Supplementary Material (ESI) for Chemical Communications

Supporting Information

Rhodium-catalysed substitutive arylation of *cis*-allylic diols with arylboroxines

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General. Infrared spectra were recorded on a Shimadzu FTIR-8100 spectrometer. Unless otherwise noted, ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Gemini 2000 (^{1}H at 300 MHz and ^{13}C at 75 MHz) spectrometer using $CHCl_3$ (^{1}H, δ = 7.26) and $CDCl_3$ (^{13}C, δ =77.0) as an internal standard. High-resolution mass spectra were recorded on a JEOL JMS-SX102A spectrometer. Preparative thin-layer chromatography was performed with silica gel 60 PF_{254} (Merck).

Materials. Unless otherwise noted, all chemicals and anhydrous solvents were obtained from commercial suppliers and used as received. 1,4-Dioxane was freshly distilled from sodium benzophenone ketyl. $[Rh(OH)(cod)_2]_2$ was prepared according to the reported procedure.[1] *cis*-But-2-ene-1,4-diol (**1a**) and *cis*-cyclopent-4-ene-1,3-diol (**1b**) were purchased from Nacalai Tesque, Inc. and Fluka. Arylboroxines **2a**–**2f** and alkenylboroxine **2g** were prepared from the commercially available boronic acids by azeotropic removal of water from its toluene solution and purified by washing the crude boroxines repeatedly with hexane.[2]

General procedure for the rhodium-catalysed substitutive arylation of *cis*-allylic diols

To an oven-dried, Ar-purged flask was added arylboroxine (**2**, 0.57 mmol, 3.0 equiv B) and $[Rh(OH)(cod)]_2$ (0.014 mmol, 5 mol% Rh). Then, a solution of substrate **1** (0.56 mmol, 1.0 equiv) in 1,4-dioxane (5 mL) was added. The resulting reaction mixture was stirred for 12 h at room temperature. An aqueous solution of 2 M NaOH (6 mL) was added, and the aqueous layer was extracted with diethyl ether (15 mL x 4). The combined extracts were dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (hexane:ethyl acetate) to give the product **3**.

2-Phenyl-but-3-en-1-ol (3aa)[3]
IR (neat): 3366, 3029, 1638, 1601, 1493, 1453, 1055 cm^{-1}; ^{1}H NMR: δ = 1.47 (t, *J* = 6.3 Hz, 1H), 3.54 (q, *J* = 7.2 Hz, 1H), 3.83 (t, *J* = 6.5 Hz, 2H), 5.14–5.25 (m, 2H), 6.01 (ddd, *J* = 7.6, 10.4, 17.0 Hz, 1H), 7.20–7.38 (m, 5H); ^{13}C NMR: δ = 52.5, 66.1, 117.0, 126.8, 127.8, 128.6, 138.1, 140.5; HRMS (EI^{+}): Calcd for $C_{10}H_{12}O$, M^{+} 148.0888. Found m/z 148.0889.

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2-(4-Methylphenyl)-but-3-en-1-ol (3ab)[3]
IR (neat): 3374, 3081, 1638, 1514, 1412, 1055 cm^{-1}; ^1H NMR: δ = 1.46 (t, *J* = 6.3 Hz, 1H), 2.33 (s, 3H), 3.50 (q, *J* = 7.3 Hz, 1H), 3.81 (t, *J* = 6.3 Hz, 2H), 5.13–5.23 (m, 2H), 5.99 (ddd, *J* = 7.7, 10.7, 17.1 Hz, 1H), 7.09–7.18 (m, 4H); ^{13}C NMR: δ = 21.0, 52.1, 66.1, 116.8, 127.7, 129.4, 136.5, 137.4, 138.3; HRMS (EI^+): Calcd for $C_{11}H_{14}O$, M^+ 162.1045. Found m/z 162.1048.

2-(4-Fluorophenyl)-but-3-en-1-ol (3ac)
IR (neat): 3378, 3081, 1603, 1509, 1225, 1057 cm^{-1}; ^1H NMR: δ = 1.45 (t, *J* = 6.3 Hz, 1H), 3.52 (q, *J* = 7.2 Hz, 1H), 3.81 (t, *J* = 6.5 Hz, 2H), 5.13–5.25 (m, 2H), 5.98 (ddd, *J* = 7.5, 10.5, 17.3 Hz, 1H), 6.98–7.07 (m, 2H), 7.16–7.24 (m, 2H); ^{13}C NMR: δ = 51.6, 66.0, 115.4 (d, *J* = 21.2 Hz), 117.1, 129.3 (d, *J* = 7.3 Hz), 136.2 (d, *J* = 3.6 Hz), 137.9, 161.6 (d, *J* = 243.2 Hz); HRMS (EI^+): Calcd for $C_{10}H_{11}FO$, M^+ 166.0794. Found m/z 166.0793.

2-(3-Methoxyphenyl)-but-3-en-1-ol (3ad)[4]
IR (neat): 3384, 3079, 1601, 1489, 1262, 1156, 1048 cm^{-1}; ^1H NMR: δ = 1.47 (t, *J* = 6.5 Hz, 1H), 3.50 (q, *J* = 7.2 Hz, 1H), 3.78–3.85 (m, 5H), 5.14–5.24 (m, 2H), 5.99 (ddd, *J* = 7.7, 10.6, 16.7 Hz, 1H), 6.76–6.86 (m, 3H), 7.22–7.30 (m, 1H); ^{13}C NMR: δ = 52.5, 55.1, 65.9, 111.9, 113.8, 117.0, 120.1, 129.6, 138.0, 142.2, 159.7; HRMS (EI^+): Calcd for $C_{11}H_{14}O_2$, M^+ 178.0994. Found m/z 178.0996.

2-(3-Chlorophenyl)-but-3-en-1-ol (3ae)
IR (neat): 3374, 3081, 1597, 1478, 1080 cm^{-1}; ^1H NMR: δ = 1.49 (t, *J* = 5.9 Hz, 1H), 3.51 (q, *J* = 7.3 Hz, 1H), 3.82 (t, *J* = 6.3 Hz, 2H), 5.15–5.27 (m, 2H), 5.97 (ddd, *J* = 7.7, 10.3, 17.1 Hz, 1H), 7.10–7.15 (m, 1H), 7.20–7.30 (m, 3H); ^{13}C NMR: δ = 52.1, 65.8, 117.6, 126.1, 127.0, 128.1, 129.9, 134.4, 137.4, 142.7; HRMS (EI^+): Calcd for $C_{10}H_{11}ClO$, M^+ 182.0498. Found m/z 182.0502.

2-(1-Naphthyl)-but-3-en-1-ol (3af)
IR (neat): 3386, 3048, 1597, 1510, 1397, 1036 cm^{-1}; ^1H NMR: δ = 3.94–4.10 (m, 2H), 4.41 (q, *J* = 7.0 Hz, 1H), 5.23–5.31 (m, 2H), 6.08–6.21 (m, 1H), 7.38–7.57 (m, 4H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.86–7.90 (m, 1H), 8.14 (d, *J* = 7.5 Hz, 1H) (–O<u>H</u> missing); ^{13}C NMR: δ = 47.0, 65.4, 117.2, 123.1, 124.2, 125.3, 125.5, 126.0, 127.3, 128.8, 131.7, 133.9, 136.3, 138.1; HRMS (EI^+): Calcd for $C_{14}H_{14}O$, M^+ 198.1045. Found m/z 198.1047.

(*E*)-4-phenyl-2-vinylbut-3-en-1-ol (3ag)[5]
IR (neat): 3382, 3081, 1638, 1495, 1449, 1048 cm^{-1}; ^1H NMR: δ = 1.54 (t, *J* = 6.6 Hz, 1H), 3.08–3.20 (m, 1H), 3.66 (t, *J* = 6.5 Hz, 2H), 5.17–5.21 (m, 1H), 5.22–5.26 (m, 1H), 5.77–5.91 (m, 1H), 6.14 (dd, *J* = 8.0, 16.1 Hz, 1H), 6.51 (d, *J* = 15.9 Hz, 1H), 7.21–7.41 (m, 5H); ^{13}C NMR: δ = 50.1, 65.2, 99.6, 117.2, 126.1, 127.4, 128.5, 132.2, 136.9, 137.2; HRMS (EI^+): Calcd for $C_{12}H_{14}O$, M^+ 174.1045. Found m/z 174.1044.

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***trans*-2-Phenyl-cyclopent-3-en-1-ol (3ba)**[5]
IR (neat): 3355, 3060, 1601, 1491, 1318, 1076 cm^{-1}; ^1H NMR (400 MHz): δ = 2.00 (br s, 1H), 2.33–2.41 (m, 1H), 2.75–2.84 (m, 1H), 3.73–3.77 (m, 1H), 4.24–4.30 (m, 1H), 5.75–5.79 (m, 1H), 5.87–5.92 (m, 1H), 7.16–7.34 (m, 5H); ^{13}C NMR (100 MHz): δ = 41.3, 60.7, 81.0, 126.6, 127.3, 128.6, 129.5, 132.2, 142.5; HRMS (EI^+): Calcd for $C_{11}H_{12}O$, M^+ 160.0888. Found m/z 160.0886.

***trans*-2-(3-Methoxyphenyl)-cyclopent-3-en-1-ol (3bd)**
IR (neat): 3374, 3056, 1601, 1487, 1264, 1157, 1051 cm^{-1}; ^1H NMR: δ = 1.88 (br s, 1H), 2.31–2.42 (m, 1H), 2.74–2.86 (m, 1H), 3.71–3.77 (m, 1H), 3.80 (s, 3H), 4.23–4.33 (m, 1H), 5.73–5.80 (m, 1H), 5.87–5.93 (m, 1H), 6.71–6.81 (m, 3H), 7.23 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR: δ = 41.3, 55.2, 60.7, 80.8, 111.8, 113.0, 119.7, 129.4, 129.5, 132.0, 144.1, 159.7; HRMS (EI^+): Calcd for $C_{12}H_{14}O_2$, M^+ 190.0994. Found m/z 190.0996.

3-Phenylbut-3-en-1-ol (4aa)[6]
^1H NMR: δ = 2.80 (dt, *J* = 0.9, 6.3 Hz, 2H), 3.73 (t, *J* = 6.3 Hz, 2H), 5.17 (d, *J* = 1.2 Hz, 1H), 5.42 (d, *J* = 1.5 Hz, 1H), 7.23–7.42 (m, 5H) (–O<u>H</u> missing).

Cyclic *cis*-allylic diol A[7]
^1H NMR (C_6D_6: δ = 7.15): δ = 4.09–4.30 (m, 4H), 5.52–5.63 (m, 2H), 7.23–7.33 (m, 3H), 8.06–8.17 (m, 2H); ^{13}C NMR (C_6D_6: δ = 128.6): δ = 62.0, 128.4, 131.4, 133.4, 135.3 (–B<u>C</u> missing); HRMS (EI^+): Calcd for $C_{10}H_{11}BO_2$, M^+ 174.0852. Found m/z 174.0853.

<u>General procedure for the asymmetric arylative addition catalyzed by a rhodium(I) complex</u>

To an oven-dried, Ar-purged flask were added $[RhCl(C_2H_4)]_2$ (0.14 mmol, 5 mol% Rh), arylboroxines **2** (0.99 mmol, 5.0 equiv B) and KOH (0.29 mmol, 0.5 equiv). Then, a solution of chiral diene ligand **9** (0.33 mmol, 5.5 mol%) in dioxane (2 mL), prepared from *R*-(–)-carvone, was added at room temperature. After being stirred for 20 min at 40 °C, a solution of **1** (0.57 mmol, 1 equiv) in dioxane (3 mL) was added. The resulting reaction mixture was stirred for 2 d at 40 °C. An aqueous solution of 2 M NaOH (6 mL) was added, and the aqueous layer was extracted with diethyl ether (15 mL x 4). The combined extracts were dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (hexane:ethyl acetate) to give the product **3**.

3aa:[8] a Daicel Chiralcel OD-H column with hexane:isopropanol = 95:5, flow rate = 0.6 mL/min, λ = 254 nm. Retention times: 29.9 min, 35.4 min.
$[\alpha]^{27}_D$ +37.4 (c 1.04, $CHCl_3$) for the sample of 83 % ee.

3ad: a Daicel Chiralcel OD-H column with hexane:isopropanol = 96:4, flow rate = 0.6 mL/min, λ = 220 nm. Retention times: 22.9 min, 24.6 min.
$[\alpha]^{29}_D$ +29.5 (c 1.07, $CHCl_3$) for the sample of 53 % ee.

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3af: a Daicel Chiralcel OD-H column with hexane:isopropanol = 95:5, flow rate = 0.6 mL/min, λ = 220 nm. Retention times: 26.4 min, 40.0 min.
$[\alpha]^{29}_{D}$ –5.5 (c 1.01, $CHCl_3$) for the sample of 88 % ee.

3bd: a Daicel Chiralcel OD-H column with hexane:isopropanol = 93:7, flow rate = 0.6 mL/min, λ = 220 nm. Retention times: 16.9 min, 25.5 min.
$[\alpha]^{27}_{D}$ –166.6 (c 1.11, $CHCl_3$) for the sample of 78 % ee.