Catalytic Asymmetric Vinylation and Dienylation of Ketones

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Supporting Information

Part 1

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General Methods. All reactions were carried out under a nitrogen atmosphere with oven-dried glassware. The progress of all reactions was monitored by thin-layer chromatography to ensure the reactions had reached completion. All manipulations involving Schwartz's reagent and dimethylzinc were carried out under an inert atmosphere in a Vacuum Atmospheres drybox with an attached MO-40 Dritrain or by using standard Schlenk or vacuum line techniques. All chemicals were obtained from Aldrich, Acros, or GFS Chemicals unless otherwise specified. All solvents were purchased from Fischer Scientific. Toluene, dichloromethane, diethyl ether and hexanes were dried through activated alumina columns. Cp_2ZrHCl was prepared according to a modification of literature protocol.^{1,2} Titanium(IV) isopropoxide and all liquid ketone substrates were distilled prior to use. Titanium(IV) isopropoxide (1.4 M in toluene) and dimethylzinc (1.0 M in toluene) were prepared and stored in a Vacuum Atmospheres drybox. NMR spectra were obtained on a Bruker 500 MHz Fourier transform spectrometer at the University of Pennsylvania NMR facility. Chemical shifts are reported in units of parts per million downfield from tetramethylsilane. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced to residual solvent. The infrared spectra were obtained using a Perkin-Elmer 1600 series spectrometer. Thin-layer chromatography was performed on Whatman precoated silica gel 60 F-254 plates and visualized by ultraviolet light or by staining with ceric ammonium molybdate or phosphomolybdic acid solutions. Silica gel (230-400 mesh, Silicycle) was used for air-flashed chromatography.

General Protocol A. Preparation of 2,2-dimethyl-propionic acid 4-hydroxy-4-phenyl-pent-2-enyl ester (S1).

To a suspension of Cp_2ZrHCl (155 mg, 0.60 mmol) in CH_2Cl_2 (2.0 mL) under N_2 was added 2,2-dimethyl-propionic acid prop-2-ynyl ester (103 mg, 0.60 mmol) and the reaction mixture was stirred for 10 min at r.t. after which it was homogeneous. 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 15 min. In another Schlenk flask were mixed ligand **1** (13.7 mg, 0.025 mmol, 5 mol %) in 1.0 mL toluene and $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.22 mL, 1.4 M toluene solution, 0.30 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 ($\text{Et}_3\text{N} / \text{SiO}_2 = 2.5\% \text{ V/V}$, hexanes : EtOAc / 90 : 10) to give the product (110 mg, 90% yield, 89% ee) as an oil: $[\alpha]_{\text{D}}^{20} = +6.7$ (c 0.99, CHCl_3); ^1H NMR (C_6D_6 , 500 MHz) δ 1.13 (s, 9H), 1.44 (s, 3H), 4.47 (d, $J = 5.8$ Hz, 2H), 5.74-5.78 (m, 1H), 5.90 (d, $J = 15.6$ Hz, 1H), 7.06 (m, 1H), 7.15-7.18 (m, 2H), 7.40-7.42 (m, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz) δ 27.3, 29.9, 38.8, 64.4, 73.9, 122.5, 125.6, 127.1, 128.4, 141.2, 147.2, 177.7 ppm; IR (neat) 3472, 2974, 2875, 1724, 1602, 1482, 1452, 1368 cm^{-1} ; HRMS m/z 244.1473 [$\text{M}-\text{H}_2\text{O}$] $^+$; calcd for $\text{C}_{16}\text{H}_{20}\text{O}_2$: 244.1464].

Preparation of 5-phenylsulfanyl-2-(3-trifluoromethyl-phenyl)-pent-3-en-2-ol (S2).

The General Procedure A was applied to acetophenone on a 76 μL (0.5 mmol) scale. 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 / 90 : 10) to give the product (160 mg, 95% yield, 88% ee) as an oil: $[\alpha]_{\text{D}}^{20} = +33.3$ (c 0.90, CHCl_3); ^1H NMR (CDCl_3 , 500 MHz) δ 1.55 (s, 3H), 1.84 (br, 1H), 3.52-3.53 (m, 2H), 5.73-5.74 (m, 2H), 7.18-7.19 (m, 1H), 7.23-7.25 (m, 2H), 7.31-7.32 (m, 2H), 7.35-7.41 (m, 2H), 7.48 (d, $J = 7.4$ Hz, 1H), 7.65 (s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz) δ 30.2, 36.7, 74.3, 122.3 (m), 123.5, 124.1 (m), 125.2, 127.2, 129.0, 129.1, 129.2, 130.8 (q), 131.5, 135.4, 139.8, 147.9 ppm; IR (neat) 3418, 3067,

2977, 2927, 1584, 1480, 1439 cm^{-1} ; HRMS-CI m/z 320.0841 $[(M-H_2O)^+]$; calcd for $\text{C}_{18}\text{H}_{15}\text{F}_3\text{S}$: 320.0846].

Preparation of 3-methyl-1-phenyl-non-4-en-1-yn-3-ol (S3).

The General Procedure A was applied to 4-phenyl-but-3-yn-2-one on a 73 μL (0.5 mmol) scale. 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 the product (85 mg, 81% yield, 79% ee) as an oil: $[\alpha]_{\text{D}}^{20} = -8.9$ (c 0.83, CHCl_3); ^1H NMR (C_6D_6 , 500 MHz) δ 0.83 (t, $J = 7.1$ Hz, 3H), 1.22-1.27 (m, 4H), 1.95 (s, 3H), 1.94-1.96 (m, 2H), 5.71 (d, $J = 15.3$ Hz, 1H), 6.10 (dt, $J = 15.3$, 6.8 Hz, 1H), 6.96-7.00 (m, 3H), 7.41-7.44 (m, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz) δ 14.1, 22.6, 31.0, 31.6, 31.9, 68.3, 84.6, 93.2, 123.6, 128.4, 128.6, 130.0, 132.0, 135.2 ppm; IR (neat) 3353, 2957, 2928, 2861, 1668, 1598, 1490, 1446 cm^{-1} ; HRMS m/z 210.1416 $[(M-H_2O)^+]$; calcd for $\text{C}_{16}\text{H}_{18}$: 210.1408].

Preparation of 2-bromo-1-hex-1-enyl-cyclohex-2-enol (S4).

The General Procedure A was applied to 2-bromo-cyclohex-2-enone on a 88 mg (0.5 mmol) scale. 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 : $\text{EtOAc} / 97 : 3$) to give the product (50 mg, 42% yield, 92% ee) as an oil: $[\alpha]_{\text{D}}^{20} = -0.1$ (c 0.67, CHCl_3); ^1H NMR (CDCl_3 , 500 MHz) δ 0.89 (t, $J = 7.2$ Hz, 3H), 1.31-1.38 (m, 4H), 1.61-1.64 (m, 1H), 1.65-1.66 (m, 1H), 1.90-1.94 (m, 2H), 2.04-2.12 (m, 4H), 2.28 (s, 1H from OH), 5.44 (d, $J = 15.5$ Hz, 1H), 5.70 (dt, $J = 15.5$, 6.9 Hz, 1H), 6.20 (t, $J = 4.1$ Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz) δ 14.3, 19.4, 22.5, 28.3, 31.7, 32.2, 37.9, 74.4, 129.9, 131.9, 132.7, 134.2 ppm; IR (neat) 3411, 2954, 2867, 1713, 1453, 1261 cm^{-1} ; HRMS m/z 240.0514 $[(M-H_2O)^+]$; calcd for $\text{C}_{12}\text{H}_{17}\text{Br}$: 240.0513].

Preparation of 4-cyclohex-1-enyl-2-phenyl-but-3-en-2-ol (S5).

The General Procedure A was applied to acetophenone on a 59 μL (0.5 mmol) scale. The crude product was purified by flash chromatography on deactivated silica gel ($\text{Et}_3\text{N} / \text{SiO}_2 = 2.5\% \text{ V/V}$, hexanes : $\text{EtOAc} / 96 : 4$) to give the product (101 mg, 89% yield, 89% ee) as an oil: $[\alpha]_{\text{D}}^{20} = -1.8$ (c 1.37, CHCl_3); ^1H NMR (C_6D_6 , 500 MHz) δ 1.41-1.52 (m, 4H), 1.54 (s, 3H), 1.95-1.97 (m, 4H), 5.64 (m, 1H), 5.82 (d, $J = 15.9$ Hz, 1H), 6.32 (d, $J = 15.9$ Hz, 1H), 7.07-7.10 (m, 1H), 7.18-7.21 (m, 2H), 7.50-7.52 (m, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz) δ 22.9, 23.0, 25.0, 26.2, 30.3, 74.6, 125.8, 126.9, 128.4, 129.7, 131.5, 133.3, 135.5, 148.2 ppm; IR (neat) 3424, 3026, 2929, 2860, 1714, 1669, 1492, 1445 cm^{-1} ; HRMS m/z 228.1509 $[\text{M}^+]$; calcd for $\text{C}_{16}\text{H}_{20}\text{O}$: 228.1514].

Preparation of 4-cyclohex-1-enyl-2-*m*-tolyl-but-3-en-2-ol (S6).

The General Procedure A was applied to 3'-methyl-acetophenone on a 55 μL (0.4 mmol) scale. 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 : $\text{EtOAc} / 96 : 4$) to give the product (89 mg, 92% yield, 92% ee) as an oil: $[\alpha]_{\text{D}}^{20} = +4.2$ (c 1.10, CHCl_3); ^1H NMR (C_6D_6 , 500 MHz) δ 1.38-1.50 (m, 4H), 1.59 (s, 3H), 1.95-1.98 (m, 4H), 2.17 (s, 3H), 5.66 (m, 1H), 5.86 (d, $J = 15.9$ Hz, 1H), 6.37 (d, $J = 15.9$ Hz, 1H), 6.94 (d, $J = 7.4$ Hz, 1H), 7.16 (dd, $J = 7.8$, 7.4 Hz, 1H), 7.36 (d, $J = 7.8$ Hz, 1H), 7.43 (s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz) δ 21.7, 22.9, 23.0, 25.0, 26.2, 30.4, 74.5, 123.0, 126.5, 127.7, 128.4, 129.7, 131.4, 133.5, 135.5, 137.8, 148.3 ppm; IR (neat) 3410, 2932, 2859, 1676, 1606, 1485, 1451, 1365 cm^{-1} ; HRMS m/z 224.1573 $[(M-H_2O)^+]$; calcd for $\text{C}_{17}\text{H}_{20}$: 224.1566].

Preparation of 4-cyclohex-1-enyl-2-(3-trifluoromethyl-phenyl)-but-3-en-2-ol (S7).

The General Procedure A was applied to 3'-(trifluoromethyl)acetophenone on a 76 μ L (0.5 mmol) scale. 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 / 96 : 4) to give the product (138 mg, 93% yield, 87% ee) as an oil: $[\alpha]_{\text{D}}^{20} = +3.5$ (c 0.99, CHCl_3); ^1H NMR (C_6D_6 , 500 MHz) δ 1.42 (s, 3H), 1.43-1.50 (m, 4H), 1.91-1.95 (m, 4H), 5.62 (m, 1H), 5.67 (d, $J = 15.9$ Hz, 1H), 6.22 (d, $J = 15.9$ Hz, 1H), 7.00 (dd, $J = 7.8, 7.7$ Hz, 1H), 7.30 (d, $J = 7.7$ Hz, 1H), 7.44 (d, $J = 7.8$ Hz, 1H), 7.96 (s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz) δ 22.7, 22.8, 24.8, 26.2, 30.3, 74.2, 122.3 (m), 123.7 (m), 126.3, 128.9, 129.4, 130.6, 130.7 (q), 132.1, 132.3, 135.2, 149.4 ppm; IR (neat) 3425, 2934, 2864, 1685, 1666, 1617, 1440, 1329 cm^{-1} ; HRMS-ESI m/z 278.1285 $[(\text{M}-\text{H}_2\text{O})^+]$; calcd for $\text{C}_{17}\text{H}_{17}\text{F}_3$: 278.1282].

Preparation of 6-methyl-2-*m*-tolyl-dodeca-3, 5-dien-2-ol (S8).

The General Procedure A was applied to 3'-methyl-acetophenone on a 55 μ L (0.4 mmol) scale. 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 / 96 : 4) to give the product (78 mg, 68% yield, 89% ee) as an oil: $[\alpha]_{\text{D}}^{20} = -8.9$ (c 0.91, CHCl_3); ^1H NMR (C_6D_6 , 500 MHz) δ 0.88 (t, $J = 6.8$ Hz, 3H), 1.23-1.28 (m, 6H), 1.34-1.39 (m, 2H), 1.57 (s, 3H), 1.65 (s, 3H), 1.99 (t, $J = 7.4$ Hz, 2H), 2.16 (s, 3H), 5.89 (d, $J = 15.2$ Hz, 1H), 5.94 (d, $J = 10.9$ Hz, 1H), 6.66 (dd, $J = 15.2, 10.9$ Hz, 1H), 6.93 (d, $J = 7.5$ Hz, 1H), 7.14 (m, 1H), 7.32 (d, $J = 7.8$ Hz, 1H), 7.39 (s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz) δ 14.3, 16.7, 21.6, 23.0, 28.3, 29.4, 30.4, 32.2, 40.3, 74.5, 122.9, 124.3, 125.0, 126.4, 127.7, 128.4, 137.7, 138.9, 139.1, 148.1 ppm; IR (neat) 3406, 2925, 2857, 1686, 1605, 1455, 1373 cm^{-1} ; HRMS m/z 268.2182 $[(\text{M}-\text{H}_2\text{O})^+]$; calcd for $\text{C}_{20}\text{H}_{28}$: 268.2191].

Preparation of 6-methyl-2-(3-trifluoromethyl-phenyl)-dodeca-3, 5-dien-2-ol (S9).

The General Procedure A was applied to 3'-(trifluoromethyl)acetophenone on a 61 μ L (0.5 mmol) scale. 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 / 96 : 4) to give the product (150 mg, 88% yield, 94% ee) as an oil: $[\alpha]_{\text{D}}^{20} = +3.0$ (c 0.99, CHCl_3); ^1H NMR (C_6D_6 , 500 MHz) δ 0.88 (t, $J = 6.8$ Hz, 3H), 1.23-1.28 (m, 6H), 1.35-1.39 (m, 5H), 1.62 (s, 3H), 1.97 (t, $J = 7.4$ Hz, 2H), 5.66 (d, $J = 15.2$ Hz, 1H), 5.86 (d, $J = 10.8$ Hz, 1H), 6.54 (dd, $J = 15.2, 10.8$ Hz, 1H), 6.95 (dd, $J = 7.8, 7.7$ Hz, 1H), 7.82 (d, $J = 7.7$ Hz, 1H), 7.40 (d, $J = 7.8$ Hz, 1H), 7.93 (s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz) δ 14.3, 16.6, 23.0, 28.1, 29.4, 30.1, 32.1, 40.2, 74.1, 122.3 (m), 123.7 (m), 124.5, 125.1, 126.2, 128.8, 129.2, 130.7 (q), 137.4, 140.1, 149.2 ppm; IR (neat) 3378, 2928, 2858, 1653, 1444, 1328 cm^{-1} ; HRMS m/z 322.1905 $[(\text{M}-\text{H}_2\text{O})^+]$; calcd for $\text{C}_{20}\text{H}_{25}\text{F}_3$: 322.1908].

Preparation of 5-methyl-2-phenyl-hexa-3, 5-dien-2-ol (S10).

The General Procedure A was applied to acetophenone on a 59 μ L (0.5 mmol) scale. 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 the product (93 mg, 99% yield, 93% ee) as an oil: $[\alpha]_{\text{D}}^{20} = -12.2$ (c 0.72, CHCl_3); ^1H NMR (C_6D_6 , 500 MHz) δ 1.50 (s, 3H), 1.67 (s, 3H), 1.97 (br, 1H), 4.90 (s, 1H), 4.94 (s, 1H), 5.88 (d, $J = 15.9$ Hz, 1H), 6.41 (d, $J = 15.9$ Hz, 1H), 7.06 (t, $J = 7.2$ Hz, 1H), 7.17 (dd, $J = 7.8, 7.5$ Hz, 2H), 7.44 (d, $J = 7.7$ Hz, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz) δ 18.7, 30.0, 74.4, 116.9, 125.6, 127.0, 128.4, 130.5, 137.2, 141.7, 147.6 ppm; IR (neat) 3409, 3028, 2976, 2930, 1886, 1676, 1607, 1446, 1367 cm^{-1} ; HRMS m/z 170.1090 $[(\text{M}-\text{H}_2\text{O})^+]$; calcd for $\text{C}_{13}\text{H}_{14}$: 170.1095].

Preparation of 5-methyl-2-(3-trifluoromethyl-phenyl)-hexa-3, 5-dien-2-ol (S11).

The General Procedure A was applied to 3'-(trifluoromethyl)acetophenone on a 76 μ L (0.5 mmol) scale. The crude product was purified by column chromatography on deactivated silica gel (Et₃N / SiO₂ = 2.5% V/V, hexanes : EtOAc / 95 : 5) to give the product (107 mg, 84% yield, 90% ee) as an oil: $[\alpha]_D^{20} = +5.6$ (*c* 1.00, CHCl₃); ¹H NMR (C₆D₆, 500 MHz) δ 1.35 (s, 3H), 1.64 (s, 3H), 4.91 (s, 1H), 4.93 (s, 1H), 5.72 (d, *J* = 15.9 Hz, 1H), 6.31 (d, *J* = 15.9 Hz, 1H), 6.98 (t, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.91 (s, 1H) ppm; ¹³C{¹H} NMR (C₆D₆, 125 MHz) δ 18.9, 29.8, 74.0, 117.6, 122.3 (m), 123.9 (m), 126.2, 128.9, 129.3, 130.8 (q), 131.3, 136.0, 141.5, 148.9 ppm; IR (neat) 3374, 2979, 2934, 1797, 1609, 1440, 1328 cm⁻¹; HRMS *m/z* 256.1062 [M⁺; calcd for C₁₄H₁₅F₃O: 256.1075].

Preparation of 2-(2-bromo-phenyl)-4-cyclohex-1-enyl-but-3-en-2-ol (S12).

The General Procedure A was applied to 2'-bromo-acetophenone on a 67 μ L (0.5 mmol) scale. The crude product was purified by column chromatography on deactivated silica gel (Et₃N / SiO₂ = 2.5% V/V, hexanes : EtOAc / 96 : 4) to give the product (65 mg, 42% yield, 87% ee) as an oil: $[\alpha]_D^{20} = -20.8$ (*c* 1.55, CHCl₃); ¹H NMR (C₆D₆, 500 MHz) δ 1.39-1.44 (m, 2H), 1.47-1.52 (m, 2H), 1.79 (s, 3H), 1.92-1.93 (m, 2H), 2.02-2.05 (m, 2H), 5.57 (m, 1H), 6.09 (d, *J* = 16.0 Hz, 1H), 6.27 (d, *J* = 16.0 Hz, 1H), 6.70 (m, 1H), 7.01 (m, 1H), 7.40 (m, 1H), 7.83 (m, 1H) ppm; ¹³C{¹H} NMR (C₆D₆, 125 MHz) δ 22.8, 22.9, 24.9, 26.2, 28.6, 75.2, 121.7, 127.5, 128.4, 128.7, 130.0, 132.0, 133.6, 135.1, 135.6, 146.4 ppm; IR (neat) 3426, 2928, 2859, 1700, 1664, 1459, 1429 cm⁻¹; HRMS *m/z* 288.0503 [(M-H₂O)⁺; calcd for C₁₆H₁₇Br: 288.0513].

Preparation of 3-(3-chloro-phenyl)-1-cyclohex-1-enyl-pent-1-en-3-ol (S13).

The General Procedure A was applied to 3'-chloropropiophenone on a 84 mg (0.5 mmol) scale. The crude product was purified by column chromatography on deactivated silica gel (Et₃N / SiO₂ = 2.5% V/V, hexanes : EtOAc / 97 : 3) to give the product (96 mg, 85% yield, 89% ee) as an oil: $[\alpha]_D^{20} = -1.9$ (*c* 0.82, CHCl₃); ¹H NMR (C₆D₆, 500 MHz) δ 0.75 (t, *J* = 7.3 Hz, 3H), 1.41-1.49 (m, 4H), 1.66-1.72 (m, 2H), 1.93-1.95 (m, 4H), 5.63 (m, 1H), 5.69 (d, *J* = 15.9 Hz, 1H), 6.26 (d, *J* = 15.9 Hz, 1H), 6.90 (dd, *J* = 7.9, 7.8 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.63 (s, 1H) ppm; ¹³C{¹H} NMR (C₆D₆, 125 MHz) δ 8.1, 22.8, 22.9, 24.9, 26.2, 35.5, 76.7, 124.3, 126.4, 126.9, 129.6, 130.2, 131.6, 132.5, 134.6, 135.3, 149.4 ppm; IR (neat) 3438, 3026, 2933, 2878, 1647, 1593, 1571, 1467 cm⁻¹; HRMS-Cl *m/z* 258.1167 [(M-H₂O)⁺; calcd for C₁₇H₁₉Cl: 258.1175].

Preparation of 3-(4-chloro-phenyl)-1-cyclohex-1-enyl-pent-1-en-3-ol (S14).

The General Procedure A was applied to 4'-chloropropiophenone on a 84 mg (0.5 mmol) scale. The crude product was purified by column chromatography on deactivated silica gel (Et₃N / SiO₂ = 2.5% V/V, hexanes : EtOAc / 97 : 3) to give the product (91 mg, 80% yield, 79% ee) as an oil: $[\alpha]_D^{20} = -12.6$ (*c* 0.98, CHCl₃); ¹H NMR (C₆D₆, 500 MHz) δ 0.77 (t, *J* = 7.3 Hz, 3H), 1.43-1.46 (m, 2H), 1.48-1.51 (m, 2H), 1.67-1.76 (m, 2H), 1.95-1.97 (m, 4H), 5.65 (m, 1H), 5.70 (d, *J* = 15.9 Hz, 1H), 6.25 (d, *J* = 15.9 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H) ppm; ¹³C{¹H} NMR (C₆D₆, 125 MHz) δ 8.1, 22.8, 22.9, 25.0, 26.2, 35.5, 76.6, 127.7, 128.4, 130.1, 132.3, 132.7, 134.6, 135.3, 145.4 ppm; IR (neat) 3431, 2934, 2862, 1681, 1591, 1489, 1455 cm⁻¹; HRMS *m/z* 258.1180 [(M-H₂O)⁺; calcd for C₁₇H₁₉Cl: 258.1175].

Preparation of 4-cyclohex-1-enyl-2-*m*-tolyl-but-3-en-2-ol (S15).

The General Procedure A was applied to cyclohexyl methyl ketone on a 69 μL (0.5 mmol) scale. 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 : $\text{EtOAc} / 96 : 4$) to give the product (102 mg, 87% yield, 77% ee) as an oil: $[\alpha]_{\text{D}}^{20} = +1.4$ (c 2.45, CHCl_3); ^1H NMR (C_6D_6 , 500 MHz) δ 0.97-1.06 (m, 4H), 1.09-1.16 (m, 1H), 1.20 (s, 3H), 1.27-1.29 (m, 1H), 1.45-1.49 (m, 2H), 1.51-1.55 (m, 2H), 1.70-1.73 (m, 2H), 1.82-1.85 (m, 2H), 2.00-2.01 (m, 2H), 2.04-2.07 (m, 2H), 5.61 (d, $J = 16.0$ Hz, 1H), 5.70 (m, 1H), 6.33 (d, $J = 16.0$ Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz) δ 22.9, 23.0, 25.0, 26.0, 26.1, 26.9, 27.0, 27.1, 27.5, 27.9, 49.1, 74.6, 128.6, 131.3, 132.5, 135.5 ppm; IR (neat) 3448, 2923, 2854, 1652, 1449, 1370, 1130 cm^{-1} ; HRMS m/z 216.1863 $[(\text{M}-\text{H}_2\text{O})^+]$; calcd for $\text{C}_{16}\text{H}_{24}$: 216.1878].

Preparation of 1-cyclohex-1-enyl-3,4-dimethyl-pent-1-en-3-ol (S16).

The General Procedure A was applied to 3-methyl-butan-2-one on a 54 μL (0.5 mmol) scale. 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 : $\text{EtOAc} / 98 : 2$) to give the product (66 mg, 68% yield, 42% ee) as an oil: $[\alpha]_{\text{D}}^{20} = +0.95$ (c 2.0, CHCl_3); ^1H NMR (C_6D_6 , 500 MHz) δ 0.91 (t, $J = 6.2$ Hz, 6H), 1.16 (s, 3H), 1.44-1.48 (m, 2H), 1.51-1.55 (m, 2H), 1.62-1.67 (m, 1H), 1.99-2.00 (m, 2H), 2.03-2.05 (m, 2H), 5.60 (d, $J = 16.0$ Hz, 1H), 5.69 (t, $J = 3.9$ Hz, 1H), 6.33 (d, $J = 16.0$ Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz) δ 17.4, 17.8, 22.9, 23.0, 25.0, 25.8, 26.1, 38.7, 75.0, 128.7, 131.6, 132.0, 135.5 ppm; IR (neat) 3440, 2962, 2923, 2870, 1713, 1662, 1451 cm^{-1} ; HRMS m/z 176.1567 $[(\text{M}-\text{H}_2\text{O})^+]$; calcd for $\text{C}_{13}\text{H}_{20}$: 176.1565].

General Procedure B. Preparation of 4-methyl-2-phenyl-pent-3-en-2-ol (S17).

The ligand **1** (27.3 mg, 10 mol%) was weighed into the well-dried Schlenk flask and loaded into the drybox. The bis(2-methyl-1-propenyl)zinc reagent (140 mg, 0.8 mmol) was weighed under N_2 and combined with 2 mL toluene, followed by titanium(IV) isopropoxide (0.43 mL, 0.6 mmol, 1.4 M toluene solution) in drybox. The reaction mixture was stirred at room temperature for 10 min and acetophenone (59 μL , 0.5 mmol) was added neat. The flask was sealed and removed from the drybox. The reaction mixture was stirred at r.t. until TLC showed completion of the ketone. The reaction was quenched with H_2O , extracted into CH_2Cl_2 , dried with MgSO_4 and concentrated under reduced pressure. 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 the product (84 mg, 95% yield, 93% ee) as an oil: $[\alpha]_{\text{D}}^{20} = -5.0$ (c 1.17, CHCl_3); ^1H NMR (C_6D_6 , 500 MHz) δ 1.39 (s, 3H), 1.48 (s, 3H), 1.55 (s, 3H), 1.69 (br, 1H), 5.62 (s, 1H), 7.06 (t, $J = 7.4$ Hz, 1H), 7.19 (dd, $J = 7.6, 7.5$ Hz, 2H), 7.52 (d, $J = 7.6$ Hz, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz) δ 19.1, 26.7, 34.1, 73.8, 125.6, 126.4, 128.2, 133.2, 136.1, 149.8 ppm; IR (neat) 3434, 3025, 2971, 2923, 1663, 1491, 1446, 1374 cm^{-1} ; HRMS m/z 158.1091 $[(\text{M}-\text{H}_2\text{O})^+]$; calcd for $\text{C}_{12}\text{H}_{14}$: 158.1095].

Preparation of 3-(3-chloro-phenyl)-5-methyl-hex-4-en-3-ol (S18).

The General Procedure B was applied to 3'-chloropropiophenone on a 67 mg (0.4 mmol) scale. 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 : $\text{EtOAc} / 97 : 3$) to the product (89 mg, 99% yield, 75% ee) as an oil: $[\alpha]_{\text{D}}^{20} = -1.3$ (c 0.80, CHCl_3); ^1H NMR (CDCl_3 , 500 MHz) δ 0.78 (t, $J = 7.4$ Hz, 3H), 1.47 (s, 3H), 1.73 (s, 3H), 1.75-1.80 (m, 2H), 1.83 (br, 1H), 5.68 (s, 1H), 7.15-7.17 (m, 1H), 7.19-7.22 (m, 1H), 7.27-7.28 (m, 1H), 7.43 (s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz) δ 8.2, 19.9, 27.2, 39.4, 76.3, 124.4, 126.4, 126.6, 129.4, 131.4, 134.2, 139.0, 150.2 ppm; IR (neat) 3475, 2970, 2927, 1661, 1593, 1570, 1463 cm^{-1} ; HRMS m/z 206.0859 $[(\text{M}-\text{H}_2\text{O})^+]$; calcd for $\text{C}_{13}\text{H}_{15}\text{Cl}$: 206.0862].

Preparation of 2, 4, 4-trimethyl-1-(2-methyl-propenyl)-cyclohex-2-enol (S19).

The General Procedure B was applied to 2,4,4-trimethyl-2-cyclohexen-1-one on a 60 μ L (0.4 mmol) scale. The crude product was purified by column chromatography on deactivated silica gel (Et_3N / SiO_2 = 2.5% V/V, hexanes : EtOAc / 96 : 4) to the product (67 mg, 86% yield, 94% ee) as an oil: $[\alpha]_{\text{D}}^{20}$ = -25.1 (*c* 1.10, CHCl_3); ^1H NMR (C_6D_6 , 500 MHz) δ 0.91 (s, 3H), 0.93 (s, 3H), 1.25 (br, 1H), 1.38-1.45 (m, 1H), 1.46-1.47 (m, 1H), 1.60 (s, 3H), 1.701 (s, 3H), 1.703 (s, 3H), 1.81-1.85 (m, 1H), 1.87-1.92 (m, 1H), 5.13 (s, 1H) 5.40 (s, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz) δ 18.2, 18.8, 27.1, 27.9, 30.4, 31.1, 33.7, 35.6, 72.9, 131.7, 132.1, 135.3, 136.6 ppm; IR (neat) 3383, 2954, 2860, 1667, 1447, 1373 cm^{-1} ; HRMS m/z 176.1561 $[(\text{M}-\text{H}_2\text{O})^+]$; calcd for $\text{C}_{13}\text{H}_{20}$: 176.1566].

Preparation of 2-cyclohex-1-enyl-4-methyl-pent-3-en-2-ol (S20).

The General Procedure B was applied to 1-acetyl-1-cyclohexene on a 51 μ L (0.4 mmol) scale. The crude product was purified by column chromatography on deactivated silica gel (Et_3N / SiO_2 = 2.5% V/V, hexanes : EtOAc / 96 : 4) to the product (50 mg, 70% yield, 96% ee) as white solid: mp. 56-58.5 $^\circ\text{C}$; $[\alpha]_{\text{D}}^{20}$ = +4.7 (*c* 1.20, CHCl_3); ^1H NMR (CDCl_3 , 500 MHz) δ 1.37 (s, 3H), 1.52-1.56 (m, 2H), 1.58-1.62 (m, 2H), 1.69 (s, 3H), 1.69 (s, 3H), 1.97-2.00 (m, 2H), 2.03-2.06 (m, 2H), 5.31 (s, 1H), 5.78-5.79 (m, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz) δ 18.7, 22.8, 23.6, 25.4, 25.6, 27.3, 29.8, 75.3, 120.1, 131.2, 135.0, 143.4 ppm; IR (neat) cm^{-1} ; HRMS m/z 162.1410 $[(\text{M}-\text{H}_2\text{O})^+]$; calcd for $\text{C}_{12}\text{H}_{18}$: 162.1409].

1-Cyclopropyl-2-(2,4,4-trimethyl-cyclohex-2-enylidene)-ethanol (S21).

^1H NMR (C_6D_6 , 500 MHz) δ 0.28-0.36 (m, 4H), 0.89 (s, 3H), 0.95 (s, 3H), 1.35-1.46 (m, 3H), 1.79 (s, 3H), 2.26-2.28 (m, 1H), 2.36-2.40 (m, 1H), 4.00 (dd, J = 8.1, 7.1 Hz, 1H), 5.36 (s, 1H), 5.56 (d, J = 8.3 Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz) δ 2.0, 2.7, 18.4, 20.4, 23.5, 29.0, 29.5, 32.3, 37.2, 71.2, 126.1, 130.8, 136.9, 138.7 ppm; IR (neat) 3333, 3079, 2952, 2859, 1638, 1618, 1449 cm^{-1} ; HRMS-CI m/z 206.1673 $[\text{M}^+]$; calcd for $\text{C}_{14}\text{H}_{22}\text{O}$: 206.1671].

1-Cyclopropyl-3-methyl-5-phenyl-penta-2,4-dien-1-ol (S22).

^1H NMR (CDCl_3 , 500 MHz) δ 0.30-0.32 (m, 1H), 0.38-0.40 (m, 1H), 0.50-0.56 (m, 1H), 0.57-0.60 (m, 1H), 1.06-1.13 (m, 1H), 1.93 (s, 3H), 4.03 (dd, J = 8.1, 8.1 Hz, 1H), 5.70 (d, J = 8.3 Hz, 1H), 6.58 (d, J = 16.1 Hz, 1H), 6.82 (d, J = 16.1 Hz, 1H), 7.23 (t, J = 7.3 Hz, 1H), 7.32 (dd, J = 7.3, 7.7 Hz, 1H), 7.42 (d, J = 7.7 Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz) δ 2.3, 3.2, 13.4, 18.3, 72.7, 126.8, 127.8, 128.6, 129.0, 133.6, 134.1, 135.9, 137.8 ppm; IR (neat) 3322, 3002, 2921, 2356, 1714, 1620, 1596, 1446 cm^{-1} ; HRMS m/z 214.1347 $[\text{M}^+]$; calcd for $\text{C}_{15}\text{H}_{18}\text{O}$: 214.1358].

1-Cyclohex-2-enylidene-hexan-2-ol (S23).

^1H NMR (CDCl_3 , 500 MHz) δ 0.88 (t, J = 12.3 Hz, 1H), 1.28-1.38 (m, 3H), 1.55-1.64 (m, 3H), 1.77-1.81 (m, 1H), 1.85-1.90 (m, 1H), 2.06-2.18 (m, 4H), 4.27 (m, 1H), 5.64 (m, 1H), 5.66-5.72 (m, 1H), 6.02 (d, J = 15.7 Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz) δ 14.4, 19.3, 22.6, 25.0, 32.0, 32.6, 32.9, 66.7, 128.5, 130.7, 132.8, 139.1 ppm; IR (neat) 3344, 3021, 2919, 1623, 1454 cm^{-1} ; HRMS m/z 162.1407 $[(\text{M}-\text{H}_2\text{O})^+]$; calcd for $\text{C}_{12}\text{H}_{18}$: 162.1408].

Conditions for the Determination of Enantiomeric Excess.

The analysis of **S2-3**, **S5-7**, **S10-14** and **S17-18** was performed by chiral HPLC using a Chiralcel OD-H or AS column. The conditions for the resolution are described below.

5-Phenylsulfanyl-2-(3-trifluoromethyl-phenyl)-pent-3-en-2-ol (S2). $t_1 = 36.4$ min, $t_2 = 39.1$ min (hexanes /2-propanol : 97 /3, 0.5 mL/min, OD-H).

3-Methyl-1-phenyl-non-4-en-1-yn-3-ol (S3). $t_1 = 16.1$ min, $t_2 = 23.0$ min (hexanes /2-propanol : 97 /3, 0.5 mL/min, OD-H).

4-Cyclohex-1-enyl-2-phenyl-but-3-en-2-ol (S5). $t_1 = 15.8$ min, $t_2 = 18.2$ min (hexanes /2-propanol : 97 / 3, 0.5 mL/min, OD-H).

4-Cyclohex-1-enyl-2-*m*-tolyl-but-3-en-2-ol (S6). $t_1 = 15.7$ min, $t_2 = 17.9$ min (hexanes /2-propanol : 97 / 3, 0.5 mL/min, OD-H).

4-Cyclohex-1-enyl-2-(3-trifluoromethyl-phenyl)-but-3-en-2-ol (S7). $t_1 = 13.9$ min, $t_2 = 16.6$ min (hexanes /2-propanol : 97 / 3, 0.5 mL/min, OD-H).

5-Methyl-2-phenyl-hexa-3, 5-dien-2-ol (S10). $t_1 = 60.1$ min, $t_2 = 64.6$ min (hexanes /2-propanol : 99 / 1, 0.2 mL/min, OD-H).

5-Methyl-2-(3-trifluoromethyl-phenyl)-hexa-3, 5-dien-2-ol (S11). $t_1 = 15.4$ min, $t_2 = 16.8$ min (hexanes /2-propanol : 98 / 2, 0.5 mL/min, OD-H).

2-(2-Bromo-phenyl)-4-cyclohex-1-enyl-but-3-en-2-ol (S12). $t_1 = 17.0$ min, $t_2 = 20.9$ min (hexanes /2-propanol : 98 / 2, 0.5 mL/min, OD-H).

3-(3-Chloro-phenyl)-1-cyclohex-1-enyl-pent-1-en-3-ol (S13). $t_1 = 19.1$ min, $t_2 = 20.6$ min (hexanes /2-propanol : 98 / 2, 0.5 mL/min, OD-H).

3-(4-Chloro-phenyl)-1-cyclohex-1-enyl-pent-1-en-3-ol (S14). $t_1 = 14.6$ min, $t_2 = 16.2$ min (hexanes /2-propanol : 98 / 2, 0.5 mL/min, OD-H).

4-Methyl-2-phenyl-pent-3-en-2-ol (S17). $t_1 = 14.2$ min, $t_2 = 15.2$ min (hexanes /2-propanol : 99.2 / 0.8, 0.5 mL/min, AS).

3-(3-Chloro-phenyl)-5-methyl-hex-4-en-3-ol (S18). $t_1 = 15.6$ min, $t_2 = 17.5$ min (hexanes /2-propanol : 99.5 / 0.5, 0.5 mL/min, OD-H).

The allylic alcohols **S1**, **S4**, **S8-9**, **S15-S16** and **S19-20** 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 μ m 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.

2,2-Dimethyl-propionic acid 4-hydroxy-4-phenyl-pent-2-enyl ester (S1). $t_1 = 57.9$ min, $t_2 = 60.2$ min (160°C, 1.0 mL/min).

2-Bromo-1-hex-1-enyl-cyclohex-2-enol (S4). $t_1 = 32.3$ min, $t_2 = 33.4$ min (145°C, 1.0 mL/min).

6-Methyl-2-*m*-tolyl-dodeca-3, 5-dien-2-ol (S8). $t_1 = 134.3$ min, $t_2 = 137.4$ min (170°C, 1.0 mL/min).

6-Methyl-2-(3-trifluoromethyl-phenyl)-dodeca-3, 5-dien-2-ol (S9). $t_1 = 153.6$ min, $t_2 = 157.5$ min (165°C, 1.0 mL/min).

4-Cyclohex-1-enyl-2-*m*-tolyl-but-3-en-2-ol (S15). $t_1 = 119.1$ min, $t_2 = 124.3$ min (150°C, 1.0 mL/min).

1-Cyclohex-1-enyl-3,4-dimethyl-pent-1-en-3-ol (S16). $t_1 = 46.7$ min, $t_2 = 48.5$ min (135°C, 1.0 mL/min).

2, 4, 4-Trimethyl-1-(2-methyl-propenyl)-cyclohex-2-enol (S19). $t_1 = 5.0$ min, $t_2 = 5.2$ min (165°C, 1.0 mL/min).

2-Cyclohex-1-enyl-4-methyl-pent-3-en-2-ol (S20). $t_1 = 39.1$ min, $t_2 = 40.3$ min (115°C, 1.0 mL/min).

Determination of the Absolute Configuration

(S)-2-phenyl-oct-3-en-2-ol (entries 1 and 2 in Table 2) Determined with the products by further transformation in eq. 1.³

$[\alpha]_D^{20} = -6.95$ (c 2.0, Et₂O); lit.⁴ (S)-diol: $[\alpha]_D^{20} = 8.94$ (c 6.8, Et₂O).

The absolute configuration of the product diol should have the opposite assignment compared to the starting compound; therefore, a diol with configuration (R) will be produced from an allylic alcohol of absolute configuration (S).

(S)-4-cyclopropyl-2-phenyl-but-3-en-2-ol (entry 3 in Table 2) Determined with the products by further transformation in eq. 1³

$[\alpha]_D^{20} = -8.33$ (c 2.1, Et₂O); lit.⁴ (S)-diol: $[\alpha]_D^{20} = 8.94$ (c 6.8, Et₂O).

(S)-5-(*tert*-butyl-diphenyl-silanyloxy)-2-phenyl-pent-3-en-2-ol (entries 4 and 5 in Table 2)

Determined with the products by further transformation in eq. 1³

$[\alpha]_D^{20} = -9.20$ (c 1.0, Et₂O); lit.⁴ (S)-diol: $[\alpha]_D^{20} = 8.94$ (c 6.8, Et₂O).

(S)-2,4-diphenyl-but-3-en-2-ol (entries 6 and 7 in Table 2) Determined with the products by further transformation in eq. 1³

$[\alpha]_D^{20} = -5.33$ (c 0.6, Et₂O); lit.⁴ (S)-diol: $[\alpha]_D^{20} = 8.94$ (c 6.8, Et₂O).

(S)-2,2-dimethyl-propionic acid 4-hydroxy-4-phenyl-pent-2-enyl ester (entries 8 and 9 in Table 2) Determined with the products by further transformation in eq. 1³

$[\alpha]_{\text{D}}^{20} = -6.53$ (*c* 1.7, Et₂O); lit.⁴ (S)-diol: $[\alpha]_{\text{D}}^{20} = 8.94$ (*c* 6.8, Et₂O).

(S)-5-methyl-2-phenyl-hexa-3, 5-dien-2-ol (entry 1 in Table 4) Determined with the products by further transformation in eq. 1³

$[\alpha]_{\text{D}}^{20} = -7.42$ (*c* 1.2, Et₂O); lit.⁴ (S)-diol: $[\alpha]_{\text{D}}^{20} = 8.94$ (*c* 6.8, Et₂O).

(S)-4-cyclohex-1-enyl-2-phenyl-but-3-en-2-ol (entry 2 in Table 4) Determined with the products by further transformation in eq. 1³

$[\alpha]_{\text{D}}^{20} = -6.80$ (*c* 0.5, Et₂O); lit.⁴ (S)-diol: $[\alpha]_{\text{D}}^{20} = 8.94$ (*c* 6.8, Et₂O).

(S)-4-methyl-2-phenyl-pent-3-en-2-ol (entries 1 and 2 in Table 5) Determined with the products by further transformation in eq. 1³

$[\alpha]_{\text{D}}^{20} = -6.86$ (*c* 1.4, Et₂O); lit.⁴ (S)-diol: $[\alpha]_{\text{D}}^{20} = 8.94$ (*c* 6.8, Et₂O).

(S)-3-phenyl-non-4-en-3-ol (entry 17 in Table 2) Determined with the products by further transformation in eq. 2³

$[\alpha]_{\text{D}}^{20} = +10.23$ (*c* 2.2, EtOH); lit.^{5,6} (S)-diol: $[\alpha]_{\text{D}}^{20} = -11.4$ (*c* 3.7, EtOH).

All the above absolute configuration of the compound was based on the (R,R)-ligand **1**; the compounds with opposite absolute configuration can also be prepared using (S,S)-ligand **1**.

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