SUPPORTING INFORMATION

Catalytic Enantioselective Nozaki-Hiyama allylation Reaction with Tethered Bis(8-Quinolinolato) (TBOx) Chromium Complex

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Experimental Section.

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 E. Merck. 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 (anhydrous, 99.9%, inhibited with 250 ppm BHT, 18L in Pure-PacTM), Toluene (anhydrous, 99.8%, 18L in Pure-PacTM) and Acetonitrile (CH₃CN) (anhydrous, 99.8%, 18L in Pure-PacTM) purchased from Aldrich were purified by M. BRAUN solvent purification system.

¹H NMR and ¹⁹F 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) from Daicel. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter.

General Procedure for Nozaki-Hiyama Allylation Reaction of Aldehydes

An oven-dried test tube was charged with a magnetic stir bar, TBOxCrCl¹ (12 mg, 0.015 mmol, 3 mol%) and Mn powder 50-mesh (83 mg, 1.5 mmol) then flushed thoroughly with argon three times. To this were added anhydrous acetonitrile (0.5 mL) and anhydrous DME (1.5 mL) then the resulting yellow-brown mixture was stirred for 10 min. at room temperature. The catalyst solution was treated with allylic-halide (0.5mmol), 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 TESCl (95 μ L, 0.55 mmol). The reaction was stirred at room temperature for a specified length of time, at which time it was quenched with saturated NaHCO₃ solution (1 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 either aqueous HCl (1M, 2 mL, 2 mmol) or TBAF (1M in THF, 1 mL, 1 mmol) in THF (5 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. All the products were known compounds. The ¹H NMR spectra of the products were identical to the known compounds in the literature report.

(*R*)-1-Phenyl-but-3-en-1-ol²

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 = 1.0 mL/min.), $t_r(R)$ = 10.9 min., $t_r(S)$ = 13.6 min. $[\alpha]_D^{24}$ = +57.8 (c = 1.0, Benzene). The reported value² for *R*-enantiomer (95% ee) is $[\alpha]_D^{22}$ = +56.5 (c = 1.0, Benzene).

(*R*)-1-(4-Chloro-phenyl)-but-3-en-1-ol⁷

Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column equipped with an AD-H guard column (hexanes : 2-propanol = 98 : 2, flow rate = 1.0 mL/min.), $t_r(R)$ = 14.8 min., $t_r(S)$ = 15.6 min. $[\alpha]_D^{24}$ = +62.9 (c = 1.0, CHCl_3). The reported value⁷ for *R*-enantiomer (94% ee) is $[\alpha]_D$ = +61.4 (c = 1.17, CHCl_3).

(*R*)-1-(4-Bromo-phenyl)-but-3-en-1-ol²

Enantiomeric excess was determined by HPLC with a Chiralcel OJ column equipped with an OJ guard column (hexanes : 2-propanol = 90 : 10, flow rate = 0.5 mL/min.), $t_r(S)$ = 17.0 min., $t_r(R)$ = 17.9 min. $[\alpha]_D^{26}$ = +24.6 (c = 1.0, Benzene). The reported value² for *R*-enantiomer (96% ee) is $[\alpha]_D^{24}$ = +23.2 (c = 1.0, Benzene).

(*R*)-1-*p*-Tolyl-but-3-en-1-ol⁵

Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes : 2-propanol = 99 : 1, flow rate = 1 mL/min.), $t_r(R)$ = 14.8 min., $t_r(S)$ = 16.4 min. $[\alpha]_D^{24}$ = +68.7 (c = 1.0, CHCl_3). The reported value⁵ for *R*-enantiomer (78% ee) is $[\alpha]_D^{25}$ = +50.3 (c = 1.0, CHCl_3).

(*R*)-1-*o*-Tolyl-but-3-en-1-ol²

Enantiomeric excess was determined by HPLC with a Chiralcel AD column equipped with an AD guard column (hexanes : 2-propanol = 95 : 5, flow rate = 0.5 mL/min.), $t_r(R)$ = 15.6 min., $t_r(S)$ = 17.4 min. $[\alpha]_D^{24}$ = +70.6 (c = 1.0, Benzene). The reported value² for *R*-enantiomer (97% ee) is $[\alpha]_D^{24}$ = +75.5 (c = 1.0, Benzene).

(*R*)-1-(3-Methoxy-phenyl)-but-3-en-1-ol⁶

Enantiomeric excess was determined by HPLC with a Chiralcel OD column equipped with an OD guard column (hexanes : 2-propanol = 98 : 2, flow rate = 1 mL/min.), $t_r(R)$ = 28.8 min., $t_r(S)$ = 35.9 min. $[\alpha]_D^{24}$ = +54.2 (c = 1.0, Benzene). The reported value⁶ for *R*-enantiomer (73% ee) is $[\alpha]_D^{25}$ = +41.0 (c = 2.22, Benzene).

(*R*)-1-Naphthalen-1-yl-but-3-en-1-ol²

Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes : 2-propanol = 90 : 10, flow rate = 0.5 mL/min.), $t_r(S)$ = 16.2 min., $t_r(R)$ = 23.9 min. $[\alpha]_D^{25}$ = +92.7 (c = 1.0, Benzene). The reported value² for *R*-enantiomer (92% ee) is $[\alpha]_D^{23}$ = +97.3 (c = 1.0, Benzene).

(*R*)-1-Naphthalen-2-yl-but-3-en-1-ol³

Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes : 2-propanol = 90 : 10, flow rate = 0.75 mL/min.), $t_r(S)$ = 11.2 min., $t_r(R)$ = 12.5 min. $[\alpha]_D^{24}$ = +32.4 (c = 1.0, MeOH). The reported value³ for *R*-enantiomer (94% ee) is $[\alpha]_D^{20}$ = +25.2 (c = 0.25, MeOH).

(*R*)-1-Furan-2-yl-but-3-en-1-ol²

Enantiomeric excess was determined by HPLC with a Chiralcel OJ column equipped with an OJ guard column (hexanes : 2-propanol = 98 : 2, flow rate = 1 mL/min.), $t_r(S)$ = 20.0 min., $t_r(R)$ = 21.5 min. $[\alpha]_D^{24}$ = +30.5 (c = 1.0, Et₂O). The reported value² for *R*-enantiomer (95% ee) is $[\alpha]_D^{26}$ = +29.9 (c = 1.0, Et₂O).

(*R*)-1-Thiophen-2-yl-but-3-en-1-ol⁸

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 = 0.75 mL/min.), $t_r(R)$ = 14.8 min., $t_r(S)$ = 16.7 min. $[\alpha]_D^{24}$ = +9.7 (c = 1.0, EtOH). The reported value⁸ for *S*-enantiomer (80% ee) is $[\alpha]_D^{27}$ = -5.8 (c = 1.2, EtOH).

(*R*),(*E*)-2-Methyl-1-phenyl-hexa-1,5-dien-3-ol¹³

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.), $t_r(R)$ = 9.9 min., $t_r(S)$ = 11.2 min. $[\alpha]_D^{24}$ = +2.4 (c = 1.0, CHCl₃). The reported value¹³ for *R*-enantiomer (50% ee) is $[\alpha]_D$ = +1.1 (c = 1.15, CHCl₃).

(*R*)-1-Cyclohexyl-but-3-en-1-ol²

$[\alpha]_{\text{D}}^{24} = +15.2$ ($c = 1.0$, EtOH). The reported value² for *R*-enantiomer (93% ee) is $[\alpha]_{\text{D}}^{25} = +13.7$ ($c = 1.0$, EtOH). The title compound was benzoylated as described below and its enantiomeric excess was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes : 2-propanol = 99.9 : 0.1, flow rate = 1.0 mL/min.), $t_{\text{r}}(R) = 10.7$ min., $t_{\text{r}}(S) = 13.1$ min.

To a solution of the title compound (20 mg, 0.064 mmol) in pyridine (2 mL) was added 4-DMAP (10 mg, 0.082 mmol) and BzCl (50 μL , excess) at room temperature. The resulting reaction mixture was stirred for 10 h then diluted with Et₂O (20 mL), washed with aqueous HCl (1M, 10 mL) and a saturated NaCl solution, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The purification with preparative TLC (10% EtOAc in hexanes) afforded the corresponding benzoylated product

(*S*)-Undec-1-en-4-ol⁹

$[\alpha]_{\text{D}}^{29} = -6.4$ ($c = 1.0$, CHCl₃). The reported value⁹ for *R*-enantiomer (97% ee) is $[\alpha]_{\text{D}}^{25} = +6.51$ ($c = 1.04$, CHCl₃). The title compound was benzoylated and its enantiomeric excess was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes : 2-propanol = 99.9 : 0.1, flow rate = 1.0 mL/min.), $t_{\text{r}}(S) = 9.5$ min., $t_{\text{r}}(R) = 10.3$ min.

(*S*)-1-Phenyl-hex-5-en-3-ol²

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 = 1 mL/min.), $t_{\text{r}}(S) = 7.8$ min., $t_{\text{r}}(R) = 11.2$ min. $[\alpha]_{\text{D}}^{24} = -30.7$ ($c = 1.0$, Benzene). The reported value² for *S*-enantiomer (86% ee) is $[\alpha]_{\text{D}}^{24} = -26.4$ ($c = 1.0$, Benzene).

(*R*)-1-Benzyloxy-pent-4-en-2-ol³

Enantiomeric excess was determined by HPLC with a Chiralcel OD column equipped with an OD guard column (hexanes : 2-propanol = 98 : 2, flow rate = 0.5 mL/min.), $t_r(S)$ = 51.3 min., $t_r(R)$ = 54.2 min. $[\alpha]_D^{24}$ = +1.8 (c = 1.0, CHCl_3). The reported value³ for *R*-enantiomer (53% ee) is $[\alpha]_D^{20}$ = +0.9 (c = 2.5, CHCl_3).

(*R*)-2,2-Dimethyl-hex-5-en-3-ol⁴

$[\alpha]_D^{24}$ = -6.1 (c = 1.4, CHCl_3). The reported value⁴ for *R*-enantiomer (>99% ee) is $[\alpha]_D^{25}$ = -6.6 (c = 2.1, CHCl_3). Enantiomeric excess was determined by ^{19}F NMR (C_6D_6) analysis of the derived Mosher ester.⁴

2-Methyl-1-phenyl-but-3-en-1-ol²

The ratio of *anti:syn* was determined by ^1H NMR analysis of a crude reaction mixture based on the literature². 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 = 1.0 mL/min.), $t_r(\text{anti-major}+\text{syn-major})$ = 12.1 min., $t_r(\text{anti-minor})$ = 13.4 min., $t_r(\text{syn-minor})$ = 26.8 min. The absolute configuration of the major *anti* isomer was determined to be (1*R*,2*R*) by comparing with the literature².

1-Phenyl-2-vinyl-pentan-1-ol¹⁰

The ratio of *anti:syn* was determined by ^1H NMR analysis of a crude reaction mixture based on the literature¹⁰. 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 = 1.0 mL/min.), $t_r(\text{anti-major}) = 17.3$ min., $t_r(\text{anti-minor}+\text{syn-major}) = 19.3$ min., $t_r(\text{syn-minor}) = 22.9$ min.

1-Phenyl-2-vinyl-heptan-1-ol¹¹

The ratio of *anti:syn* was determined by ¹H NMR analysis of a crude reaction mixture based on the literature¹¹. 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 = 1.0 mL/min.), $t_r(\text{anti-major}) = 16.1$ min., $t_r(\text{anti-minor}+\text{syn-major}) = 18.4$ min., $t_r(\text{syn-minor}) = 21.9$ min.

1-Cyclohexyl-2-methyl-but-3-en-1-ol¹⁰

The ratio of *anti:syn* was determined by ¹H NMR analysis of a crude reaction mixture based on the literature¹⁰. The title compound was transferred to (*R*)-MTPA ester as described below and its enantiomeric excess was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes : 2-propanol = 100 : 0, flow rate = 1.0 mL/min.), $t_r(\text{anti-minor}) = 17.8$ min., $t_r(\text{syn-minor}) = 18.7$ min., $t_r(\text{anti-major}) = 19.8$ min., $t_r(\text{syn-major}) = 21.9$ min.

To a solution of the title compound (10 mg, 0.032 mmol) in pyridine (2 mL) was added 4-DMAP (10 mg, 0.082 mmol) and (*R*)-MTPA-Cl (50 μ L, excess) at room temperature. The resulting reaction mixture was stirred for 40 h then diluted with Et₂O (20 mL), washed with aqueous HCl (1M, 10 mL) and a saturated NaCl solution, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The purification with preparative TLC (10% EtOAc in hexanes) afforded the corresponding (*R*)-MTPA ester.

4-Methyl-1-phenyl-hex-5-en-3-ol¹²

The ratio of *anti:syn* (4.4 : 1) was determined by ¹H NMR analysis of a crude reaction mixture based on the literature¹². Enantiomeric excess was determined by HPLC with a Chiralcel OD column equipped with an OD guard column (hexanes : 2-propanol = 97 : 3, flow rate = 1.0 mL/min.), *t_r*(*anti*-major) = 12.0 min., *t_r*(*syn*-major) = 13.3 min., *t_r*(*anti*-minor) = 22.2 min., *t_r*(*syn*-minor) = 25.3 min. The absolute configuration of the major *anti* isomer was determined to be (3*S*,4*R*) by comparing with the literature¹².

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