SUPPORTING INFORMATION

Catalytic Enantioselective Allenylation Reactions of Aldehydes with Tethered Bis(8-quinolinolato) (TBOx) Chromium Complex

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General Procedures.

All reactions were carried out in oven- or flame-dried glassware under an atmosphere of dry argon unless otherwise noted. Except as otherwise indicated, all reactions were magnetically stirred and monitored by analytical thin-layer chromatography using Whatman pre-coated silica gel flexible plates (0.25 mm) with F₂₅₄ indicator or Merck pre-coated silica gel plates with F₂₅₄ indicator. Visualization was accomplished by UV light (256 nm), with combination of potassium permanganate and/or phosphomolybdic acid solution as an indicator. Flash column chromatography was performed according to the method of Still using silica gel 60 (mesh 230-400) supplied by SILICYCLE. Yields refer to chromatographically and spectrographically pure compounds, unless otherwise noted.

Commercial grade reagents and solvents were used without further purification except as indicated below. Liquid aldehydes and chlorosilanes were freshly distilled under an atmosphere of dry argon, and solid aldehydes were purified by flash chromatography on silica gel. THF (ultra low water, 99.9%, 18L, BakerDRYTM), purchased from J. T. Baker was purified by M. BRAUN solvent purification system.

¹H NMR spectra were recorded on a Bruker Avance 400 (400 MHz ¹H) or a Bruker Avance 500 (500 MHz ¹H). High-performance liquid chromatography (HPLC) was performed on a Varian ProStar Series equipped with a variable wavelength detector using chiral stationary columns (0.46 cm x 25 cm) equipped with guard columns from Daicel. Analytical gas-liquid chromatograph (GLC) was performed on a Shimadzu GC-17A instrument equipped with a flame ionization detector and capillary column of B-DM (0.25mm x 20m) using nitrogen as carrier gas. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter.

General Procedure for Allenylation Reactions of Aldehydes

An oven-dried test tube was charged with a magnetic stir bar, TBOxCrCl^{1,2} (18 mg, 0.025 mmol, 5 mol%) and Mn powder 50-mesh (83 mg, 1.5 mmol) then flushed thoroughly with argon three times. To this were added anhydrous THF (2 mL), then the resulting yellow-brown mixture was stirred for 10 min. at room temperature. The catalyst solution was treated with substituted propargylic halides (0.75mmol), and the mixture was stirred for 30 minutes. To the reaction mixture was added neat aldehyde (0.5 mmol) followed by drop-wise addition of neat Silyl chloride (0.5 mmol). The reaction was stirred at room temperature for a specified length of time, at which time it was quenched with saturated NaHCO₃ solution (0.5 mL) and filtered through a short pad of Celite®. After removal of volatiles *in vacuo*, the residue was taken up into Et₂O (20 mL) then washed with a saturated NaCl solution (20 mL), dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The resulting crude silyl ether was treated with TBAF (1M in THF, 1 mL, 1 mmol) in THF (4 mL) at room temperature until it was completely desilylated (by TLC). The reaction mixture was diluted with Et₂O (20 mL), washed with a saturated NaCl solution (20 mL), and dried over anhydrous Na₂SO₄. The crude product was purified by flash chromatography on silica gel, which had to be fast to prevent the decomposition of the products. The ¹H NMR spectra of the products were identical to the known compounds in the literature report.

Scheme 1

As shown in Scheme 1, the silyl group of the propargylic bromide affected the yields and enantioselectivities. TES substituted propargylic bromide generated the desired α-allenic alcohol in lower yield with the same enantioselectivity as 1-

trimethylsilyl-3-bromopropyne. If the size of the silyl group increased further (TBDMS and TIPS), the yields and enantioselectivities of the products went down dramatically. TES, TBDMS, and TIPS substituted propargylic bromides were synthesized according to the known procedures.³

Scheme 2

As shown in Scheme 2, if the crude product was treated with aqueous HCl (0.5N, 2 mL, 1 mmol) at room temperature until it was completely desilylated (by TLC), 1-Phenyl-2-trimethylsilylbuta-2,3-dien-1-ol³ was obtained in 80% yield. This TMS substituted α -allenic alcohol could be further transferred into 1-phenylbuta-2,3-dien-1-ol in almost quantitative yield by TBAF in THF.

Scheme 3

As shown in Scheme 3, the unique *cis*- β transition state provided very good enantioselective environment for allenylation reactions.

Scheme 4

As shown in Scheme 4, the reaction could be scaled up by using only 4 mol% TBOxCr(III)Cl. After 48 h, at RT, the desired product was obtained in 82% yield with 94% ee.

(*R*)-1-Phenyl-buta-2,3-dien-1-ol⁴

¹H NMR (400 MHz, CDCl₃, ppm): 7.42-7.25 (m, 5H), 5.46-5.43 (m, 1H), 5.29-5.28 (m, 1H), 4.95-4.93 (m, 2H), 2.10 (d, 1H). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes : 2-propanol = 95 : 5, flow rate = 0.5 mL/min.), *t_r*(major, *R*) = 19.1 min., *t_r*(minor, *S*) = 25.7 min. $[\alpha]_{\text{D}}^{24} = +98.8$ (*c* = 1.1, CHCl₃). The reported value for *R*-enantiomer (47% ee) is $[\alpha]_{\text{D}}^{25} = +45.6$ (*c* = 1.2, CCl₄).

(*S*)-1-Phenyl-2-trimethylsilyl-buta-2,3-dien-1-ol³

¹H NMR (400 MHz, CDCl₃, ppm): 7.37-7.27 (m, 5H), 5.24-5.22 (m, 1H), 4.69-4.63 (m, 2H), 2.29 (d, 1H), -0.01 (s, 9H). $[\alpha]_{\text{D}}^{24} = +101.9$ (*c* = 1.0, CHCl₃). The reported value for *R*-enantiomer (76% ee) is $[\alpha]_{\text{D}}^{21} = -95.5$ (*c* = 0.55, CHCl₃).

1-*o*-Tolyl-buta-2,3-dien-1-ol⁸

^1H NMR (400 MHz, CDCl_3 , ppm): 7.50-7.49 (m, 1H), 7.23-7.14 (m, 3H), 5.48-5.42 (m, 1H), 5.41-5.38 (m, 1H), 4.92-4.89 (m, 2H), 2.36 (s, 3H), 2.05 (d, 1H). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes : 2-propanol = 97.5 : 2.5, flow rate = 1 mL/min.), $t_r(\text{major})$ = 14.0 min., $t_r(\text{minor})$ = 16.7 min.

1-*p*-Tolyl-buta-2,3-dien-1-ol⁸

^1H NMR (400 MHz, CDCl_3 , ppm): 7.41-7.30 (m, 2H), 7.19-7.16 (m, 2H), 5.45-5.41 (m, 1H), 5.25-5.23 (m, 1H), 4.94-4.91 (m, 2H), 2.34 (s, 3H), 2.12 (br, 1H). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes : 2-propanol = 95 : 5, flow rate = 0.5 mL/min.), $t_r(\text{major})$ = 16.6 min., $t_r(\text{minor})$ = 19.4 min.

1-(3-Methoxy-phenyl)-buta-2,3-dien-1-ol⁸

^1H NMR (400 MHz, CDCl_3 , ppm): 7.29-7.26 (m, 1H), 6.99-6.97 (m, 2H), 6.84-6.82 (m, 1H), 5.46-5.41 (m, 1H), 5.26 (m, 1H), 4.95-4.93 (m, 2H), 3.82 (s, 3H), 2.12 (br, 1H). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes : 2-propanol = 97.5 : 2.5, flow rate = 1 mL/min.), $t_r(\text{major})$ = 23.0 min., $t_r(\text{minor})$ = 33.0 min.

1-(4-Methoxy-phenyl)-buta-2,3-dien-1-ol⁹

^1H NMR (400 MHz, CDCl_3 , ppm): 7.46-7.33 (m, 2H), 6.99-6.88 (m, 2H), 5.45-5.42 (m, 1H), 5.23 (m, 1H), 4.96-4.88 (m, 2H), 3.88 (s, 3H), 2.16 (br, 1H). Enantiomeric excess

was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes : 2-propanol = 92.5 : 2.5, flow rate = 1 mL/min.), $t_r(\text{major}) = 20.1 \text{ min.}$, $t_r(\text{minor}) = 26.1 \text{ min.}$

1-(4-Chloro-phenyl)-buta-2,3-dien-1-ol⁸

^1H NMR (400 MHz, CDCl_3 , ppm): 7.57-7.54 (m, 2H), 7.37-7.32 (m, 2H), 5.41-5.38 (m, 1H), 5.26-5.25 (m, 1H), 4.95-4.92 (m, 2H), 2.14 (br, 1H). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes : 2-propanol = 97.5 : 2.5, flow rate = 1 mL/min.), $t_r(\text{major}) = 13.4 \text{ min.}$, $t_r(\text{minor}) = 14.1 \text{ min.}$

1-(4-Bromo-phenyl)-buta-2,3-dien-1-ol⁸

^1H NMR (400 MHz, CDCl_3 , ppm): 7.48-7.46 (m, 2H), 7.30-7.26 (m, 2H), 5.40-5.38 (m, 1H), 5.22-5.19 (m, 1H), 4.93-4.91 (m, 2H), 2.11 (br, 1H). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes : 2-propanol = 98.5 : 1.5, flow rate = 1 mL/min.), $t_r(\text{major}) = 21.6 \text{ min.}$, $t_r(\text{minor}) = 22.8 \text{ min.}$

1-Naphthalen-2-yl-buta-2,3-dien-1-ol⁸

^1H NMR (400 MHz, CDCl_3 , ppm): 7.86-7.82 (m, 4H), 7.53-7.46 (m, 3H), 5.55-5.51 (m, 1H), 5.46-5.45 (m, 1H), 4.98-4.95 (m, 2H), 2.15 (br, 1H). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes : 2-propanol = 97 : 3, flow rate = 1 mL/min.), $t_r(\text{major}) = 24.9 \text{ min.}$, $t_r(\text{minor}) = 26.2 \text{ min.}$

1-Furan-2-yl-buta-2,3-dien-1-ol¹⁰

¹H NMR (400 MHz, CDCl₃, ppm): 7.40-7.39 (m, 1H), 6.35-6.33 (m, 1H), 6.31-6.30 (m, 1H), 5.54-5.51 (m, 1H), 5.28-5.27 (m, 1H), 4.98-4.96 (m, 2H), 2.17 (d, 1H). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes : 2-propanol = 97.5 : 2.5, flow rate = 1 mL/min.), *t_r*(major) = 17.6 min., *t_r*(minor) = 21.7 min.

2-Methyl-1-phenyl-hexa-1,4,5-trien-3-ol¹¹

¹H NMR (400 MHz, CDCl₃, ppm): 7.44-7.20 (m, 5H), 6.58 (s, 1H), 5.35-5.33 (m, 1H), 4.97-4.95 (m, 2H), 4.74 (m, 1H), 2.04 (d, 1H), 1.89 (s, 3H). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes : 2-propanol = 97.5 : 2.5, flow rate = 1 mL/min.), *t_r*(major) = 15.9 min., *t_r*(minor) = 18.8 min.

(*S*)-1-Phenyl-hexa-4,5-dien-3-ol⁵

¹H NMR (400 MHz, CDCl₃, ppm): 7.30-7.27 (m, 3H), 7.24-7.21 (m, 2H), 5.28-5.26 (m, 1H), 4.89-4.87 (m, 2H), 4.12-4.11 (m, 1H), 2.78-2.73 (m, 2H), 2.04 (d, 1H), 1.90-1.86 (m, 2H). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes : 2-propanol = 95 : 5, flow rate = 0.5 mL/min.), *t_r*(major, *S*) = 21.6 min., *t_r*(minor, *R*) = 31.2 min. $[\alpha]_D^{24} = +11.8$ (*c* = 1.0, CHCl₃). The reported value for *S*-enantiomer (88% ee) is $[\alpha]_D^{20} = +9.5$ (*c* = 0.21, CHCl₃).

(S)- 1-Cyclohexyl-buta-2,3-dien-1-ol⁶

¹H NMR (400 MHz, CDCl₃, ppm): 5.24-5.21 (m, 1H), 4.85-4.83 (m, 2H), 3.93 (m, 1H), 1.85 (br, 1H), 1.90-0.82 (m, 11H). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes : 2-propanol = 99.5 : 0.5, flow rate = 1 mL/min.), *t_r*(major, *S*) = 11.9 min., *t_r*(minor, *R*) = 12.5 min. $[\alpha]_D^{24} = +14.2$ (*c* = 1.1, Benzene). The reported value for *S*-enantiomer (79% ee) is $[\alpha]_D^{24} = +10.5$ (*c* = 1.02, Benzene).

(S)-Undeca-1,2-dien-4-ol⁷

¹H NMR (400 MHz, CDCl₃, ppm): 5.26-5.22 (m, 1H), 4.86-4.85 (m, 2H), 4.17 (m, 1H), 1.85 (br, 1H), 1.64-0.86 (m, 15H). Enantiomeric excess was determined by Analytical gas-liquid chromatograph (GLC) with capillary column of B-DM (0.25mm x 20m) using nitrogen as carrier gas (130°C injection temp., 110°C column temp., 100Kpa), *t_r*(major, *S*) = 14.6 min., *t_r*(minor, *R*) = 15.3 min. $[\alpha]_D^{24} = -18.8$ (*c* = 1.2, MeOH). The reported value for *S*-enantiomer (92% ee) is $[\alpha]_D^{20} = -16.5$ (*c* = 0.95, MeOH).

2-Methyl-1-phenyl-buta-2,3-dien-1-ol^{12,13}

¹H NMR (400 MHz, CDCl₃, ppm): 7.39-7.25 (m, 5H), 5.10 (m, 1H), 4.92-4.89 (m, 2H), 2.27 (d, 1H), 1.58-1.56 (m, 3H). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes : 2-propanol = 95 : 5, flow rate = 0.5 mL/min.), *t_r*(major) = 15.9 min., *t_r*(minor) = 17.9 min.

2-Methyl-1-p-tolyl-buta-2,3-dien-1-ol¹²

^1H NMR (400 MHz, CDCl_3 , ppm): 7.34-7.32 (m, 2H), 7.16-7.14 (m, 2H), 5.07 (m, 1H), 4.90-4.89 (m, 2H), 2.44 (br, 1H), 2.38 (s, 3H), 1.58-1.56 (m, 3H). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes : 2-propanol = 98.5 : 1.5, flow rate = 1 mL/min.), $t_r(\text{major})$ = 13.3 min., $t_r(\text{minor})$ = 15.2 min.

1-(4-Chloro-phenyl)-2-methyl-buta-2,3-dien-1-ol¹²

^1H NMR (400 MHz, CDCl_3 , ppm): 7.30-7.28 (m, 4H), 5.09 (m, 1H), 4.90-4.89 (m, 2H), 2.33 (br, 1H), 1.56-1.54 (m, 3H). Enantiomeric excess was determined by HPLC with a Chiralcel OJ-H column equipped with an OJ-H guard column (hexanes : 2-propanol = 95 : 5, flow rate = 0.5 mL/min.), $t_r(\text{major})$ = 17.9 min., $t_r(\text{minor})$ = 19.5 min.

(S)- 4-Methyl-1-phenyl-hexa-4,5-dien-3-ol⁵

^1H NMR (400 MHz, CDCl_3 , ppm): 7.30-7.17 (m, 5H), 4.81-4.78 (m, 2H), 4.06 (m, 1H), 2.76-2.67 (m, 2H), 2.04 (br, 1H), 1.94-1.85 (m, 2H), 1.72-1.71 (m, 3H). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes : 2-propanol = 95 : 5, flow rate = 0.5 mL/min.), $t_r(\text{major}, S)$ = 22.1 min., $t_r(\text{minor}, R)$ = 26.3 min. $[\alpha]_D^{24} = +57.1$ ($c = 1.0$, CHCl_3). The reported value for *R*-enantiomer (93% ee) is $[\alpha]_D^{25} = -51.3$ ($c = 0.1$, CHCl_3).

2-Ethyl-1-phenyl-buta-2,3-dien-1-ol¹³

¹H NMR (400 MHz, CDCl₃, ppm): 7.38-7.26 (m, 5H), 5.12-5.11 (m, 1H), 5.04-5.02 (m, 2H), 2.21 (d, 1H), 1.86-1.80 (m, 2H), 0.97 (t, 3H). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes : 2-propanol = 95 : 5, flow rate = 0.5 mL/min.), *t_r*(major) = 15.3 min., *t_r*(minor) = 17.2 min.

(S)-4-Ethyl-1-phenyl-hexa-4,5-dien-3-ol⁵

¹H NMR (400 MHz, CDCl₃, ppm): 7.30-7.18 (m, 5H), 4.92-4.90 (m, 2H), 4.07 (m, 1H), 2.77-2.67 (m, 2H), 2.04 (br, 1H), 1.99-1.97 (m, 2H), 1.86-1.83 (m, 2H), 1.03 (t, 3H). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes : 2-propanol = 95 : 5, flow rate = 0.5 mL/min.), *t_r*(major, *S*) = 20.6 min., *t_r*(minor, *R*) = 23.9 min. $[\alpha]_D^{24} = +29.2$ (*c* = 1.0, CHCl₃). The reported value for *R*-enantiomer (92% ee) is $[\alpha]_D^{25} = -23.7$ (*c* = 0.1, CHCl₃).

1,2-Diphenyl-buta-2,3-dien-1-ol¹²

¹H NMR (400 MHz, CDCl₃, ppm): 7.46-7.44 (m, 2H), 7.37-7.24 (m, 7H), 7.19-7.17 (m, 1H), 5.72 (m, 1H), 5.29-5.26 (m, 2H), 2.31 (d, 1H). Enantiomeric excess was determined by HPLC with a Chiralcel OJ-H column equipped with an OJ-H guard column (hexanes : 2-propanol = 95 : 5, flow rate = 1 mL/min.), *t_r*(major) = 32.1 min., *t_r*(minor) = 36.0 min.

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