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General Procedure: All palladium catalyzed reactions were performed under an atmosphere of argon. Solvents were deoxygenated by passing a stream of argon through them for 15 min. Palladium catalysts, ligand and phenol nucleophile were weighed into the reaction vessel, which was then deoxygenated by three cycles of vacuum followed by refilling with argon. The reaction vessel is then charged with the appropriate amount of deoxygenated solvent.

## 1'-Methylprop-2-enyl-4-methoxyphenyl ether 9a

A purple solution of phenol **7a** (50 mg, 0.403 mmol), Pd<sub>2</sub>dba<sub>3</sub>.CHCl<sub>3</sub> (4 mg, 0.003 mmol), the ligand **4** (8 mg, 0.016 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.8 mL) is stirred at 0° for 15 min. To the solution, which slowly becomes orange, is added allyl carbonate **8a** (52 mg, 0.40 mmol) and the mixture stirred at 0° for 4 h. The resulting yellow solution is applied directly onto a silica gel column. Flash chromatography eluting with 6:1 pet. ether:ether affords 63 mg (88%) of a 12.2:1 mixture of **9a:10a** as a colorless liquid. Enantiomers are separated on the chiralcel OD eluting with 99.9:0.1 heptane:iso-propanol (1mL/min.); minor 14.92, major 15.75.

[α]<sub>D</sub><sup>25</sup> = +1.0 (c=1.0, CH<sub>2</sub>Cl<sub>2</sub>). IR (film): 2980, 2933, 2834, 1507, 1465, 1442, 1228, 1039, 928, 826 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 6.83 (m, 4H), 5.90 (m, 1H), 5.23 (dd, J=17.3, 1.3 Hz, 1H), 5.23 (dd, J=10.5, 1.3 Hz, 1H), 4.68 (quin., J=6.3 Hz, 1H), 3.76 (s, 3H), 1.42 (d, J=6.4 Hz, 3H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz): δ 154.0; 152.1, 139.6, 117.5, 115.7, 115.6, 114.6, 114.5, 75.7, 55.6, 21.2. Anal. Calc'd for C<sub>11</sub>H<sub>14</sub>O<sub>2</sub>: C, 74.11; H, 7.93. Found: C, 73.95; H, 7.79.

## 1',2'-Dimethylprop-2-enyl-4-methoxyphenyl ether 9b

A purple solution of **7b** (107 mg, 0.69 mmol), Pd<sub>2</sub>dba<sub>3</sub>.CHCl<sub>3</sub> (7 mg, 0.0068 mmol) and the ligand **6** (16 mg, 0.020 mmol) in THF (1.4 mL) is stirred at 25° for 15 min. To the resulting orange solution is added allyl carbonate **8b** (100 mg. 0.69 mmol) and the mixture

stirred for 12 h. The resulting yellow solution is diluted with ether (5 mL) and washed with 2N NaHCO<sub>3</sub> (5 mL), dried (MgSO<sub>4</sub>) and concentrated *in vacuo*. Flash chromatography eluting with 3:1 pet. ether:ether affords 88 mg (58%) of a 10.4:1 mixture of **9b:10b** as a colorless liquid. Enantiomers are separated on the chiralcel OD eluting with 99.5:0.5 heptane:iso-propanol (1mL/min.); major 7.25, minor 8.20 (regioisomer, 10.42).

[α]<sub>D</sub><sup>25</sup> = +16.0 (c=1.6, CH<sub>2</sub>Cl<sub>2</sub>). IR (film): 2980, 2938, 2840, 1599, 1475, 1205, 1152, 1067, 903, 820 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 6.08 (d, J=2.2 Hz, 2H), 6.05 (t, J=2.2 Hz, 1H), 5.00 (d, J=1.4 Hz, 1H), 4.89 (d, J=1.4 Hz, 1H), 4.68 (quin., J=6.5 Hz, 1H), 3.75 (s, 6H), 1.72 (s, 3H), 1.42 (d, J=6.5 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 161.2, 159.9, 145.6, 111.3, 94.4, 92.7, 77.2, 55.1, 20.5, 17.2. MS: m/e(rel %), 222(48), 207(8), 193(8), 154(100), 125(42), 94(6), 69(17). HRMS: Calc'd for C<sub>13</sub>H<sub>18</sub>O<sub>3</sub>: 222.1256. Found: 222.1256.

## Allyl aryl ether 13b

A purple solution of 11 (1.0 g, 6.02 mmol), Pd<sub>2</sub>dba<sub>3</sub>.CHCl<sub>3</sub> (62 mg, 0.060 mmol) and the ligand 4 (124 mg, 0.180 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (12 mL) is stirred at room temperature for 15 min. The solution, which becomes orange, is treated with geranyl methyl carbonate 12a (850 mg, 4.52 mmol) and stirring continued for 16 h. The resulting yellow solution is concentrated and then applied onto a silica gel column. Flash chromatography eluting with 5% ether in pet. ether, affords 43 mg (61%) of 13b as a colorless liquid. Enantiomers are separated on the chiralcel OD eluting with 99.9:0.1 heptane:iso-propanol (1mL/min.); major 7.38, minor 9.59.

 $[\alpha]_D^{25} = -3.6 \text{ (c=2.2, CH}_2\text{Cl}_2).$  IR (film): 2979, 2930, 2834, 1478, 1229, 1088, 1008 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  6.71 (s, 1H), 6.07 (dd, J=17.9, 10.7 Hz, 1H), 5.18(m 3H), 3.64 (s, 3H), 2.19 (s, 3H), 2.17 (s, 3H), 2.12 (s, 3H), 1.75 (m, 4H), 1.69 (s, 3H), 1.57 (s, 3H), 1.35 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  151.3, 149.9, 144.1,

131.5, 130.1, 127.7, 126.9, 124.3, 119.4, 113.7, 81.3, 59.9, 42.1, 25.7, 22.6, 17.5, 16.2, 13.1, 12.7. Anal. Calc'd for  $C_{20}H_{30}O_2$ : C, 79.42; H, 10.00. Found: C, 79.56; H, 9.88.

# 6-Methoxy-2,5,7,8-tetramethyl-2-(4-methyl-pent-3-enyl)-chroman 14<sup>13a</sup>

A solution of 13b (100 mg, 0.357 mmol) and tris(triphenylphosphine)rhodium(I) chloride in THF (0.4 mL) is stirred at room temperature until a homogenous orange solution is obtained. To the reaction mixture is added 1.0M catecholborane (0.7 mL, 0.7 mmol) and the resulting orange solution stirred at room temperature for 4h. After 4 h, the resulting brownish-green reaction mixture is quenched with 3N NaOH/30%  $H_2O_2$  and stirred at room temperature for an additional 1 h. The biphasic solution is extracted with ether (3 x 10 mL), and the combined ethereal extracts washed with 3N NaOH (10 mL), dried (MgSO<sub>4</sub>) and concentrated. Flash chromatography eluting with 6:1 to 2:1 pet. ether:ether affords the desired alcohol (93 mg, 88%) as a colorless liquid.

[ $\alpha$ ] = -28.1 (c=2.2, CH<sub>2</sub>Cl<sub>2</sub>). IR (film): 3416, 2834, 1478, 1228, 1082, 1007 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  6.72 (s, 1H), 5.08 (t, J=7.0 Hz, 3H), 3.94 (t, J=6.0 Hz, 2H), 3.65 (s, 3H), 2.85 (br s, 1H), 2.23 (s, 3H), 2.17 (s, 3H), 2.13 (s, 3H), 1.90-2.04 (m, 4H), 1.6-1.80 (m, 2H), 1.70 (s, 3H), 1.57 (s, 3H), 1.27 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  152.4, 148.6, 131.7, 130.5, 129.4, 127.5, 123.8, 122.1, 84.0, 59.9, 59.6, 41.2, 39.4, 25.6, 24.2, 23.1, 17.5, 16.1, 13.9, 12.8. Anal. Calc'd for C<sub>20</sub>H<sub>32</sub>O<sub>3</sub>: C, 74.96; H, 10.06. Found: C, 74.69; H, 9.83.

To a solution of the alcohol (270 mg, 0.906 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (465 mg, 2.27 mmol) in  $CH_2Cl_2$  (4 mL) at 0°C is slowly added trifluoromethanesulfonic anhydride (170  $\mu$ L, 1.01 mmol) and the resulting yellow solution stirred at 0° for 15 min. The solution is diluted with 1N HCl (15 mL) and extracted with ether (3 x 15 mL). The

combined extracts are dried (MgSO<sub>4</sub>) and concentrated. Flash chromatography eluting with 5% ether:pet ether affords 197 mg (78%) of **14** as slightly yellow oil.

 $[\alpha]_D^{25} = -7.8$  (c=1.0, benzene). IR (film): 2971, 2932, 1454, 1404, 1376, 1253, 1225, 1089, 1009 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  5.15 (tt, J=7.1, 1.4 Hz, 3H), 3.63 (s, 3H), 2.61 (t, J=6.9 Hz, 2H), 2.20 (s, 3H), 2.16 (s, 3H), 2.12 (s, 3H), 1.83 (t, J=6.9 Hz, 2H), 1.75-1.83 (m, 2H), 1.70 (s, 3H), 1.54-1.64 (m, 2H), 1.60 (s, 3H), 1.25 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  149.4, 147.7, 131.4, 127.7, 125.6, 124.5, 122.9, 117.4, 74.5, 60.3, 39.7.2, 31.3, 25.6, 23.8, 22.3, 20.6, 17.5, 13.5, 11.7, 11.6.

## 5,7-Dihydroxy-2,2-dimethylchroman (16)

A slurry of zinc powder (9.0 g, 0.14 mol) and chroman-4-one **15** (3.0 g, 0.014 mol), in methanol (50 mL) is carefully added conc. Hydrochloric acid (20 mL) and the resulting clear yellow solution is stirred at room temperature for 2 h. The solid zinc is removed by filtration, and the filtrate is diluted with brine (25 mL) and extracted with ether (3 x 25 mL). The combined ethereal extracts are dried (MgSO<sub>4</sub>) and concentrated to afford **16** as a yellow oil, which slowly solidifies (2.69 g, 99% yield), and is used in the next reaction without further purification. The solid can be recrystallized from benzene to afford pale yellow plates, mp 160-163 °C (lit. mp. 162-163 °C).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 5.92 (s, 2H), 5.20 (br s, 2H), 2.56 (t, J=6.7 Hz, 2H), 1.78 (t, J=6.7 Hz, 2H), 1.31 (s, 6H).

## Coumarins 18 and 19

To a solution of the phenol 16 (2.3 g, 0.012 mol),  $Pd_2dba_3$  (310 mg, 0.3 mmol) in formic acid (1 ml) is added methyl pent-2-ynoate 17 (3.4 g, 0.024 mol) and the resulting brown solution stirred at room temperature for 12 h. The reaction mixture is diluted with  $CH_2Cl_2$  (10 mL), washed with water (2 x 25 mL), dried (MgSO<sub>4</sub>) and concentrated *in vacuo*. Flash chromatography eluting with 1:1 pentanes:ether affords 18 (1.50 g, 43%) and 19 (0.39 g, 11%) as white solids. Coumarin 18 was generally used in subsequent reactions

without further purification, but can be recrystallized from CH<sub>2</sub>Cl<sub>2</sub>:hexanes, (mp. 208-210°C).

**18:** IR (film): 3251, 2971, 2871, 1688, 1606, 1425, 1364, 1150, 1085, 825 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.25 (br s, 1H), 6.77 (s, 1H), 5.93 (s, 1H), 2.89 (t, J=7.6 Hz, 2H), 2.70 (t, J=6.7 Hz, 2H), 1.82 (t, J=6.7 Hz, 2H), 1.63 (m, 2H), 1.39 (s, 6H), 1.02 (t, J=6.6 Hz, 3H) . <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  163.3, 160.6, 158.5, 155.0, 153.0, 109.4, 105.7, 103.7, 95.6, 75.7, 38.9, 31.4, 26.5, 23.3, 16.8, 13.9. Anal. Calc'd for C<sub>17</sub>H<sub>20</sub>O<sub>4</sub>: C, 70.81; H, 6.99. Found: C, 70.60; H, 6.99.

**19:** IR (film): 3217, 2972, 2932, 2871, 1687, 1593, 1431, 1384, 1357, 1159, 1118 cm<sup>-1</sup> H NMR (300 MHz, CDCl<sub>3</sub>): δ 6.65 (br s, 1H), 6.22 (s, 1H), 5.98 (s, 1H), 2.95 (t, J=7.6 Hz, 2H), 2.78 (t, J=6.8 Hz, 2H), 1.79 (t, J=6.8 Hz, 2H), 1.69 (m, 2H), 1.32 (s, 6H), 1.00 (t, J=8.0 Hz, 3H).

## Allyl aryl ether 20

A solution of 18 (467 mg, 3.2 mmol), Pd<sub>2</sub>dba<sub>3</sub>.CHCl<sub>3</sub> (70 mg, 0.068 mmol) and the ligand 6 (162 mg, 0.20 mmol) in THF (2 mL) is stirred for 15 min. at which point the methyl carbonate 8b (780 mg, 2.7 mmol) in THF (4 mL) is added to the orange solution. The reaction mixture, which slowly becomes yellow, is stirred at room temperature for 12 h. After 12 h, the solvent is removed *in vacuo*, and the residual oil chromatographed eluting with CH<sub>2</sub>Cl<sub>2</sub> to afford 785 mg (85%) of 20 (11:1 regioselectivity) as a colorless liquid. Enantiomers are separated on the chiralcel OD eluting with 95:5 heptane:iso-propanol (1mL/min.); minor 6.39, major 7.14 (regioisomer, 11.39).

 $[α]_D^{25}$  = +7.9 (c=2.0, CH<sub>2</sub>Cl<sub>2</sub>). IR (film): 2974, 2934, 2871, 1727, 1604, 1419, 1362, 1152, 1105 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 6.38 (s, 1H), 5.93 (m, 1H), 5.02 (s, 1H), 4.94 (s, 1H), 4.71 (quart, J=6.4, 1H), 2.90 (t, J=7.5 Hz, 2H), 2.69 (m, 2H), 1.81 (t, J=6.7 Hz, 2H), 1.74 (m, 3H), 1.69 (m, 2H), 1.49 (d, J=6.4 Hz, 3H), 1.39 (s, 6H), 1.03 (t, J=7.3 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 161.9, 158.9, 158.6, 155.4,

152.4, 144.8, 112.3, 110.5, 106.3, 103.8, 93.4, 77.6, 75.5, 38.7, 31.4, 26.6, 26.4, 23.1, 20.3, 17.2, 17.0, 13.8. Anal. Calc'd for  $C_{22}H_{28}O_4$ : C, 74.13; H, 7.92. Found: C, 73.94; H, 7.92.

## Aryl allyl ether 21

To a solution of **20** (100 mg, 0.39 mmol) in dry dioxane (4 mL), at 100°, is added DDQ (266 mg, 1.13 mmol) and the resulting brown solution heated at reflux for 4 h. The brown solution is cooled to 0° and the precipitate removed by filtration, and washed with ether (25 mL). The filtrate is washed with 1N aqueous sodium hydroxide (25 mL), brine (25 mL), dried (MgSO<sub>4</sub>) and concentrated. Flash chromatography eluting with CH<sub>2</sub>Cl<sub>2</sub> affords 73 mg (74%) of **21** as a colorless oil (becomes pink on standing).

[ $\alpha$ ]<sub>D</sub><sup>25</sup> = -28.1 (c=1.9, CH<sub>2</sub>Cl<sub>2</sub>). IR (film): 3075, 2973, 2933, 2872, 1732, 1641, 1563, 1420, 1367, 1159, 1121, 1105 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  6.69 (d, J=10.0 Hz, 1H), 6.36 (s, 1H), 5.93 (s, 1H), 5.53 (d, J=10.0 Hz, 1H), 5.00 (d, J=1.3 Hz, 1H), 4.92 (d, J=1.3 Hz, 1H), 4.75 (quart, J=6.6, 1H), 2.88 (m, 2H), 1.71 (s, 3H), 1.64 (m, 2H), 1.49 (s, 6H), 1.47 (d, J=6.6 Hz, 3H), 1.03 (t, J=7.3 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  161.5, 158.2, 156.2, 156.1, 151.7, 144.6, 126.8, 116.8, 112.6, 110.8, 107.5, 104.0, 94.8, 78.1, 77.5, 38.3, 27.8, 27.6, 23.1, 20.3, 17.2, 13.9. Anal. Calc'd for C<sub>22</sub>H<sub>26</sub>O<sub>4</sub>: C, 74.53; H, 7.39. Found: C, 74.31; H, 7.41.

#### Alcohol 22

To a solution of **21** (330 mg, 1.02 mmol) in THF (5 mL) is added freshly prepared 9-BBN dimer (250 mg, 1.02 mmol) and the resulting yellow tinged solution stirred at room temperature for 4 h. After 4 h, the solution is quenched with 30% NaOH (10 mL) and 30%  $H_2O_2$  (5 mL) and stirred for 1 h. The biphasic solution is extracted with ether (3 x 25 mL), and the combined ethereal extracts dried (MgSO<sub>4</sub>) and concentrated. Flash chromatography eluting with 3:1 ether:pet. ether affords 278 mg (76%) of **22**, 93:7

mixture of diastereomeric alcohols, as a thick pale yellow oil (becomes a foam under vacuum).

IR (film): 3375, 2971, 2932, 1615, 1158, 1141, 1098 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 6.63 (d, J=10.0 Hz, 1H), 6.46 (s, 1H), 5.94 (s, 1H), 5.52 (d, J=10.0 Hz, 1H), 4.51 (quint, J=6.1 Hz, 1H), 3.70 (m, 2H), 2.90 (t, J=7.8 Hz, 2H), 2.11 (m, 2H), 1.76 (br s, 1H). 1.67 (m, 2H), 1.51 (s, 3H), 1.51 (s, 6H), 1.34 (d, J=6.3 Hz, 3H), 1.06 (t, J=6.9 Hz, 3H), 1.04 (d, J=7.3 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)L δ 161.3, 158.1, 156.2, 155.8, 151.8, 126.4, 116.6, 110.9, 107.8, 104.0, 94.2, 77.6, 76.4, 65.0, 38.4, 27.8, 27.7, 23.2, 16.3, 14.0, 12.5.

## Calanolide B (2)

To a suspension of 22 (66 mg, 0.183 mmol) and sodium bicarbonate (23 mg, 0.275 mmol) in  $CH_2Cl_2$  is added portionwise the Dess-Martin periodinane (43 mg, 0.220 mmol) and the resulting yellow suspension stirred at room temperature for 1 h. The suspension is directly applied to a silica gel column and chromatographed eluting with 3:1 ether:pet ether, affording 57 mg (87%) of the desired aldehyde as a clear colorless liquid.

IR (film): 2973, 2935, 2873, 1731, 1603, 1367, 1157, 1106 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 9.79 (d, J=2.0 Hz, 1H), 6.56 (d, J=10.0 Hz, 1H), 6.42 (s, 1H), 5.98 (s, 1H), 5.55 (d, J=10.0 Hz, 1H), 4.73 (quint, J=6.0 Hz, 1H), 2.90 (t, J=7.7 Hz, 2H), 2.79 (m, 2H), 1.66 (m, 2H), 1.50 (s, 3H), 1.49 (s, 3H), 1.42 (d, J=6.2 Hz, 3H), 1.22 (d, J=7.2 Hz, 3H), 1.04 (t, J=7.2 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 202.4, 161.1, 158.0, 156.1, 155.0, 151.9, 127.0, 116.3, 111.1, 107.7, 104.3, 93.9, 77.7, 74.7, 51.2, 38.3, 27.8, 27.7, 23.1, 16.9, 13.9, 10.0.

To the aldehyde (48 mg, 0.186 mmol) at  $0^{\circ}$  is added 1.0M zinc(II) chloride in ether (370  $\mu$ L, 0.37 mmol) and the resulting yellow solution stirred at  $0^{\circ}$  for 2 h. The resulting solution is diluted with 1M hydrochloric acid (5 mL) and extracted with ether (2 x 5 mL).

The combined organic extracts are dried (MgSO<sub>4</sub>) and concentrated *in vacuo*. Flash chromatography eluting with 2:1 ether:pet. ether affords  $2^2$  (32 mg, 66 %) as a clear film.  $[\alpha]_D^{25} = -48.2$  (c=0.3, acetone). IR (film): 3429, 2972, 2934, 2873, 1732, 1587, 1376, 1137, 1128 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  6.66 (d, J=9.9 Hz, 1H), 5.97 (s, 1H), 5.55 (d, J=9.9 Hz, 1H), 5.00 (d, J=3.1 Hz, 1H), 4.28 (m, 1H), 2.92 (m, 2H), 2.48 (br s, 1H), 1.78 (m, 1H), 1.68 (sextet, J=7.1 Hz, 2H), 1.52 (s, 3H), 1.50 (s, 3H), 1.46 (d, J=6.4 Hz, 3H), 1.17 (d, J=7.0 Hz, 3H), 1.06 (t, J=7.1 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  160.9, 158.7, 153.9, 153.1, 151.4, 126.8, 116.5, 110.3, 106.3, 103.5, 77.7, 73.0, 61.9, 38.6, 38.2, 27.8, 27.7, 23.3, 18.8, 14.0, 12.5.

## Calanolide A (1)

To a solution of 2 (14 mg, 0.039 mmol) in THF (2mL), at -78 °C, is added diethyl azodicarboxylate (126 μL, 0.8 mmol) followed by 1.0M trimethyl phosphine (0.8 mL, 0.8 mmol). To the resulting yellow solution is added chloroacetic acid (70 mg, 0.74 mmol) and the reaction mixture stirred at -78 °C for 3 h. After 3 h, the reaction mixture is concentrated and the residual solid flushed through a small column of silica eluting with 1:1 ether:pet. ether. At this stage calanolide A and calanolide B chloroacetates can be separated, but generally the crude reaction mixture was carried on without further purification. The resulting clear film is dissolved in methanol (2 mL), cooled to 0 °C, and treated with K<sub>2</sub>CO<sub>3</sub> (27 mg, 0.195 mmol). The suspension is stirred at 0 °C for 30 min, filtered, and the filtrate concentrated *in vacuo*. Flash chromatography eluting with 1:1 ether:pet. ether affords 1² (8 mg, 57% yield) as a clear film.

[ $\alpha$ ]<sub>D</sub><sup>25</sup> = -64.2 (c=0.5, CHCl<sub>3</sub>). IR (film): 3435, 2973, 2873, 1732, 1584, 1376, 1129, 1118 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  6.61 (d, J=10.0 Hz, 1H), 5.94 (s, 1H), 5.54 (d, J=10.0 Hz, 1H), 4.70 (d, J=7.9 Hz, 1H), 3.92 (m, 1H), 2.90 (m, 2H), 3.58 (br s, 1H), 1.91 (m, 1H), 1.65 (m, 2H), 1.50 (s, 3H), 1.49 (s, 3H), 1.48 (d, J=6.4 Hz, 3H), 1.16 (d, J=6.5 Hz, 3H), 1.03 (t, J=7.5 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  160.4.

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158.9, 154.4, 153.1, 151.1, 126.9, 116.5, 110.2, 106.3, 104.1, 77.7, 76.7, 67.2, 40.9, 38.6, 28.0, 27.7, 23.3, 18.9, 15.1, 14.1.

Table 1. Asymmetric Aryl Ether Formation with Allyl Carbonates<sup>a</sup>

entry	phenol	substrate	% Pd2dba3	ligand	solvent	temp (°C)	isolated yield	ratio 9:10 <sup>b</sup>	% ee 6°	config
<del></del> -	7a	8a	1	4	THF	25	85	86:14	60	R
2	7a	8a	ī	4	CH <sub>2</sub> Cl <sub>2</sub>	25	91	92:8	68	R
3	7a	8a	ī	4	CH <sub>2</sub> Cl <sub>2</sub>	0	90	92:8	77	R
4	7a	8a	1	4	CH <sub>2</sub> Cl <sub>2</sub>	-20	62	91:9	71	R
5	7a	8a	0.1	4	CH <sub>2</sub> Cl <sub>2</sub>	0	75	95:5	81	R
6d	7a	8a	0.1	4	CH <sub>2</sub> Cl <sub>2</sub>	0	76	94:6	83	R
7	7b	8b	1	4	$CH_2Cl_2$	25	72	84:16	90	R
Ŕ	7b	8b	1	6	CH <sub>2</sub> Cl <sub>2</sub>	25	43	87:13	75	S
9	7b	8b	ı	6	THF	25	58	91:9	87	S

<sup>&</sup>lt;sup>a</sup> Reaction performed with 1 equiv of phenol at 0.5 M concentration unless otherwise stated. <sup>b</sup> Ratio determined by <sup>1</sup>H NMR. <sup>c</sup> Enantiomeric excess determined by chiral HPLC (Chiralcel OD column) using 99.9:0.1 heptane—isopropanol as the eluting solvent. <sup>d</sup> Reaction run at 0.1 M in phenol.