (*R*)-1-(4'-i-propylphenyl)buta-2,3-dien-1-ol acetate [(*R*)-2f] The reaction of racemic 1-(4'-*i*-propylphenyl)buta-2,3-dien-1-ol (96 mg), vinyl acetate (5 mL) and CCL (70 mg) afforded (*S*)-**1f** (60 mg, 63%) and (*R*)-**2f** (17 mg, 17%).

(*S*)-**1f**: 9% *ee* [HPLC conditions: Chiralcel OD column (0.46 cmϕ×25 cm); λ: 254 nm; rate: 0.7 mL/min; eluent: hexane∶*i*-PrOH=95∶5]; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.24 (d, J=7.8 Hz, 2H), 7.14 (d, J=7.8 Hz, 2H), 5.40—5.30 (m, 1H), 5.25—5.12 (m, 1H), 5.00—4.80 (m, 2H), 2.90—2.65 (m, 1H), 2.09 (bs, 1H), 1.16 (d, J=6.9 Hz, 6H); IR (neat) v: 3353, 1948 cm^{-1}; MS (70 eV) *m/z* (%): 188 (M^+, 13.66), 145 (100); HRMS calcd for $C_{13}H_{16}O$ (M^+): 188.1201, found 188.1195.

(*R*)-**2f**: 14% *ee* [HPLC conditions: Chiral-Pak AS

column (0.46 cmϕ × 25 cm); λ: 254 nm; rate: 0.7 mL/min; eluent: hexane∶*i*-PrOH=100∶1], liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.24 (d, J=8.2 Hz, 2H), 7.16 (d, J=8.2 Hz, 2H), 6.28—6.18 (m, 1H), 5.33 (q, J =6.7 Hz, 1H), 4.90—4.78 (m, 2H), 2.90—2.75 (m, 1H), 2.03 (s, 3H), 1.19 (d, J=6.9 Hz, 6H); IR (neat) v: 1956, 1738 cm^{-1}; MS (70 eV) *m/z* (%): 230 (M^+, 0.96), 171 (100); HRMS calcd for $C_{15}H_{18}O_2$ (M^+): 230.1307, found 230.1298.

Synthesis of (*S*)-(+)-1-phenylbuta-2,3-dien-1-ol [(*S*)-1g][10a] **and (*R*)-1-phenylbuta-2,3-dien-1-ol acetate (2g)** The reaction of racemic 1-phenylbuta-2,3-dien-1-ol (96 mg), vinyl acetate (5 mL) and CCL (70 mg) afforded (*S*)-**1g** (53 mg, 55%) and (*R*)-**2g** (25 mg, 20%).

(*S*)-**1g**: 20% *ee* [HPLC conditions: Chiralcel OD column (0.46 cmϕ × 25 cm); λ: 254 nm; rate: 0.7 mL/min; eluent: hexane∶*i*-PrOH=95∶5], liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.60—7.10 (m, 5H), 5.44 (q, J=6.7 Hz, 1H), 5.30—5.20 (m, 1H), 5.08—4.80 (m, 2H), 2.21 (bs, 1H); IR (neat) v: 3185, 1947 cm^{-1}; MS (70 eV) *m/z* (%): 146 (M^+, 3.13), 105 (100).

(*R*)-**2g**: 62% *ee* [HPLC conditions: ChiralPak AS column (0.46 cmϕ × 25 cm); λ: 254 nm; rate: 0.7 mL/min; eluent: hexane∶*i*-PrOH=100∶4], liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.50—7.10 (m, 5H), 6.30—6.20 (m, 1H), 5.39 (q, J=6.6 Hz, 1H), 4.95—4.40 (m, 2H), 2.04 (s, 3H); IR (neat) v: 1958, 1742 cm^{-1}; MS *m/z* (%): 188 (M^+, 0.55), 146 (M^++1−$COCH_3$, 83.11), 145 (M^+−$COCH_3$, 36.72), 129 (100); HRMS calcd for $C_{12}H_{12}O_2$ (M^+): 188.0837, found 188.0840.

Synthesis of (*S*)-1-(1'-naphthyl)buta-2,3-dien-1-ol [(*S*)-1l][16] **and (*R*)-(−)-1-(1'-naphthyl)buta-2,3-dien-1-ol acetate [(*R*)-(−) 2l]** The reaction of racemic 1-(1'-naphthyl)buta-2,3-dien-1-ol (96 mg), vinyl acetate (5 mL) and CCL (70 m g) afforded (*S*)-**1l** (52 mg, 54%) and (*R*)-**2l** (25 mg, 21%).

(*S*)-**1l**: 33% *ee* [HPLC conditions: Chiralcel OD column (0.46 cmϕ × 25 cm); λ: 254 nm; rate: 0.7 mL/min; eluent: hexane∶*i*-PrOH=95∶5], liquid, ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.16 (d, J=7.5 Hz, 1H), 7.89 (d, J=7.2 Hz, 1H), 7.81 (d, J=8.1 Hz, 1H), 7.70 (d, J=7.2 Hz, 1H), 7.60—7.40 (m, 3H), 6.05—5.95 (m, 1H), 5.61 (q, J=6.3 Hz, 1H), 4.96 (d, J=2.4 Hz, 1H), 4.94 (d, J=2.4 Hz, 1H), 2.20 (d, J=6.9 Hz, 1H); IR (neat) v: 3365, 1946 cm^{-1}; MS(70 eV) *m/z* (%): 196(M^+, 24.55), 129 (100).

(*R*)-**2l**: 93% *ee* [HPLC conditions: ChiralPak AS column (0.46 cmϕ×25 cm); λ: 254 nm; rate: 0.7 mL/min; eluent: hexane∶*i*-PrOH=100∶1], liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.06 (d, J=7.8 Hz, 1H), 7.90—7.70 (m, 2H), 7.56 (d, J=6.4 Hz, 1H), 7.50—7.28 (m, 3H), 7.00—6.82 (m, 1H), 5.50 (q, J=6.4 Hz, 1H), 4.90—4.70 (m, 2H), 2.07 (s, 3H); IR (neat) v: 1954, 1739 cm^{-1}; MS (70 eV) *m/z* (%): 238 (M^+, 0.92), 196 (M^++1−$COCH_3$, 41.11), 178 (100.0); HRMS calcd for $C_{14}H_{12}O$ (M^+ − $COCH_3$ + 1): 196.0888, found 196.0876.

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