

## SUPPLEMENTARY MATERIAL

### **Water-Accelerated Tandem Claisen Rearrangement – Catalytic Asymmetric Carboalumination**

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Experimental parts.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.

**General:** All air- and moisture-sensitive reactions were performed under an atmosphere of  $N_2$  and all glassware was dried at 140 °C prior to use. THF and  $Et_2O$  were dried by distillation from Na/benzophenone, and dry  $CH_2Cl_2$  and toluene were obtained by distillation from  $CaH_2$ . A 10% solution of MAO in toluene was obtained from Aldrich. Unless otherwise stated, other solvents or reagents were used without further purification. NMR spectra were recorded in  $CDCl_3$  (unless otherwise noted) at either 300 MHz ( $^1H$ ) or 75 MHz ( $^{13}C$ ). Chemical shifts ( $\delta$ ) are reported in parts per million and the residual solvent peak was used as an internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, s = sextet, m = multiplet, b = broad), integration and coupling constants. IR spectra were obtained on an IBM IR/32 FT-IR spectrometer or on a Nicolet AVATAR 360 FTIR E.S.P. Spectrometer. Mass spectra were obtained on a VG-70-70 HF. Optical rotations were measured on a Perkin-Elmer 241 polarimeter.

**(*R*)-2-(3-Hydroxy-2-methyl-propyl)-phenol (3). General procedure A.**

A solution of 0.315 g (4.37 mmol) of  $Me_3Al$  and 0.029 g (0.043 mmol) of Erker's catalyst **2** in 6 mL of  $CH_2Cl_2$  was treated at -30 °C with 18  $\mu L$  (1.0 mmol) of  $H_2O$ . The cooling bath was immediately removed and the mixture was allowed to warm to room temperature. The resulting red/orange homogeneous solution was cooled to 0 °C prior to the addition of 137  $\mu L$  (1.00 mmol) of allyl phenyl ether **1** (the addition of **1** was accompanied by an immediate change in color from red/orange to light yellow). The reaction mixture was kept at 0 °C for 12 h and quenched by bubbling  $O_2$  through the solution until all volatiles were evaporated. The resulting slurry was washed with  $CH_2Cl_2$  and 2 N NaOH. The combined aqueous layers were neutralized with 1 N HCl and extracted with  $CH_2Cl_2$ . The combined organic layers were dried ( $MgSO_4$ ), filtered, concentrated and chromatographed on  $SiO_2$  (EtOAc/Hexanes, 1:4) to afford 0.124 g (0.747 mmol, 75%) of **3** as a colorless oil (75% ee by Mosher ester analysis): IR (neat) 3318, 2958, 2931, 2874, 1592, 1489, 1456, 1380, 1244, 1026, 753  $cm^{-1}$ ;  $^1H$  NMR  $\delta$  7.15 - 7.07 (m, 2 H), 6.88 - 6.84 (m, 2 H), 3.57 (dd, 1 H,  $J$  = 10.7, 4.1 Hz), 3.36 (dd, 1 H,  $J$  = 10.7, 6.7 Hz), 2.72 (d, 2 H,  $J$  = 6.2 Hz), 2.07 - 1.96 (m, 1 H) 1.02 (d, 3 H,  $J$  = 7.0 Hz);  $^{13}C$  NMR  $\delta$  154.8, 131.9, 127.8, 125.9, 120.6, 116.3, 65.9, 36.4, 32.7, 17.2; MS (EI)  $m/z$  (rel intensity) 166 ( $M^+$ , 17), 148 (9), 133 (25), 119 (5), 115 (7), 107 (100), 91 (22); HRMS (EI)  $m/z$  calcd for  $C_{10}H_{14}O_2$  166.0994, found 166.0998.

**Ent-3. General procedure B.** A solution of 0.304 g (4.22 mmol) of  $Me_3Al$  and 0.031 g (0.046 mmol) of Erker's catalyst *ent-2* in 6 mL of  $CH_2Cl_2$  was treated at

room temperature with 1 mL (1 mmol) of a 10% solution of MAO in toluene. The resulting dark purple homogeneous solution was cooled to 0 °C prior to the addition of 0.136 g (1.01 mmol) of **1** (the addition of allylphenyl ether was accompanied by an immediate change in color from dark purple to light yellow). The reaction mixture was kept at 0 °C for 12 h and quenched by bubbling O<sub>2</sub> through the solution until all volatiles were evaporated. The resulting slurry was washed with CH<sub>2</sub>Cl<sub>2</sub> and 2 N NaOH. The combined aqueous extracts were neutralized with 1 N HCl and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried (MgSO<sub>4</sub>), filtered, concentrated and chromatographed on SiO<sub>2</sub> (EtOAc/Hexanes, 1:4) to afford 0.120 g (71%) of **ent-3** (75% ee based on Mosher ester analysis): [ $\alpha$ ]<sub>D</sub> -2.4 (c 0.58, EtOH).

**(R)-4-Fluoro-2-(3-hydroxy-2-methyl-propyl)-phenol (5).** According to general procedure A, 0.313 g (4.34 mmol) of Me<sub>3</sub>Al, 0.031 g (0.046 mmol) of **2**, 18  $\mu$ L (1.0 mmol) of water and 0.152 g (0.997 mmol) of allyl phenyl ether **4** in 6 mL of CH<sub>2</sub>Cl<sub>2</sub> afforded 0.143 g (0.777 mmol, 78%) of **5** as a light yellow oil (75% ee by Mosher ester analysis): IR (neat) 3300, 2960, 2877, 1496, 1442, 1381, 1245, 1198, 1145, 1026, 963, 876, 812, 743 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  6.81-6.78 (m, 3 H), 3.55 (dd, 1 H, *J* = 10.8, 4.1 Hz), 3.34 (dd, 1 H, *J* = 10.8, 6.7 Hz), 2.68 (d, 2 H, *J* = 6.3 Hz), 2.03-1.96 (m, 1 H), 1.02 (d, 3 H, *J* = 6.9 Hz); <sup>13</sup>C NMR  $\delta$  157.0 (d, *J* = 236.0 Hz), 150.8, 127.4 (d, *J* = 7.1 Hz), 117.7 (d, *J* = 22.1 Hz), 117.2 (d, *J* = 8.2 Hz), 114.1 (d, *J* = 22.7 Hz), 65.7, 36.2, 32.7, 17.1; MS (EI) *m/z* (rel intensity) 184 (M<sup>+</sup>, 36), 166 (28), 151 (53), 137 (16), 133 (11), 125 (100), 109 (19), 103 (8), 96 (22); HRMS (EI) *m/z* calcd for C<sub>10</sub>H<sub>13</sub>O<sub>2</sub>F 184.0900, found 184.0898.

**Ent-5.** According to general procedure B, 0.308 g (4.27 mmol) of Me<sub>3</sub>Al, 0.0345 g (0.0516 mmol) of **ent-2**, 2 mL (2 mmol) of a 10% solution of MAO in toluene and 0.154 g (1.01 mmol) of **4** in 6 mL of CH<sub>2</sub>Cl<sub>2</sub> afforded 0.149 g (0.809 mmol, 80%) of **ent-5** (76% ee based on Mosher ester analysis): [ $\alpha$ ]<sub>D</sub> -3.1 (c 0.8, EtOH).

**(R)-2-(3-Hydroxy-2-methyl-propyl)-4-(triisopropyl-silanyloxy)-phenol (7).** According to general procedure A, 0.332 g (4.61 mmol) of Me<sub>3</sub>Al, 0.031 g (0.046 mmol) of **2**, 18  $\mu$ L (1.0 mmol) of water and 0.308 g (1.00 mmol) of allyl phenyl ether **6** in 6mL of CH<sub>2</sub>Cl<sub>2</sub> afforded 0.173 g (0.511 mmol, 51%) of **7** as a colorless oil (74% ee based on Mosher ester analysis): IR (neat) 3313, 2945, 2867, 1499, 1463, 1432, 1385, 1293, 1247, 1208, 1029, 981, 883, 851, 815, 679 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  6.72-6.61 (m, 3 H), 3.53 (dd, 1 H, *J* = 10.7, 4.0 Hz), 3.33 (dd, 1 H, *J* = 10.7, 6.5 Hz), 2.64 (d, 2 H, *J* = 6.4 Hz), 1.98-1.93 (m, 1 H), 1.26-1.16 (m,

3 H), 1.09 (d, 18 H,  $J = 6.7$  Hz), 1.01 (d, 3 H,  $J = 6.9$  Hz);  $^{13}\text{C}$  NMR  $\delta$  149.6, 148.9, 126.7, 122.7, 118.8, 116.9, 65.8, 36.4, 32.7, 18.1, 17.1, 12.8; MS (EI)  $m/z$  (rel intensity) 338 ( $\text{M}^+$ , 65), 277 (23), 253 (100), 221 (10), 205 (33), 131 (25), 103 (26), 91 (15); HRMS (EI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{34}\text{O}_3\text{Si}$  338.2277, found 338.2284.

**Ent-7.** According to general procedure B, 0.326 g (4.52 mmol) of  $\text{Me}_3\text{Al}$ , 0.0120 g (0.0180 mmol) of *ent-2*, 1 mL (1 mmol) of a 10% solution of MAO in toluene and 0.309 g (1.01 mmol) of **6** in 6 mL of  $\text{CH}_2\text{Cl}_2$  afforded 0.198 g (0.585 mmol, 58%) of **ent-7** (75% ee based on Mosher ester analysis):  $[\alpha]_{\text{D}} -2.4$  (c 1.1, EtOH).

**(R)-2-(3-Hydroxy-2-methyl-propyl)-4-[3-(triisopropyl-silanyloxy)-propyl]-phenol (9).** According to general procedure A, 0.201 g (2.79 mmol) of  $\text{Me}_3\text{Al}$ , 0.014 g (0.021 mmol) of **2**, 9  $\mu\text{L}$  (0.5 mmol) of water and 0.175 g (0.502 mmol) of allyl phenyl ether **8** in 3 mL of  $\text{CH}_2\text{Cl}_2$  afforded 0.115 g (0.302 mmol, 60%) of **9** as a colorless oil (73% ee based on Mosher ester analysis): IR (neat) 3317, 2942, 2866, 1462, 1257, 1105, 882, 679  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.27 (bs, 1 H), 6.96-6.91 (m, 2 H), 6.78 (d, 1 H,  $J = 8.0$  Hz), 3.71 (t, 2 H,  $J = 6.4$  Hz), 3.55 (dd, 1 H,  $J = 10.6, 4.0$  Hz), 3.37-3.34 (m, 1 H), 3.00 (bs, 1 H), 2.68 (d, 2 H,  $J = 6.3$  Hz), 2.62 (t, 2 H,  $J = 7.7$  Hz), 2.10-1.90 (m, 1 H), 1.87-1.80 (m, 2 H), 1.15-1.05 (m, 21 H), 1.02 (d, 3 H,  $J = 6.9$  Hz);  $^{13}\text{C}$  NMR  $\delta$  152.8, 134.3, 131.8, 127.7, 125.6, 116.1, 65.8, 62.8, 36.5, 35.1, 32.6, 31.4, 30.5, 18.2, 17.2, 12.2; MS (EI)  $m/z$  (rel intensity) 380 ( $\text{M}^+$ , 62), 368 (38), 319 (14), 253 (10), 189 (100), 161 (88), 147 (31), 119 (16), 103 (19); HRMS (EI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{40}\text{O}_3\text{Si}$  380.2747, found 380.2756.

**Ent-9.** According to general procedure B, 0.202 g (2.80 mmol) of  $\text{Me}_3\text{Al}$ , 0.014 g (0.021 mmol) of *ent-2*, 0.5 mL (0.5 mmol) of a 10% solution of MAO in toluene and 0.174 g (0.499 mmol) of **8** in 3 mL of  $\text{CH}_2\text{Cl}_2$  afforded 0.105 g (0.276 mmol, 55%) of **ent-9** (74% ee based on Mosher ester analysis):  $[\alpha]_{\text{D}} -1.1$  (c 0.65, EtOH).

**(R)-2-(3-Hydroxy-2-methyl-propyl)-4-methyl-phenol (11).** According to general procedure A, 0.290 g (4.02 mmol) of  $\text{Me}_3\text{Al}$ , 0.031 g (0.046 mmol) of **2**, 18  $\mu\text{L}$  (1.0 mmol) of water and 0.148 g (1.00 mmol) of allyl phenyl ether **10** in 6 mL of  $\text{CH}_2\text{Cl}_2$  afforded 0.134 g (0.744 mmol, 74%) of **11** as a colorless oil (76% ee based on Mosher ester analysis): IR (neat) 3299, 3014, 2958, 2929, 2873, 1506, 1458, 1380, 1260, 1212, 1027, 813  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  6.91 (d, 2 H,  $J = 7.5$  Hz), 6.76 (d, 1 H,  $J = 7.9$  Hz), 5.7 (bs, 2 H), 3.55 (dd, 1 H,  $J = 10.8, 4.0$  Hz), 3.34 (dd, 1 H,  $J = 10.8, 6.5$  Hz), 2.68 (d, 2 H,  $J = 6.4$  Hz), 2.27 (s, 3 H), 2.02-1.96 (m, 1 H),

1.02 (d, 3 H,  $J = 6.9$  Hz);  $^{13}\text{C}$  NMR  $\delta$  152.5, 132.4, 129.7, 128.3, 125.7, 116.1, 65.8, 36.5, 32.6, 20.7, 17.3; MS (EI)  $m/z$  (rel intensity) 180 ( $\text{M}^+$ , 40), 162 (14), 147 (53), 133 (11), 121 (100), 105 (14), 91 (37); HRMS (EI)  $m/z$  calcd for  $\text{C}_{11}\text{H}_{16}\text{O}_2$  180.1150, found 180.1147.

**Ent-11.** According to general procedure B, 0.302 g (4.19 mmol) of  $\text{Me}_3\text{Al}$ , 0.032 g (0.048 mmol) of **ent-2**, 1 mL (1 mmol) of a 10% solution of MAO in toluene and 0.152 g (1.03 mmol) of **9** in 6 mL of  $\text{CH}_2\text{Cl}_2$  afforded 0.139 g (0.771 mmol, 75%) of **ent-11** (74% ee based on Mosher ester analysis):  $[\alpha]_{\text{D}} -2.8$  ( $c$  0.47, EtOH).

**(R)-2-(3-Hydroxy-2-methyl-propyl)-6-methyl-phenol (13)** and **(R)-4-(3-hydroxy-2-methyl-propyl)-2-methyl-phenol (14)**. According to general procedure A, 0.315 g (4.37 mmol) of  $\text{Me}_3\text{Al}$ , 0.032 g (0.048 mmol) of **2**, 18  $\mu\text{L}$  (1.0 mmol) of water and 0.151 g (1.02 mmol) of allyl phenyl ether **12** in 6 mL of  $\text{CH}_2\text{Cl}_2$  afforded 0.093 g (0.517 mmol, 51%) of **13** as a colorless solid (74% ee based on Mosher ester analysis) and 0.0527 g (0.293 mmol, 29 %) of **14** as a colorless oil (70% ee based on Mosher ester analysis). **13**: mp 34-35  $^{\circ}\text{C}$ ; IR (neat) 3360, 2957, 2927, 2874, 1593, 1469, 1380, 1324, 1264, 1200, 1065, 1028, 981, 771, 746  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.01 (dd, 1 H,  $J = 7.3$ , 0.88 Hz), 6.95 (dd, 1 H,  $J = 7.5$ , 1.4 Hz), 6.76 (t, 1 H,  $J = 7.4$  Hz), 3.59 (dd, 1 H,  $J = 10.4$ , 4.1 Hz), 3.38 (dd, 1 H,  $J = 10.4$ , 6.8 Hz), 2.72-2.69 (m, 2 H), 2.27 (s, 3 H), 2.02-1.97 (m, 1 H), 1.03 (d, 3 H,  $J = 6.9$  Hz);  $^{13}\text{C}$  NMR  $\delta$  153.3, 129.4, 129.2, 125.3, 125.1, 120.0, 65.9, 36.3, 32.9, 30.5, 17.1, 16.6; MS (EI)  $m/z$  (rel intensity) 180 ( $\text{M}^+$ , 53), 147 (13), 135 (18), 121 (100); HRMS (EI)  $m/z$  calcd for  $\text{C}_{11}\text{H}_{16}\text{O}_2$  180.1150, found 180.1145. **14**: IR (neat) 3350, 3015, 2955, 2925, 2874, 1508, 1459, 1263, 1213, 1120, 1026  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  6.93-6.85 (m, 2 H), 6.68 (d, 1 H,  $J = 8.0$  Hz), 5.11 (bs, 1 H), 3.55 (dd, 1 H,  $J = 10.6$ , 5.9 Hz), 3.48 (dd, 1 H,  $J = 10.6$ , 6.9 Hz), 2.64 (dd, 1 H,  $J = 13.6$ , 6.5 Hz), 2.35 (dd, 1 H,  $J = 13.6$ , 7.8 Hz), 2.23 (s, 3 H), 1.94-1.87 (m, 1 H), 1.50 (bs, 1 H), 0.92 (d, 3 H,  $J = 6.7$  Hz);  $^{13}\text{C}$  NMR  $\delta$  152.3, 132.7, 131.9, 127.7, 123.8, 114.9, 68.0, 39.1, 38.1, 30.5, 16.7, 16.0; MS (EI)  $m/z$  (rel intensity) 180 ( $\text{M}^+$ , 34), 147 (8), 135 (15), 121 (100); HRMS (EI)  $m/z$  calcd for  $\text{C}_{11}\text{H}_{16}\text{O}_2$  180.1150, found 180.1155.

**Ent-13** and **ent-14**. According to general procedure B, 0.322 g (4.47 mmol) of  $\text{Me}_3\text{Al}$ , 0.012 g (0.018 mmol) of **ent-2**, 1 mL (1 mmol) of a 10% solution of MAO in toluene and 0.152 g (1.03 mmol) of **12** in 6 mL of  $\text{CH}_2\text{Cl}_2$  afforded 0.112 g (0.622 mmol, 60%) of **ent-13** as a colorless solid (77% ee based on Mosher ester analysis) and, after flushing the column with EtOAc, 0.0463g (0.257

mmol, 25%) of **ent-14** as an oil (73% ee based on Mosher ester analysis). **Ent-13**: mp 34-35 °C;  $[\alpha]_D$  -4.4 (c 0.9, EtOH). **Ent-14**:  $[\alpha]_D$  -7.0 (c 1.4, EtOH).

**(R)-4-(3-Hydroxy-2-methyl-propyl)-2,6-dimethyl-phenol (16).**

According to general procedure A, 0.302 g (4.19 mmol) of Me<sub>3</sub>Al, 0.031 g (0.045 mmol) of **2**, 18 μL (1.0 mmol) of water and 0.162 g (1.00 mmol) of allyl phenyl ether **15** in 6 mL of CH<sub>2</sub>Cl<sub>2</sub> afforded, after chromatography on SiO<sub>2</sub> (EtOAc/Hexanes, 3:7), 0.152 g (0.783 mmol, 78%) of **16** as a colorless oil (75% ee based on  $[\alpha]_D$  comparison with **ent-16**):  $[\alpha]_D$  +6.3 (c 0.65, EtOH); IR (neat) 3382, 3008, 2922, 1489, 1460, 1380, 1304, 1213, 1151, 1028 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 6.79 (s, 2 H), 4.56 (s, 1 H), 3.54-3.47 (m, 2 H), 2.61 (dd, 1 H, *J* = 13.5, 6.6 Hz), 2.32 (dd, 1 H, *J* = 13.5, 7.7 Hz), 2.23 (s, 6 H), 1.95-1.85 (m, 1 H), 1.32 (bs, 1 H), 0.92 (d, 3 H, *J* = 6.6 Hz); <sup>13</sup>C NMR δ 150.5, 132.3, 129.4, 123.0, 68.0, 39.1, 38.1, 16.8, 16.2; MS (EI) *m/z* (rel intensity) 194 (M<sup>+</sup>, 77), 176 (10), 161 (34), 147 (20), 135 (100), 121 (48), 115 (28), 105 (35), 91 (74); HRMS (EI) *m/z* calcd for C<sub>12</sub>H<sub>18</sub>O<sub>2</sub> 194.1307, found 194.1305.

**Ent-16.** According to general procedure B, 0.342 g (4.74 mmol) of Me<sub>3</sub>Al, 0.013 g (0.019 mmol) of **ent-5**, 1 mL (1 mmol) of a 10% solution of MAO in toluene and 0.164 g (1.01 mmol) of **15** in 6 mL of CH<sub>2</sub>Cl<sub>2</sub> afforded 0.153 g (0.789 mmol, 78%) of **ent-16** (72% ee based on Mosher ester analysis):  $[\alpha]_D$  -6.0 (c 1.0, EtOH).

**(R)-4-(3-Hydroxy-2-methyl-propyl)-2,5-dimethyl-phenol (18)** and **2-allyl-3,6-dimethyl-phenol (19)**. According to general procedure A, 0.327 g (4.54 mmol) of Me<sub>3</sub>Al, 0.014 g (0.021 mmol) of **2**, 18 μL of water and 0.167 g (1.03 mmol) of **17** in 6 mL of CH<sub>2</sub>Cl<sub>2</sub> afforded 0.0779 g (0.401 mmol, 39%) of **18** as a colorless solid (60% ee based on Mosher ester analysis) and 0.0921 g (0.569 mmol, 55%) of **19**<sup>1</sup> as a colorless oil. **18**: mp 70-72 °C; IR (neat) 3360, 2925, 2870, 1513, 1461, 1413, 1281, 1199, 1027 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 6.86 (s, 1 H), 6.58 (s, 1 H), 4.90 (s, 1 H), 3.61-3.47 (m, 2 H), 2.64 (dd, 1 H, *J* = 13.8, 6.7 Hz), 2.33 (dd, 1 H, *J* = 13.8, 7.8 Hz), 2.23 (s, 3 H), 2.20 (s, 3 H), 1.93-1.86 (m, 1 H), 1.46 (bs, 1 H), 0.95 (d, 3 H, *J* = 6.7 Hz); <sup>13</sup>C NMR δ 152.1, 135.1, 132.7, 131.1, 120.9, 116.9, 68.3, 37.2, 36.4, 19.3, 17.0, 15.5; MS (EI) *m/z* (rel intensity) 194 (M<sup>+</sup>, 58), 135 (100); HRMS (EI) *m/z* calcd for C<sub>12</sub>H<sub>18</sub>O<sub>2</sub> 194.1307, found 194.1309.

**Ent-18 and 19.** According to general procedure B, 0.325 g (4.51 mmol) of Me<sub>3</sub>Al, 0.014 g (0.021 mmol) of **ent-5**, 1 mL (1 mmol) of a 10% solution of MAO in toluene and 0.163 g (1.01 mmol) of **17** in 6 mL of CH<sub>2</sub>Cl<sub>2</sub> afforded 0.0665 g (0.343

<sup>1</sup> Sharma, G. V. M.; Ilangoan, A.; Sreenivas, P.; Mahalingam, A. K. *Synlett* **2000**, 615.

mmol, 34%) of **ent-18** (74% ee based on Mosher ester analysis) and 0.0972 g (0.600 mmol, 59%) of **19**. **Ent-18**:  $[\alpha]_D$  -5.7 (c 0.3, EtOH).

**(R)-2-(3-Hydroxy-2-methyl-propyl)-naphthalen-1-ol (21)**. According to general procedure A, 0.303 g (4.20 mmol) of  $\text{Me}_3\text{Al}$ , 0.030 g (0.045 mmol) of **2**, 18  $\mu\text{L}$  (1.0 mmol) of water and 0.1845 g (1.003 mmol) of **20** in 6 mL of  $\text{CH}_2\text{Cl}_2$  afforded 0.162 g (0.750 mmol, 75%) of **21** as a colorless crystalline solid (80% ee based on Mosher ester analysis): mp 112-114 °C; IR (neat) 3379, 3055, 2957, 2874, 1573, 1465, 1388, 1269, 1019, 820, 754, 678  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  8.31-8.27 (m, 1 H), 7.79-7.76 (m, 1 H), 7.48-7.42 (m, 2 H), 7.37 (d, 1 H,  $J$  = 8.3 Hz), 7.20 (d, 1 H,  $J$  = 8.3 Hz), 3.62 (dd, 1 H,  $J$  = 10.3, 3.9 Hz), 3.38 (dd, 1 H,  $J$  = 10.3, 6.8 Hz), 2.96-2.81 (m, 2 H), 2.13-2.07 (m, 1 H), 1.08 (d, 3 H,  $J$  = 7.0 Hz);  $^{13}\text{C}$  NMR  $\delta$  150.6, 133.8, 129.9, 127.5, 125.8, 125.6, 125.2, 122.5, 119.7, 118.6, 65.6, 36.1, 32.7, 17.3; MS (EI)  $m/z$  (rel intensity) 216 ( $\text{M}^+$ , 74), 198 (50), 183 (48), 169 (10), 165 (15), 157 (100), 141 (19), 128 (64), 115 (27), 102 (10); HRMS (EI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{16}\text{O}_2$  216.1150, found 216.1150.

**Ent-21**. According to general procedure B, 0.302 g (4.19 mmol) of  $\text{Me}_3\text{Al}$ , 0.031 g (0.046 mmol) of **ent-5**, 1 mL (1 mmol) of a 10% solution of MAO in toluene and 0.189 g (1.03 mmol) of **20** in 6 mL of  $\text{CH}_2\text{Cl}_2$  afforded 0.165 g (0.765 mmol, 74%) of **ent-21** (76% ee based on Mosher ester analysis):  $[\alpha]_D$  -2.6 (c 0.8, EtOH).

**(R)-2-(3-Hydroxy-2-ethyl-propyl)-phenol (22)**. According to general procedure A, 0.472 g (4.13 mmol) of  $\text{Et}_3\text{Al}$ , 0.030 g (0.045 mmol) of **2**, 18  $\mu\text{L}$  (1.0 mmol) of  $\text{H}_2\text{O}$  and 137  $\mu\text{L}$  (1 mmol) of allyl phenyl ether **1** in 6 mL of  $\text{CH}_2\text{Cl}_2$  afforded 0.0720 g (0.400 mmol, 40%) of **22** as a colorless oil (92% ee based on Mosher ester analysis):  $[\alpha]_D$  -10.7 (c 0.8, EtOH); IR (neat) 3285, 2960, 2932, 2876, 1592, 1489, 1456, 1380, 1247, 1185, 1037, 1011, 753  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.15 - 7.09 (m, 2 H), 6.89 - 6.85 (m, 2 H), 3.58 (dd, 1 H,  $J$  = 10.8, 3.7 Hz), 3.44 (dd, 1 H,  $J$  = 10.9, 6.1 Hz), 2.74 (d, 2 H,  $J$  = 6.0 Hz), 1.75 - 1.67 (m, 1 H), 1.52 - 1.36 (m, 2 H), 1.02 (t, 3 H,  $J$  = 7.4 Hz);  $^{13}\text{C}$  NMR  $\delta$  154.9, 131.7, 127.8, 126.3, 120.7, 116.3, 63.6, 43.7, 30.6, 24.3, 12.2; MS (EI)  $m/z$  (rel intensity) 180 ( $\text{M}^+$ , 32), 162 (10), 147 (8), 133 (54), 120 (10), 107 (100); HRMS (EI)  $m/z$  calcd for  $\text{C}_{11}\text{H}_{16}\text{O}_2$  180.1150, found 180.1154.

**(R)-3-Methyl-chroman (25)**. A solution of 0.0850 g (0.512 mmol) of phenol **3** and 0.163 g (0.620 mmol) of  $\text{PPh}_3$  in 2 mL of THF was treated at 0 °C with 90  $\mu\text{L}$  (0.57 mmol) of diethyl azodicarboxylate (DEAD). After 10 min, the reaction mixture was concentrated under reduced pressure. The resulting slurry was chromatographed on  $\text{SiO}_2$  (EtOAc/Hexanes, 1:19) to afford 0.0717 g (0.484 mmol,

95%) of **25**<sup>2</sup> as a colorless oil:  $[\alpha]_D -43.1$  (c 0.2, CHCl<sub>3</sub>): <sup>1</sup>H NMR  $\delta$  7.10 - 7.03 (m, 2 H), 6.87 - 6.80 (m, 2 H), 4.21 (ddd, 1 H,  $J = 10.6, 3.4, 2.0$  Hz), 3.70 (dd, 1 H,  $J = 10.4, 9.6$  Hz), 2.84 (ddd, 1 H,  $J = 16.2, 5.2, 1.7$  Hz), 2.46 (dd, 1 H,  $J = 16.1, 9.8$  Hz), 2.19 - 2.14 (m, 1 H), 1.06 (d, 3 H,  $J = 6.7$  Hz).

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<sup>2</sup> Rajesh, C. S.; Thanulingam, T. L.; Das, S. *Tetrahedron* **1997**, 53, 16817.



















































