Catalytic Asymmetric Vinylation of Ketones

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Supporting Information

Table of Contents	Page
General Methods	S2
General Procedure for the Preparation of Allylic Alcohols	S2
Characterization of S1 – S15	S2
Conditions for the Determination of Enantiomeric Excess	S13
Reference	S15
¹ H and ¹³ C { ¹ H} NMR spectra	S16

General Methods. All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. All chemicals were obtained from Aldrich or Acros Organics unless otherwise specified. All solvents were purchased from Fischer Scientific. Cp_2ZrHCl and Me_2Zn 2.0 M toluene solution were purchased from the Aldrich Chemical Company. Titanium (IV) isopropoxide and all liquid ketone substrates were distilled prior to use. Titanium (IV) isopropoxide (1.4 M in toluene) was prepared and stored in a Vacuum Atmospheres dry box. Toluene, dichloromethane, and hexanes were dried through activated alumina columns. NMR spectra were obtained on a Brüker 500 MHz Fourier transform spectrometer at the University of Pennsylvania NMR facility. ^1H NMR spectra were referenced to tetramethylsilane in CDCl_3 ; ^{13}C $\{^1\text{H}\}$ NMR spectra were referenced to residual solvent. The infrared spectra were obtained using a Perkin-Elmer 1600 series spectrometer.

General Protocol A. Preparation of 2-phenyl-oct-3-en-2-ol (S1).

To a suspension of Cp_2ZrHCl (155 mg, 0.60 mmol) in CH_2Cl_2 (2.0 mL) under N_2 was added 1-hexyne (70 μL , 0.60 mmol) and the reaction mixture was stirred for 10 min at r.t. after which it was a homogeneous yellow solution. The solvent was removed *in vacuo* and the residue was dissolved in dry toluene (2.0 mL), cooled to -78°C , treated with Me_2Zn (0.30 mL, 2.0 M in toluene, 0.60 mmol) for 10 min. In another Schlenk flask were mixed ligand **1** (27.3 mg, 0.05 mmol, 10 mol %) in 1.0 mL toluene, Me_2Zn (0.10 mL, 2.0 M in toluene, 0.20 mmol) and $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.43 mL, 1.4 M toluene solution, 0.60 mmol) at r.t. and stirred for 15 min. The resulting solution was added to the Schlenk flask

containing the vinylzirconocene and dimethylzinc at -78°C . After the addition, the solution was warmed to 0°C , and acetophenone (59 μL , 0.50 mmol) was added. The reaction mixture was warmed to r.t. and stirred until TLC showed complete consumption of the ketone. The reaction mixture was quenched with saturated NaHCO_3 (5 mL), diluted with EtOAc, filtered through Celite, and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 40 mL) and the combined organic layers were washed with brine, dried over MgSO_4 , and concentrated. The residue was purified by flash chromatography on deactivated silica gel ($\text{Et}_3\text{N}/\text{SiO}_2 = 2.5\%$ V/V, hexanes : EtOAc / 96:4) to give **S1** (103 mg, 85% yield, 93% ee) as an oil: $[\alpha]_{\text{D}}^{20} = +0.4$ (c 2.0, CHCl_3); ^1H NMR (CDCl_3 , 500 MHz) δ 0.89 (t, $J = 7.1$ Hz, 3H), 1.26-1.40 (m, 4H), 1.62 (s, 3H), 2.03-2.09 (m, 2H), 5.63-5.69 (m, 1H), 5.77 (d, $J = 15.5$ Hz, 1H), 7.21-7.24 (m, 1H), 7.32 (dd, $J = 7.9, 7.5$ Hz, 2H), 7.45 (d, $J = 7.4$ Hz, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz) δ 14.4, 22.7, 30.4, 31.8, 32.3, 74.8, 125.6, 127.2, 128.5, 129.5, 137.3, 147.8 ppm; IR (film) 3388, 3025, 2956, 2874, 2358, 1667, 1601, 1492, 1446, 1369 cm^{-1} ; HRMS-Cl m/z 187.1477 $[(\text{M}-\text{OH})^+]$; calcd for $\text{C}_{14}\text{H}_{19}$: 187.1487; HRMS-Cl m/z 186.1403 $[(\text{M}-\text{H}_2\text{O})^+]$; calcd for $\text{C}_{14}\text{H}_{18}$: 186.1408].

Preparation of 4-cyclopropyl-2-phenyl-but-3-en-2-ol (**S2**).

The product was prepared by General Procedure A using Cp_2ZrHCl (155 mg, 0.60 mmol), cyclopropyl acetylene (40 mg, 0.60 mmol), Me_2Zn (0.30 mL, 0.60 mmol, 2.0 M in toluene), ligand **1** (27.3 mg, 0.05 mmol, 10 mol %), Me_2Zn (0.10 mL, 0.20 mmol, 2.0 M in toluene), $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.43 mL, 0.60 mmol, 1.4 M toluene solution) and acetophenone (59

μL , 0.50 mmol). The crude product was purified by column chromatography on deactivated silica gel ($\text{Et}_3\text{N}/\text{SiO}_2 = 2.5\% \text{ V/V}$, hexanes : $\text{EtOAc} / 95:5$) to give **S2** (85 mg, 90% yield, 95% ee) as an oil: $[\alpha]_{\text{D}}^{20} = -5.0$ (c 2.00, CHCl_3); ^1H NMR (CDCl_3 , 500 MHz) δ 0.35-0.36 (m, 2H), 0.68-0.70 (m, 2H), 1.36-1.40 (m, 1H), 1.60 (s, 3H), 5.14-5.19 (m, 1H), 5.84 (d, $J = 15.5$ Hz, 1H), 7.20-7.25 (m, 1H), 7.29-7.32 (m, 2H), 7.40-7.45 (m, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz) δ 7.2, 14.0, 30.4, 74.7, 125.7, 127.2, 128.5, 133.4, 135.1, 147.8 ppm; IR (film) 3391, 3081, 3004, 2977, 2927, 1663, 1600, 1493, 1446, 1369 cm^{-1} ; HRMS-CI m/z 188.1194 [M^+ ; calcd for $\text{C}_{13}\text{H}_{16}\text{O}$: 188.1201].

Preparation of 5-(*tert*-butyl-diphenyl-silanyloxy)-2-phenyl-pent-3-en-2-ol (**S3**).

The product was prepared by General Procedure A using Cp_2ZrHCl (93 mg, 0.36 mmol), *tert*-butyl-diphenyl-prop-2-ynyloxy-silane (106 mg, 0.36 mmol), Me_2Zn (0.18 mL, 0.36 mmol, 2.0 M in toluene), ligand **1** (16.4 mg, 0.03 mmol, 10 mol %), Me_2Zn (0.06 mL, 0.12 mmol, 2.0 M in toluene), $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.25 mL, 0.36 mmol, 1.4 M toluene solution) and acetophenone (35 μL , 0.30 mmol). The crude product was purified by column chromatography on deactivated silica gel ($\text{Et}_3\text{N}/\text{SiO}_2 = 2.5\% \text{ V/V}$, hexanes : $\text{EtOAc} / 94:6$) to give **S3** (115 mg, 92% yield, 89% ee) as an oil: $[\alpha]_{\text{D}}^{20} = -3.6$ (c 2.20, CHCl_3); ^1H NMR (C_6D_6 , 500 MHz) δ 1.16 (s, 9H), 1.45 (s, 3H), 4.17 (d, $J = 4.9$ Hz, 2H), 5.72-5.77 (m, 1H), 5.99 (d, $J = 15.5$ Hz, 1H), 7.07-7.10 (m, 1H), 7.17-7.24 (m, 8H), 7.43-7.44 (m, 2H), 7.73-7.77 (m, 4H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz) δ 19.5, 27.1, 30.1, 64.6, 74.0, 125.6, 127.0, 128.1, 128.4, 130.1, 134.2, 136.1, 137.9, 147.7 ppm;

IR (film) 3564, 3406, 3069, 3028, 2930, 2856, 1589, 1492, 1472, 1446, 1428, 1377 cm^{-1} ;
HRMS-Cl m/z 439.2053 $[(M+Na)^+]$; calcd for $\text{C}_{27}\text{H}_{32}\text{O}_2\text{SiNa}$: 439.2070].

Preparation of 2,4-diphenyl-but-3-en-2-ol (**S4**).

The product was prepared by General Procedure A using Cp_2ZrHCl (155 mg, 0.60 mmol), phenylacetylene (71 μL , 0.60 mmol), Me_2Zn (0.30 mL, 0.60 mmol, 2.0 M in toluene), ligand **1** (27.3 mg, 0.05 mmol, 10 mol %), Me_2Zn (0.10 mL, 0.20 mmol, 2.0 M in toluene), $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.43 mL, 0.60 mmol, 1.4 M toluene solution) and acetophenone (59 μL , 0.50 mmol). The crude product was purified by column chromatography on deactivated silica gel ($\text{Et}_3\text{N}/\text{SiO}_2 = 2.5\%$ V/V, hexanes : EtOAc / 93:7) to give **S4** (103 mg, 92% yield, 87% ee) as an oil: $[\alpha]_{\text{D}}^{20} = +11.6$ (c 2.40, CHCl_3). Spectra data for this compound is consistent with the previous characterization.¹

Preparation of 4-phenyl-2-(3-trifluoromethyl-phenyl)-but-3-en-2-ol (**S5**).

The product was prepared by General Procedure A using Cp_2ZrHCl (155 mg, 0.60 mmol), phenylacetylene (71 μL , 0.60 mmol), Me_2Zn (0.30 mL, 0.60 mmol, 2.0 M in toluene), ligand **1** (27.3 mg, 0.05 mmol, 10 mol %), Me_2Zn (0.10 mL, 0.20 mmol, 2.0 M in toluene), $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.43 mL, 0.60 mmol, 1.4 M toluene solution) and 3'-(trifluoromethyl)acetophenone (76 μL , 0.50 mmol). The crude product was purified by column chromatography on deactivated silica gel ($\text{Et}_3\text{N}/\text{SiO}_2 = 2.5\%$ V/V, hexanes : EtOAc / 93:7) to give **S5** (123 mg, 84% yield, 88% ee) as an oil: $[\alpha]_{\text{D}}^{20} = +14.8$ (c 2.33,

CHCl₃); ¹H NMR (C₆D₆, 500 MHz) δ 1.37 (s, 3H), 6.21 (d, *J* = 16.0 Hz, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.95-7.00 (m, 1H), 7.03-7.16 (m, 5H), 7.28-7.29 (m, 1H), 7.38-7.40 (d, *J* = 7.8 Hz, 1H), 7.97 (s, 1H) ppm; ¹³C{¹H} NMR (C₆D₆, 125 MHz) δ 29.8, 74.2, 122.3, 124.0, 127.0, 128.0, 128.6, 128.9, 129.0, 129.4, 130.8, 136.0, 137.0, 148.7 ppm; IR (film) 3272, 3061, 3028, 2980, 2931, 1598, 1494, 1448, 1329 cm⁻¹; HRMS-CI *m/z* 274.0971 [(M-H₂O)⁺; calcd for C₁₇H₁₃F₃: 274.0970].

Preparation of 6-(*tert*-butyl-diphenyl-silanyloxy)-2-(3-trifluoromethyl-phenyl)-hex-3-en-2-ol (S6).

The product was prepared by General Procedure A using Cp₂ZrHCl (93 mg, 0.36 mmol), *tert*-butyl-but-3-ynyloxy-diphenyl-silane (111 mg, 0.36 mmol), Me₂Zn (0.18 mL, 0.36 mmol, 2.0 M in toluene), ligand **1** (16.4 mg, 0.03 mmol, 10 mol %), Me₂Zn (0.06 mL, 0.12 mmol, 2.0 M in toluene), Ti(O^{*i*}Pr)₄ (0.25 mL, 0.36 mmol, 1.4 M toluene solution) and 3'-(trifluoromethyl)acetophenone (46 μL, 0.30 mmol). The crude product was purified by column chromatography on deactivated silica gel (Et₃N/SiO₂ = 2.5% V/V, hexanes : EtOAc / 92:8) to give **S6** (140 mg, 94% yield, 90% ee) as an oil: [α]_D²⁰ = +1.0 (*c* 3.27, CHCl₃); ¹H NMR (C₆D₆, 500 MHz) δ 1.14 (s, 9H), 1.33 (s, 3H), 2.13-2.16 (m, 2H), 3.62 (t, *J* = 6.4 Hz, 2H), 5.56-5.57 (m, 2H), 6.98 (t, *J* = 7.8 Hz, 1H), 7.23-7.24 (m, 6H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.73-7.75 (m, 4H), 7.92 (s, 1H) ppm; ¹³C{¹H} NMR (C₆D₆, 125 MHz) δ 19.5, 27.1, 30.0, 35.9, 63.8, 73.9, 122.4, 123.7, 126.2, 128.1, 128.3, 128.8, 129.3, 130.1, 134.3, 136.0, 138.8, 149.1 ppm; IR (film) 3564, 3408,

3071, 2931, 2858, 1668, 1590, 1488, 1472, 1428 cm^{-1} ; HRMS-CI m/z 521.2085 $[(M+Na)^+]$; calcd for $\text{C}_{29}\text{H}_{33}\text{F}_3\text{O}_2\text{SiNa}$: 521.2100].

Preparation of 5,5-dimethyl-2-*m*-tolyl-hex-3-en-2-ol (S7)

The product was prepared by General Procedure A using Cp_2ZrHCl (155 mg, 0.60 mmol), 3,3-dimethyl-1-butyne (75 μL , 0.60 mmol), Me_2Zn (0.30 mL, 0.60 mmol, 2.0 M in toluene), ligand **1** (27.3 mg, 0.05 mmol, 10 mol %), Me_2Zn (0.10 mL, 0.20 mmol, 2.0 M in toluene), $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.43 mL, 0.60 mmol, 1.4 M toluene solution) and 3'-methylacetophenone (68 μL , 0.50 mmol). The crude product was purified by column chromatography on deactivated silica gel ($\text{Et}_3\text{N}/\text{SiO}_2 = 2.5\%$ V/V, hexanes : EtOAc / 96:4) to give **S7** (101 mg, 93% yield, 92% ee) as an oil: $[\alpha]_D^{20} = -3.9$ (c 2.33, CHCl_3); ^1H NMR (C_6D_6 , 500 MHz) δ 0.97 (s, 3H), 1.55 (s, 3H), 2.18 (s, 3H), 5.72 (d, $J = 15.8$ Hz, 1H), 5.77 (d, $J = 15.8$ Hz, 1H), 6.92 (d, $J = 7.4$ Hz, 1H), 7.15 (d, $J = 7.7$ Hz, 1H), 7.32 (d, $J = 7.7$ Hz, 1H), 7.41 (s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz) δ 21.7, 29.8, 30.5, 32.7, 74.2, 122.9, 126.4, 127.6, 128.4, 133.1, 137.6, 139.0, 148.4 ppm; IR (film) 3382, 3022, 2958, 2865, 1662, 1606, 1588, 1462, 1362 cm^{-1} . HRMS-CI m/z 200.1573 $[(M-\text{H}_2\text{O})^+]$; calcd for $\text{C}_{15}\text{H}_{20}$: 200.1567].

Preparation of 8-chloro-2-*m*-tolyl-oct-3-en-2-ol (S8).

The product was prepared by General Procedure A using Cp_2ZrHCl (155 mg, 0.60 mmol), 6-chloro-hex-1-yne (73 μL , 0.60 mmol), Me_2Zn (0.30 mL, 0.60 mmol,

2.0 M in toluene), ligand **1** (27.3 mg, 0.05 mmol, 10 mol %), Me₂Zn (0.10 mL, 0.20 mmol, 2.0 M in toluene), Ti(O^{*i*}Pr)₄ (0.43 mL, 0.60 mmol, 1.4 M toluene solution) and 3'-methylacetophenone (68 μL, 0.50 mmol). The crude product was purified by column chromatography on deactivated silica gel (Et₃N/SiO₂ = 2.5% V/V, hexanes : EtOAc / 93:7) to give **S8** (124 mg, 98% yield, 90% ee) as an oil: [α]_D²⁰ = −0.9 (*c* 2.40, CHCl₃); ¹H NMR (C₆D₆, 500 MHz) δ 1.18-1.24 (m, 2H), 1.38-1.44 (m, 2H), 1.52 (s, 3H), 1.76-1.80 (m, 2H), 2.19 (s, 3H), 3.08 (t, *J* = 6.6 Hz, 2H), 5.50-5.56 (m, 1H), 5.68 (d, *J* = 15.0 Hz, 1H), 6.93 (d, *J* = 7.3 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.37 (s, 1H) ppm; ¹³C{¹H} NMR (C₆D₆, 125 MHz) δ 21.7, 26.7, 30.3, 31.7, 32.4, 44.8, 74.3, 122.9, 126.4, 127.5, 127.7, 128.4, 137.7, 138.6, 148.1 ppm; IR (film) 3397, 3023, 2931, 2860, 1606, 1588, 1487, 1454, 1369 cm^{−1}; HRMS-Cl *m/z* 234.1179 [(M-H₂O)⁺; calcd for C₁₅H₁₉Cl: 234.1176].

Preparation of 2,4-dimethyl-dec-5-en-4-ol (**S9**).

The product was prepared by General Procedure A using Cp₂ZrHCl (155 mg, 0.60 mmol), 1-hexyne (70 μL, 0.60 mmol), Me₂Zn (0.30 mL, 0.60 mmol, 2.0 M in toluene), ligand **1** (27.3 mg, 0.05 mmol, 10 mol %), Me₂Zn (0.10 mL, 0.20 mmol, 2.0 M in toluene), Ti(O^{*i*}Pr)₄ (0.43 mL, 0.60 mmol, 1.4 M toluene solution) and 4-methyl-pentan-2-one (62.5 μL, 0.50 mmol). The crude product was purified by column chromatography on deactivated silica gel (Et₃N/SiO₂ = 2.5% V/V, hexanes : EtOAc / 96:4) to give **S9** (78 mg, 85% yield, 79% ee) as an oil: [α]_D²⁰ = +3.4 (*c* 2.50, CHCl₃); ¹H NMR (CDCl₃, 500 MHz) δ 0.88 (t, *J* = 7.1 Hz, 3H), 0.91 (d, *J* = 2.9 Hz, 3H), 0.92 (d, *J* = 2.9 Hz, 3H), 1.25 (s, 3H),

1.28-1.39 (m, 4H), 1.40-1.44 (m, 2H), 1.68-1.74 (m, 1H), 2.00-2.04 (m, 2H), 5.51 (d, J = 15.6 Hz, 1H), 5.55-5.61 (m, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz) δ 14.3, 22.6, 24.8, 24.9, 25.0, 29.3, 31.9, 32.3, 51.9, 73.6, 127.8, 137.9 ppm; IR (film) 3414, 2955, 2923, 2870, 1668, 1466, 1366 cm^{-1} ; HRMS-CI m/z 167.1799 [$(\text{M}-\text{OH})^+$; calcd for $\text{C}_{12}\text{H}_{23}$: 167.1800].

Preparation of 3-methyl-1-phenyl-nona-1,4-dien-3-ol (S10).

The product was prepared by General Procedure A using Cp_2ZrHCl (155 mg, 0.60 mmol), 1-hexyne (70 μL , 0.60 mmol), Me_2Zn (0.30 mL, 0.60 mmol, 2.0 M in toluene), ligand **1** (27.3 mg, 0.05 mmol, 10 mol %), Me_2Zn (0.10 mL, 0.20 mmol, 2.0 M in toluene), $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.43 mL, 0.60 mmol, 1.4 M toluene solution) and *trans*-4-phenyl-3-buten-2-one (73 mg, 0.50 mmol). The crude product was purified by column chromatography on deactivated silica gel ($\text{Et}_3\text{N}/\text{SiO}_2$ = 2.5% V/V, hexanes : EtOAc / 95:5) to give **S10** (100 mg, 87% yield, 92% ee) as an oil: $[\alpha]_{\text{D}}^{20} = -12.4$ (c 2.48, CHCl_3); ^1H NMR (C_6D_6 , 500 MHz) δ 0.86 (t, J = 7.1 Hz, 3H), 1.23-1.30 (m, 4H), 1.39 (s, 3H), 1.95-2.00 (m, 2H), 5.59-5.63 (m, 1H), 5.67-5.73 (m, 1H), 6.30 (d, J = 16.0 Hz, 1H), 6.68 (d, J = 16.0 Hz, 1H), 7.03-7.06 (m, 1H), 7.11-7.14 (m, 2H), 7.27-7.29 (m, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz) δ 14.2, 22.7, 28.9, 31.9, 32.4, 73.0, 126.9, 127.5, 127.6, 128.8, 128.9, 136.7, 136.7, 137.7 ppm; IR (film) 3366, 3025, 2957, 2928, 2856, 1664, 1599, 1578, 1494, 1448 cm^{-1} ; HRMS-CI m/z 230.1674 [M^+ ; calcd for $\text{C}_{16}\text{H}_{22}\text{O}$: 230.1671].

Preparation of 1-hex-1-enyl-2,4,4-trimethyl-cyclohex-2-enol (S11).

The product was prepared by General Procedure A using Cp_2ZrHCl (155 mg, 0.60 mmol), 1-hexyne (70 μL , 0.60 mmol), Me_2Zn (0.30 mL, 0.60 mmol, 2.0 M in toluene), ligand **1** (27.3 mg, 0.05 mmol, 10 mol %), Me_2Zn (0.10 mL, 0.20 mmol, 2.0 M in toluene), $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.43 mL, 0.60 mmol, 1.4 M toluene solution) and 2,4,4-trimethyl-2-cyclohexen-1-one (75 μL , 0.50 mmol). The crude product was purified by column chromatography on deactivated silica gel ($\text{Et}_3\text{N}/\text{SiO}_2 = 2.5\% \text{ V/V}$, hexanes : EtOAc / 95:5) to give **S11** (104 mg, 94% yield, 97% ee) as an oil: $[\alpha]_{\text{D}}^{20} = -72.0$ (c 0.60, CHCl_3); ^1H NMR (CDCl_3 , 500 MHz) δ 0.88 (t, $J = 7.0$ Hz, 3H), 0.95 (s, 3H), 0.99 (s, 3H), 1.28-1.35 (m, 4H), 1.36-1.39 (m, 2H), 1.61 (s, 3H), 1.73-1.77 (m, 2H), 2.06-2.07 (m, 2H), 5.24 (s, 1H), 5.41 (d, $J = 15.5$ Hz, 1H), 5.53-5.59 (m, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz) δ 14.3, 18.4, 22.6, 29.6, 30.2, 32.0, 32.3, 32.6, 34.2, 36.7, 74.2, 130.4, 134.2, 134.8, 136.6 ppm; IR (film) 3378, 2954, 2925, 2858, 2359, 1668, 1451, 1377, 1359 cm^{-1} ; HRMS-Cl m/z 222.1980 [M^+ ; calcd for $\text{C}_{15}\text{H}_{26}\text{O}$: 222.1984].

Preparation of 1-[4-(*tert*-butyl-diphenyl-silanyloxy)-but-1-enyl]-2,4,4-trimethyl-cyclohex-enol (S12).

The product was prepared by General Procedure A using Cp_2ZrHCl (93 mg, 0.36 mmol), *tert*-butyl-but-3-ynyloxy-diphenyl-silane (111 mg, 0.36 mmol), Me_2Zn (0.18 mL, 0.36 mmol, 2.0 M in toluene), ligand **1** (16.4 mg, 0.03 mmol, 10 mol %), Me_2Zn (0.06 mL, 0.12 mmol, 2.0 M in toluene), $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.25 mL,

0.36 mmol, 1.4 M toluene solution) and 2,4,4-trimethyl-2-cyclohexen-1-one (45 μ L, 0.30 mmol). The crude product was purified by column chromatography on deactivated silica gel ($\text{Et}_3\text{N}/\text{SiO}_2 = 2.5\%$ V/V, hexanes : EtOAc / 95:5) to give **S12** (115 mg, 85% yield, 94% ee) as an oil: $[\alpha]_{\text{D}}^{20} = -43.8$ (c 3.10, CHCl_3); ^1H NMR (C_6D_6 , 500 MHz) δ 0.92 (s, 3H), 0.93 (s, 3H), 1.17 (s, 9H), 1.44-1.46 (m, 2H), 1.67-1.79 (5H), 2.25-2.28 (m, 2H), 3.69 (t, $J = 6.5$ Hz, 2H), 5.18 (s, 1H), 5.51 (d, $J = 15.5$ Hz, 1H), 5.69-5.74 (m, 1H), 7.23-7.26 (m, 6H), 7.76-7.79 (m, 4H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz) δ 18.4, 19.5, 27.2, 29.4, 30.1, 32.4, 34.2, 35.8, 36.1, 64.2, 73.6, 126.2, 128.1, 130.0, 134.4, 134.9, 135.8, 136.1, 137.6 ppm; IR (film) 3397, 3070, 3049, 2953, 1662, 1589, 1568, 1471, 1428 cm^{-1} ; HRMS-Cl m/z 471.2696 $[(\text{M}+\text{Na})^+]$; calcd for $\text{C}_{29}\text{H}_{40}\text{O}_2\text{SiNa}$: 471.2696].

Preparation of 5-(*tert*-butyl-diphenyl-silanyloxy)-2-cyclohex-1-enyl-pent-3-en-2-ol (S13).

The product was prepared by General Procedure A using Cp_2ZrHCl (93 mg, 0.36 mmol), *tert*-butyl-diphenyl-prop-2-ynyloxy-silane (106 mg, 0.36 mmol), Me_2Zn (0.18 mL, 0.36 mmol, 2.0 M in toluene), ligand **1** (16.4 mg, 0.03 mmol, 10 mol %), Me_2Zn (0.06 mL, 0.12 mmol, 2.0 M in toluene), $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.25 mL, 0.36 mmol, 1.4 M toluene solution) and 1-cyclohex-1-enyl-ethanone (39 μ L, 0.30 mmol). The crude product was purified by column chromatography on deactivated silica gel ($\text{Et}_3\text{N}/\text{SiO}_2 = 2.5\%$ V/V, hexanes : EtOAc / 92:8) to give **S13** (123 mg, 98% yield, 92% ee) as an oil: $[\alpha]_{\text{D}}^{20} = -1.5$ (c 3.07, CHCl_3); ^1H NMR (C_6D_6 , 500 MHz) δ 1.17 (s, 9H), 1.28 (s, 3H), 1.45-1.47 (m, 2H), 1.52-1.54 (m, 2H), 1.94-1.97 (m, 2H), 2.00-2.01 (m, 2H), 4.22 (d, $J = 3.5$ Hz, 2H),

5.74-5.84 (m, 3H), 7.21-7.26 (m, 6H), 7.75-7.80 (m, 4H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz) δ 19.6, 22.8, 23.5, 24.6, 25.6, 27.1, 27.2, 64.7, 74.7, 120.6, 126.7, 128.1, 130.0, 134.4, 136.0, 137.2, 142.6 ppm; IR (film) 3564, 3377, 3069, 3047, 2920, 2837, 1447, 1436, 1427, 1376 cm^{-1} ; HRMS-Cl m/z 402.2372 $[(\text{M}-\text{H}_2\text{O})^+]$; calcd for $\text{C}_{27}\text{H}_{34}\text{OSi}$: 402.2380].

Preparation of 3-phenyl-non-4-en-3-ol (S14).

The product was prepared by General Procedure A using Cp_2ZrHCl (155 mg, 0.60 mmol), 1-hexyne (70 μL , 0.60 mmol), Me_2Zn (0.30 mL, 0.60 mmol, 2.0 M in toluene), ligand **1** (27.3 mg, 0.05 mmol, 10 mol %), Me_2Zn (0.10 mL, 0.20 mmol, 2.0 M in toluene), $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.43 mL, 0.60 mmol, 1.4 M toluene solution) and propiophenone (67 μL , 0.50 mmol). The crude product was purified by column chromatography on deactivated silica gel ($\text{Et}_3\text{N}/\text{SiO}_2 = 2.5\%$ V/V, hexanes : EtOAc / 97:3) to give **S14** (98 mg, 90% yield, 94% ee) as an oil: $[\alpha]_{\text{D}}^{20} = -11.0$ (c 2.13, CHCl_3); ^1H NMR (C_6D_6 , 500 MHz) δ 0.82-0.85 (m, 6H), 1.19-1.25 (m, 4H), 1.72-1.78 (m, 1H), 1.79-1.88 (m, 1H), 1.92-1.96 (m, 2H), 5.58-5.64 (m, 1H), 5.73 (d, $J = 15.5$ Hz, 1H), 7.09 (t, $J = 7.3$ Hz, 1H), 7.21 (t, $J = 7.5$ Hz, 2H), 7.46 (d, $J = 7.3$ Hz, 2H), ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz) δ 8.2, 14.2, 22.6, 31.9, 32.4, 35.6, 76.7, 126.0, 126.7, 128.3, 129.0, 137.2, 147.0 ppm; IR (film) 3459, 3024, 2953, 2916, 2872, 1665, 1601, 1493, 1466, 1446 cm^{-1} ; HRMS-Cl m/z 200.1567 $[(\text{M}-\text{H}_2\text{O})^+]$; calcd for $\text{C}_{15}\text{H}_{20}$: 200.1565].

Preparation of 3-(3-chloro-phenyl)-non-4-en-3-ol (S15).

The product was prepared by General Procedure A using Cp_2ZrHCl (155 mg, 0.60 mmol), 1-hexyne (70 μL , 0.60 mmol), Me_2Zn (0.30 mL, 0.60 mmol, 2.0 M in toluene), ligand **1** (27.3 mg, 0.05 mmol, 10 mol %), Me_2Zn (0.10 mL, 0.20 mmol, 2.0 M in toluene), $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.43 mL, 0.60 mmol, 1.4 M toluene solution) and 3-chloropropiophenone (84 mg, 0.50 mmol). The crude product was purified by column chromatography on deactivated silica gel ($\text{Et}_3\text{N}/\text{SiO}_2 = 2.5\%$ V/V, hexanes : EtOAc / 97:3) to give **S15** (117 mg, 93% yield, 93% ee) as an oil: $[\alpha]_{\text{D}}^{20} = -3.2$ (c 2.02, CHCl_3); ^1H NMR (C_6D_6 , 500 MHz) δ 0.74 (t, $J = 7.4$ Hz, 3H), 0.84 (t, $J = 7.0$ Hz, 3H), 1.20-1.25 (m, 4H), 1.56-1.71 (m, 2H), 1.87-1.91 (m, 2H), 5.50-5.57 (m, 2H), 6.90 (t, $J = 7.9$ Hz, 1H), 7.05 (m, 1H), 7.16 (d, $J = 7.7$ Hz, 1H), 7.59 (t, $J = 1.8$ Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz) δ 8.0, 14.1, 22.6, 31.8, 32.3, 35.4, 76.4, 124.2, 126.4, 126.9, 129.5, 129.6, 134.5, 136.7, 149.4 ppm; IR (film) 3455, 3024, 2958, 2927, 2872, 1665, 1595, 1572, 1466, 1420 cm^{-1} ; HRMS- CI m/z 234.1175 $[(\text{M}-\text{H}_2\text{O})^+]$; calcd for $\text{C}_{15}\text{H}_{19}\text{Cl}$: 234.1175].

Conditions for the Determination of Enantiomeric Excess.

The allylic alcohols **S1-S2**, **S7**, **S9**, **S11** and **S14-S15** were analyzed by chiral capillary GC. The specifications for the GC analyses were as follows: Fused silica chiral capillary column (Supelco β -Dex 120): 30 m x 0.25 mm (id) x 0.25 μm film thickness. Carrier gas:

nitrogen. Inlet temperature: 250 °C. Detector: FID, 270 °C. The conditions for the resolution of the racemates by GC are given below.

2-Phenyl-oct-3-en-2-ol (S1). $t_1 = 72.6$ min, $t_2 = 77.1$ min (130°C, 1.0 mL/min).

4-Cyclopropyl-2-phenyl-but-3-en-2-ol (S2). $t_1 = 34.9$ min, $t_2 = 35.7$ min (140°C, 1.0 mL/min).

5,5-Dimethyl-2-*m*-tolyl-hex-3-en-2-ol (S7). $t_1 = 51.9$ min, $t_2 = 55.0$ min (125°C, 1.5 mL/min).

2,4-Dimethyl-dec-5-en-4-ol (S9). $t_1 = 13.4$ min, $t_2 = 14.2$ min (120°C, 1.0 mL/min).

1-Hex-1-enyl-2,4,4-trimethyl-cyclohex-2-enol (S11). $t_1 = 13.6$ min, $t_2 = 14.4$ min (145°C, 1.0 mL/min).

3-Phenyl-non-4-en-3-ol (S14). $t_1 = 25.6$ min, $t_2 = 26.6$ min (130°C, 1.0 mL/min).

3-(3-Chloro-phenyl)-non-4-en-3-ol (S15). $t_1 = 54.6$ min, $t_2 = 56.5$ min (135°C, 1.0 mL/min).

The analysis of **S3-S6, S8, S10** and **S12-S13** was performed by chiral HPLC using a Chiralcel OD-H column. The conditions for the resolution are described below.

5-(*tert*-Butyl-diphenyl-silanyloxy)-2-phenyl-pent-3-en-2-ol (S3). $t_1 = 30.0$ min, $t_2 = 32.7$ min (hexane /2-propanol : 98 / 2, 0.3 mL/min).

2,4-Diphenyl-but-3-en-2-ol (S4). $t_1 = 12.2$ min, $t_2 = 15.6$ min (hexane /2-propanol : 92 / 8, 0.8 mL/min).

4-Phenyl-2-(3-trifluoromethyl-phenyl)-but-3-en-2-ol (S5). $t_1 = 19.4$ min, $t_2 = 30.8$ min (hexane /2-propanol : 92 / 8, 0.5 mL/min).

6-(tert-Butyl-diphenyl-silanyloxy)-2-(3-trifluoromethyl-phenyl)-hex-3-en-2-ol (S6).
 $t_1 = 28.0$ min, $t_2 = 30.8$ min (hexane /2-propanol : 99.5 / 0.5, 0.5 mL/min).

8-Chloro-2-m-tolyl-oct-3-en-2-ol (S8). $t_1 = 17.7$ min, $t_2 = 19.0$ min (hexane /2-propanol : 97 / 3, 0.5 mL/min).

3-Methyl-1-phenyl-nona-1,4-dien-3-ol (S10). $t_1 = 24.8$ min, $t_2 = 28.7$ min (hexane /2-propanol : 97 / 3, 0.5 mL/min).

1-[4-(tert-Butyl-diphenyl-silanyloxy)-but-1-enyl]-2,4,4-trimethyl-cyclohex-enol (S12).
 $t_1 = 8.6$ min, $t_2 = 11.0$ min (hexane /2-propanol : 97 / 3, 0.5 mL/min).

5-(tert-Butyl-diphenyl-silanyloxy)-2-cyclohex-1-enyl-pent-3-en-2-ol (S13). $t_1 = 20.5$ min, $t_2 = 21.7$ min (hexane /2-propanol : 98 / 2, 0.3 mL/min).

Reference

1) Garcia C.; Walsh P. J. *Org. Lett.* **2003**, 3641-3644.

2-Phenyl-oct-3-en-2-ol

2-Phenyl-oct-3-en-2-ol

4-Cyclopropyl-2-phenyl-but-3-en-2-ol

4-Cyclopropyl-2-phenyl-but-3-en-2-ol

5-(*tert*-Butyl-diphenyl-silanyloxy)-2-phenyl-pent-3-en-2-ol

4-Phenyl-2-(3-(trifluoromethyl)-phenyl)-but-3-en-2-ol

6-(*tert*-Butyl-diphenyl-silanyloxy)-2-(3-trifluoromethyl-phenyl)-hex-3-en-2-ol

5,5-Dimethyl-2-*m*-tolyl-hex-3-en-2-ol

5,5-Dimethyl-2-*p*-tolyl-hex-3-en-2-ol

8-Chloro-2-(4-chlorophenyl)-oct-3-en-2-ol

8-Chloro-2-*m*-tolyl-oct-3-en-2-ol

2,4-Dimethyl-dec-5-en-4-ol

2,4-Dimethyl-dec-5-en-4-ol

3-Methyl-1-phenyl-nona-1,4-dien-3-ol

3-Methyl-1-phenyl-nona-1,4-dien-3-ol

1-Hex-1-enyl-2,4,4-trimethyl-cyclohex-2-enol

1-Hex-1-enyl-2,4,4-trimethyl-cyclohex-2-enol

1-[4-(*tert*-Butyl-diphenyl-silyloxy)-but-1-enyl]-2,4,4-trimethyl-cyclohex-2-enol

1-[4-(*tert*-Butyl-diphenyl-silanyloxy)-but-1-enyl]-2,4,4-trimethyl-cyclohex-2-enol

5-(*tert*-Butyl-diphenyl-silanyloxy)-2-cyclohex-1-enyl-pent-3-en-2-ol

5-(*tert*-Butyl-diphenyl-silyloxy)-2-cyclohex-1-enyl-pent-3-en-2-ol

3-Phenyl-non-4-en-3-ol

3-(3-Chloro-phenyl)-non-4-en-3-ol

3-(3-Chloro-phenyl)-non-4-en-3-ol