Catalytic Enantioselective Synthesis of 2-Aryl Chromenes

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General Information

All reactions were carried out under a nitrogen atmosphere in flame-dried glassware with magnetic stirring. THF, toluene, and dichloromethane were purified by passage through a bed of activated alumina. Reagents were purified prior to use unless otherwise stated following the guidelines of Perrin and Armarego. Purification of reaction products was carried out by flash chromatography using EM Reagent or Silicycle silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and ceric ammonium nitrate stain or potassium permanganate stain followed by heating. Infrared spectra were recorded on a Bruker Tensor 37 FT-IR spectrometer. $^1$H-NMR spectra were recorded on a Bruker Avance 500 MHz w/direct cryoprobe (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl$_3$ at 7.26 ppm). Data are reported as (ap = apparent, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration). Proton-decoupled $^{13}$C-NMR spectra were recorded on a Bruker Avance 500 MHz w/direct cryoprobe (125 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl$_3$ at 77.2 ppm). Mass spectra data were obtained on a Waters Acquity Single Quadrupole ESI Spectrometer, Micromass Quadro II Spectrometer and Agilent 7890 GC-TOF.

Benzaldehyde and 2'-hydroxyacetophenone derivatives were obtained from commercial sources (Sigma Aldrich, Oakwood). Chalcones and phosphoramidites were prepared according to published procedures.

General Procedure for the Synthesis of 2'-Hydroxychalcone Derivatives

2'-Hydroxychalcones were prepared using a modified literature procedure. Into a round bottom flask equipped with magnetic stirring bar was dissolved acetophenone derivative (15 mmol, 1 equiv) in methanol (100 mL) and 50% w/v KOH (17 mL). The reaction was stirred at 0 °C for 30 min. The aldehyde (18 mmol, 1.2 equiv) was added in one portion, and the mixture was stirred at 23 °C for 12-24 h. The solution was neutralized with 12 M HCl. The precipitate was removed by vacuum filtration, washed with water, dried, and recrystallized from methanol or dichloromethane/hexanes. When no precipitate was formed upon neutralization, the solution was extracted with EtOAc, and the combined organics were dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography using

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10% EtOAc/hexanes or recrystallization with hot methanol to afford the chalcones as a yellow solid.

**General Procedure for the Synthesis of Bis-acetates**

Into a round bottom flask equipped with magnetic stir bar was loaded 2’-hydroxychalcone derivative (2.5 mmol, 1 equiv), CeCl$_3$·7H$_2$O (5.5 mmol, 2.2 equiv), ethanol (200 proof, 8.8 equiv), and THF (0.1 M 25 mL). The mixture was cooled to 0 °C before NaBH$_4$ (5.5 mmol, 2.2 equiv) was added in one portion and allowed to slowly warmed to 23 °C. Upon consumption of the 2’-hydroxychalcone, 4-dimethylaminopyridine (3.75 mmol, 1.5 equiv), pyridine (37.5 mmol, 15 equiv), and acetic anhydride (37.5 mmol, 15 equiv) were successively added. The reaction was stirred for 12-18 h and concentrated. The unpurified residue was taken up in EtOAc and quenched with a saturated solution of sodium bicarbonate. The layers were separated and the aqueous layer was back extracted with EtOAc. The combined organics were washed with DI H$_2$O, saturated copper(II) sulfate, and brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography using EtOAc/hexanes to afford the corresponding bis-acetates.

**(E)-1-(2-Acetoxy-3-methylphenyl)-3-phenylallyl acetate (1a).** Prepared according to the general procedure using (E)-2-(1-hydroxy-3-phenylallyl)-phenol. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford 1a as a clear crystal (450 mg, 74%). Analytical data for 1a: $^1$H NMR (500 MHz, CDCl$_3$) δ 7.52 (dt, $J$ = 7.7, 1.5 Hz, 1H), 7.39 – 7.34 (m, 3H), 7.35 – 7.23 (m, 4H), 7.11 (dt, $J$ = 8.1, 1.3 Hz, 1H), 6.62 (d, $J$ = 16.0, 1H), 6.61 (d, $J$ = 6.5 Hz, 1H), 6.35 (dd, $J$ = 15.8, 6.6 Hz, 1H), 2.32 (s, 3H), 2.11 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 170.0, 169.5, 148.4, 136.2, 132.9, 131.1, 129.5, 128.7, 128.6, 128.3, 126.8, 126.5, 126.2, 123.3, 71.3, 21.3, 21.2; IR (film): 3061, 3027, 2938, 1765, 1738, 1650, 1586, 1491, 1452, 1369, 1233, 1197, 1173, 1098, 1063, 1015, 964, 911, 877 cm$^{-1}$; LRMS (ESI): Mass calculated for [M+H]$^+$ C$_{19}$H$_{19}$O$_4$: 311.1; found: 311.1.

**(E)-2-(1-Acetoxy-3-(naphthalen-1-yl)allyl)phenyl acetate (1b).** Prepared according to the general procedure using (E)-1-(2-hydroxyphenyl)-3-(naphthalen-1-yl)prop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford 1b as a
colorless oil (290 mg, 40%). Analytical data for 1b: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 8.05 (d, J = 8.6, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.59 (d, J = 7.8, 1.7 Hz, 1H), 7.57 (d, J = 7.2 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.49 – 7.39 (m, 3H), 7.34 (td, J = 7.6, 1.3 Hz, 1H), 7.17 (dd, J = 8.0, 1.3 Hz, 1H), 6.76 (dd, J = 6.5, 1.3 Hz, 1H), 6.41 (dd, J = 15.6, 6.5 Hz, 1H), 2.36 (s, 3H), 2.18 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta 170.0, 169.6, 148.5, 134.0, 133.7, 131.7, 131.1, 130.4, 129.6, 129.4, 128.8, 128.7, 128.6, 126.5, 126.4, 126.0, 125.7, 124.3, 123.8, 123.4, 71.5, 21.4, 21.2; IR (film): 3060, 3046, 3014, 2936, 1765, 1737, 1369, 1233, 1198 cm\(^{-1}\); LRMS (ESI): Mass calculated for [M+H]\(^+\) \(\text{C}_{23}\text{H}_{21}\text{O}_4\): 361.1; found: 361.0.

(\(E\))-2-(1-Acetoxy-3-(naphthalen-2-yl)allyl)phenyl acetate (1c). Prepared according to the general procedure using (\(E\))-1-(2-hydroxyphenyl)-3-(naphthalen-2-yl)prop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford 1c as a colorless oil (250 mg, 57%). Analytical data for 1c: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.81 – 7.73 (m, 4H), 7.57 (ddd, J = 9.4, 8.2, 1.7 Hz, 2H), 7.49 – 7.42 (m, 2H), 7.38 (td, J = 7.6, 1.7 Hz, 1H), 7.30 (td, J = 7.6, 1.3 Hz, 1H), 7.12 (dd, J = 8.1, 1.2 Hz, 1H), 6.78 (d, J = 15.9 Hz, 1H), 6.67 (dd, J = 6.5, 1.3 Hz, 1H), 6.47 (dd, J = 15.9, 6.4 Hz, 1H), 2.33 (s, 3H), 2.14 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta 170.0, 169.6, 148.5, 134.0, 133.7, 131.7, 131.1, 129.5, 128.8, 128.4, 128.2, 127.8, 127.2, 126.54, 126.51, 126.49, 126.3, 123.6, 123.3, 71.3, 21.3, 21.2; IR (film): 3057, 2936, 1766, 1737, 1651, 1607, 1507, 1369, 1233, 1198, 1174 cm\(^{-1}\); LRMS (ESI): Mass calculated for [M+H]\(^+\) \(\text{C}_{20}\text{H}_{21}\text{O}_4\): 361.1; found: 361.3.

(\(E\))-2-(1-Acetoxy-3-\((\text{o}-\text{tolyl})\)allyl)phenyl acetate (1d). Prepared according to the general procedure using (\(E\))-1-(2-hydroxyphenyl)-3-\((\text{o}-\text{tolyl})\)prop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford 1d as a colorless oil (290 mg, 40%). Analytical data for 1d: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.53 (dd, J = 7.7, 1.6 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.37 (td, J = 7.8, 1.7 Hz, 1H), 7.28 (td, J = 7.6, 1.2 Hz, 1H), 7.19 – 7.09 (m, 4H), 6.85 (dd, J = 15.9, 1.3 Hz, 1H), 6.62 (dd, J = 6.6, 1.3 Hz, 1H), 6.24 (dd, J = 15.7, 6.6 Hz, 1H), 2.34 (s, 3H), 2.33 (s, 3H), 2.11 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta 169.9, 169.4, 148.3, 135.8, 135.2, 131.1, 130.9, 130.4, 129.4, 128.6, 128.0, 127.4, 126.4, 126.2, 125.8, 123.2, 71.5, 21.2, 21.1, 19.8; IR (film): 3098,3063, 3017, 2912, 2860, 1924, 1724, 1719, 1572, 1463, 1426 cm\(^{-1}\); LRMS (ESI): Mass calculated for [M+H]\(^+\) \(\text{C}_{20}\text{H}_{21}\text{O}_4\): 325.1; found: 325.5.
(E)-2-(1-Acetoxy-3-(p-tolyl)allyl)phenyl acetate (1e). Prepared according to the general procedure using (E)-1-(2-hydroxyphenyl)-3-(p-tolyl)prop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford 1e as a colorless oil (170 mg, 62%). Analytical data for 1e: 1H NMR (500 MHz, CDCl₃) δ 7.52 (dd, J = 7.7, 1.7 Hz, 1H), 7.36 (td, J = 7.7, 1.7 Hz, 1H), 7.29 – 7.26 (m, 3H), 7.11 (d, J = 8.1 Hz, 2H), 7.10 (dd, J = 8.3, 1.3 Hz, 1H), 6.60 (d, J = 7.5 Hz, 1H), 6.59 (d, J = 15.4 Hz, 1H), 6.34 – 6.25 (m, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 2.11 (s, 3H); 13C NMR (125 MHz, CDCl₃) δ 170.0, 169.5, 148.4, 138.2, 133.4, 132.9, 131.2, 129.4, 128.7, 126.7, 126.4, 125.1, 123.3, 71.4, 21.4, 21.3, 21.2; IR (film): 3087, 3023, 2973, 2921, 2858, 1777, 1769, 1371, 1282, 1245 cm⁻¹; LRMS (ESI): Mass calculated for [M+H]+ C₂₀H₂₁O₄: 325.1.

(E)-2-(1-Acetoxy-3-(3-methoxyphenyl)allyl)phenyl acetate (1f). Prepared according to the general procedure using (E)-1-(2-hydroxyphenyl)-3-(3-methoxyphenyl)prop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford 1f as a colorless oil (330 mg, 42%). Analytical data for 1f: 1H NMR (500 MHz, CDCl₃) δ 7.52 (dd, J = 7.7, 1.7 Hz, 1H), 7.37 (ddd, J = 8.1, 7.4, 1.7 Hz, 1H), 7.28 (td, J = 7.8, 1.5 Hz, 1H), 7.23 (t, J = 7.9 Hz, 1H), 7.11 (dd, J = 8.1, 1.2 Hz, 1H), 6.97 (dt, J = 7.6, 1.2 Hz, 1H), 6.90 (dd, J = 2.6, 1.5 Hz, 1H), 6.81 (ddd, J = 8.3, 2.6, 0.9 Hz, 1H), 6.61 (d, J = 6.5 Hz, 1H), 6.60 (d, J = 15.9 Hz, 1H), 6.34 (dd, J = 15.6, 6.7 Hz, 1H), 3.80 (s, 3H), 2.32 (s, 3H), 2.11 (s, 3H); 13C NMR (125 MHz, CDCl₃) δ 169.7, 169.3, 159.6, 148.1, 137.3, 132.5, 130.8, 129.5, 128.5, 126.2, 123.0, 119.2, 113.7, 111.7, 70.9, 55.1, 21.0, 20.9; IR (film): 3063, 3038, 3005, 2959, 2940, 1766, 1599, 1489, 1466, 1370, 1234, 1042 cm⁻¹; LRMS (ESI): Mass calculated for [M+H]+ C₂₀H₂₁O₅: 341.1; found: 341.1.

(E)-2-(1-Acetoxy-3-(2-fluorophenyl)allyl)phenyl acetate (1g). Prepared according to the general procedure using (E)-3-(2-fluorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford 1g as a colorless oil (229 mg, 47%). Analytical data for 1g: 1H NMR (500 MHz, CDCl₃) δ 7.52 (dd, J = 7.7, 1.7 Hz, 1H), 7.42 (td, J = 7.7, 1.7 Hz, 1H), 7.37 (td, J = 7.7, 1.7 Hz, 1H), 7.28 (dd, J = 7.6, 1.3 Hz, 1H), 7.22 (ddd, J = 8.1, 7.1, 5.2, 1.8 Hz, 1H), 7.11 (dd, J = 8.2, 1.3 Hz, 1H), 7.08 (td, J = 7.6, 1.2 Hz, 1H), 7.03 (ddd, J = 10.8, 8.3, 1.2 Hz, 1H), 6.80 (dd, J = 16.3, 1.2 Hz, 1H), 6.61 (dd, J = 6.6, 1.3 Hz, 1H), 6.43 (dd, J = 16.1, 6.5 Hz, 1H), 2.33 (s, 3H), 2.12 (s, 3H); 13C NMR (125 MHz, CDCl₃) δ 169.9, 169.5, 160.5 (d, J = 249.8 Hz), 148.4, 130.9, 129.56 (d, J = 8.6 Hz), 129.56, 128.74 (d, J = 5.5 Hz), 128.69, 127.8 (d, J = 3.5 Hz), 126.5, 125.1 (d, J = 3.6 Hz), 124.3 (d, J = 3.6 Hz), 124.0 (d, J = 12.0 Hz), 123.3, 115.9 (d, J = 22.0 Hz), 71.3, 21.3, 21.2; 19F NMR (376 MHz, CDCl₃) δ -117.57; IR (film): 3064, 3040, 2935, 2853, 1766, 1741, 1609, 1579, 1488, 1455, 1370, 1231, 1199, 1174, 1096, 1066, 1016, 968 cm⁻¹; LRMS (ESI): Mass calculated for [M+H]+ C₁₉H₁₆FO₄: 329.1; found: 329.2.
(E)-2-(1-Acetoxy-3-(4-fluorophenyl)allyl)phenyl acetate (1h). Prepared according to the general procedure using (E)-3-(4-fluorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford 1h as a white solid (285 mg, 39%). Analytical data for 1h: 1H NMR (500 MHz, CDCl$_3$) δ 7.51 (dd, $J = 7.7$, 1.7 Hz, 1H), 7.40 – 7.30 (m, 3H), 7.29 (dd, $J = 7.6$, 1.3 Hz, 1H), 7.10 (dd, $J = 8.1$, 1.3 Hz, 1H), 6.99 (t, $J = 8.7$ Hz, 2H), 6.59 – 6.55 (m, 2H) 6.26 (dd, $J = 15.6$, 6.9 Hz, 1H), 2.31 (s, 3H), 2.11 (s, 3H); 13C NMR (125 MHz, CDCl$_3$) δ 170.0, 169.5, 162.7 (d, $J = 247.8$ Hz), 148.3, 132.3 (d, $J = 3.2$ Hz), 131.8, 131.0, 129.5, 128.7, 128.4 (d, $J = 8.0$ Hz), 126.5, 126.0 (d, $J = 2.3$ Hz), 123.3, 115.7 (d, $J = 21.7$ Hz), 71.2, 21.3, 21.2; 19F NMR (376 MHz, CDCl$_3$) δ -113.62; IR (film): 3041, 2937, 1769, 1765, 1736, 1729, 1655, 1509, 1489, 1453, 1431, 1371, 1297, 1158, 1096, 1040, 1012, 970 cm$^{-1}$; LRMS (ESI): Mass calculated for [M-H] $C_{19}H_{16}FO_4$: 327.1; found: 327.0.

(E)-2-(1-Acetoxy-3-(3-chlorophenyl)allyl)phenyl acetate (1i). Prepared according to the general procedure using (E)-3-(3-chlorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford 1i as a colorless oil (683 mg, 64%). Analytical data for 1i: 1H NMR (500 MHz, CDCl$_3$) δ 7.53 (dd, $J = 7.7$, 1.6 Hz, 1H), 7.41 (dd, $J = 7.7$, 1.7 Hz, 1H), 7.39 (t, $J = 1.6$ Hz, 1H), 7.31 (td, $J = 7.6$, 1.2 Hz, 1H), 7.26 (m, 3H), 7.14 (dd, $J = 8.1$, 1.3 Hz, 1H), 6.63 (dd, $J = 6.2$, 1.3 Hz, 1H), 6.58 (dd, $J = 15.9$, 1.4 Hz, 1H), 6.39 (dd, $J = 15.9$, 6.3 Hz, 1H), 2.35 (s, 3H), 2.14 (s, 3H); 13C NMR (125 MHz, CDCl$_3$) δ 169.9, 169.5, 148.4, 138.0, 134.7, 131.3, 130.8, 130.0, 129.6, 128.7, 128.2, 127.8, 126.7, 126.5, 125.1, 123.3, 70.9, 21.25, 21.18; IR (film): 3064, 3038, 2936, 2850, 1765, 1739, 1593, 1566, 1489, 1453, 1428, 1369, 1232, 1198, 1174, 1096, 1077, 1066, 1015, 962, 911, 777, 757 cm$^{-1}$; LRMS (ESI): Mass calculated for [M+H]$^+$ $C_{19}H_{18}ClO_4$: 345.1; found: 345.1.

(E)-2-(1-Acetoxy-3-(4-(trifluoromethyl)phenyl)allyl)phenyl acetate (1j). Prepared according to the general procedure using (E)-1-(2-hydroxyphenyl)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford 1j as a colorless oil (230 mg, 49%). Analytical data for 1j: 1H NMR (500 MHz, CDCl$_3$) δ 7.56 (d, $J = 8.1$ Hz, 2H), 7.50 (dd, $J = 7.7$, 1.7 Hz, 1H), 7.46 (d, $J = 8.2$ Hz, 2H), 7.38 (td, $J = 7.8$, 1.7 Hz, 1H), 7.29 (td, $J = 7.5$, 1.3 Hz, 1H), 7.11 (dd, $J = 8.0$, 1.2 Hz, 1H), 6.63 (d, $J = 15.9$ Hz, 1H), 6.62 (d, $J = 6.5$ Hz, 1H); 13C NMR (125 MHz, CDCl$_3$) δ 169.9, 169.5, 148.4, 139.7, 131.2, 130.7, 130.0 (d, $J = 32.4$ Hz), 129.7, 129.0, 128.8, 127.0, 126.6, 125.7 (q, $J = 3.8$ Hz), 124.2 (d, $J = 272.0$ Hz), 123.4, 70.8, 21.3, 21.2; 19F NMR (376 MHz, CDCl$_3$) δ -62.62; IR (film): 3085, 3044, 2937, 1726, 1782, 1726, 1657, 1615,
(E)-2-(1-Acetoxy-3-(3,4-dichlorophenyl)allyl)phenyl acetate (1k). Prepared according to the general procedure using its (E)-3-(3,4-dichlorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford 1k as a colorless oil (230 mg, 28%). Analytical data for 1k: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.39 (dd, \(J = 7.7, 1.7\) Hz, 1H), 7.35 (s, 1H), 7.31 – 7.26 (m, 2H), 7.22 – 7.14 (m, 1H), 7.08 (dd, \(J = 8.3, 2.1\) Hz, 1H), 7.01 (dd, \(J = 8.0, 1.3\) Hz, 1H), 6.49 (dd, \(J = 6.1, 1.4\) Hz, 1H), 6.40 (dd, \(J = 15.9, 1.4\) Hz, 1H), 6.24 (dd, \(J = 15.9, 6.2\) Hz, 1H), 2.22 (s, 3H), 2.02 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) 169.9, 169.5, 148.3, 136.3, 132.9, 131.9, 130.64, 130.60, 130.2, 129.7, 128.7, 128.5, 128.4, 126.6, 126.0, 123.3, 70.7, 21.24, 21.18; IR (film): 3063, 3038, 2926, 2852, 1767, 1739, 1608, 1587, 1554, 1473, 1454, 1431, 1370, 1198, 1174, 1133, 1026 cm\(^{-1}\); LRMS (ESI): Mass calculated for [M+H]+ C\(_{19}\)H\(_{17}\)Cl\(_2\)O\(_4\): 379.1; found: 379.1.

(E)-2-(1-Acetoxy-3-(3-nitrophenyl)allyl)phenyl acetate (1l). Prepared according to the general procedure using (E)-1-(2-hydroxyphenyl)-3-(3-nitrophenyl)prop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford 1l as a colorless oil (352 mg, 54%). Analytical data for 1l: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.23 (t, \(J = 1.9\) Hz, 1H), 8.10 (ddd, \(J = 8.4, 2.3, 1.1\) Hz, 1H), 7.66 (dt, \(J = 8.0, 1.3\) Hz, 1H), 7.57 – 7.45 (m, 2H), 7.40 (dd, \(J = 8.1, 1.3\) Hz, 1H), 6.65 (d, \(J = 16.0\) Hz, 1H), 6.63 (d, \(J = 6.0\) Hz, 1H), 6.49 (dd, \(J = 16.0, 5.9\) Hz, 1H), 2.34 (s, 3H), 2.20 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) 169.9, 169.5, 148.3, 138.0, 132.6, 130.4, 130.2, 129.8, 129.7 (2C), 128.8, 126.6, 123.4, 122.8, 121.4, 70.6, 21.24, 21.20; IR (film): 3087, 3068, 3039, 2937, 2869, 2310, 2281, 1825, 1780, 1721, 1656, 1608, 1587, 1490, 1431, 1378, 1341, 1262, 1158, 1043, 1023, 975 cm\(^{-1}\); LRMS (ESI): Mass calculated for [M+H]+ C\(_{19}\)H\(_{18}\)NO\(_6\): 356.1; found: 356.2.

(E)-2-(1-Acetoxy-3-phenylallyl)-5-fluorophenyl acetate (1m). Prepared according to the general procedure using (E)-1-(2-hydroxyphenyl)-3-(3-nitrophenyl)prop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford 1m as a colorless oil (485 mg, 70%). Analytical data for 1m: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.48 (dd, \(J = 8.7, 6.2\) Hz, 1H), 7.39 – 7.27 (m, 5H), 6.99 (dd, \(J = 8.6, 7.9, 2.6\) Hz, 1H), 6.89 (dd, \(J = 9.1, 2.6\) Hz, 1H), 6.60 (d, \(J = 16.0\) Hz, 1H), 6.57 (dd, \(J = 6.4, 1.4\) Hz, 1H), 6.32 (dd, \(J = 15.9, 6.4\) Hz, 1H), 2.32 (s, 3H), 2.10 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) 169.9, 169.0, 162.5 (d, \(J = 249.3\))
Hz), 149.1 (d, J = 10.9 Hz), 136.0, 132.9, 129.9 (d, J = 9.6 Hz), 128.8, 128.4, 127.2 (d, J = 3.6 Hz), 126.8, 126.0, 113.6 (d, J = 21.3 Hz), 111.2 (d, J = 24.4 Hz), 70.7, 21.3, 21.1; 19F NMR (376 MHz, CDCl3) δ -112.10; IR (film): 3082, 3028, 2938, 1951, 1890, 1732, 1651, 1603, 1578, 1504, 1425, 1371, 1235, 1143, 1091 and 1015 cm⁻¹; LRMS (ESI): Mass calculated for [M+H]⁺ C19H18FO4: 329.1; found: 329.2.

(E)-2-(1-Acetoxy-3-phenylallyl)-4-fluorophenyl acetate (1n). Prepared according to the general procedure using (E)-1-(5-fluoro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford 1n as a yellow oil (382.1 mg, 63%). Analytical data for 1n: 1H NMR (500 MHz, CDCl3) δ 7.39 – 7.29 (m, 4H), 7.28 – 7.24 (m, 1H), 7.22 (dd, J = 8.9, 2.8 Hz, 1H), 7.10 – 7.02 (m, 2H), 6.63 (dd, J = 15.9, 1.3 Hz, 1H), 6.56 (dd, J = 6.8, 1.3 Hz, 1H), 6.28 (dd, J = 15.9, 6.6 Hz, 1H), 2.30 (s, 3H), 2.13 (s, 3H); 13C NMR (125 MHz, CDCl3) 169.8, 169.5, 160.4 (d, J = 245.3 Hz), 144.0 (d, J = 2.9 Hz), 135.9, 133.5, 133.1 (d, J = 7.4 Hz), 128.8, 128.4, 126.8, 125.5, 124.7 (d, J = 8.5 Hz), 116.1 (d, J = 23.4 Hz), 115.1 (d, J = 24.4 Hz), 70.7, 21.3, 21.1; 19F NMR (376 MHz, CDCl3) δ -115.63; IR (film): 3082, 3060, 3028., 2935, 2851, 1766, 1651, 1619, 1579, 1494, 1370, 1269, 1205, 1171, 1065, 1017, 968, 941, 901, 879 cm⁻¹; LRMS (ESI): Mass calculated for [M+H]⁺ C19H18FO4: 329.1; found: 329.1.

(E)-2-(1-Acetoxy-3-phenylallyl)-4-methoxyphenyl acetate (1o). Prepared according to the general procedure using (E)-1-(2-hydroxy-5-methoxyphenyl)-3-phenylprop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford 1o as a colorless oil (380 mg, 61%). Analytical data for 1o: 1H NMR (500 MHz, CDCl3) δ 7.37 (d, J = 7.0 Hz, 2H), 7.31 (t, J = 7.4 Hz, 2H), 7.24 (d, J = 7.3 Hz, 1H), 7.03 (d, J = 1.8 Hz, 1H), 7.02 (d, J = 4.1 Hz, 1H), 6.88 (dd, J = 8.9, 3.1 Hz, 1H), 6.62 (dd, J = 15.9, 1.3 Hz, 1H), 6.55 (dd, J = 6.5, 1.4 Hz, 1H), 6.32 (dd, J = 15.9, 6.5 Hz, 1H), 3.81 (s, 3H), 2.29 (s, 3H), 2.12 (s, 3H); 13C NMR (125 MHz, CDCl3) δ 169.93, 169.91, 157.6, 141.7, 136.1, 133.0, 132.0, 128.7, 128.3, 126.8, 126.0, 124.0, 114.2, 113.9, 71.2, 55.8, 21.3, 21.1; IR (film): 3086, 3061, 3032, 2999, 2917, 2849, 2832, 1608, 1578, 1488, 1433, 1372, 1307, 1269, 1165, 1029 cm⁻¹; LRMS (ESI): Mass calculated for [M+H]⁺ C20H21O5: 341.1; found 341.1.
(E)-1-(2-Acetoxy-3-methylphenyl)-3-phenylallyl acetate (1p). Prepared according to the general procedure using (E)-1-(2-hydroxy-3-methylphenyl)-3-phenylprop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford 1p as a yellow oil (280 mg, 47%). Analytical data for 1p: 1H NMR (500 MHz, CDCl3) δ 7.40 – 7.15 (m, 8H), 6.62 (dd, J = 15.9, 1.4 Hz, 1H), 6.55 (m, 1 H), 6.36 (dd, J = 15.9, 6.5 Hz, 1H), 2.33 (s, 3H), 2.17 (s, 3H), 2.10 (s, 3H); 13C NMR (125 MHz, CDCl3) δ 170.0, 169.0, 147.4, 136.2, 131.5, 131.4, 131.3, 128.7, 128.2, 127.3, 126.8, 126.5, 126.4, 126.3, 76.2, 21.3, 20.9, 16.5; IR (film): 3060, 3027, 2957, 2925, 2855, 1762, 1740, 1598, 1577, 1496, 1468, 1437, 1369, 1232, 1209, 1165, 1089, 1016, 966 and 907 cm−1; LRMS (ESI): Mass calculated for [M+H]+ C20H21O4: 325.1; found: 325.1.

General Procedure for Enantioselective Synthesis of Chromenes

Into an oven-dried, screw-capped reaction tube-vial equipped with magnetic stirbar was loaded bis-acetate (0.36 mmol, 1 equiv). The vial was taken into a nitrogen-filled drybox at which time Pd2(dba)3 (7.2 µmol, 0.02 equiv) and phosphoramidite (29 µmol, 0.08 equiv) were added. The vial was capped with a septum cap, removed from the drybox and put under positive N2 pressure. The mixture was diluted with CH2Cl2 (3.6 mL) and stirred for 10 min under static nitrogen pressure. A solution of K2CO3 (0.36 mmol, 1 equiv) in methanol:water (1.8 mL:1.8 mL) was added. The resulting biphasic mixture was stirred at 23 °C for 19-48 h. Reaction was extracted with CH2Cl2. The combined organic layers were filtered through a Biotage ISOLUTE® phase separator, and the organic filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography using EtOAc/hexanes to afford the corresponding chromene.

2-Phenyl-2H-chromene (2a). Prepared according to the general procedure using 1a. The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford 2a as a light yellow oil (53 mg, 71%). Analytical data for 2a: 1H NMR (500 MHz, CDCl3) δ 7.52 – 7.43 (m, 2H), 7.43 – 7.36 (m, 2H), 7.36 – 7.31 (m, 1H), 7.12 (td, J = 7.8, 1.7 Hz, 1H), 7.02 (dd, J = 7.5, 1.7 Hz, 1H), 6.87 (td, J = 7.4, 1.1 Hz, 1H), 6.80 (d, J = 8.1 Hz, 1H), 6.54 (dd, J = 9.8, 1.9 Hz, 1H), 5.93 (dd, J = 3.4, 1.9 Hz, 1H), 5.81 (dd, J = 9.8, 3.4 Hz, 1H); 13C NMR (125 MHz, CDCl3) δ 153.5, 141.2, 129.9, 129.1, 128.8, 127.4, 127.0, 125.2, 124.4, 121.7, 121.6, 116.4, 77.5; IR (film): 3043, 2919, 2851,1573, 1510, 1456, 1456, 1227, 1201, 1112, 1060, 857 cm−1; HRMS (EI): Mass calculated for [M]+ C15H12O: 208.0888; found 208.0869; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OJ-H; 100% hexanes; 0.7 mL/min, 280 nm), Rt1 (minor) = 61.4. Rt2 (major) = 74.8 min; er = 95:5. The absolute configuration of the chromenes was determined by comparison of optical rotation to literature value of the known enantiomer.5

2-(Naphthalen-1-yl)-2H-chromene (2b). Prepared according to the general procedure using 1b. The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford 2b as a light yellow oil (66 mg, 71%). Analytical data for 2b: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.32 (d, $J = 8.4$ Hz, 1H), 7.90 (dd, $J = 7.9$, 1.7 Hz, 1H), 7.84 (d, $J = 8.2$ Hz, 1H), 7.65 (dd, $J = 7.0$, 1.1 Hz, 1H), 7.54 (dd, $J = 20.2$, 8.0, 6.7, 1.4 Hz, 2H), 7.45 (dd, $J = 8.2$, 7.1 Hz, 1H), 7.11 (td, $J = 7.7$, 1.7 Hz, 1H), 7.08 (dd, $J = 7.4$, 1.6 Hz, 1H), 6.90 (td, $J = 7.4$, 1.1 Hz, 1H), 6.79 (d, $J = 8.0$ Hz, 1H), 6.65 (dd, $J = 9.7$, 2.1 Hz, 1H), 6.62 (t, $J = 2.7$ Hz, 1H), 5.92 (dd, $J = 9.8$, 3.3 Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 153.9, 135.8, 134.5, 131.3, 129.9, 129.6, 129.2, 127.1, 126.8, 126.24, 126.16, 125.7, 125.3, 125.2, 124.4, 122.0, 121.7, 116.6, 75.2; IR (film): 3072, 3042, 1640, 1605, 1510, 1485, 1456, 1307, 1228, 1200, 1112, 1060, 1036, 1010, 959, 944 cm$^{-1}$; HRMS (EI): Mass calculated for [M]$^+$ C$_{19}$H$_{14}$O: 258.1045; found 258.1036; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OJ-H; 100% hexanes; 0.7 mL/min, 280 nm), $R_t$ (minor) = 61.2, $R_t$ (major) = 83.9 min; er = 94:6.

2-(Naphthalen-2-yl)-2H-chromene (2c). Prepared according to the general procedure using 1c. The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford 2c as a light yellow oil (81 mg, 87%). Analytical data for 2c: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.89 – 7.81 (m, 4H), 7.61 (dd, $J = 8.5$, 1.8 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.12 (td, $J = 7.8$, 1.7 Hz, 1H), 7.04 (dd, $J = 7.5$, 1.6 Hz, 1H), 6.88 (td, $J = 7.5$, 1.2 Hz, 1H), 6.81 (dt, $J = 8.2$, 1.0 Hz, 1H), 6.59 (dd, $J = 10.0$, 1.9, 0.8 Hz, 1H), 6.09 (dd, $J = 3.4$, 1.9 Hz, 1H), 5.88 (dd, $J = 9.9$, 3.4 Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 153.9, 135.8, 134.5, 131.3, 129.9, 129.6, 129.2, 127.1, 126.8, 126.24, 126.16, 125.7, 125.3, 125.2, 124.4, 122.0, 121.7, 116.6, 75.2; IR (film): 3072, 3042, 1640, 1510, 1485, 1456, 1307, 1228, 1200, 1112, 1060, 1036, 1010, 959, 944 cm$^{-1}$; HRMS (EI): Mass calculated for [M]$^+$ C$_{19}$H$_{14}$O: 258.1045; found 258.1022; Enantiomeric ratio was measured by chiral phase HPLC (Whelk-O; 100% hexanes; 0.7 mL/min, 280 nm), $R_t$ (minor) = 35.7, $R_t$ (major) = 66.8 min; er = 91:9.

2-(o-Tolyl)-2H-chromene (2d). Prepared according to the general procedure using 1d. The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford 2d as a yellow oil (58 mg, 72%). Analytical data for 2d: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.48 (dt, $J = 7.0$, 1.2 Hz, 1H), 7.24 – 7.18 (m, 3H), 7.11 (td, $J = 7.8$, 1.7 Hz, 1H), 7.02 (dd, $J = 7.4$, 1.7 Hz, 1H), 6.87 (td, $J = 7.4$, 1.1 Hz, 1H), 6.77 (dt, $J = 8.1$, 0.9 Hz, 1H), 6.56 (dd, $J = 9.8$, 2.1 Hz, 1H), 6.15 (dd, $J = 3.1$, 1H).
2.1 Hz, 1H), 5.75 (dd, J = 9.8, 3.2 Hz, 1H), 2.47 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 153.6, 138.4, 136.1, 131.0, 129.5, 128.5, 127.8, 126.7, 126.3, 124.7, 124.6, 121.5, 121.3, 116.1, 74.8, 19.4; IR (film): 3061, 3022, 2971, 2924, 1646, 1633, 1586, 1563, 1485 cm\(^{-1}\); HRMS (EI): Mass calculated for [M]\(^+\) \(C_{16}H_{14}O\): 222.1045; found 222.1018; Enantiomeric ratio was measured by chiral phase HPLC (Whelk-O; 100% hexanes; 0.1 mL/min, 280 nm), \(R_t\) (minor) = 100.9, \(R_t\) (major) = 118.5 min; \(\text{er} = 92:8\).

2-(\(p\)-Tolyl)-2\(H\)-chromene (2e). Prepared according to the general procedure using 1e. The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford 2e as a yellow oil (58 mg, 73%). Analytical data for 2e: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.39 – 7.35 (m, 2H), 7.20 (d, J = 7.9 Hz, 2H), 7.12 (td, J = 7.7, 1.7 Hz, 1H), 7.03 (dd, J = 7.4, 1.7 Hz, 1H), 6.88 (td, J = 7.5, 1.2 Hz, 1H), 6.80 (dt, J = 8.1, 0.9 Hz, 1H), 6.55 (dd, J = 9.9, 1.9 Hz, 1H), 5.90 (dd, J = 3.4, 1.9 Hz, 1H), 5.81 (dd, J = 9.8, 3.4 Hz, 1H), 2.37 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 153.3, 138.4, 138.0, 129.6, 129.5, 127.2, 126.7, 125.1, 124.1, 121.5, 121.3, 116.2, 77.4, 21.6; IR (film): 3044, 2958, 2851, 1633, 1484 cm\(^{-1}\); HRMS (EI): Mass calculated for [M]\(^+\) \(C_{16}H_{14}O\): 222.1045; found 222.1015; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OJ-H; 100% hexanes; 0.7 mL/min, 280 nm), \(R_t\) (major) = 62.3, \(R_t\) (minor) = 124.4 min; \(\text{er} = 93:7\).

2-(3-Methoxyphenyl)-2\(H\)-chromene (2f). Prepared according to the general procedure using 1f. The residue was purified by flash chromatography using 1.5% EtOAc/hexanes to afford 2f as a light yellow oil (67 mg, 78%). Analytical data for 2f: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.29 (t, J = 7.9 Hz, 1H), 7.14 – 7.08 (m, 1H), 7.06 – 6.98 (m, 3H), 6.89 – 6.84 (m, 2H), 6.80 (dt, J = 8.0, 0.9 Hz, 1H), 6.55 – 6.50 (m, 1H), 5.91 – 5.87 (m, 1H), 5.79 (dd, J = 9.8, 3.4 Hz, 1H), 3.80 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 160.2, 153.5, 142.8, 130.1, 129.9, 127.0, 125.2, 124.4, 121.7, 121.6, 119.7, 116.4, 114.2, 112.9, 55.6, 53.8; IR (film): 3043, 2958, 2851, 1613, 1485 cm\(^{-1}\); HRMS (EI): Mass calculated for [M]\(^+\) \(C_{16}H_{14}O_2\): 238.0994; found 238.0983; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OJ-H; 100% hexanes; 0.7 mL/min, 280 nm), \(R_t\) (minor) = 102.8, \(R_t\) (major) = 127.3 min; \(\text{er} = 94:6\).

2-(2-Fluorophenyl)-2\(H\)-chromene (2g). Prepared according to the general procedure using 1g. The residue was purified by flash chromatography using 0.8% EtOAc/hexanes to afford 2g as a light yellow oil (61 mg, 75%). Analytical data for 2g: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.51 (td, J = 7.9 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.21 – 7.16 (m, 1H), 7.10 – 7.00 (m, 3H), 6.89 – 6.84 (m, 2H), 6.80 (dt, J = 8.0, 0.9 Hz, 1H), 6.55 – 6.50 (m, 1H), 5.91 – 5.87 (m, 1H), 5.79 (dd, J = 9.8, 3.4 Hz, 1H), 3.80 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 160.2, 153.5, 142.8, 130.1, 129.9, 127.0, 125.2, 124.4, 121.7, 121.6, 119.7, 116.4, 114.2, 112.9, 55.6, 53.8; IR (film): 3043, 2930, 2851, 1610, 1485, 1286, 1227, 788 cm\(^{-1}\); HRMS (EI): Mass calculated for [M]\(^+\) \(C_{16}H_{14}F\): 234.0994; found 234.0983; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OJ-H; 100% hexanes; 0.7 mL/min, 280 nm), \(R_t\) (minor) = 102.8, \(R_t\) (major) = 127.3 min; \(\text{er} = 94:6\).
7.6, 1.8 Hz, 1H), 7.30 (dddd, J = 8.2, 7.2, 5.3, 1.8 Hz, 1H), 7.15 – 7.11 (m, 2H), 7.08 (dd, J = 10.3, 8.3, 1.2 Hz, 1H), 7.01 (dd, J = 7.5, 1.7 Hz, 1H), 6.88 (td, J = 7.4, 1.1 Hz, 1H), 6.81 (dt, J = 8.1, 1.0 Hz, 1H), 6.54 (ddd, J = 9.9, 1.9, 0.8 Hz, 1H), 6.29 (dd, J = 3.6, 1.9 Hz, 1H), 5.79 (ddd, J = 10.0, 3.6, 1.1 Hz, 1H); 13C NMR (125 MHz, CDCl₃) δ 159.6 (d, J = 247.4 Hz), 153.2, 130.0 (d, J = 8.2 Hz), 129.7, 128.7 (d, J = 3.9 Hz), 128.1 (d, J = 13.4 Hz), 126.8, 124.5 (d, J = 3.6 Hz), 124.4, 123.8, 121.5, 121.2, 116.1, 115.7 (d, J = 21.4 Hz), 71.2 (d, J = 3.8 Hz); IR (film): 3044, 2923, 2851, 1641, 1485 cm⁻¹; HRMS (EI): Mass calculated for [M]⁺ C₁₅H₁₁FO: 226.0794; found: 226.0808; Enantiomer ratio was measured by chiral phase HPLC (Chiralcel OJ-H; 100% hexanes; 0.7 mL/min, 280 nm), Rt₁ (minor) = 22.2, Rt₂ (major) = 35.3 min; er = 91:9.

2-(4-Fluorophenyl)-2H-chromene (2h). Prepared according to the general procedure using 1h. The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford 2h as a light yellow oil (69 mg, 84%). Analytical data for 2h: 1H NMR (500 MHz, CDCl₃) δ 7.43 (td, J = 5.9, 1.9 Hz, 2H), 7.12 (td, J = 7.8, 1.7 Hz, 1H), 7.05 (t, J = 8.7 Hz, 2H), 7.02 (dd, J = 7.5, 1.7 Hz, 1H), 6.88 (td, J = 7.4, 1.1 Hz, 1H), 6.77 (d, J = 7.9 Hz, 1H), 6.56 (dd, J = 9.9, 1.9 Hz, 1H), 5.90 (dd, J = 3.5, 1.9 Hz, 1H), 5.78 (dd, J = 9.9, 3.4 Hz, 1H); 13C NMR (125 MHz, CDCl₃) δ 162.8 (d, J = 246.8 Hz), 153.0, 136.7 (d, J = 3.2 Hz), 129.7, 129.1 (d, J = 8.3 Hz), 126.8, 124.6, 124.4, 121.44, 121.35, 116.2, 115.7 (d, J = 21.5 Hz), 76.5; 19F NMR (376 MHz, CDCl₃) δ -113.75; IR (film): 2922, 2852, 1719, 1603, 1509, 1484, 1457, 1224, 1204 cm⁻¹; HRMS (EI): Mass calculated for [M]⁺ C₁₅H₁₁FO: 226.0794; found: 226.0764; Enantiomeric ratio was measured by chiral phase HPLC (Whelk-O; 100% hexanes; 1.0 mL/min, 280 nm), Rt₁ (minor) = 9.5, Rt₂ (major) = 10.5 min; er = 95:5.

2-(3-Chlorophenyl)-2H-chromene (2i). Prepared according to the general procedure using 1i. The residue was purified by flash chromatography using 0.6% EtOAc/hexanes to afford 2i as a light yellow oil (71 mg, 81%). Analytical data for 2i: 1H NMR (500 MHz, CDCl₃) δ 7.46 (q, J = 1.4 Hz, 1H), 7.34 (qd, J = 4.3, 1.5 Hz, 1H), 7.32 – 7.30 (m, 2H), 7.14 (td, J = 7.8, 1.7 Hz, 1H), 7.03 (dd, J = 7.5, 1.7 Hz, 1H), 6.89 (td, J = 7.4, 1.2 Hz, 1H), 6.81 (d, J = 8.1 Hz, 1H), 6.56 (dd, J = 9.9, 1.9 Hz, 1H), 5.90 (dd, J = 3.5, 1.9 Hz, 1H), 5.78 (dd, J = 9.9, 3.4 Hz, 1H); 13C NMR (125 MHz, CDCl₃) δ 152.9, 142.9, 134.6, 130.1, 129.8, 128.6, 127.3, 126.8, 125.2, 124.6, 124.1, 121.6, 121.2, 116.1, 76.4; IR (film): 3048, 2923, 2847, 1638, 1602, 1574, 1483, 1457, 1430, 1349 cm⁻¹; HRMS (EI): Mass calculated for [M]⁺ C₁₅H₁₁ClO: 242.0498; found: 242.0508; Enantiomeric ratio was measured by chiral phase HPLC (Whelk-O; 100% hexanes; 0.35 mL/min, 280 nm), Rt₁ (minor) = 27.0, Rt₂ (major) = 31.7 min; er = 93:7.
2-(4-(Trifluoromethyl)phenyl)-2H-chromene (2j). Prepared according to the general procedure using 1j. The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford 2j as a light yellow oil (66 mg, 84%). Analytical data for 2j: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.63 (d, \(J = 8.1\) Hz, 2H), 7.57 (d, \(J = 8.1\) Hz, 2H), 7.14 (td, \(J = 7.8, 1.6\) Hz, 1H), 7.02 (dd, \(J = 7.4, 1.6\) Hz, 1H), 6.89 (td, \(J = 7.5, 1.1\) Hz, 1H), 6.81 (d, \(J = 8.0\) Hz, 1H), 6.57 (dd, \(J = 9.8, 1.8\) Hz, 1H), 5.97 (s, 1H), 5.79 (dd, \(J = 9.8, 3.5\) Hz, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 152.9, 144.8, 130.5 (d, \(J = 32.4\) Hz), 129.9, 127.3, 126.9, 125.8 (q, \(J = 3.8\) Hz), 124.7, 124.1 (d, \(J = 272.0\) Hz), 124.0, 121.7, 121.2, 116.1, 76.4; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -62.64; IR (film): 3047, 2925, 2854, 1620, 1574, 1485, 1457, 1418, 1325 cm\(^{-1}\); HRMS (EI): Mass calculated for [M]\(^+\) C\(_{16}\)H\(_{11}\)F\(_3\)O: 276.0762; found: 276.0736; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OJ-H; 100% hexanes; 0.7 mL/min, 280 nm), \(R_t\) (minor) = 30.8, \(R_t\) (major) = 44.4 min; \(\text{er} = 83:17\).

2-(3,4-Dichlorophenyl)-2H-chromene (2k). Prepared according to the general procedure using 1k. The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford 2k as a light yellow oil (74 mg, 74%). Analytical data for 2k: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.54 (d, \(J = 2.1\) Hz, 1H), 7.43 (d, \(J = 8.3\) Hz, 1H), 7.29 (dd, \(J = 8.3, 2.1\) Hz, 1H), 7.13 (td, \(J = 7.8, 1.7\) Hz, 1H), 7.02 (dd, \(J = 7.5, 1.7\) Hz, 1H), 6.89 (td, \(J = 7.5, 1.1\) Hz, 1H), 6.79 (dt, \(J = 8.0, 0.9\) Hz, 1H), 6.57 (dd, \(J = 9.7, 1.4\) Hz, 1H), 5.87 (dd, \(J = 3.6, 1.8\) Hz, 1H), 5.76 (dd, \(J = 9.8, 3.5\) Hz, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 153.0, 141.3, 133.1, 132.7, 131.0, 130.2, 129.5, 127.2, 126.7, 125.2, 123.9, 122.0, 121.4, 116.4, 76.0; IR (film): 3076, 2924, 2827, 1641, 1486 cm\(^{-1}\); HRMS (EI): Mass calculated for [M]\(^+\) C\(_{15}\)H\(_{10}\)Cl\(_2\)O: 276.0109; found: 276.0137; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OJ-H; 100% hexanes; 0.5 mL/min, 280 nm), \(R_t\) (major) = 78.0, \(R_t\) (minor) = 133.5 min; \(\text{er} = 90:10\).

2-(3-Nitrophenyl)-2H-chromene (2l). Prepared according to the general procedure using 1l. The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford 2l as a light yellow oil (65 mg, 71%). Analytical data for 2l: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.32 (q, \(J = 1.9\) Hz, 1H), 8.18 (ddt, \(J = 8.4, 2.6, 1.3\) Hz, 1H), 7.81 (dt, \(J = 7.8, 1.5\) Hz, 1H), 7.55 (td, \(J = 8.0, 1.8\) Hz, 1H), 7.15 (tt, \(J = 7.6, 1.7\) Hz, 1H), 7.04 (dt, \(J = 7.6, 1.8\) Hz, 1H), 6.90 (tt, \(J = 7.5, 1.4\) Hz, 1H), 6.82 (d, \(J = 8.1\) Hz, 1H), 6.62 (dt, \(J = 10.0, 1.9\) Hz, 1H), 6.02 (dd, \(J = 3.7, 1.9\) Hz, 1H), 5.83 (dd, \(J = 9.8, 3.6, 1.7\) Hz, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 152.7, 148.5, 143.0, 133.2, 130.0, 129.8, 127.0, 125.3, 123.4, 123.3, 122.1, 121.9, 121.2, 116.2, 75.7; IR (film): 3065, 3032, 2920, 2845, 1645, 1612, 1587, 1500, 1454, 1432, 1264, 1160, 1138, 1105, 1036, 982 cm\(^{-1}\); HRMS
(EI): Mass calculated for [M]+ C_{15}H_{11}NO_3: 253.0739; found: 253.0715; Enantiomeric ratio was measured by chiral phase HPLC (Whelk-O; 100% hexanes; 0.2 mL/min, 280 nm), Rt_1 (minor) =48.0, Rt_2 (major) =51.8 min; er = 92:8.

7-Fluoro-2-phenyl-2H-chromene (2m). Prepared according to the general procedure using 1m. The residue was purified by flash chromatography using 0.5% EtOAc/hexanes to afford 2m as a light yellow oil (56 mg, 69%). Analytical data for 2m: 1H NMR (500 MHz, CDCl_3) δ 7.45 – 7.32 (m, 5H), 6.96 (dd, J = 8.3, 6.4 Hz, 1H), 6.57 (td, J = 8.4, 2.5 Hz, 1H), 6.51 (ddd, J = 10.0, 3.7, 2.1 Hz, 2H), 5.91 (q, J = 3.1, 1.9 Hz, 1H), 5.76 (dd, J = 9.9, 3.4 Hz, 1H); 13C NMR (125 MHz, CDCl_3) δ 163.4 (d, J = 246.7 Hz), 154.5 (d, J = 12.4 Hz), 140.5 (d, J = 12.4 Hz), 128.9, 128.7, 127.55 (d, J = 10.0 Hz), 127.2, 123.6 (d, J = 2.6 Hz), 123.3, 117.7 (d, J = 3.2 Hz), 108.0 (d, J = 21.9 Hz), 104.1 (d, J = 21.9 Hz), 77.4; IR (film): 3065, 3032, 2920, 2845, 1645, 1612, 1587, 1500, 1454, 1432, 1264, 1160, 1137, 1105, 1036, 982, 852 cm⁻¹; HRMS (EI): Mass calculated for [M]+ C_{15}H_{11}FO: 226.0794; found: 226.0804; Enantiomeric ratio was measured by chiral phase HPLC (Whelk-O; 100% hexanes; 0.2 mL/min, 280 nm), Rt_1 (minor) =45.9, Rt_2 (major) =52.6 min; er = 90:10.

6-Fluoro-2-phenyl-2H-chromene (2n). Prepared according to the general procedure using 1n. The residue was purified by flash chromatography using 0.5% EtOAc/hexanes to afford 2n as white solids (59 mg, 72%). Analytical data for 2n: 1H NMR (500 MHz, CDCl_3) δ 7.43 (dt, J = 6.9, 2.1, 1.6 Hz, 2H), 7.40 – 7.31 (m, 3H), 6.79 (td, J = 8.5, 3.0 Hz, 1H), 6.76 – 6.69 (m, 2H), 6.49 (dt, J = 7.7, 3.1, 2.6 Hz, 1H), 5.91 – 5.85 (m, 2H); 13C NMR (125 MHz, CDCl_3) δ 157.4 (d, J = 238.3 Hz), 149.1 (d, J = 1.8 Hz), 140.3, 128.7, 128.6, 127.1, 126.4, 123.6 (d, J = 2.1 Hz), 122.3 (d, J = 8.4 Hz), 116.9 (d, J = 8.1 Hz), 115.5 (d, J = 23.2 Hz), 112.8 (d, J = 23.8 Hz), 77.2; 19F NMR (376 MHz, CDCl_3) δ -123.28; IR (film): 3063, 3032, 2954, 2921, 2851, 1645, 1612, 1587, 1500, 1454, 1432, 1264, 1160, 1137, 1105, 1036, 982, 852 cm⁻¹; HRMS (EI): Mass calculated for [M]+ C_{15}H_{11}FO: 226.0794; found: 226.0804; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OJ-H; 100% hexanes; 0.7 mL/min, 280 nm), Rt_1 (minor) =66.2, Rt_2 (major) =77.0 min; er = 97:3.

6-Methoxy-2-phenyl-2H-chromene (2o). Prepared according to the general procedure using 1o. The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford 2o as a light yellow oil (68 mg, 80%). Analytical data for 2o: 1H NMR (500 MHz, CDCl_3) δ 7.47 – 7.42 (m, 2H), 7.40 – 7.29 (m, 3H), 6.73 (d, J = 8.8 Hz, 1H), 6.67 (ddd, J = 8.9, 3.1, 1.2 Hz, 1H), 6.59 (dd, J = 3.2, 1.2 Hz, 1H), 6.54 – 6.46 (m, 1H), 5.88 – 5.82 (m, 2H), 3.76 (d, J = 1.4 Hz, 3H); 13C NMR (125 MHz, CDCl_3) δ 154.1, 147.1, 140.8, 128.8, 128.5, 127.2, 126.0, 124.3, 122.2, 116.7,
114.6, 111.9, 77.1, 55.9; IR (film): 3033, 2998, 2915, 2831, 1609, 1576, 1490, 1429, 1344, 1307, 1265, 1208, 1158, 1117, 1045 cm$^{-1}$; HRMS (EI): Mass calculated for [M]$^+$ C$_{16}$H$_{14}$O$_2$: 238.0994; found 238.0970; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OJ-H; 40% IPA/ hexanes; 1.0 mL/min, 280 nm), Rt$_1$ (minor) =23.4, Rt$_2$ (major) =33.6 min; er = 86:14.

8-Methyl-2-phenyl-2H-chromene (2p). Prepared according to the general procedure using 1p. The residue was purified by flash chromatography using 0.1% EtOAc/hexanes to afford 2p as a light yellow oil (58 mg, 73%). Analytical data for 2p: $^1$H NMR (500 MHz, CDCl$_3$) δ 7.45 (d, $J$ = 7.5 Hz, 2H), 7.39 – 7.29 (m, 3H), 6.98 (d, $J$ = 7.5 Hz, 1H), 6.86 (d, $J$ = 7.5 Hz, 1H), 6.77 (t, $J$ = 7.5 Hz, 1H), 6.52 (dd, $J$ = 9.9, 1.8 Hz, 1H), 5.94 (dd, $J$ = 3.7, 1.8 Hz, 1H), 5.82 (dd, $J$ = 9.8, 3.6 Hz, 1H), 2.16 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 151.5, 141.6, 131.3, 128.9 (2C), 128.5, 127.1 (2C), 125.6, 124.9, 124.7 (2C), 121.3, 120.9, 77.0, 16.0; IR (film): 3062, 3044, 3029, 2920, 2851, 1644, 1602, 1494, 1455, 1390, 1344, 1304, 1264, 1208, 1178, 1156, 1082, 1055, 1029, 1001, 968, 939, 917 cm$^{-1}$; HRMS (EI): Mass calculated for [M]$^+$ C$_{16}$H$_{14}$O: 222.1045; found 222.1031; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OJ-H; 5 %IPA/ hexanes; 1.0 mL/min, 280 nm), Rt$_1$ (minor) =8.7, Rt$_2$ (major) =12.5 min; er = 85:15.

**General Procedure for Racemic Synthesis of Chromenes**

To a round bottom flask equipped with magnetic stir bar was dissolved 2’-hydroxychalcone derivative (0.5 mmol, 1 equiv) in isopropanol (5 mL). Mixture was heated to 70 °C before NaBH$_4$ (1.5 mmol, 3 equiv.) was added in one portion and was slowly cooled to 23 °C. Ice was added and the resulting solution was acidified using 10% glacial acetic acid to pH 5. The solution was extracted with CH$_2$Cl$_2$, organics washed with brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography with EtOAc/hexanes to afford the corresponding chromenes.

**Synthesis of Ligand**

To a solution of diol (2.94 mmol, 1 equiv) and triethylamine (14.68 mmol, 5 equiv) in dry, oxygen-free THF (18 mL) at 0 °C was added PCl$_3$ (3.52 mmol, 1.2 equiv). After stirring for 2 h at 23 °C under positive N$_2$ pressure, reaction was cooled to 0 °C before a solution of piperidine (5.87 mmol, 2 equiv) in dry, oxygen-free THF (10 mL) was slowly added via cannula. The resulting mixture was slowly warmed to 23 °C and stirred for 20 h under positive N$_2$ pressure. Reaction was diluted with Et$_2$O, filtered through a plug of Celite®, and concentrated under reduced pressure. The residue was purified by flash chromatography using EtOAc/hexanes to afford the corresponding phosphoramidites.
1-((5R,6R)-5,6-Dimethoxy-4,4,7,7-tetraphenyl-1,3,2-dioxaphosphepan-2-yl)piperidine (L4). Prepared according to the general procedure using (2R,3R)-2,3-dimethoxy-1,1,4,4-tetraphenylbutane-1,4-diol. The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford L4 as a white foam (44 mg, 65%). Analytical data for L4: 1H NMR (500 MHz, CDCl3) δ 7.73 (d, J = 7.0 Hz, 2H), 7.53 (d, J = 7.3 Hz, 2H), 7.43 (d, J = 7.3 Hz, 2H), 7.36 – 7.18 (m, 14H), 4.50 (dd, J = 7.3, 3.6 Hz, 1H), 4.30 (d, J = 7.3 Hz, 1H), 3.26 (s, 3H), 3.16 (dtd, J = 15.1, 7.0, 3.1 Hz, 2H), 2.83 (m, 2H), 2.58 (s, 3H), 1.54 – 1.37 (m, 6H); 13C NMR (126 MHz, CDCl3) δ 146.6, 146.5, 142.3, 141.92, 141.89, 129.10, 129.08, 128.7, 128.0, 127.6, 127.43, 127.39, 127.3, 127.24, 127.22, 126.88, 126.85, 126.8, 84.74, 84.69, 83.7, 82.4, 82.3, 81.0, 80.9, 59.7, 59.4, 45.1, 44.9, 26.94, 26.91, 25.1; 31P NMR (162 MHz, CDCl3) δ 133.2; IR (film): 3089, 3057, 3034, 3024, 2932, 2848, 2831, 1599, 1582, 1492, 1445, 1372, 1334, 1316, 1265, 1213, 1184.22, 1128, 1126, 1124, 1041, 974, 947, 805 cm⁻¹; LRMS (ESI): Mass calculated for [M+H]+ C35H39NO4P: 568.3; found 568.4.

(3aR,8aR)-N-cyclohexyl-4,4,8,8-tetraakis(3,5-dimethylphenyl)-N,2,2-trimethyltetrahydro[1,3]dioxol[4,5-e][1,3,2]dioxaphosphepin-6-amine (L3j). Prepared according to the general procedure using ((4R,5R)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(bis(3,5-dimethylphenyl)methanol). The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford L3j as a white foam (195 mg, 77%). Analytical data for L3j: 1H NMR (500 MHz, CDCl3) δ 7.45 (s, 2H), 7.21 (s, 2H), 7.06 (d, J = 10.2 Hz, 4H), 6.88 – 6.78 (m, 4H), 5.07 (dd, J = 8.5, 3.5 Hz, 1H), 4.65 (d, J = 8.5 Hz, 1H), 3.25 (tdd, J = 11.8, 8.2, 3.4 Hz, 1H), 2.81 (d, J = 7.6 Hz, 3H), 2.29 (s, 6H), 2.27 (s, 6H), 2.26 (s, 12H), 1.88 – 1.70 (m, 4H), 1.60 (d, J = 14.4 Hz, 1H), 1.54 – 1.47 (m, 2H), 1.45 (s, 3H), 1.27 (ddt, J = 20.8, 12.7, 3.6 Hz, 2H), 1.05 (dd, J = 16.6, 8.4, 3.5 Hz, 1H), 0.22 (s, 3H); 13C NMR (126 MHz, CDCl3) δ 147.5, 147.04, 147.02, 142.3, 142.1, 137.1, 136.8, 136.7, 136.3, 129.0, 128.9, 128.8, 128.7, 127.1, 126.64, 126.61, 125.2, 111.2, 83.61, 83.59, 83.0, 82.8, 81.2, 81.1, 80.72, 80.70, 57.5, 57.2, 32.60, 32.55, 32.5, 32.4, 27.9, 27.6, 27.5, 26.50, 26.48, 25.9, 25.4, 21.84, 21.78, 21.7; 31P NMR (162 MHz, CDCl3) δ 140.0; IR (film): 3047, 2990, 2930, 2855, 2731, 1787, 1754, 1600, 1450, 1380, 1265, 1214,
1159, 1066, 969, 942, 861, 785, 738, 690, 601, 574, 508, 413 cm\(^{-1}\); LRMS (ESI): Mass calculated for [M+H]\(^+\) \(\text{C}_{46}\text{H}_{59}\text{NO}_4\text{P}\): 720.4; found 720.6.

1-((3a\text{R},8a\text{R})-4,4,8,8-Tetrakis(3,5-diethylphenyl)-2,2-dimethyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepin-6-yl)piperidine (L3k). Prepared according to the general procedure using \(\text{(4R,5R)}-2,2\text{-dimethyl-1,3-dioxolane-4,5-diyl)}\text{bis(3,5-diethylphenyl)methanol}\). The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford L3k as a white foam (2.15 g, 91%). Analytical data for L3k: \(^1\text{H} NMR\) (500 MHz, CDCl\(_3\)) \(\delta\) 7.45 (d, \(J = 1.6\) Hz, 2H), 7.30 (d, \(J = 1.6\) Hz, 2H), 7.13 (s, 2H), 7.05 (d, \(J = 1.6\) Hz, 2H), 6.92-6.82 (m, 4H), 5.15 (dd, \(J = 8.5, 3.1\) Hz, 1H), 4.78 (d, \(J = 8.5\) Hz, 1H), 3.38 – 3.26 (m, 2H), 3.16 (ddd, \(J = 15.0, 8.8, 5.4\) Hz, 2H), 2.66 – 2.51 (m, 16H), 1.65 – 1.51 (m, 6H) 1.36 (s, 3H), 1.19 (dtt, \(J = 7.1, 4.3, 2.1\) Hz, 24H), 0.18 (s, 3H); \(^{13}\text{C} NMR\) (125 MHz, CDCl\(_3\)) \(\delta\) 147.2, 146.9, 143.4, 142.9, 142.5, 142.1, 142.0, 126.3, 126.2, 126.2, 126.04, 125.99, 125.96, 124.4, 124.3, 110.9, 83.33, 83.31, 82.4, 82.8, 82.7, 81.6, 81.5, 81.3, 45.1, 44.9, 29.1, 29.0, 28.93, 28.91, 27.7, 27.2, 27.1, 25.3, 25.1, 15.9, 15.6, 15.4; \(^{31}\text{P} NMR\) (162 MHz, CDCl\(_3\)) \(\delta\) 137.2; IR (film): 2964, 2933, 2873, 1600, 1459, 1371, 1333, 1247, 1215, 1160, 1072, 1038, 949, 875, 853, 783, 739, 703, 506, 432, 411 cm\(^{-1}\); LRMS (ESI): Mass calculated for [M+H]\(^+\) \(\text{C}_{52}\text{H}_{71}\text{NO}_4\text{P}\): 804.5; found 804.5.

Synthesis of \([\text{Pd}(\eta^3-1,3\text{-diphenylallyl})\{(S,S)-L3g}\}]\text{BF}_4\). Bis\([\mu\text{-chloro}](\eta^3-1,3\text{-diphenylallyl})\text{palladium(II)}\). Prepared according to procedure described by Pregosin and co-workers.\(^6\) PdCl\(_2\) (350 mg, 1.95 mmol) and LiCl (350 mg, 8.3 mmol) were stirred in H\(_2\)O (2.3 mL) for 45 min. Ethanol (3.9 mL) and (rac)-\((\text{E})-3\text{-acetoxy-1,3-diphenyl-1-propene}\) (1 g, 3.97 mmol) in THF (11 mL) were then added, and the brown solution was cooled to 0 °C. After the addition of 1.2 mL of concentrated HCl, carbon monoxide was slowly bubbled through the solution for 15 min. Another 0.8 mL of concentrated HCl was added and CO bubbled for 1.5 h. The stream of CO was then stopped and the solution stirred under CO atmosphere for 7 h at 23 °C. The yellow mixture was filtered, washed with MeOH and Et\(_2\)O, and dried under vacuum overnight. Spectroscopic data was consistent with those previously reported.\(^5\)

\([\text{Pd}(\eta^3-1,3\text{-diphenylallyl})\{(S,S)-L3g}\}]\text{BF}_4\). To a solution of bis\([\mu\text{-chloro}](\eta^3-1,3\text{-diphenylallyl})\text{palladium(II)}\) (12 mg, 0.018 mmol) in anhydrous acetone was added \((S,S)-L3g\) (25 mg, 0.035 mmol). The mixture was stirred for 2 h at 23 °C. To the yellow solution was added

a solution of silver tetrafluoroborate (7.59 mg, 0.039 mmol) in THF. The filtrate was concentrated at reduced pressure, and CH$_2$Cl$_2$ was added. Pentane was carefully layered on top to induce crystallization and afford $[\text{Pd(η}^3\text{-1,3-diphenylallyl)}\{(S,S)-\text{L3g})\}]\text{BF}_4$ as yellow needles.

**Synthetic Transformations**

(2R,3S)-2-Phenylchroman-3-ol (7). A solution of 2-phenyl-2H-chromene (2a) (167 mg, 0.8 mmol) and 1 molar BH$_3$-THF (16 mL) was stirred for 2 h at 23 °C. Solution was cooled to 0 °C before a 20% (w/w) aqueous solution of NaOH (4.8 mL) and 30% (w/w) aqueous solution of H$_2$O$_2$ (4.9 mL) were added. The reaction was slowly warmed to 23 °C and stirred for 12 h. The solution was then diluted with Et$_2$O and H$_2$O followed by acidification with 10% (w/w) aqueous HCl and extraction with Et$_2$O. The organics were combined, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Purification by flash chromatography with 10% EtOAc/hexanes afforded 7 as a white solid (115 mg, 63%). Spectroscopic data was consistent with those previously reported.$^2$

(2R,3S)-2-Phenylchroman-3-yl 3,4,5-trihydroxybenzoate (8). Prepared using a modified literature procedure.$^7$ To a solution of (2R,3S)-2-phenylchroman-3-ol (7) (91 mg, 0.4 mmol) in CH$_2$Cl$_2$ (2 mL) was added DMAP (28 mg, 0.23 mmol), Et$_3$N (0.167 mL, 1.2 mmol) and tri-OBn gallic acid chloride (184 mg, 0.4 mmol). The reaction was stirred for 12 h at 23 °C, washed with H$_2$O followed by brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The protected gallate ester was taken up in EtOAc (4 mL). To the solution was added 10 wt. % Pd/C (255 mg, 2.4 mmol). The mixture was stirred under an atmosphere of H$_2$ for 14 h, filtered through a plug of Celite®, dried over sodium sulfate, filtered, and concentrated under reduced pressure. Purification by flash chromatography with 30% EtOAc/hexanes afforded 8 as a white solid (89 mg, 59%). Analytical data for 8: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.40 (dd, $J = 7.5$, 1.8 Hz, 2H), 7.34 (t, $J = 7.4$ Hz, 2H), 7.29 (d, $J = 7.2$ Hz, 1H), 7.21 (td, $J = 7.8$, 7.4, 1.7 Hz, 1H), 7.10 (s, 2H), 7.09 – 7.05 (m, 1H), 7.01 (dd, $J = 8.2$, 1.2 Hz, 1H), 6.93 (td, $J = 7.4$, 1.2 Hz, 1H), 6.50 (bs, 1H), 5.55 (td, $J = 6.0$, 4.9 Hz, 1H), 5.46 (bs, 2H), 5.33 (d, $J = 5.7$ Hz, 1H), 3.11 (dd, $J = 16.7$, 4.8 Hz, 1H), 2.96 (dd, $J = 16.6$, 6.1 Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 143.1,

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138.2, 129.8, 128.6, 128.3, 127.9, 126.2, 121.0, 116.5, 109.9, 78.4, 69.9, 28.6. Other spectroscopic data was consistent with those previously reported.\(^6\)

(2\textit{R},3\textit{S},4\textit{S})-2-(3-Chlorophenyl)chromane-3,4-diol (9). To a solution of 2-(3-chlorophenyl)-2\textit{H}-chromene (2\textit{i}) (72.8 mg, 0.3 mmol) and 4-methylmorpholine \textit{N}-oxide (52.7 mg, 0.45 mmol) in THF (3 mL) and water (0.116 mL) was added a 2.5 wt % solution of osmium tetraoxide in \textit{t}-BuOH (0.118 mL). The mixture was stirred at 23 \textdegree C for 16 h and was then quenched with a saturated solution of sodium thiosulfate. The mixture was extracted with EtOAc. The combined organics was washed with brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude was purified by flash chromatography using 20% EtOAc/hexanes to afford 9 as an off-white solid (76 mg, 91%). Analytical data for 9: \(\text{\textit{H NMR (500 MHz, CDCl}_3 \text{)}} \delta 7.53 – 7.48 (m, 1H), 7.39 (dd, \text{\textit{J}} = 7.6, 1.7 Hz, 1H), 7.37 (d, \text{\textit{J}} = 1.4 Hz, 3H), 7.30 (ddd, \text{\textit{J}} = 8.6, 7.3, 1.7 Hz, 1H), 7.02 (td, \text{\textit{J}} = 7.4, 1.2 Hz, 1H), 6.96 (dd, \text{\textit{J}} = 8.2, 1.1 Hz, 1H), 5.05 (d, \text{\textit{J}} = 9.5 Hz, 1H), 4.81 (t, \text{\textit{J}} = 3.7 Hz, 1H), 4.04 (ddd, \text{\textit{J}} = 9.5, 6.6, 3.7 Hz, 1H), 2.57 (d, \text{\textit{J}} = 3.7 Hz, 1H), 2.25 (d, \text{\textit{J}} = 6.6 Hz, 1H); \text{\textit{C NMR (125 MHz, CDCl}_3 \text{)}} \delta 154.0, 139.9, 134.8, 130.9, 130.7, 130.1, 129.0, 127.8, 125.9, 122.0, 121.7, 117.0, 76.2, 71.1, 66.2; IR (film): 3407, 2919, 2851, 1583, 1485, 1455, 1239, 1036, 1012, 754, 701, 511 cm\(^{-1}\); LRMS (ESI): Mass calculated for [M+H]\(^{+}\) \text{C}_{15}\text{H}_{14}\text{ClO}_3: 277.1; found 277.1.

(\textit{2R,3R})-2-(3-Chlorophenyl)-3-hydroxychroman-4-one (10). To a solution of (\textit{2R},3\textit{S},4\textit{S})-2-(3-chlorophenyl)chromane-3,4-diol (9) (28 mg, 0.1 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (2 mL) was added manganese dioxide (44 mg, 0.5 mmol). The mixture was stirred at 23 \textdegree C for 24 h, filtered through a plug of Celite\textsuperscript{®}, and concentrated under reduced pressure. The crude was purified by flash chromatography using 7% EtOAc/hexanes to afford 10 as a solid (16 mg, 59%). Analytical data for 9: \(\text{\textit{H NMR (500 MHz, CDCl}_3 \text{)}} \delta 7.93 (dd, \text{\textit{J}} = 7.9, 1.7 Hz, 1H), 7.62 (d, \text{\textit{J}} = 2.0 Hz, 1H), 7.58 (ddd, \text{\textit{J}} = 8.6, 7.2, 1.8 Hz, 1H), 7.48 – 7.45 (m, 1H), 7.42 – 7.38 (m, 2H), 7.14 (ddd, \text{\textit{J}} = 8.0, 7.2, 1.0 Hz, 1H), 7.07 (dd, \text{\textit{J}} = 8.4, 1.0 Hz, 1H), 5.12 (d, \text{\textit{J}} = 12.3 Hz, 1H), 4.57 (dd, \text{\textit{J}} = 12.3, 1.9 Hz, 1H), 3.70 (d, \text{\textit{J}} = 1.9 Hz, 1H); \text{\textit{C NMR (125 MHz, CDCl}_3 \text{)}} \delta 193.8, 161.5, 138.3, 137.1, 134.6, 129.9, 129.4, 127.6, 127.4, 125.8, 122.4, 118.4, 118.1, 83.0, 73.6; IR (film): 3461, 2921, 2851, 2361, 2341, 1695, 1608, 1579, 1466, 1300, 1229, 1138, 1104, 1009, 861, 764, 693, 419, 405 cm\(^{-1}\); LRMS (ESI): Mass calculated for [M+H]\(^{+}\) \text{C}_{15}\text{H}_{12}\text{ClO}_3: 275.0; found 275.1.
Selected NMR Spectra

$^1$H NMR Spectrum of $1a$ (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of $1a$ (125 MHz, CDCl$_3$):
$^1$H NMR Spectrum of 1b (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of 1b (125 MHz, CDCl$_3$):
$^1$H NMR Spectrum of 1c (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of 1c (125 MHz, CDCl$_3$):
$^1$H NMR Spectrum of 1d (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of 1d (125 MHz, CDCl$_3$):
$^1$H NMR Spectrum of 1e (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of 1e (125 MHz, CDCl$_3$):
$^1$H NMR Spectrum of 1f (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of 1f (125 MHz, CDCl$_3$):
$^1$H NMR Spectrum of 1g (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of 1g (125 MHz, CDCl$_3$):
\( ^1H \) NMR Spectrum of 1h (500 MHz, CDCl\(_3\)):

\( ^{13}C \) NMR Spectrum of 1h (125 MHz, CDCl\(_3\)):
$^1$H NMR Spectrum of 1i (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of 1i (125 MHz, CDCl$_3$):
$^1$H NMR Spectrum of 1j (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of 1j (125 MHz, CDCl$_3$):
$^1$H NMR Spectrum of 1k (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of 1k (125 MHz, CDCl$_3$):
$^1$H NMR Spectrum of II (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of II (125 MHz, CDCl$_3$):
$^1$H NMR Spectrum of 1m (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of 1m (125 MHz, CDCl$_3$):
$^1$H NMR Spectrum of 1n (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of 1n (125 MHz, CDCl$_3$):
$^1$H NMR Spectrum of 1o (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of 1o (125 MHz, CDCl$_3$):
$^1$H NMR Spectrum of \textbf{1p} (500 MHz, CDCl$_3$):

\begin{center}
\includegraphics[width=0.5\textwidth]{1h_nmr_spectrum}
\end{center}

$^{13}$C NMR Spectrum of \textbf{1p} (125 MHz, CDCl$_3$):

\begin{center}
\includegraphics[width=0.5\textwidth]{13c_nmr_spectrum}
\end{center}
$^1$H NMR Spectrum of 2a (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of 2a (125 MHz, CDCl$_3$):
$^1$H NMR Spectrum of 2b (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of 2b (125 MHz, CDCl$_3$):
\(^1\)H NMR Spectrum of 2c (500 MHz, CDCl\(_3\)):

\(^{13}\)C NMR Spectrum of 2c (125 MHz, CDCl\(_3\)):
$^1$H NMR Spectrum of 2d (500 MHz, CDCl$_3$):

\[ \text{Diagram of 2d} \]

$^{13}$C NMR Spectrum of 2d (125 MHz, CDCl$_3$):

\[ \text{Diagram of 2d} \]
\(^1\)H NMR Spectrum of 2e (500 MHz, CDCl\(_3\)):

\(^{13}\)C NMR Spectrum of 2e (125 MHz, CDCl\(_3\)):
$^1$H NMR Spectrum of 2f (500 MHz, CDCl$_3$):

\[
\text{\includegraphics{image1.png}}
\]

$^{13}$C NMR Spectrum of 2f (125 MHz, CDCl$_3$):

\[
\text{\includegraphics{image2.png}}
\]
$^1$H NMR Spectrum of 2g (500 MHz, CDCl$_3$):

\[ \text{Diagram of} \ 2g \text{ with chemical shifts} \]

$^{13}$C NMR Spectrum of 2g (125 MHz, CDCl$_3$):

\[ \text{Diagram of} \ 2g \text{ with chemical shifts} \]
$^1$H NMR Spectrum of 2h (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of 2h (125 MHz, CDCl$_3$):
\(^1\text{H NMR Spectrum of } 2i \ (500 \text{ MHz, CDCl}_3):\)

\(^{13}\text{C NMR Spectrum of } 2i \ (125 \text{ MHz, CDCl}_3):\)
$^1$H NMR Spectrum of $2j$ (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of $2j$ (125 MHz, CDCl$_3$):
$^1$H NMR Spectrum of 2k (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of 2k (125 MHz, CDCl$_3$):
$^1$H NMR Spectrum of 21 (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of 21 (125 MHz, CDCl$_3$):
$^1$H NMR Spectrum of 2m (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of 2m (125 MHz, CDCl$_3$):
$^1$H NMR Spectrum of 2n (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of 2n (125 MHz, CDCl$_3$):
$^1$H NMR Spectrum of 2o (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of 2o (125 MHz, CDCl$_3$):
$^1$H NMR Spectrum of 2p (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectrum of 2p (125 MHz, CDCl$_3$):
HPLC Traces of Racemic and Enantioenriched Compounds

Racemic 2a:

Enantioenriched 2a:
Racemic 2b:

Enantioenriched 2b:
Racemic 2c:

Enantioenriched 2c:
Racemic 2d:

![Chromatogram for Racemic 2d]

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</thead>
<tbody>
<tr>
<td>1</td>
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<tr>
<td>2</td>
<td>117.735</td>
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</tbody>
</table>

Enantioenriched 2d:

![Chromatogram for Enantioenriched 2d]

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</tr>
</thead>
<tbody>
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Racemic 2e:

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Enantioenriched 2e:

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Racemic 2f:

Enantioenriched 2f:

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Racemic 2g:

Enantioenriched 2g:
Racemic 2h:

Enantioenriched 2h:
Racemic 2i:

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Enantioenriched 2i:

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Racemic 2j:

Enantioenriched 2j:
Racemic 2k:

Enantioenriched 2k:
Racemic 2l:

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Enantioenriched 2l:

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Racemic 2m:

(Columns: N,N-DMF, 0.5 g, 60°C, 4 h, CD, Injection 1 DAD A, Sip=194.4 Ref=160.186 Chromatogram)

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Enantioenriched 2m:

(Columns: N,N-DMF, 0.5 g, 60°C, 4 h, CD, Injection 1 DAD A, Sip=194.4 Ref=160.186 Chromatogram)

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<td>52.612 89.53</td>
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Racemic 2n:

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Enantioenriched 2n:

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Racemic 2o:

Enantioenriched 2o:
Racemic 2p:

Enantioenriched 2p:
Bis-Benzoylated vs. Bis-Acetated Substrates

\[
\begin{align*}
\text{OR} & \quad \text{OR} \\
\text{R} = \text{Ac}, \text{Bz}
\end{align*}
\]

\[
\begin{align*}
\text{2 mol} \% \text{Pd}_2\text{(dba)}_3 \\
\text{4 mol} \% \text{Ligand} \\
\text{K}_2\text{CO}_3, \text{MeOH/H}_2\text{O} \\
\text{CH}_2\text{Cl}_2
\end{align*}
\]

\[
\begin{align*}
\text{Ligand:}
\end{align*}
\]

% Conversion vs. Time

% ee vs. Time
Determination of Absolute Stereochemistry of L3k

The absolute stereochemistry of L3k was determined by the X-ray diffraction. Recrystallized from ethanol.

![L3k](image)

X-ray crystal structure of 1-((3aR,8aR)-4,4,8,8-tetrakis(3,5-diethylphenyl)-2,2-dimethyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepin-6-yl)piperidine:

X-ray diffraction was performed at 100 K and raw frame data were processed using SAINT. Molecular structures was solved using direct methods and refined on F2 by full-matrix least-square techniques. The GOF = 1.033 for 1065 variables refined to R1 = 0.0349 for 15189 reflections with I>2σ(I). A multi-scan absorption correction was performed and the Flack parameter was 0.014(3). Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 984483.
Determination of Structure of $[\text{Pd}(\eta^3\text{-1,3-diphenylallyl})\{(S,S)-\text{L3g}\}]\text{BF}_4$

The structure of $[\text{Pd}(\eta^3\text{-1,3-diphenylallyl})\{(S,S)-\text{L3g}\}]\text{BF}_4$ was determined by the X-ray diffraction. Recrystallized from $\text{CH}_2\text{Cl}_2$:pentane.

X-ray crystal structure of $[\text{Pd}(\eta^3\text{-1,3-diphenylallyl})\{(S,S)-\text{L3g}\}]\text{BF}_4$:

X-ray diffraction was performed at 100 K and raw frame data were processed using SAINT. Molecular structures was solved using direct methods and refined on F2 by full-matrix least-square techniques. The GOF = 0.919 for 677 variables refined to R1 = 0.0234 for 8799 reflections with I>2σ(I). A multi-scan absorption correction was performed and the Flack parameter was -0.009(3). Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 969569.