# **Supporting Information**

# Asymmetric Synthesis of $\alpha$ -Chiral $\beta$ -Hydroxy Allenes: Copper-Catalyzed y-Selective Borylative Coupling of Vinyl **Arenes and Propargyl Phosphates**

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#### **General Methods**

CuCl, LiO*t*Bu, bis(pinacolato)diboron, and other commercial reagents were purchased from Aldrich and used as received. (*R*,*S*)-Josiphos (L8) was purchased from Strem. 1g<sup>1</sup>, 1h<sup>2</sup>, 1i<sup>3</sup>, 1j<sup>4</sup>, 1k<sup>5</sup>, 2a–2h<sup>6</sup> were prepared by following literature procedures. Reactions with oxygen- and moisture-sensitive materials were carried out with standard Schlenk technique. DMA was distilled from calcium hydride under nitrogen. Flash chromatography was performed on silica gel from Merck (70–230 mesh). Deactivated silica gel was prepared by stirring a slurry of the silica gel in a NaOAc aqueous solution for 30 minutes. Then, the deactivated silica gel was collected by filtration and then dried in a 120 °C oven for 3 days. All <sup>1</sup>H NMR spectra were obtained on Bruker at 500 systems and reported in parts per million (ppm) downfield from tetramethylsilane. <sup>13</sup>C NMR spectra are reported in ppm referenced to deuteriochloroform (77.16 ppm). Infrared spectra (IR) were obtained on Nicolet 205 FT-IR and were recorded in cm<sup>-1</sup>. Optical rotation was measured with Model 343 plus polarimeter equipped with a sodium lamp (589 nm). High performance liquid chromatography (HPLC) was performed using Younglin Acme 9100 series. High resolution mass spectra (HRMS) were obtained at Korea Basic Science Institute (Cheongju, Korea) and reported in the form of *m/z* (intensity relative to peak = 100).

# General Procedure for the Copper-Catalyzed Allenylboration of Vinyl Arenes with Propargylic Phosphates



A mixture of CuCl (5 mol %, 0.025 mmol), (*R*,*S*)-Josiphos (5.5 mol %, 0.0275 mmol), bis(pinacolato)diboron (1.5 equiv, 0.75 mmol) and LiO*t*Bu (1.5 equiv, 0.75 mmol) in DMA (0.5 mL) were stirred for 15 min in a Schlenk tube under an atmosphere of nitrogen. Substrate **1** dissolved in DMA (0.5mL) and **2** (1.5 equiv, 0.75 mmol) were added to the reaction mixture. The reaction mixture was stirred at room temperature and monitored by TLC. Upon completion of the reaction, the reaction mixture was diluted with diethyl ether (10 mL). The aqueous layer was extracted with diethyl ether, and the combined organic layers were dried over  $Na_2SO_4$  and concentrated in vacuo. To the mixture was in THF (2 mL) and water (2 mL) was added sodium perborate (3 equiv). The reaction mixture was

vigorously stirred for 5 h at room temperature. After the reaction was quenched with water and then, extracted with diethyl ether. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The product **4** was purified by silica gel chromatography. Rapid silica gel chromatography within 10 minutes is critical for reproducible yields due to instability of allenols on silica gel.

#### **Characterization of 4**

Me

4ba

 (S)-2,3-diphenylpenta-3,4-dien-1-ol: By following the general procedure, 4aa was obtained in 79% yield (pale yellow oil). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.37– 7.34 (m, 4H), 7.31–7.28 (m, 2H), 7.24–7.20 (m, 3H), 7.24–7.20 (m, 3H), 7.15– 7.12 (m, 1H), 5.35 (s, 2H), 4.03–3.96 (m, 2H), 3.86–3.81 (m, 1H), 1.70 (brs, 1H);
 <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 208.3, 140.3, 135.5, 128.7, 128.4, 128.3, 127.2, 126.9, 105.7, 80.4, 66.9, 48.4; IR (neat) 3386, 3014, 2935, 1254 cm<sup>-1</sup>; HRMS

(ESI) calcd for  $[C_{17}H_{16}O+H^+]$ : 237.1279, found: 237.1280; 95:5 er were measured by chiral HPLC on AD-H column (*i*-PrOH:hexane = 1:99, 1.0 mL/min);  $t_{R}$  = 34.49 min (minor),  $t_{R}$  = 39.51 min (major).



(S)-3-phenyl-2-(o-tolyl)penta-3,4-dien-1-ol: By following the general procedure,
4ba was obtained in 62% yield (pale yellow oil). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ
7.34–7.33 (m, 2H), 7.29–7.26 (m, 2H), 7.24–7.22 (m, 2H), 7.21–7.18 (m, 1H),
7.03–7.01 (m, 2H), 5.31 (s, 2H), 4.02–3.93 (m, 2H), 3.86–3.73 (m, 1H), 2.24 (s,
3H), 1.84 (brs, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 208.1,140.5, 136.7, 132.5,
131.5, 129.2, 128.7, 128.3, 127.1, 126.5, 105.6, 80.3, 67.0, 48.4, 21.0; IR (neat)

3396, 3028, 2928, 1276 cm<sup>-1</sup>; HRMS (ESI) calcd for [C<sub>18</sub>H<sub>18</sub>O+H<sup>+</sup>]: 251.1436, found: 251.1432; 96:4

er were measured by chiral HPLC on AD-H column (*i*-PrOH:hexane = 1:99, 1.0 mL/min);  $t_{\rm R}$  = 28.04 min (minor),  $t_{\rm R}$  = 31.16 min (major).



CI OH 4ca (*S*)-2-(3-chlorophenyl)-3-phenylpenta-3,4-dien-1-ol: By following the general procedure, 4ca was obtained in 74% yield (colorless oil). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.33–7.32 (m, 3H), 7.27–7.22 (m, 5H), 7.21–7.18 (m, 1H), 7.17–7.14 (m, 1H), 5.36 (s, 2H), 3.98–3.95 (m, 2H), 3.83–3.78 (m, 1H), 1.72 (brs, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 208.3, 142.6, 134.6, 131.6, 130.0,

128.5, 128.3, 127.4, 127.1, 126.6, 126.5, 105.4, 80.7, 66.7, 48.1; IR (neat) 3262, 3124, 2885, 1522 cm<sup>-1</sup>; HRMS (ESI) calcd for  $[C_{17}H_{15}OCI+H^+]$ : 271.0890, found: 271.0892; 92:8 er was measured by chiral HPLC on OJ-H column (*i*-PrOH:hexane = 1:99, 1.0 mL/min);  $t_R = 6.61$  min (major),  $t_R = 7.83$  min (major).







(*S*)-2-(4-fluorophenyl)-3-phenylpenta-3,4-dien-1-ol: By following the general procedure, 4da was obtained in 74% yield (pale yellow oil). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.34–7.28 (m, 7H), 7.25–7.21 (m, 1H), 6.93–6.89 (m, 2H), 5.35 (s, 2H), 3.99–3.93 (m, 2H), 3.84–3.80 (m, 1H), 1.67 (brs, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 208.0, 161.8 (d, J = 245.1 Hz), 140.0, 133.3 (d, J = 8.1 Hz), 128.8,

128.2, 128.1 (d, J = 7.9 Hz), 127.3, 115.3 (d, J = 21.5 Hz), 104.9, 80.6, 66.9, 48.6; IR (neat) 3146, 3025, 2925, 1578 cm<sup>-1</sup>; HRMS (ESI) calcd for [C<sub>17</sub>H<sub>15</sub>OF+H<sup>+</sup>]: 255.1185, found: 255.1187; 92:8 er was measured by chiral HPLC on AD-H column (*i*-PrOH:hexane = 1:99, 1.0 mL/min);  $t_{\rm R} = 43.95$  min (major),  $t_{\rm R} = 53.54$  min (major).



Me 4ea

(S)-3-phenyl-2-(p-tolyl)penta-3,4-dien-1-ol: By following the general procedure, 4ea was obtained in 62% yield (pale yellow oil). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.36–7.34 (m, 2H), 7.25–7.21 (m, 4H), 7.15–7.10 (m, 3H), 5.35 (s, 2H), 3.99–3.94 (m, 2H), 3.82–3.78 (m, 1H), 2.30 (s, 3H), 1.68 (brs, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 208.2, 137.1, 136.8, 135.6, 131.6, 129.5, 128.4,

126.9, 126.5, 105.8, 80.4, 67.0, 47.9, 21.1; IR (neat) 3390, 3052, 2837, 1360 cm<sup>-1</sup>; HRMS (ESI) calcd for [C<sub>18</sub>H<sub>18</sub>O+H<sup>+</sup>]: 251.1436, found: 251.1435; 96:4 er was measured by chiral HPLC on OD-H column (*i*-PrOH:hexane = 1:99, 1.0 mL/min);  $t_{\rm R}$  = 4.43 min (major),  $t_{\rm R}$  = 4.72 min (minor).



RT[분]	면적[mV*sec]	면적비[%]
4,4333	5153,5031	50, 51
83	5049, 1250	49,49

(S)-2-(4-methoxyphenyl)-3-phenylpenta-3,4-dien-1-ol: By following the general procedure, 4fa was obtained in 59% yield (pale yellow oil). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.35–7.34 (m, 2H), 7.28–7.21 (m, 5H), 7.15–7.12 (m, 1H), 6.85–6.82 (m, 2H), 5.33 (s, 2H), 3.97–3.93 (m, 2H), 3.80–3.78 (m, 1H), 3.76 (s, 3H), 1.68 (brs, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 208.2, 158.7,

135.6, 132.2, 129.2, 128.4, 126.9, 126.6, 114.2, 105.9, 80.3, 67.0, 55.2, 47.5; IR (neat) 3390, 3076, 2935, 1462 cm<sup>-1</sup>; HRMS (ESI) calcd for  $[C_{18}H_{18}O_2+H^+]$ : 267.1385, found: 267.1382; 98:2 er was measured by chiral HPLC on AS-H column (*i*-PrOH:hexane = 10:90, 1.0 mL/min);  $t_{\rm R}$  = 15.46 min (major),  $t_{\rm R}$  = 15.98 min (minor).



(*S*)-2-(4-(methylthio)phenyl)-3-phenylpenta-3,4-dien-1-ol: By following the general procedure, 4ga was obtained in 65% yield (pale yellow oil). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.34–7.32 (m, 2H), 7.28–7.23 (m, 4H), 7.20–7.18 (m, 2H), 7.16–7.13 (m, 1H), 5.35 (s, 2H), 3.99–3.97 (m, 2H), 3.82–3.78 (m, 1H), 2.44 (s, 3H), 1.68 (brs, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 208.2, 137.1,

135.4, 131.5, 128.7, 128.4, 126.9, 126.5, 105.6, 80.5, 66.8, 47.8, 29.7, 15.8; IR (neat) 3390, 3076, 2935, 1462 cm<sup>-1</sup>; HRMS (ESI) calcd for [C<sub>18</sub>H<sub>18</sub>OS+Na<sup>+</sup>]: 305.0976, found: 305.0980; 90:10 er was measured by chiral HPLC on OZ-H column (*i*-PrOH:hexane = 10:90, 1.0 mL/min);  $t_{\rm R}$  = 10.74 min (minor),  $t_{\rm R}$  = 14.83 min (major).

.OH

4ga

MeS



(*S*)-2-(benzo[*d*][1,3]dioxol-5-yl)-3-phenylpenta-3,4-die-1-ol: By following the general procedure, **4ha** was obtained in 64% yield (pale yellow oil). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.35–7.34 (m, 2H), 7.25–7.22 (m, 2H), 7.16–7.13 (m, 1H), 6.83–6.81 (m, 2H), 6.74–6.72 (m, 1H), 5.90 (d, *J* = 6.0 Hz, 2H), 5.34 (s, 2H), 3.95–3.90 (m, 2H), 3.79–3.73 (m, 1H), 1.75 (brs, 1H); <sup>13</sup>C NMR (125 MHz,

CDCl<sub>3</sub>)  $\delta$  208.1, 148.0, 146.7, 135.4, 134.1, 131.5, 128.4, 127.0, 126.5, 121.6, 108.4, 108.3, 105.9, 101.0, 80.4, 66.9, 48.0; IR (neat) 3375, 2925, 2870, 1488 cm<sup>-1</sup>; HRMS (ESI) calcd for [C<sub>18</sub>H<sub>16</sub>O<sub>3</sub>+H<sup>+</sup>]: 281.1178, found: 281.1180; 96:4 er was measured by chiral HPLC on AD-H column (*i*-PrOH:hexane = 5:95, 1.0 mL/min);  $t_{\rm R}$  = 27.72 min (minor),  $t_{\rm R}$  = 33.85 min (major).





OH

4ha

റ

(*R*)-tert-butyl 3-(1-hydroxy-3-phenylpenta-3,4-dien-2-yl)-1H-indole-1carboxylate: By following the general procedure, 4ia was obtained in 58% yield (pale yellow oil). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.09 (brs, 1H), 7.39 (d, J = 7.5 Hz, 2H), 7.33–7.30 (m, 2H), 7.27–7.23 (m, 4H), 7.17–7.14 (m, 1H), 5.35–5.28 (m, 2H), 4.28–4.25 (m, 1H), 4.07–4.01 (m, 2H), 1.64 (s, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  208.1, 135.4, 131.6, 129.8, 128.5, 128.2, 127.1, 126.4, 124.5, 124.2, 122.6, 122.5, 119.6, 119.2, 115.5, 105.5, 80.7, 65.4, 39.7, 28.2; IR (neat) 3375, 2925, 2870, 1488 cm<sup>-1</sup>; HRMS (ESI) calcd for [C<sub>24</sub>H<sub>25</sub>NO<sub>3</sub>+H<sup>+</sup>]: 376.1913, found: 376.1910; 98:2 er was measured by chiral HPLC on OD-H column (*i*-PrOH:hexane = 1:99, 1.0 mL/min);  $t_{\rm R}$  = 28.22 min (major),  $t_{\rm R}$  = 48.92 min (minor).



(*R*)-3-phenyl-2-(thiophen-3-yl)penta-3,4-dien-1-ol: By following the general procedure, **4ja** was obtained in 57% yield (pale yellow oil). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.37–7.36 (m, 3H), 7.28–7.27 (m, 2H), 7.17–7.15 (m, 2H), 7.06 (d, *J* = 4.5 Hz, 1H), 5.29 (s, 2H), 4.13–4.10 (m, 1H), 3.98–3.94 (m, 1H), 3.88–3.84 (m, 1H), 1.69 (brs, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 208.0, 141.2, 135.5, 131.6,

128.4, 127.3, 126.4, 122.2, 106.1, 80.4, 66.2, 43.8, 29.7; IR (neat) 3388, 2927, 1640, 1512, 1206 cm<sup>-1</sup>; HRMS (ESI) calcd for [ $C_{15}H_{14}OS+H^+$ ]: 243.0844, found: 243.0841; 98:2 er was measured by chiral HPLC on OD-H column (*i*-PrOH:hexane = 5:95, 1.0 mL/min);  $t_R$  = 11.67 min (major),  $t_R$  = 19.78 min (minor).

OH

4ja





4ka

(*R*)-2-(benzofuran-3-yl)-3-phenylpenta-3,4-dien-1-ol: By following the general procedure, **4ka** was obtained in 70% yield (pale yellow oil). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.68–7.66 (m, 1H), 7.52 (s, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.41–7.40 (m, 2H), 7.30–7.25 (m, 4H), 7.19–7.16 (m, 1H), 5.34–5.27 (m, 2H), 4.26–4.23 (m, 1H), 4.09–4.06 (m, 2H), 1.81 (brs, 1H); <sup>13</sup>C NMR (125 MHz,

CDCl<sub>3</sub>)  $\delta$  208.0, 155.6, 143.1, 131.6, 128.5, 128.3, 127.2, 126.4, 124.4, 122.6, 120.0, 119.4, 111.7, 105.1, 80.7, 65.1, 38.8; IR (neat) 3375, 2925, 2870, 1488 cm<sup>-1</sup>; HRMS (ESI) calcd for [C<sub>19</sub>H<sub>16</sub>O<sub>2</sub>+Na<sup>+</sup>]: 299.1048, found: 299.1048; 95:5 er was measured by chiral HPLC on AS-H column (*i*-PrOH:hexane = 1:99, 1.0 mL/min); *t*<sub>R</sub> = 9.89 min (major), *t*<sub>R</sub> = 10.71 min (minor).





(*S*)-2-phenyl-3-(p-tolyl)penta-3,4-dien-1-ol: By following the general procedure, **4ab** was obtained in 82% yield (pale yellow oil). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.35–7.33 (m, 2H), 7.30–7.27 (m, 2H), 7.24–7.19 (m, 3H), 7.03–7.02 (m, 2H), 5.32 (s, 2H), 4.00–3.94 (m, 2H), 3.83–3.79 (m, 1H), 2.25 (s, 3H), 1.74 (brs, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 208.1, 140.4, 136.7, 132.5, 129.1, 128.7, 128.3, 127.1, 126.4, 105.6, 80.3, 66.9, 48.4, 21.0; IR

(neat) 3393, 3085, 2928, 1647, 1267 cm<sup>-1</sup>; HRMS (ESI) calcd for  $[C_{18}H_{18}O+H^+]$ : 251.1436, found: 251.1440; 95:5 er was measured by chiral HPLC on AD-H column (*i*-PrOH:hexane = 1:99, 1.0 mL/min);  $t_R$  = 16.31 min (major),  $t_R$  = 24.62 min (minor).





[chiral]



(*S*)-3-(4-methoxyphenyl)-2-phenylpenta-3,4-dien-1-ol: By following the general procedure, **3ac** was obtained in 77% yield (pale yellow oil). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.35–7.33 (m, 2H), 7.30–7.24 (m, 4H), 7.22–7.19 (m, 1H), 6.76 (d, *J* = 9.0 Hz, 2H), 5.32 (s, 2H), 3.97–3.93 (m, 2H), 3.80–3.77 (m, 1H), 3.72 (s, 3H), 1.80 (brs, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 207.9, 158.6, 140.4, 128.7, 128.2, 127.7, 127.6, 127.2, 113.9, 105.2, 80.4, 55.2, 48.5; IR

(neat) 3396, 3071, 2928, 1625, 1275 cm<sup>-1</sup>; HRMS (ESI) calcd for  $[C_{18}H_{18}O2+H^+]$ : 267.1385, found: 267.1387; 85:15 er was measured by chiral HPLC on AD-H column (*i*-PrOH:hexane = 5:95, 1.0 mL/min);  $t_{\rm R}$  = 9.02 min (major),  $t_{\rm R}$  = 10.45 min (minor).







(*S*)-3-(4-fluorophenyl)-2-phenylpenta-3,4-dien-1-ol: By following the general procedure, **3ad** was obtained in 75% yield (pale yellow oil). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.34–7.27 (m, 6H), 7.24–7.21 (m, 1H), 6.92–6.89 (m, 2H), 5.34 (s, 2H), 3.98–3.93 (m, 2H), 3.83–3.78 (m, 1H), 1.77 (brs, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  208.0, 140.0, 133.3 (d, *J* = 8.1 Hz), 128.8, 128.2, 128.1 (d, *J* = 7.9 Hz), 127.3, 115.3 (d, *J* = 21.5 Hz), 104.9, 80.6, 66.9, 48.6;

IR (neat) 3382, 3086, 2940, 164.0, 1482 cm<sup>-1</sup>; HRMS (ESI) calcd for  $[C_{17}H_{15}OF+H^+]$ : 255.1185, found: 255.1187; 95:5 er was measured by chiral HPLC on AS-H column (*i*-PrOH:hexane = 1:99, 0.5 mL/min);  $t_{\rm R} = 6.91$  min (major),  $t_{\rm R} = 10.41$  min (minor).

F OH 4ad



(S)-2-phenyl-3-(o-tolyl)penta-3,4-dien-1-ol: By following the general procedure, 4ae was obtained in 69% yield (pale yellow oil). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ 7.29-7.20 (m, 5H), 7.10-7.02 (m, 3H), 7.02-7.01 (m, 1H), 5.01 (s, 2H), 4.07-4.02 (m, 1H), 3.89–3.84 (m, 1H), 3.71–3.68 (m, 1H), 2.23 (s, 3H), 1.68 (brs, 1H); OH. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 206.1, 139.9, 136.4, 136.1, 130.4, 128.5, 128.4, 128.3, 127.2, 127.1, 125.8, 104.6, 77.5, 66.1, 52.1, 20.1; IR (neat) 3364, 2942, 2861, 1479 cm<sup>-1</sup>; HRMS (ESI) calcd for [C18H18O+Na+]: 273.1255, found: 273.1255; 82:18 er was

measured by chiral HPLC on OD-H column (*i*-PrOH:hexane = 1:99, 1.0 mL/min);  $t_R$  = 19.03 min (major),  $t_{R} = 21.26$  min (minor).





Me

4ae

(S)-2-phenyl-3-(m-tolyl)penta-3,4-dien-1-ol: By following the general procedure, 4af was obtained in 58% yield (pale yellow oil). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ 7.36-7.34 (m, 2H), 7.31-7.28 (m, 2H), 7.23-7.19 (m, 2H), 7.12-7.09 (m, 2H), 6.95 (d, J = 6.5 Hz, 1H), 5.33 (s, 2H), 4.01–3.95 (m, 2H), 3.84–3.80 (m, 1H), 2.27 (s, 3H), 1.74 (brs, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 208.3, 140.4, 137.9,

135.4, 128.7, 128.3, 128.2, 127.8, 127.4, 127.2, 123.5, 105.8, 80.3, 66.9, 48.4, 21.5; IR (neat) 3378, 2945, 2872, 1468 cm<sup>-1</sup>; 95:5 er was measured by chiral HPLC on OZ-H column (*i*-PrOH:hexane = 1:99, 1.0 mL/min);  $t_{\rm R}$  = 5.00 min (minor),  $t_{\rm R}$  = 7.17 min (major).



H<sub>3</sub>C OH 4ag **(S)-3-methyl-2-phenylpenta-3,4-dien-1-ol:** By following the general procedure, **4ag** was obtained in 72% yield (colorless oil). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.33– 7.30 (m, 6H), 7.26–7.23 (m, 3H), 4.87–4.84 (m, 2H), 3.89–3.85 (m, 1H), 3.72– 3.68 (m, 1H), 3.31–3.27 (m, 1H), 1.74 (brs, 1H), 1.60 (dd, *J* = Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 205.6, 140.2, 128.6, 128.3, 127.2, 99.1, 66.1, 52.0, 18.4; IR

(neat) 3382, 3086, 2940, 164.0, 1482 cm<sup>-1</sup>; HRMS (ESI) calcd for  $[C_{12}H_{14}O+H^+]$ : 175.1123, found: 175.1120; 91:9 er was measured by chiral HPLC on OD-H column (*i*-PrOH:hexane = 1:99, 0.5 mL/min);  $t_{\rm R}$  = 22.97 min (minor),  $t_{\rm R}$  = 23.98 min (major).





(*R*)-2-phenyl-3-(trimethylsilyl)penta-3,4-dien-1-ol: By following the general procedure, 4ah was obtained in 59% yield (pale yellow oil). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.32–7.29 (m, 2H), 7.27–7.22 (m, 3H), 4.60–4.59 (m, 2H), 3.94–3.89 (m, 1H), 3.78–3.73 (m, 1H), 3.43–3.39 (m, 1H), 1.64 (brs, 1H), -0.05 (s, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ207.9, 128.5, 128.4, 127.9, 127.0, 70.7, 67.3, 47.9,

24.7, -1.6; IR (neat) 3382, 3086, 2940, 164.0, 1482 cm<sup>-1</sup>; HRMS (ESI) calcd for  $[C_{14}H_{20}OSi+H^+]$ : 233.1362, found: 233.1361; 95:5 er was measured by chiral HPLC on OD-H column (*i*-PrOH:hexane = 1:99, 1.0 mL/min);  $t_{\rm R}$  = 23.25 min (minor),  $t_{\rm R}$  = 35.62 min (major).



[chiral]



CH<sub>3</sub> (S)-5-methy CH<sub>3</sub> procedure, CH<sub>3</sub> CDCl<sub>3</sub>) ō 7. (m, 1H), 4. 4ai 3H), 1.92 (s

(*S*)-5-methyl-2,3-diphenylhexa-3,4-dien-1-ol: By following the general procedure, **4ai** as obtained in 51% yield (pale yellow oil). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.36–7.34 (m, 2H), 7.31–7.28 (m, 4H), 7.22–7.19 (m, 3H), 7.12–7.09 (m, 1H), 4.02–3.99 (m, 1H), 3.92–3.88 (m, 1H), 3.78–3.74 (m, 1H), 1.93 (s, 3H), 1.92 (s, 3H), 1.64 (brs, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 201.7, 140.7,

137.3, 128.7, 128.3, 128.2, 127.0, 126.6, 126.5, 104.0, 100.9, 67.3, 49.2, 20.6, 20.5; IR (neat) 3410, 2932, 2836, 1647, 1515 cm<sup>-1</sup>; HRMS (ESI) calcd for  $[C_{19}H_{20}O+H^+]$ : 265.1592, found: 265.1591; 90:10 er was measured by chiral HPLC on OD-H column (*i*-PrOH:hexane = 1:99, 1.0 mL/min);  $t_{\rm R}$  = 17.48 min (minor),  $t_{\rm R}$  = 18.38 min (major).



RT[분]	면적[mV*sec]	면적비[%]
17,5817	8137,0672	50,84
18,9900	7867,6586	49,16



(S)-2,3-diphenylhexa-3,4-dien-1-ol: By following the general procedure, 4aj as obtained in 97% yield (pale yellow oil). Major diastereomer: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.37–7.27 (m, 6H), 7.23–7.20 (m, 3H), 7.13–7.10 (m, 1H), 5.78–5.71 (m, 1H), 4.03–3.99 (m, 1H), 3.97–3.90 (m, 1H), 3.83–3.75 (m, 1H), 1.87 (d, *J* = 7.0 Hz, 3H), 1.64 (brs, 1H); minor diastereomer: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.37–7.27 (m, 6H), 7.23–7.20 (m, 3H), 7.13–7.10 (m, 1H), 5.78–5.71 (m, 1H),

4.03–3.99 (m, 1H), 3.97–3.90 (m, 1H), 3.83–3.75 (m, 1H), 1.90 (d, J = 7.0 Hz, 3H), 1.70 (brs, 1H); Major diastereomer: <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  204.7, 140.6, 136.5, 128.7, 128.3, 128.2, 127.1, 126.7, 126.6, 105.6, 91.2, 67.2, 48.8, 14.5; minor diastereomer: <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  204.4, 140.4, 136.5, 128.7, 128.3, 128.2, 127.1, 126.7, 126.6, 105.8, 91.3, 67.1, 49.0, 14.6; IR (neat) 3378, 3075, 2946, 1645, 1472 cm<sup>-1</sup>; HRMS (ESI) calcd for [C<sub>18</sub>H<sub>18</sub>O+Na<sup>+</sup>]: 273.1255, found: 273.1256; 95:5 er major diastereomer 98:2 er minor diastereomer were measured by chiral HPLC on AD-H column (*i*-PrOH:hexane = 1:99, 1.0 mL/min); major diastereomer:  $t_R = 27.73$  min (minor),  $t_R = 40.78$  min (major); major diastereomer:  $t_R = 33.49$  min (minor),  $t_R = 38.10$  min (major)





5862, 6852

60,04

41,6500

[rac]

#### Hammett Plot for the Reaction (Scheme 3)



For the allenol products derived from **1a**, **1d**, **1e**, **1f**, **2a**, **2b** and **2d**, enantiomeric ratio (er) values were obtained from Table 2. The log(er) for each substrate is shown below with a Hammett plot.



R	er	log(er)	<b>σ</b> para	
OMe	49	1.7	-0.27	
Ме	32	1.5	-0.14	
н	19	1.3	0	
F	12	1.1	0.15	



R	er	log(er)	$\sigma_{para}$	
Me	19	1.3	-0.14	
н	19	1.3	0	
F	19	1.3	0.15	

#### Gold-catalyzed cyclization of an allenol product (Scheme 5, (a))



A mixture of IPrAuCl (5 mol %, 0.015 mmol) and AgOTf (5 mol %, 0.015 mmol) in toluene (1 mL) was stirred at room temperature for 5 min. **4aa** (0.3 mmol) dissolved in toluene (1 mL) was added to the reaction mixture. The reaction mixture was stirred at room temperature and monitored by TLC. The crude mixture was filtered through a pad of Celite and concentrated. The product **5** was purified by silica gel chromatography. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.30–7.24 (m, 6H), 7.22–7.19 (m, 2H), 7.17–7.13 (m, 2H), 6.35–6.34 (m, 1H), 4.52–4.47 (m, 1H), 4.43–4.39 (m, 1H), 4.04 (dd, *J* = 11.0 Hz, 3.0 Hz, 1H), 3.86–3.85 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  142.1, 139.6, 136.4, 128.5, 128.4, 128.3, 127.1, 126.5, 125.6, 124.5, 71.5, 66.3, 43.3; 95:5 er was measured

by chiral HPLC on AS-H column (*i*-PrOH:hexane = 1:99, 0.7 mL/min);  $t_{\rm R}$  = 27.73 min (minor),  $t_{\rm R}$  = 33.86 min (major).



Palladium-Catalyzed Cyclization of an Allenol Product (Scheme 5, (b))



A mixture of Pd(OAc)<sub>2</sub> (5 mol %, 0.015 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (3 equiv, 0.015 mmol) in DMF (1 mL) and H<sub>2</sub>O (0.1 mL) was stirred at room temperature for 5 min. **4aa** (0.3 mmol) dissolved in DMF (1 mL) was added to the reaction mixture. The reaction mixture was stirred at 70 °C and monitored by TLC. The crude mixture was filtered through a pad of Celite and concentrated. The product **6** was purified by silica gel chromatography. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.27–7.22 (m, 4H), 7.19–7.15 (m, 3H), 7.10–7.09 (m, 2H), 6.06–7.03 (m, 1H), 4.70 (dd, *J* = 10.0 Hz, 8.5 Hz, 1H), 4.49–4.45 (m, 1H), 4.17 (dd, *J* = 8.5 Hz, 5.5 Hz, 1H), 2.14 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  152.6, 143.8, 135.2, 128.7, 128.2, 127.6, 127.1, 126.7, 125.3, 112.6, 52.3, 13.6; IR (neat) 3396, 3028, 2928, 1276 cm<sup>-1</sup>; HRMS (ESI) calcd for [C<sub>17</sub>H<sub>16</sub>O+H<sup>+</sup>]: 237.1279, found: 237.1275; 95:5 er was measured by chiral HPLC on AD-H column (*i*-PrOH:hexane = 1:99, 1.0 mL/min); *t*<sub>R</sub> = 15.53 min (major), *t*<sub>R</sub> = 17.42 min (minor).



**Determination of Absolute Configuration of 4ah** 



A mixture of CuCl (5 mol %, 0.05 mmol), (*R*,*S*)-Josiphos (5.5 mol %, 0.055 mmol), bis(pinacolato)diboron (1.5 equiv, 1.5 mmol) and LiO*t*Bu (1.5 equiv, 1.5 mmol) in DMA (1 mL) were stirred for 15 min in a Schlenk tube under an atmosphere of nitrogen. **1a** dissolved in DMA (1 mL) and **2h** (1.5 equiv, 1.5 mmol) were added to the reaction mixture. The reaction mixture was stirred at room temperature and monitored by TLC. Upon completion of the reaction, the reaction mixture was diluted with diethyl ether (15 mL). The aqueous layer was extracted with diethyl ether, and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. To the mixture in THF (2 mL) was added 1.0 M solution of TBAF in THF (3 equiv, 3 mmol) at -78 °C. The reaction mixture was stirred for 4 h at -78 °C. After the reaction was quenched with water and then, extracted with diethyl ether. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The corresponding boronate product was purified by silica gel chromatography. The resulting boronate in THF (2 mL) and

water (2 mL) was added sodium perborate (3 equiv). The reaction mixture was vigorously stirred for 5 h at room temperature. After the reaction was quenched with water and then, extracted with diethyl ether. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The resulting crude in MeOH (2 mL) was added to Pd/C (10 mol %) under H<sub>2</sub> (1 atm). The solution was stirred for 4 h at room temperature. The mixture was filtered by a pad of Celite and concentrated. The corresponding product **7** was purified by chromatography on silica gel. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.35–7.20 (m, 5H), 3.75–3.64 (m, 3H), 2.80–2.75 (m, 1H), 1.67–1.53 (m, 2H), 1.25–1.15 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  143.5, 128.6, 128.0, 124.8, 65.5, 48.2, 34.5, 20.2, 14.5; [ $\alpha$ ]<sub>D</sub> = -4.8 (c = 1.16, CHCl<sub>3</sub>), (lit.<sup>7</sup> [ $\alpha$ ]<sub>D</sub> = -7.8 (c = 1.16, CHCl<sub>3</sub>)); 95:5 er was measured by chiral HPLC on OZ-H column (*i*-PrOH:hexane = 1:99, 1.0 mL/min); *t*<sub>R</sub> = 11.73 min (minor), *t*<sub>R</sub> = 32.34 min (major).

## **Optimization Studies and Extra data**

## Table S1. Optimization (racemic conditions)





3aa

Entry	LG	Copper salt	Ligand	Base	Solvent	T (°C)	NMR vield (%)ª
1	OP(O)(OEt) <sub>2</sub>	CuCl	L1	LiO <i>t</i> Bu	THF	60	57
2	OP(O)(OEt) <sub>2</sub>	CuCl	L1	LiO <i>t</i> Bu	toluene	60	42
3	OP(O)(OEt) <sub>2</sub>	CuCl	L1	LiO <i>t</i> Bu	DMA	60	71
4	OP(O)(OEt) <sub>2</sub>	CuCl	L1	LiOMe	DMA	60	59
5	OP(O)(OEt) <sub>2</sub>	CuCl	L1	NaOMe	DMA	60	44
6	OP(O)(OEt) <sub>2</sub>	CuCl	L1	LiO <i>t</i> Bu	DMA	RT	84
7	OCO <sub>2</sub> Me	CuCl	L1	LiO <i>t</i> Bu	DMA	RT	46
8	OBn	CuCl	L1	LiO <i>t</i> Bu	DMA	RT	<10
9	OP(O)(OEt) <sub>2</sub>	CuTC	L1	LiO <i>t</i> Bu	DMA	RT	63
10	OP(O)(OEt) <sub>2</sub>	[Cu(CH <sub>3</sub> CN) <sub>4</sub> ]BF <sub>4</sub>	L1	LiO <i>t</i> Bu	DMA	RT	54
11	OP(O)(OEt) <sub>2</sub>	MesCu	L1	LiO <i>t</i> Bu	DMA	RT	64
12	OP(O)(OEt) <sub>2</sub>	CuCl	L1	LiO <i>t</i> Bu (4 equiv)	DMA	RT	56
13	OP(O)(OEt) <sub>2</sub> (3 equiv)	CuCl	L1	LiO <i>t</i> Bu	DMA	RT	47
14	OP(O)(OEt) <sub>2</sub>	CuCl (10 mol%)	<b>L1</b> (11 mol %)	LiO <i>t</i> Bu	DMA	RT	63
15	OP(O)(OEt) <sub>2</sub>	CuCl	PCy <sub>3</sub>	LiO <i>t</i> Bu	DMA	RT	<10
16	OP(O)(OEt) <sub>2</sub>	IMes–CuCl (5 mol %)		LiO <i>t</i> Bu	DMA	RT	<10

<sup>a</sup> NMR yield of **3aa** was determined by <sup>1</sup>H NMR analysis using DMF as an internal standard.



IMes-CuCl





## Scheme S2. Allenylboration of 1a with CF3 Substituted Aryl Propargylic Phosphate



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