Supporting Information

Unexpected Effect of the Fluorine Atom on the Optimal Ligand-to-Palladium Ratio in the Enantioselective Pd-Catalyzed Allylation Reaction of Fluorinated Enol Carbonates

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The following includes general experimental procedures, specific details for representative reactions, and isolation and spectroscopic information for the new compounds prepared. $^1$H, $^{13}$C, and $^{19}$F NMR spectra were recorded on a VARIAN Inova 400 MHz in CDCl$_3$ at ambient temperature using tetramethylsilane ($^1$H NMR) or residual CHCl$_3$ ($^1$H and $^{13}$C NMR) as the internal standard, or CFCl$_3$ ($^{19}$F NMR) as the external standard. Infrared spectra were recorded on a Bomem FT-IR MB-Series spectrometer. High-resolution mass spectra were performed on a LC/MS-TOF Agilent 6210 using electrospray ionization (ESI) or by AIMS Lab (University of Toronto) on an ABI/Sciex QStar mass spectrometer using ESI. Enantiomeric excesses were determined by HPLC analysis with a Hewlett Packard 1200 Series. Optical rotation [$\alpha$]$_D$ were measured on a Jasco DIP-360 Polarimeter. Melting points were recorded on a Uni-Met capillary melting point apparatus and are uncorrected. (S)-t-Bu-PHOX was prepared using literature procedure.$^1$

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Synthesis of the α-fluoroketones

The fluoroketones were prepared as described previously or as indicated thereafter.

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**2-Fluoro-7-methoxy-1-tetralone** The fluoroketone was prepared following a literature protocol. On a 1.7 mmol scale, the desired product (258 mg, 78%) was isolated as a white solid by flash chromatography using 10% Et₂O/hexane. mp 84-85 °C; IR (neat) ν = 3018, 2958, 2908, 2843, 1693, 1495, 1320, 1276, 1070, 1002, 870 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, 1H, J = 2.7 Hz), 7.18 (d, 1H, J = 8.5 Hz), 7.11 (dd, 1H, J = 8.5, 2.7 Hz), 5.15 (ddd, 1H, J = 47.9, 12.3, 5.2 Hz), 3.85 (s, 3H), 3.07 (m, 2H), 2.62–2.53 (m, 1H), 2.40–2.28 (m, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ -190.8 (m, 1F); ¹³C NMR (100 MHz, CDCl₃) δ 193.7 (d, J_C-F = 14.5 Hz), 158.9, 135.9, 132.3, 130.2, 123.1, 109.1, 91.6 (d, J_C-F = 187.7 Hz), 55.9, 30.6 (d, J_C-F = 18.6 Hz), 26.5 (d, J_C-F = 11.7 Hz); HRMS-ESI cald for C₁₁H₁₂FO₂ [M+H]⁺ 195.0816, found 195.0823.

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**2-Fluoro-thiochroman-4-one** To a 0 °C solution of LiHMDS (4.6 mL, 4.6 mmol, 1.0 M in THF) in THF (6 mL) was added a solution of the thioketone (750 mg, 4.6 mmol) in THF (2 mL) dropwise over 15 minutes and stirred 1.5 h at 0 °C. The resulting enolate solution was added dropwise over 15 minutes to a

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-78 °C solution of NFSI (1.58 g, 5.02 mmol) in THF (12 mL). The reaction mixture was allowed to warm to rt overnight. The reaction was transferred into a mixture of CH₂Cl₂ and satd NH₄Cl. The layers were separated, the aqueous layer was extracted with CH₂Cl₂ (3×). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and the solvent was evaporated to give the crude product. The pure product (684 mg, 82%) was isolated as a white solid by flash chromatography using 10% acetone/hexane. mp 82-85 °C; IR (neat) ν = 3158, 3068, 2933, 2903, 1703, 1591, 1441, 1381, 1270, 1218, 1147, 1122 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, 1H, J = 8.0 Hz), 7.43 (t, 1H, J = 7.6 Hz), 7.30–7.21 (m, 2H), 5.42 (ddd, 1H, J = 47.6, 13.4, 4.8 Hz), 3.60 (dt, 1H, J = 12.9, 2.8 Hz), 3.32–3.25 (m, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ -184.4 (ddd, 1F, J = 47.6, 9.2, 2.9 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 140.7, 134.3, 130.5, 130.2 (d, J_C,F = 2.2 Hz), 127.3, 125.8, 90.5, 85.6, 31.1 (d, J_C,F = 23.5 Hz); HRMS-ESI cald for C₉H₁₁NSFO [M+NH₄]⁺ 200.0540, found 200.0540.

1) NaI, TMSCl, Et₃N, pentane/CH₃CN
2) Selectfluor™, CH₃CN

63%

2-Fluoro-1-propiophenone The fluoroketone was prepared following a literature protocol.⁴ Spectroscopic data were in agreement with the literature.³

Allyl-2-fluoro-3,4-dihydronaphthalen-1-yl carbonate (1) (General protocol) To a 0 °C solution of LiHMDS (3.2 mL, 3.2 mmol, 1.0 M in THF) in THF (4 mL) was added a solution of the fluoroketone (500 mg, 3.0 mmol) in THF (1 mL) dropwise over 15 minutes and was stirred 1.5 h at 0 °C. The resulting enolate solution was added dropwise over 15 minutes to a -78 °C solution of allylchloroformate (0.39 ml, 3.65 mmol) in THF (8 ml). The reaction mixture was allowed to warm to rt overnight. The reaction was transferred into a mixture of CH₂Cl₂ and satd NH₄Cl. The layers were separated, the aqueous layer was extracted with CH₂Cl₂ (3×). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and the solvent was evaporated to give the crude product. The pure product (633 mg, 85%) was isolated as a colorless oil by flash chromatography using 5% acetone/hexane. IR (neat) ν = 3072, 3025, 2949, 2897, 2840, 1769, 1707, 1370, 1295, 1149, 992, 768 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.27-7.11 (m, 4H), 6.06-5.96 (m, 1H), 5.44 (d, 1H, J = 17.2 Hz), 5.34 (d, 1H, J = 10.4 Hz), 4.76 (d, 2H, J = 5.8 Hz), 3.06 (t, 2H, J = 8.3 Hz), 2.73 (m, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -118.9 (m, 1F); ¹³C NMR (100 MHz, CDCl₃) δ 152.6 (d, J_C-F = 2.1 Hz), 151.5 (d, J_C-F = 271.3 Hz), 132.5, 131.3, 130.0 (d, J_C-F = 7.1 Hz), 119.7, 69.8, 27.9 (d, J_C-F = 7.2 Hz), 24.5 (d, J_C-F = 20.1 Hz); HRMS-ESI cald for C₁₄H₁₇NFO₃ [M+NH₄]⁺ 266.1187, found 266.1191.
Allyl-2-fluoro-6-methoxy-3,4-dihyronaphthalen-1-yl carbonate Following the general protocol on a 2.57 mmol scale, the desired product (457 mg, 64%) was isolated as colorless oil by flash chromatography using 15% Et₂O/hexane. IR (neat) ν = 3087, 2998, 2949, 2839, 1769, 1709, 1502, 1333, 1252, 1227, 1150, 958 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.08 (d, 1H, J = 8.3 Hz), 6.72 (m, 2H), 6.05–5.95 (m, 1H), 5.43 (d, 1H, J = 17.2 Hz), 5.34 (d, 1H, J = 10.4 Hz), 4.75 (d, 2H, J = 5.8 Hz), 3.79 (s, 3H), 3.02 (t, 2H, J = 8.2 Hz), 2.71 (m, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -122.6 (m, 1F); ¹³C NMR (100 MHz, CDCl₃) δ 159.2 (d, J_C-F = 2.5 Hz), 152.6 (d, J_C-F = 2.1 Hz), 149.7 (d, J_C-F = 268.6 Hz), 134.5, 131.3, 127.9 (d, J_C-F = 12.2 Hz), 122.7, 122.0 (d, J_C-F = 7.3 Hz), 119.7, 114.4, 111.4, 69.7, 55.6, 28.2 (d, J_C-F = 5.7 Hz), 24.5 (d, J_C-F = 20.4 Hz); HRMS-ESI cald for C₁₅H₁₉NFO₄ [M+NH₄]⁺ 296.1293, found 296.1288.

Allyl-2-fluoro-7-methoxy-3,4-dihyronaphthalen-1-yl carbonate Following the general protocol on a 1.33 mmol scale, the desired product (309 mg, 83 %) was isolated as colorless oil by flash chromatography using 10 % Et₂O/hexane. IR (neat) ν = 3097, 3030, 2999, 2960, 2894, 2839, 1765, 1705, 1494, 1370, 1295, 1227, 1183, 1044, 998 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.03 (d, 1H, J = 8.2 Hz), 6.74 (d, 1H, J = 2.5 Hz), 6.68 (dd, 1H, J = 8.2, 2.5 Hz), 6.05-5.95 (m, 1H), 4.75 (d, 1H, J = 5.7 Hz), 3.78 (s, 3H), 2.98 (t, 2H, J = 8.2 Hz), 2.70 (m, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -118.1 (m, 1F); ¹³C NMR (100 MHz, CDCl₃) δ 159.0, 153.5, 152.5 (d, J_C-F = 2.1 Hz), 150.3, 131.3, 128.6, 128.0 (d, J_C-F = 12.2 Hz),
124.6, 119.7, 112.1 (d, $J_{C-F} = 2.5$ Hz), 107.4 (d, $J_{C-F} = 7.2$ Hz), 69.8, 55.6, 27.0 (d, $J_{C-F} = 7.3$ Hz), 24.8 (d, $J_{C-F} = 19.9$ Hz); HRMS-ESI cald for C$_{15}$H$_{19}$NFO$_4$ [M+NH$_4$]$^+$ 296.1293, found 296.1338.

**Allyl-3-fluoro-2H-thiochromen-4-yl carbonate** Following the general protocol on a 2.74 mmol scale, the desired product (603 mg, 83%) was isolated as colorless oil by flash chromatography using 10% Et$_2$O/hexane. IR (neat) $\nu = 3064, 3023, 2958, 2895, 2823, 1767, 1704, 1471, 1439, 1365, 1297, 1242, 1165, 1069, 942$ cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.23–7.13 (m, 4H), 6.04–5.95 (m, 1H), 5.44 (d, 1H, $J = 17.2$ Hz), 5.35 (d, 1H, $J = 10.4$ Hz), 4.76 (d, 2H, $J = 5.8$ Hz), 3.81 (d, 2H, $J = 6.9$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -114.4 (t, 1F, $J = 6.9$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.3 (d, $J_{C-F} = 2.2$ Hz), 146.3 (d, $J_{C-F} = 276.8$ Hz), 131.1, 129.5 (d, $J_{C-F} = 14.1$ Hz), 129.1, 128.8, 128.5 (d, $J_{C-F} = 2.5$ Hz), 126.9, 126.3, 122.9 (d, $J_{C-F} = 6.7$ Hz), 119.9, 70.0, 25.6 (d, $J_{C-F} = 25.7$ Hz); HRMS-ESI cald for C$_{13}$H$_{15}$NSFO$_3$ [M+NH$_4$]$^+$ 284.0751, found 284.0758.

**Allyl-2-fluoro-1H-inden-3-yl carbonate** Following the general protocol on a 3.33 mmol scale, the desired product (367 mg, 47%) was isolated as colorless oil by flash chromatography using 5% Et$_2$O/hexane. IR (neat) $\nu = 3082, 3054, 3029, 2953, 2903, 1776, 1691, 1461, 1330, 1243, 1166, 1154, 969$ cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32 (m, 2H), 7.24 (m, 2H), 6.08–5.98 (m, 1H), 5.47 (d, 1H, $J = 17.2$ Hz), 5.37 (d, 1H, $J = 10.4$ Hz), 4.80 (d, 2H, $J = 5.8$ Hz), 3.54 (s, 2H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -
132.7 (m, 1F); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.2 (d, $J_{C-F} = 282.3$ Hz), 151.9 (d, $J_{C-F} = 2.2$ Hz), 137.0 (d, $J_{C-F} = 1.2$ Hz), 131.9 (d, $J_{C-F} = 8.0$ Hz), 131.1, 127.7 (d, $J_{C-F} = 7.7$ Hz), 127.3, 125.7 (d, $J_{C-F} = 4.5$ Hz), 124.3 (d, $J_{C-F} = 1.1$ Hz), 120.1, 118.2 (d, $J_{C-F} = 6.7$ Hz), 70.0, 32.8 (d, $J_{C-F} = 17.8$ Hz); HRMS-ESI cald for C$_{13}$H$_{15}$NFO$_3$ [M+NH$_4$]$^+$ 252.1031, found 252.1034.

**Allyl-8-fluoro-6,7-dihydro-5H-benzo[7]annulen-9-yl carbonate** Following the general protocol on a 2.84 mmol scale, the desired product (725 mg, 97%) was isolated as colorless oil by flash chromatography using 5% Et$_2$O/hexane. IR (neat) $\nu$ = 3072, 3024, 2945, 2901, 2871, 2850, 1766, 1451, 1373, 1238, 1176, 981, 770 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 (d, 2H, $J = 7.5$ Hz), 7.23 (m, 2H), 7.14 (d, 1H, $J = 7.1$ Hz), 6.02–5.93 (m, 1H), 5.40 (d, 1H, $J = 17.2$ Hz), 5.31 (d, 1H, $J = 10.5$ Hz), 4.71 (d, 2H, $J = 5.7$ Hz), 2.85 (m, 2H), 2.65 (q, 2H, $J = 7.0$ Hz), 1.99 (m, 2H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -106.3 (t, 1F, $J = 6.8$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.6 (d, $J_{C-F} = 256.8$ Hz), 153.2 (d, $J_{C-F} = 1.7$ Hz) 140.1 (d, $J_{C-F} = 17.4$ Hz), 131.4, 131.0 (d, $J_{C-F} = 17.4$Hz), 130.3 (d, $J_{C-F} = 1.9$ Hz), 129.4, 128.4 (d, $J_{C-F} = 1.4$ Hz), 126.8, 125.8 (d, $J_{C-F} = 5.7$ Hz), 119.4, 69.5, 34.3, 30.0 (d, $J_{C-F} = 24.1$ Hz), 25.7 (d, $J_{C-F} = 10.0$ Hz); HRMS-ESI cald for C$_{15}$H$_{19}$NFO$_3$ [M+NH$_4$]$^+$ 280.1344, found 280.1368.

**PhOCO$_2$allyl**

**(Z)-allyl-2-fluoro-1-phenylprop-1-enyl carbonate** Following the general protocol on a 1.64 mmol scale, the desired product (139 mg, 36%) was isolated as colorless oil by flash chromatography using 5% acetone/hexane. IR (neat) $\nu$ = 3088, 3063, 3033, 2958, 2928, 1764, 1446, 1388, 1240, 1136, 1040, 985
cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.43-734\) (m, 5H), 5.99-5.89 (m, 1H), 5.37 (d, 1H, \(J = 17.2\) Hz), 5.29 (d, 1H, \(J = 10.5\) Hz), 4.67 (d, 2H, \(J = 5.7\) Hz), 2.13 (d, 3H, \(J = 18.0\) Hz); \(^1\)H NMR (376 MHz, CDCl\(_3\)) \(\delta -110.6\) (q, 1F, \(J = 18.0\) Hz); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 153.1\) (d, \(J_{C-F} = 1.7\) Hz), 151.8, 149.2, 132.2 (d, \(J_{C-F} = 2.6\) Hz), 131.4 (d, \(J_{C-F} = 17.2\) Hz), 131.3, 129.1, 128.7, 128.6 (d, \(J_{C-F} = 2.8\) Hz), 119.4, 69.5, 15.3 (d, \(J_{C-F} = 26.2\) Hz); HRMS-ESI cald for C\(_{13}\)H\(_{17}\)NFO\(_3\) [M+NH\(_4\)]\(^+\) 254.1187, found 254.1190.

Allyl-2-chloro-3,4-dihydronaphthalen-1-yl carbonate Following the general protocol on a 3.20 mmol scale of 2-chlorotetralone\(^5\), the desired product (624 mg, 74%) was isolated as colorless oil by flash chromatography using 5% Et\(_2\)O/hexane. IR (neat) \(\nu = 3071, 3025, 2947, 2895, 2838, 1768, 1652, 1488, 1364, 1233, 1149, 943, 765\) cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.24-7.14\) (m, 4H), 6.06-5.96 (m, 1H), 5.45 (d, 1H, \(J = 17.2\) Hz), 5.35 (d, 1H, \(J = 10.4\) Hz), 4.77 (d, 2H, \(J = 5.7\) Hz), 3.02 (t, 2H, \(J = 8.2\) Hz), 2.80 (t, 2H, \(J = 8.2\) Hz); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 152.1, 141.6, 134.5, 131.3, 130.0, 128.5, 127.8, 127.1, 122.9, 121.0, 119.7, 69.8, 31.1, 28.3; HRMS-ESI cald for C\(_{14}\)H\(_{17}\)NClO\(_3\) [M+NH\(_4\)]\(^+\) 282.0892, found 282.0894.

Representative procedure for the enantioselective Pd-catalyzed allylation reaction

\[
\begin{align*}
\text{CO}_2\text{allyl} & \quad \text{Pd}_2(\text{dba})_3 (2.5 \text{ mol\%}) \\
& \quad (\text{S})-\text{t}-\text{Bu-PHOX} (1.25 \text{ mol\%}) \\
toluene (0.1 \text{ M}), 40 \, ^\circ \text{C}, 17 \text{ h} & \quad 3 (93\%, 92\% \text{ ee})
\end{align*}
\]

\((R)-2-\text{Allyl}-2-\text{fluoro}-1-\text{tetralone} (3)\) (General protocol for the Pd-catalyzed allylation reaction)

\((\text{Table 1 – entry 1})\) A 25 ml round-bottom flask under nitrogen was charged with \(\text{Pd}_2(\text{dba})_3\) (27.7 mg, 0.030 mmol, 2.5 mol\%) and \((\text{S})-\text{t}-\text{Bu-PHOX}\) (5.9 mg, 0.015 mmol, 1.25 mol\%, L/Pd = 1 : 4) followed by toluene (8 mL). After stirring 30 minutes at RT, a solution of the fluorinated allyl enol carbonate \(1\) (300 mg, 1.2 mmol) in toluene (4 mL) was added and the reaction mixture was heated at 40 \(^\circ\)C for 17 h. \(\text{H}_2\text{O}\) and \(\text{Et}_2\text{O}\) were added and the layers were separated. The aqueous phase was extracted with \(\text{Et}_2\text{O}\) \((3 \times)\). The combined organic layers were dried over anhydrous \(\text{Na}_2\text{SO}_4\), and concentrated. The desired product (229 mg, 93\%) was isolated as a colorless oil by flash chromatography using 5\% \(\text{Et}_2\text{O}\)/hexane. The enantioselectivity was 92\% ee (OJ-H, 254 nm, hexane:2-propanol = 99.9:0.1, flow rate 0.5 ml/min, \(t_r\) (minor) = 34.4 min, \(t_r\) (major) = 38.2 min). All spectroscopic data were in agreement with the literature.\(^6\)

When the reaction was conducted under similar conditions using 3.0 mol\% of \((\text{S})-\text{t}-\text{Bu-PHOX}\) (L/Pd = 1 : 1.67), the desired product was isolated in 97\% yield and 93\% ee (Table 1 - entry 2). When the reaction was conducted using 6.25 mol\% of \((\text{S})-\text{t}-\text{Bu-PHOX}\) (L/Pd = 1.25 : 1), \(3\) was isolated in 85\% yield and 59\% ee (Table 1 - entry 3).

Effect of L/Pd ratio on the enantioselectivity for the allylation of allyl enol carbonate 1

![Chemical structure](image)

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<th>Entry</th>
<th>L/Pd ratio</th>
<th>(S)-t-Bu-PHOX (mol%)</th>
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<sup>a</sup> Average of at least 2 independent runs; <sup>b</sup> Isolated yield; <sup>c</sup> Determined by chiral HPLC.
(R)-2-Allyl-2-fluoro-6-methoxy-1-tetralone (Table 1 - entry 4) Following the general protocol on a 0.26 mmol scale using 1.25 mol% of (S)-t-Bu-PHOX (L/Pd = 1 : 4), the desired product (53 mg, 87%) was isolated as a colorless oil by flash chromatography using 10% acetone/hexane. The enantioselectivity was 92% ee (AD-H, 254 nm, hexane:2-propanol = 99:1, flow rate 1.0 ml/min, t_{r (minor)} = 17.7 min, t_{r (major)} = 19.4 min). All spectroscopic data were in agreement with the literature. When the reaction was conducted under similar conditions using 6.25 mol% of (S)-t-Bu-PHOX (L/Pd = 1.25 : 1), the desired product was isolated in 98% yield and 57% ee (Table 1 - entry 5).

(R)-2-Allyl-2-fluoro-7-methoxy-1-tetralone (Table 1 - entry 6) Following the general protocol on a 0.25 mmol scale using 1.25 mol% of (S)-t-Bu-PHOX (L/Pd = 1 : 4), the desired product (55 mg, 92%) was isolated as a colorless oil by flash chromatography using 10% Et2O/hexane. The enantioselectivity was 94% ee (OJ-H, 254 nm, hexane:2-propanol = 99:1, flow rate 0.5 ml/min, t_{r (minor)} = 29.1 min, t_{r (major)} = 36.2 min). The absolute configurations were assigned based on the established stereochemical outcome of the reaction. [α]_{D}^{22} = -36.9 (c 0.82, CHCl3); IR (neat) ν = 3077, 3008, 2942, 2839, 1698, 1611, 1498,
1283, 1251, 1035, 923, 828 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, J = 2.3 Hz, 1H), 7.17–7.09 (m, 2H), 5.89 (m, 1H), 5.19 (m, 2H), 3.84 (s, 3H), 3.07–2.91 (m, 2H), 2.75–2.51 (m, 2H), 2.44–2.30 (m, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -160.3 (m, 1F); ¹³C NMR (100 MHz, CDCl₃) δ 194.3 (d, J_C-F = 17.6 Hz), 158.9, 135.5, 131.9 (d, J_C-F = 1.1 Hz), 131.1 (d, J_C-F = 3.9 Hz), 130.2, 123.0, 120.1, 110.0 (d, J_C-F = 1.5 Hz), 95.3 (d, J_C-F = 184.3 Hz), 55.8, 38.2 (d, J_C-F = 23.5 Hz), 32.4 (d, J_C-F = 22.3 Hz), 25.4 (d, J_C-F = 10.3 Hz); HRMS-ESI cald for C₁₄H₁₆FO₂ [M+H]⁺ 235.1126, found 235.1136. When the reaction was conducted under similar conditions using 6.25 mol% of (S)-t-Bu-PHOX (L/Pd = 1.25 : 1), the desired product was isolated in 86% yield and 56% ee (Table 1 - entry 7).

(R)-3-allyl-3-fluorothiochroman-4-one (Table 1 - entry 8) Following the general protocol on a 0.30 mmol scale using 1.25 mol% of (S)-t-Bu-PHOX (L/Pd = 1 : 4), the desired product (59 mg, 90%) was isolated as a colorless oil by flash chromatography using 10% Et₂O/hexane. The enantioselectivity was 92% ee (OJ-H, 254 nm, hexane:2-propanol = 95:5, flow rate 0.8 ml/min, tᵣ (minor) = 13.1 min, tᵣ (major) = 13.9 min). The absolute configurations were assigned based on the established stereochemical outcome of the reaction. [α]D²² -62.4 (c 1.07, CHCl₃); IR (neat) ν = 3079, 3014, 2982, 2917, 1698, 1591, 1460, 1438, 1301, 1274, 1259, 1199, 929 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, 1H, J = 8.0 Hz), 7.43 (t, 1H, J = 7.0 Hz), 7.27–7.21 (m, 2H), 5.95–5.85 (m, 1H), 5.29 (d, 2H, J = 12.2 Hz), 3.62 (dd, 2H, J = 13.1, 6.4 Hz), 3.17 (dd, 2H, J = 13.1, 7.6 Hz), 2.95–2.69 (m, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -160.1 (m, 1F); ¹³C NMR (100 MHz, CDCl₃) δ 191.3 (d, J_C-F = 17.3 Hz), 140.7, 134.1, 130.7, 130.1, 129.7, 127.2, 125.6, 121.4, 93.8 (d, J_C-F = 190.2 Hz), 36.8 (d, J_C-F = 22.6 Hz), 33.0 (d, J_C-F = 28.2 Hz); HRMS-ESI cald for
C_{12}H_{12}OFS [M+H]^+ 223.0587, found 223.0592. When the reaction was conducted under similar conditions using 6.25 mol% of (S)-t-Bu-PHOX (L/Pd = 1.25 : 1), the desired product was isolated in 93% yield and 42% ee (Table 1 - entry 9).

\[
\begin{array}{c}
\text{OCO}_2\text{allyl} & \xrightarrow{\text{Pd}_2(\text{dba})_3 \ (2.5 \text{ mol})} \ \text{F} \\
\text{toluene (0.1 M), 40 °C, 17 h} & \text{OCO}_2\text{allyl} \\
3.0 \text{ mol} \% \ (L/Pd = 1 : 1.67) & 91\%, 82\% \text{ ee} \\
6.25 \text{ mol} \% \ (L/Pd = 1.25 : 1) & 90\%, 30\% \text{ ee}
\end{array}
\]

(S)-2-allyl-2-fluoro-1-indanone (Table 1 - entry 10) Following the general protocol on a 0.33 mmol scale using 3.0 mol% of (S)-t-Bu-PHOX (L/Pd = 1 : 1.67), the desired product (57 mg, 91%) was isolated as a colorless oil by flash chromatography using 5% Et\text{2}O/hexane. The enantioselectivity was 82% ee (AD-H, 254 nm, hexane:2-propanol = 99:1, flow rate 0.8 ml/min, t_{\text{r (major)}} = 9.2 min, t_{\text{r (minor)}} = 11.7 min). All spectroscopic data were in agreement with the literature.\textsuperscript{2,6} When the reaction was conducted under similar conditions using 6.25 mol% of (S)-t-Bu-PHOX (L/Pd = 1.25 : 1), the desired product was isolated in 90% yield and 30% ee (Table 1 - entry 11).

\[
\begin{array}{c}
\text{allylO}_2\text{CO} & \xrightarrow{\text{Pd}_2(\text{dba})_3 \ (2.5 \text{ mol})} \ \text{F} \\
\text{toluene (0.1 M), 40 °C, 17 h} & \text{OCO}_2\text{allyl} \\
1.25 \text{ mol} \% \ (L/Pd = 1 : 4) & 83\%, 88\% \text{ ee} \\
6.25 \text{ mol} \% \ (L/Pd = 1.25 : 1) & 87\%, 76\% \text{ ee}
\end{array}
\]

(R)-2-allyl-2-fluoro-1-benzosuberone (Table 1 - entry 12) Following the general protocol on a 0.29 mmol scale using 1.25 mol% of (S)-t-Bu-PHOX (L/Pd = 1 : 4), the desired product (49 mg, 83%) was isolated as a colorless oil by flash chromatography using 5% Et\text{2}O/hexane. The enantioselectivity was 88% ee (OJ-H, 254 nm, hexane:2-propanol = 99:1, flow rate 0.8 ml/min, t_{\text{r (major)}} = 12.3 min, t_{\text{r (minor)}} =
16.5 min). All spectroscopic data were in agreement with the literature.\textsuperscript{2,6} When the reaction was conducted under similar conditions using 6.25 mol\% of (S)-t-Bu-PHOX (L/Pd = 1.25 : 1), the desired product was isolated in 87\% yield and 76\% ee (Table 1 - entry 13).

(R)-2-fluoro-2-methyl-1-phenylpent-4-en-1-one (Table 1 - entry 14) Following the general protocol on a 0.29 mmol scale using 3.0 mol\% of (S)-t-Bu-PHOX (L/Pd = 1 : 1.67), the desired product (32 mg, 58\%) was isolated as a colorless oil by flash chromatography using 5\% Et\textsubscript{2}O/hexane. The enantioselectivity was 34\% ee (OD-H, 254 nm, hexane:2-propanol = 99.9:0.1, flow rate 0.5 ml/min, \(t_{r\text{ (minor)}} = 17.8\) min, \(t_{r\text{ (major)}} = 19.8\) min). All spectroscopic data were in agreement with the literature.\textsuperscript{6} When the reaction was conducted under similar conditions using 6.25 mol\% of (S)-t-Bu-PHOX (L/Pd = 1.25 : 1), the desired product was isolated in 75\% yield and 36\% ee (Table 1 - entry 15).

**Allylation of non-fluorinated allyl enol carbonates**

(S)-2-allyl-2-methyl-1-tetralone (5) (Scheme 1) Following the general protocol on a 0.30 mmol scale using 3.0 mol\% of (S)-t-Bu-PHOX (L/Pd = 1 : 1.67), the desired product (51 mg, 84\%) was isolated as a
colorless oil by flash chromatography using 5% Et₂O/hexane. The enantioselectivity was 92% ee (OD-H, 254 nm, hexane:2-propanol = 99.9:0.1, flow rate 0.7 ml/min, tᵣ (major) = 22.9 min, tᵣ (minor) = 25.5 min). All spectroscopic data were in agreement with the literature.⁷ When the reaction was conducted under similar conditions using 6.25 mol% of (S)-t-Bu-PHOX (L/Pd = 1.25 : 1), the desired product was isolated in 91% and 92% ee.

(R)-2-Allyl-2-chloro-1-tetralone (Reference 15) Following the general protocol on a 0.29 mmol scale using 1.25 mol% of (S)-t-Bu-PHOX (L/Pd = 1 : 4), the desired product (7 mg, 11%) was isolated as a colorless oil by flash chromatography using 5% Et₂O/hexane. The enantioselectivity was 49% ee (OD-H, 254 nm, hexane:2-propanol = 99.5:0.5, flow rate 0.5 ml/min, tᵣ (major) = 13.4 min, tᵣ (minor) = 15.7 min). The absolute configurations were assigned based on the established stereochemical outcome of the reaction. [α]D⁺²² +14.5 (c 0.60, CHCl₃); IR (neat) ν = 3076, 2980, 2937, 2844, 1690, 1602, 1455, 1239, 1224, 996, 922, 746 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, 1H, J = 7.9 Hz), 7.52 (t, 1H, J = 7.4 Hz), 7.35 (t, 1H, J = 7.6 Hz), 7.26 (d, 1H, J = 7.0 Hz), 5.89 (m, 1H), 5.23 (d, 1H, J = 6.0 Hz), 5.20 (s, 1H), 3.35 (m, 1H), 3.01–2.86 (m, 3H), 2.47-2.29 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 191.0, 143.3, 134.1, 132.6, 130.3, 129.2, 128.9, 127.3, 120.1, 70.0, 43.1, 35.3, 26.0; HRMS-ESI cald for C₁₃H₁₄OCl [M+H]⁺ 221.0727, found 221.0736. When the reaction was conducted under similar conditions using 6.25 mol% of (S)-t-Bu-PHOX (L/Pd = 1.25 : 1), the desired product was isolated in 80% yield and 34% ee.

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Allylation of alternative fluorinated precursors

(R)-2- Allyl-2-fluoro-1-tetralone (3) (Scheme 2) Following the published protocol on a 0.27 mmol scale of 6 using 1.25 mol% of (S)-t-Bu-PHOX (L/Pd = 1 : 4), the desired product (44 mg, 79%) was isolated as a colorless oil by flash chromatography using 5% Et₂O/hexane. The enantioselectivity was 91% ee. When the reaction was conducted under similar conditions using 6.25 mol% of (S)-t-Bu-PHOX (L/Pd = 1.25 : 1), the desired product was isolated in 91% yield and 91% ee.

(R)-2-Allyl-2-fluoro-1-tetralone (3) (Scheme 2) Following the general procedure on a 0.32 mmol scale of 7 using 1.25 mol% (S)-t-Bu-PHOX (L/Pd = 1 : 4), the desired product (33 mg, 50%) was isolated as a colorless oil by flash chromatography using 5% Et₂O/hexane. The enantioselectivity was 89% ee. When the reaction was conducted under similar conditions using 6.25 mol% of (S)-t-Bu-PHOX (L/Pd = 1.25 : 1), the desired product was isolated in 94% yield and 93% ee.
OCO$_2$allyl

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