# Supporting Information

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General Information

All reactions were carried out under a nitrogen atmosphere in oven-dried glassware with magnetic stirring. CH₂Cl₂, THF, and toluene 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 potassium permanganate stain followed by heating. Infrared spectra were recorded on a Bruker Tensor 37 FT-IR spectrometer. ¹H-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 (CDCl₃ at 7.26 ppm, d₆-DMSO at 2.50 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 ¹³C-NMR spectra were recorded on a Bruker Avance 500 MHz w/ direct cryoprobe (126 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl₃ at 77.0 ppm, d₆-DMSO at 39.5 ppm). ³¹P-NMR spectra were recorded on a 400 MHz Agilent 400MR-DD2 spectrometer equipped with an OneNMR probe and a 7600AS autosampler. Mass spectra data were obtained on a Gas Chromatography Mass Spectrometer (Agilent 7890A/5975C GCMS System).

(E)-3-(2-hydroxyphenyl)acrylaldehyde derivatives were prepared according to reported protocol.

Optimization of reaction conditions

Selected examples of solvents:

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<th>solvent</th>
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<tr>
<td>1</td>
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<tr>
<td>2</td>
<td>CH₂ClCH₂Cl</td>
<td>44%</td>
</tr>
<tr>
<td>3</td>
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</tr>
<tr>
<td>4</td>
<td>toluene</td>
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</tr>
<tr>
<td>5</td>
<td>PhCl</td>
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</tr>
<tr>
<td>6</td>
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<td>56%</td>
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Selected examples of ligand optimization:\(^5\)

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</tr>
<tr>
<td>102°</td>
<td>55%</td>
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<td>62%</td>
</tr>
<tr>
<td>131°</td>
<td>8%</td>
</tr>
</tbody>
</table>
General Procedure for Synthesis of (E)-3-(2-hydroxyphenyl)acrylaldehyde derivatives

Method A:

\[
\begin{align*}
\text{R} & \quad \text{H} & \quad \text{O} \\
\text{OH} & \quad \text{Cl} & \quad \text{O} \\
\text{H} & \quad \text{O} & \quad \text{H}
\end{align*}
\]

To a solution of the (E)-3-(2-hydroxyphenyl)acrylaldehyde derivative (1.0 equiv) in toluene (0.2 M) was added Et₃N (1.3 equiv) at 0 °C. Then allyl chloroformate (1.2 equiv) was added slowly. The reaction mixture was stirred for 2 h at room temperature. Then water was added to quench the reaction and organic phase was separated. The aqueous solution was extracted with EtOAc for three times. The combined organic phase was washed with brine and dried over Na₂SO₄. After evaporation of the volatile, the residue was purified by column chromatography (Hexane:EtOAc = 10:1) to afford the products as colorless oil/solid.

Method B:

\[
\begin{align*}
\text{R} & \quad \text{H} & \quad \text{O} \\
\text{OH} & \quad \text{Cl} & \quad \text{O} \\
\text{H} & \quad \text{O} & \quad \text{H}
\end{align*}
\]

Freshly prepared \(d_2\)-allyl chloroformate\(^4\) derivative (1.5 equiv) was added slowly to a solution of (E)-3-(2-hydroxyphenyl)acrylaldehyde (1.0 equiv) and Et₃N (2.0 equiv) in toluene (0.2 M) at 0 °C. The reaction mixture was stirred for 2 h at room temperature. Then water was added to quench the reaction and organic phase was separated. The aqueous solution was extracted with EtOAc for three times. The combined organic phase was washed with brine and dried over Na₂SO₄. After evaporation of the volatile, the residue was purified by column chromatography (Hexane:EtOAc = 10:1) to afford the product as colorless oil.

(E)-allyl (2-(3-oxoprop-1-en-1-yl)phenyl) carbonate (1a): Prepared according to Method A using (E)-3-(2-hydroxyphenyl)acrylaldehyde (1.48 g, 10.00 mmol). The residue was purified using column chromatography to afford 1a as colorless oil (2.05 g, 88%). Analytical data for 1a: \(^1\)H NMR (500 MHz, CDCl₃) 9.74 (d, \(J = 7.6\) Hz, 1H), 7.70 (dd, \(J = 7.8\) 1.6 Hz, 1H), 7.68 (d, \(J = 16.1\) Hz, 1H), 7.51 (ddd, \(J = 8.2, 7.4, 1.6\) Hz, 1H), 7.37 – 7.29 (m, 2H), 6.78 (dd, \(J = 16.1, 7.7\) Hz, 1H), 5.79 (ddd, \(J = 10.6, 7.7, 1.6\) Hz, 1H), 5.01 (ddd, \(J = 10.6, 7.7, 1.6\) Hz, 1H), 4.80 (ddd, \(J = 10.6, 7.7, 1.6\) Hz, 1H), 2.74 (dd, \(J = 16.1, 7.7\) Hz, 1H), 2.06 (dd, \(J = 16.1, 7.7\) Hz, 1H), 1.97 (dd, \(J = 16.1, 7.7\) Hz, 1H), 1.08 (s, 3H), 0.91 (s, 3H).
Hz, 1H), 6.07 – 6.02 (m, 1H), 5.49 (dd, J = 17.3, 1.3 Hz, 1H), 5.40 (dd, J = 10.5, 1.2 Hz, 1H), 4.81 (dt, J = 5.9, 1.3 Hz, 2H); 13C NMR (126 MHz, CDCl$_3$) δ 193.6, 152.9, 149.5, 145.3, 132.2, 130.8, 130.5, 128.0, 126.7, 126.5, 122.7, 120.0, 69.6; IR (film) cm$^{-1}$ 3067, 1750, 1706, 1682, 1606, 1487, 1457, 1418, 1263, 1218, 1175, 1124, 1079, 984, 964, 766; LRMS (EI): Mass calcd for [M]$^+$ C$_{13}$H$_{12}$O$_4$: 232.1; found 232.1.

\[
\begin{align*}
\text{(E)-allyl (4-methyl-2-(3-oxoprop-1-en-1-yl)phenyl) carbonate (1b):} & \text{ Prepared according to Method A using (E)-3-(2-hydroxy-5-methylphenyl)acrylaldehyde (0.81 g, 5.00 mmol). The residue was purified using column chromatography to afford 1b as colorless oil (0.77 g, 63%).} \\
\text{Analytical data for 1b:} & \text{ H NMR (500 MHz, CDCl$_3$) 9.73 (d, J = 7.7 Hz, 1H), 7.64 (d, J = 16.1 Hz, 1H), 7.48 (d, J = 2.0 Hz, 1H), 7.30 (dd, J = 8.4, 2.2 Hz, 1H), 7.19 (d, J = 8.3, 1H), 6.75 (dd, J = 16.1, 7.7 Hz, 1H), 6.16 – 6.01 (m, 1H), 5.48 (dq, J = 16.9, 1.3 Hz, 1H), 5.39 (dq, J = 10.4, 1.1 Hz, 1H), 4.86 – 4.74 (m, 2H), 2.41 (s, 3H); C NMR (126 MHz, CDCl$_3$) 193.8, 153.2, 147.5, 145.6, 136.6, 133.0, 130.8, 128.3, 126.1, 122.4, 120.0, 69.6, 20.9; IR (film) cm$^{-1}$ 2954, 1740, 1665, 1629, 1490, 1363, 1297, 1211, 1128, 1087, 979, 952, 778; LRMS (EI): Mass calcd for [M]$^+$ C$_{14}$H$_{14}$O$_4$: 246.1; found 246.0.} \\
\end{align*}
\]

\[
\begin{align*}
\text{(E)-allyl (2-(4-tert-butyl-3-oxoprop-1-en-1-yl)phenyl) carbonate (1d):} & \text{ Prepared according to Method A using (E)-3-(2-hydroxy-5-tert-butylphenyl)acrylaldehyde (0.41 g, 2.00 mmol).} \\
\end{align*}
\]
residue was purified using column chromatography to afford 1d as colorless solid (0.43 g, 75%). Analytical data for 1d: 1H NMR (500 MHz, CDCl₃) 9.73 (d, J = 7.8 Hz, 1H), 7.66 (t, J = 7.9 Hz, 2H), 7.52 (d, J = 8.5 Hz, 1H), 7.22 (d, J = 8.6 Hz, 1H), 6.79 (dd, J = 16.0, 7.7 Hz, 1H), 6.06–6.00 (m, 1H), 5.47 (d, J = 17.2 Hz, 1H), 5.38 (d, J = 10.4, 1H), 4.79 (d, J = 6.0, 2H), 1.35 (s, 9H); 13C NMR (126 MHz, CDCl₃) δ 193.8, 153.1, 149.7, 147.4, 146.1, 130.8, 130.2, 129.7, 125.7, 124.8, 122.2, 120.0, 69.6, 34.68, 31.3; IR (film) cm⁻¹ 2954, 1755, 1676, 1629, 1604, 1493, 1381, 1259, 1205, 1132, 1048, 975, 777; LRMS (EI): Mass calcd for [M]+ C₁₇H₂₀O₄: 288.1; found 288.1.

(E)-allyl (4,5-dimethyl-2-(3-oxoprop-1-en-1-yl)phenyl) carbonate (1e): Prepared according to Method A using (E)-3-(2-hydroxy-4,5-dimethylphenyl)acrylaldehyde (0.35 g, 2.00 mmol). The residue was purified using column chromatography to afford 1e as colorless oil (0.39 g, 75%). Analytical data for 1e: 1H NMR (500 MHz, CDCl₃) 9.69 (d, J = 7.7 Hz, 1H), 7.59 (d, J = 16.0 Hz, 1H), 7.07 (s, 1H), 6.72 (dd, J = 16.0, 7.7 Hz, 1H), 6.07 – 5.99 (m, 1H), 5.48 (d, J = 17.1 Hz, 1H), 5.38 (d, J = 10.4 Hz, 1H), 4.79 (d, J = 5.8 Hz, 2H), 2.32 (s, 3H), 2.30 (s, 3H); 13C NMR (126 MHz, CDCl₃) δ 193.9, 153.3, 147.6, 145.8, 142.2, 135.4, 130.9, 129.4, 128.7, 123.7, 123.5, 120.0, 69.6, 20.2, 19.3; IR (film) cm⁻¹ 2980, 1774, 1744, 1676, 1616, 1616, 1362, 1295, 1258, 1236, 1182, 1123, 1035, 990, 780; LRMS (EI): Mass calcd for [M]+ C₁₅H₁₆O₄: 260.1; found 260.1.

(E)-allyl (6-(3-oxoprop-1-en-1-yl)-2,3-dihydro-1H-inden-5-yl) carbonate (1f): Prepared according to Method A using (E)-3-(6-hydroxy-2,3-dihydro-1H-inden-5-yl)acrylaldehyde (0.37 g, 2.00 mmol). The residue was purified using column chromatography to afford 1f as colorless oil (0.47 g, 86%). Analytical data for 1f: 1H NMR (500 MHz, CDCl₃) 9.69 (d, J = 7.7 Hz, 1H), 7.62 (d, J = 15.9 Hz, 1H), 7.51 (s, 1H), 7.13 (s, 1H), 6.71 (dd, J = 15.9, 7.7 Hz, 1H), 6.07 – 5.99 (m, 1H), 5.47 (d, J = 17.1 Hz, 1H), 5.38 (d, J = 10.4 Hz, 1H), 4.78 (d, J = 5.8 Hz, 2H), 2.98 – 2.92 (m, 4H), 2.17 – 2.11 (m, 2H); 13C NMR (126 MHz, CDCl₃) δ 193.9, 153.3, 150.0, 148.4, 146.2, 143.0, 130.9, 129.2, 124.2, 123.0, 119.9, 118.5, 69.6, 33.3, 32.2, 25.6; IR (film) cm⁻¹ 2980, 1774, 1743, 1674, 1616, 1363, 1295, 1256, 1234, 1189, 1122, 1029, 978, 780; LRMS (EI): Mass calcd for [M]+ C₁₆H₁₆O₄: 272.1; found 272.1.
(E)-allyl (4-phenyl-2-(3-oxoprop-1-en-1-yl)phenyl) carbonate (1g): Prepared according to Method A using (E)-3-(2-hydroxy-5-phenylphenyl)acrylaldehyde (0.45 g, 2.00 mmol). The residue was purified using column chromatography to afford 1g as colorless oil (0.57 g, 93%). Analytical data for 1g: \(^1\)H NMR (500 MHz, CDCl\(_3\)) 9.74 (d, \(J = 7.6\) Hz, 1H), 7.83 (d, \(J = 16.1\) Hz, 1H), 7.72 – 7.65 (m, 2H), 7.58 – 7.56 (m, 2H), 7.49 – 7.46 (m, 2H), 7.42 – 7.37 (m, 2H), 6.83 (dd, \(J = 16.1, 7.6\) Hz, 1H), 6.10 – 6.02 (m, 1H), 5.50 (dd, \(J = 17.2, 2.6\) Hz, 1H), 5.41 (d, \(J = 10.4\) Hz, 1H), 4.82 (d, \(J = 5.7\) Hz, 2H); \(^1^3\)C NMR (126 MHz, CDCl\(_3\)) 193.8, 153.2, 149.0, 145.5, 140.2, 139.6, 131.1, 130.9, 129.2, 128.2, 127.3, 126.9, 126.8, 123.2, 120.3, 69.9; IR (film) cm\(^{-1}\): 2980, 1795, 1744, 1670, 1524, 1364, 1321, 1255, 1210, 1187, 1123, 1030, 977, 768; LRMS (EI): Mass calcd for [M]+ C\(_{19}\)H\(_{16}\)O\(_4\): 308.1; found 308.1.

(E)-allyl (3-(3-oxoprop-1-en-1-yl)naphthalen-2-yl) carbonate (1h): Prepared according to Method A using (E)-3-(2-hydroxy-5-phenylphenyl)acrylaldehyde (0.50 g, 2.50 mmol). The residue was purified using column chromatography to afford 1h as colorless solid (0.55 g, 78%). Analytical data for 1h: \(^1\)H NMR (500 MHz, CDCl\(_3\)) 9.73 (d, \(J = 7.7\) Hz, 1H), 7.81 (s, 1H), 7.88 (dd, \(J = 8.2, 1.3\) Hz, 1H), 7.81 – 7.79 (m, 1H), 7.73 – 7.70 (m, 2H), 7.55 – 7.51 (m, 2H), 6.89 (dd, \(J = 16.1, 7.7\) Hz, 1H), 6.06 – 5.98 (m, 1H), 5.48 – 5.44 (m, 1H), 5.38 – 5.35 (m, 1H), 4.79 – 4.77 (m, 2H); \(^1^3\)C NMR (126 MHz, CDCl\(_3\)) 193.8, 153.2, 146.5, 146.3, 134.7, 131.2, 130.8, 129.4, 128.6, 128.4, 127.6, 126.9, 125.8, 120.1, 120.0, 69.7; IR (film) cm\(^{-1}\): 2983, 1797, 1740, 1673, 1525, 1365, 1321, 1255, 1211, 1190, 1123, 1032, 978, 768; LRMS (EI): Mass calcd for [M]+ C\(_{17}\)H\(_{14}\)O\(_4\): 282.1; found 282.1.

(E)-allyl (2-(3-oxoprop-1-en-1-yl)phenyl) carbonate (1i): Prepared according to Method A using (E)-3-(2-hydroxy-5-(trimethylsilyl)phenyl)acrylaldehyde (0.44 g, 2.00 mmol). The residue was purified using column chromatography to afford 1i as colorless oil (0.53 g, 86%). Analytical data for 1i: \(^1\)H NMR (500 MHz, CDCl\(_3\)) 9.54 (d, \(J = 7.7\) Hz, 1H), 7.59 (d, \(J = 1.7\) Hz, 1H), 7.49 (d, \(J = 16.1\) Hz, 1H), 7.44 (dd, \(J = 8.0, 1.6\) Hz, 1H), 7.10 – 7.04 (m, 1H), 6.61 (dd, \(J = 16.1, 7.7\) Hz, 1H), 6.05 (dd, \(J = 10.4, 7.7\) Hz, 1H), 5.40 (d, \(J = 10.4\) Hz, 1H), 4.82 (d, \(J = 5.7\) Hz, 2H); \(^1^3\)C NMR (126 MHz, CDCl\(_3\)) 193.8, 153.2, 146.5, 146.3, 134.7, 131.2, 130.8, 129.4, 128.6, 128.4, 127.6, 126.9, 125.8, 120.1, 120.0, 69.7; IR (film) cm\(^{-1}\): 2983, 1797, 1740, 1673, 1525, 1365, 1321, 1255, 1211, 1190, 1123, 1032, 978, 768; LRMS (EI): Mass calcd for [M]+ C\(_{19}\)H\(_{16}\)O\(_4\): 308.1; found 308.1.
Hz, 1H), 5.87 – 5.82 (m, 1H), 5.29 (d, J = 17.2, 1.4 Hz, 1H), 5.20 (dd, J = 10.4, 1.4 Hz, 1H), 4.66 – 4.65 (m, 2H), 0.12 (m, 9H); ^13^C NMR (126 MHz, CDCl_3) 193.79, 152.89, 149.99, 145.80, 139.48, 137.25, 133.12, 130.41, 125.65, 121.83, 120.05, 69.64, -1.24; IR (film) cm\(^{-1}\) 2981, 1740, 1666, 1630, 1489, 1381, 1297, 1259, 1233, 1211, 1108, 1050, 994, 779; LRMS (EI): Mass calcd for [M]^+ C\(_{16}\)H\(_{20}\)O\(_4\)Si: 304.1; found 304.1.

(E)-allyl (2-(4-methoxy-3-oxoprop-1-en-1-yl)phenyl) carbonate (1j): Prepared according to Method A using (E)-3-(2-hydroxy-5-methoxyphenyl)acrylaldehyde (0.35 g, 2.00 mmol). The residue was purified using column chromatography to afford 1j as colorless solid (0.45 g, 86%). Analytical data for 1j: ^1^H NMR (500 MHz, CDCl_3) 9.72 (d, J = 7.8 Hz, 1H), 7.61 (d, J = 16.1 Hz, 1H), 7.20 (d, J = 9.0 Hz, 1H), 7.13 (s, 1H), 7.02 (d, J = 9.0 Hz, 1H), 6.73 (dd, J = 15.8, 7.7 Hz, 1H), 6.05 – 5.99 (m, 1H), 5.46 (d, J = 17.2 Hz, 1H), 5.37 (d, J = 10.5, 1H), 4.78 (d, J = 6.2, 2H), 3.85 (s, 3H); ^13^C NMR (126 MHz, CDCl_3) δ 193.7, 157.6, 153.3, 145.3, 143.3, 130.8, 130.5, 127.2, 123.6, 120.0, 118.1, 111.7, 69.6, 55.7; IR (film) cm\(^{-1}\) 2980, 1744, 1673, 1495, 1443, 1420, 1282, 1246, 1205, 1146, 975, 936, 780; LRMS (EI): Mass calcd for [M]^+ C\(_{14}\)H\(_{14}\)O\(_5\): 262.2; found 262.0.

(E)-allyl (4-(methylthio)-2-(3-oxoprop-1-en-1-yl)phenyl) carbonate (1k): Prepared according to Method A using (E)-3-(2-hydroxy-5-(methylthio)phenyl)acrylaldehyde (0.44 g, 2.00 mmol). The residue was purified using column chromatography to afford 1k as colorless solid (0.53 g, 86%). Analytical data for 1k: ^1^H NMR (500 MHz, CDCl_3) 9.70 (d, J = 7.6 Hz, 1H), 9.59 (d, J = 16.1 Hz, 1H), 7.47 (d, J = 2.4 Hz, 1H), 7.33 (dd, J = 8.6, 2.3 Hz, 1H), 7.21 (d, J = 8.6 Hz, 1H), 6.73 (dd, J = 16.0, 7.6 Hz, 1H), 6.03 – 5.97 (m, 1H), 5.47 – 5.43 (m, 1H), 5.36 (d, J = 10.3 Hz, 1H), 4.76 (d, J = 6.0, 2H), 2.50 (s, 3H); ^13^C NMR (126 MHz, CDCl_3) δ 193.6, 153.0, 147.0, 144.8, 137.4, 130.8, 130.7, 130.2, 126.9, 125.5, 123.1, 120.2, 69.8, 16.2; IR (film) cm\(^{-1}\) 2954, 1786, 1744, 1673, 1618, 1524, 1461, 1363, 1293, 1255, 1212, 1186, 1125, 978, 777; LRMS (EI): Mass calcd for [M]^+ C\(_{14}\)H\(_{14}\)O\(_4\)S: 278.1; found 278.0.

(E)-allyl (5-methyl-4-(methylthio)-2-(3-oxoprop-1-en-1-yl)phenyl) carbonate (1l): Prepared according to Method A using (E)-3-(2-hydroxy-4-methyl-5-(methylthio)phenyl)acrylaldehyde
(0.42 g, 2.00 mmol). The residue was purified using column chromatography to afford 1l as colorless solid (0.57 g, 97%). Analytical data for 1l: \(^1\)H NMR (500 MHz, CDCl\(_3\)) 9.70 (d, \(J = 8.1\) Hz, 1H), 7.60 (d, \(J = 16.1\) Hz, 1H), 7.36 (s, 1H), 7.09 (s, 1H), 6.73 (dd, \(J = 15.3, 7.9\) Hz, 1H), 6.06 – 5.98 (m, 1H), 5.47 (d, \(J = 17.3\) Hz, 1H), 5.38 (d, \(J = 10.6\) Hz, 1H), 4.78 (d, \(J = 6.7\), 2H), 2.50 (s, 3H), 2.37 (s, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) 193.7, 153.1, 146.7, 145.2, 141.0, 137.0, 130.8, 129.8, 124.5, 123.8, 123.3, 120.1, 69.7, 20.3, 15.5; IR (film) cm\(^{-1}\) 2990, 1745, 1677, 1635, 1517, 1382, 1270, 1210, 1180, 1121, 1051, 939, 887; LRMS (EI): Mass calcd for [M]+ C\(_{15}\)H\(_{16}\)O\(_4\)S: 292.1; found 292.0.

\((E)\)-allyl (6-(3-oxoprop-1-en-1-yl)benzo[d][1,3]dioxol-5-yl) carbonate (1m): Prepared according to Method A using \((E)\)-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)acrylaldehyde (0.33 g, 1.70 mmol) 1m as colorless solid (0.43 g, 90%). Analytical data for 1m: \(^1\)H NMR (500 MHz, CDCl\(_3\)) 9.59 (d, \(J = 7.7\) Hz, 1H), 7.49 (d, \(J = 15.9\) Hz, 1H), 6.98 (s, 1H), 6.70 (s, 1H), 6.50 (dd, \(J = 15.9, 7.7\) Hz, 1H), 6.00 (s, 2H), 5.97 – 5.91 (m, 1H), 5.42 – 5.41 (m, 1H), 5.32 – 5.29 (m, 1H), 4.70 (dt, \(J = 6.0, 1.3\) Hz, 2H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) 193.6, 153.1, 150.9, 146.5, 145.2, 145.0, 130.7, 128.4, 120.2, 119.9, 105.1, 104.0, 102.6, 69.8; IR (film) cm\(^{-1}\) 2981, 1754, 1666, 1626, 1606, 1503, 1492, 1375, 1293, 1248, 1221, 1163, 1121, 1034, 991, 772; LRMS (EI): Mass calcd for [M]+ C\(_{14}\)H\(_{12}\)O\(_6\): 276.0; found 276.0.

\((E)\)-allyl (4-fluoro-2-(3-oxoprop-1-en-1-yl)phenyl) carbonate (1n): Prepared according to Method A using \((E)\)-3-(2-hydroxy-5-fluorophenyl)acrylaldehyde (0.17 g, 1.00 mmol). The residue was purified using column chromatography to afford 1n as colorless solid (0.23 g, 94%). Analytical data for 1n: \(^1\)H NMR (500 MHz, CDCl\(_3\)) 9.71 (d, \(J = 7.6\) Hz, 1H), 7.32 (d, \(J = 8.7, 3.0\) Hz, 1H), 7.29 – 7.26 (m, 1H), 7.25 – 7.24 (m, 1H), 7.19 – 7.11 (m, 1H), 6.69 (dd, \(J = 16.1, 7.6\) Hz, 1H), 6.03 – 5.96 (m, 1H), 5.45 (d, \(J = 17.2, 1.4\) Hz, 1H), 5.37 (d, \(J = 10.4, 1.2\) Hz, 1H), 4.76 (dt, \(J = 5.8, 1.3\) Hz, 2H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) 193.3, 161.3, 159.3, 153.0, 145.4 (d, \(J_{\text{CF}} = 2.8\) Hz), 143.9 (d, \(J_{\text{CF}} = 2.3\) Hz), 131.0 (d, \(J_{\text{CF}} = 79.4\) Hz), 128.1 (d, \(J_{\text{CF}} = 8.1\) Hz), 124.3 (d, \(J_{\text{CF}} = 8.6\) Hz), 120.2, 119.0 (d, \(J_{\text{CF}} = 23.8\) Hz), 113.9 (d, \(J_{\text{CF}} = 24.2\) Hz), 69.8; IR (film) cm\(^{-1}\) 3028, 1751, 1683, 1632, 1516, 1460, 1262, 1254, 1185, 1177, 1044, 972, 735; LRMS (EI): Mass calcd for [M]+ C\(_{13}\)H\(_{11}\)FO\(_4\): 250.1; found 250.1.
(E)-allyl (4-chloro-2-(3-oxoprop-1-en-1-yl)phenyl) carbonate (10): Prepared according to Method A using (E)-3-(2-hydroxy-5-fluorophenyl)acrylaldehyde (0.18 g, 1.00 mmol). The residue was purified using column chromatography to afford 10 as colorless solid (0.24 g, 88%). Analytical data for 10: $^1$H NMR (500 MHz, CDCl$_3$) 9.73 (d, $J = 7.6$ Hz, 1H), 7.64 – 7.57 (m, 2H), 7.45 – 7.43 (m, 1H), 7.29 – 7.26 (m, 1H), 6.73 (dd, $J = 16.6, 7.7$ Hz, 1H), 6.05 – 5.99 (m, 1H), 5.50– 5.46 (m, 1H), 5.41– 5.38 (m, 1H), 4.79 (dt, $J = 5.8, 1.4$ Hz, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) 193.2, 152.7, 147.8, 143.7, 132.3, 131.9, 131.3, 130.6, 128.0, 127.6, 124.1, 120.3, 69.9; IR (film) cm$^{-1}$ 3064, 1752, 1675, 1634, 1520, 1360, 1256, 1211, 1179, 1122, 1051, 979, 772; LRMS (EI): Mass calcd for [M]$^+$ C$_{13}$H$_{11}$ClO$_4$: 266.0; found 266.0.

(E)-allyl-1,1-$d_2$ (2-(3-oxoprop-1-en-1-yl)phenyl) carbonate (8): Prepared according to Method B using (E)-3-(2-hydroxyphenyl)acrylaldehyde (0.59 g, 4.00 mmol) and allyl-1,1-$d_2$ carbonochloridate. The residue was purified using column chromatography to afford 8 as colorless oil (0.34 g, 36%). Analytical data for 8: $^1$H NMR (500 MHz, CDCl$_3$) 9.74 (d, $J = 7.6$ Hz, 1H), 7.70 – 7.66 (m, 2H), 7.53 – 7.49 (m, 1H), 7.37 – 7.29 (m, 2H), 6.77 (dd, $J = 16.1, 7.6$ Hz, 1H), 6.72 (dd, $J = 17.2, 10.4$ Hz, 1H), 5.49 (dd, $J = 17.2, 1.2$ Hz, 1H), 5.04 (dd, $J = 10.4, 1.2$ Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) 193.7, 152.9, 149.5, 145.4, 145.2, 132.3, 130.5, 128.0, 128.6, 126.5, 122.7, 120.3, 69.1 (p, $J = 22.6, 22.2$ Hz); IR (film) cm$^{-1}$ 2982, 1751, 1667, 1625, 1375, 1248, 1162, 1123, 1025, 991, 772; LRMS (EI): Mass calcd for [M]$^+$ C$_{13}$H$_{10}$D$_2$O$_4$: 234.1; found 234.0.

(E)-cinnamyl (2-(3-oxoprop-1-en-1-yl)phenyl) carbonate (11): Prepared according to Method B using (E)-3-(2-hydroxyphenyl)acrylaldehyde (0.29 g, 2.00 mmol) and cinnamyl carbonochloridate. The residue was purified using column chromatography to afford 11 as colorless oil (0.25 g, 40%). Analytical data for 11: $^1$H NMR (500 MHz, CDCl$_3$) 9.72 (d, $J = 7.7$ Hz, 1H), 7.71 – 7.68 (m, 2H), 7.52 – 7.49 (m, 1H), 7.47 – 7.44 (m, 2H), 7.41 – 7.29 (m, 5H), 6.80 – 6.77 (m, 2H), 6.40 (dt, $J = 15.9, 6.6$ Hz, 1H), 4.97 (dd, $J = 6.8, 1.3$ Hz, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) 193.7, 153.0, 149.5, 145.35, 136.2, 135.7, 132.3, 130.5, 128.7, 128.6, 128.0,
126.8, 126.8, 126.5, 121.4, 69.8; IR (film) cm$^{-1}$: 2980, 1754, 1669, 1626, 1485, 1396, 1245, 1217, 1163, 1122, 1096, 1025, 972, 771; LRMS (EI): Mass calcd for [M]$^+$ C$_{19}$H$_{16}$O$_4$: 308.1; found 308.1.

**Allyl (2-chlorophenyl) carbonate (14):** Prepared according to Method A using 2-chlorophenol (1.29 g, 10.00 mmol) and allyl carbonochloridate. The residue was purified using column chromatography to afford 12 as colorless oil (2.09 g, 98%). Analytical data for 12: $^1$H NMR (500 MHz, CDCl$_3$) 7.48 (d, $J$ = 7.9, 1.6 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.29 – 7.23 (m, 2H), 6.06 – 6.00 (m, 1H), 5.47 (dq, $J$ = 17.2, 1.4 Hz, 1H), 5.37 (dq, $J$ = 10.3, 1.1 Hz, 1H), 4.80 (dt, $J$ = 5.7, 1.4 Hz, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) 152.6, 147.1, 130.9, 130.5, 127.9, 127.4, 126.9, 123.3, 119.6, 69.6; IR (film) cm$^{-1}$: 2991, 1764, 1689, 1636, 1517, 1477, 1277, 1242, 1211, 1105, 983, 940, 794; LRMS (EI): Mass calcd for [M]$^+$ C$_{10}$H$_9$ClO$_3$: 212.0; found 212.1.

**Allyl (2,6-dimethylphenyl) carbonate (6):** Prepared according to Method A using 2,6-dimethylphenol (2.44 g, 20.00 mmol) and allyl carbonochloridate. Colorless oil (3.80 g, 92%). Analytical data: $^1$H NMR (500 MHz, CDCl$_3$) 7.09 (br, 3H), 6.05 – 6.00 (m, 1H), 5.46 (dt, $J$ = 17.1, 1.4 Hz, 1H), 5.36 (dd, $J$ = 10.4, 1.3 Hz, 1H), 4.78 (d, $J$ = 5.6 Hz, 2H), 2.24 (s, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$) 152.8, 148.3, 131.3, 130.2, 128.7, 126.1, 119.4, 69.1, 16.1; IR (film) cm$^{-1}$: 2981, 1756, 1691, 1652, 1637, 1381, 1236, 1178, 1143, 1047, 984, 767; LRMS (EI): Mass calcd for [M]$^+$ C$_{12}$H$_{14}$O$_3$: 206.1; found 206.0.

**General procedure for NHC-catalyzed reaction**

Into an oven-dried, screw-capped vial equipped with a magnetic stirbar was weighed Pd$_2$(dba)$_3$ (0.016 mmol, 0.04 equiv) and dppf (0.064 mmol, 0.16 equiv) in a nitrogen-filled drybox. The vial was capped with a septum cap and degassed CH$_2$Cl$_2$ (0.6 mL) was added into the vial, and the solution was stirred for 10 min.

Into another oven-dried, screw-capped vial equipped with a magnetic stirbar was weighed aldehyde 1 (0.400 mmol, 1 equiv). The vial was taken into a nitrogen-filled drybox at which time azolium salt A (0.08 mmol, 0.20 equiv) was added. Into the vial were then successively added CH$_2$Cl$_2$ (1.0 mL) and the premixed Pd-dppf solution via cannula (washed with 2 × 0.2 mL degassed CH$_2$Cl$_2$). Then allyl 2-chlorophenylcarbonate 12 (0.400 mmol, 1.0 equiv) was added via a syringe. The reaction was stirred at room temperature in drybox for 24 h (all reactions were completed within 24 h). The reaction mixture was filtered over a short pad of silica gel eluted with dichloromethane and concentrated under reduced pressure. Purification by flash chromatography with EtOAc/hexanes afforded the corresponding 3-allyldihydrocoumarins.
3-allyl-dihydrocoumarin (2a): Prepared according to the general procedure using 1a. The NMR yield was determined using Me₃SiPh as internal standard. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford 2a as a colorless oil. Analytical data for 2a: ¹H NMR (500 MHz, CDCl₃) δ 7.26 – 7.21 (m, 1H), 7.17 – 7.13 (m, 1H), 7.09 – 7.02 (m, 2H), 5.88 – 5.77 (m, 1H), 5.14 – 5.10 (m, 2H), 2.98 (dd, J = 14.6, 5.0 Hz, 1H), 2.81 – 2.65 (m, 3H), 2.37 – 2.29 (m, 1H); LRMS (EI): Mass calcd for [M]+ C₁₂H₁₂O₂: 188.1; found 188.1.

4-allyl-dihydrocoumarin (3a): Prepared according to the general procedure using 1a. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford 3a as a colorless oil. Analytical data for 3a: ¹H NMR (500 MHz, CDCl₃) δ 7.27 – 7.20 (m, 1H), 7.19 (dd, J = 7.6, 1.6 Hz, 1H), 7.11 – 7.09 (m, 1H), 7.05 (dd, J = 8.0, 1.3 Hz, 1H), 5.77 – 5.67 (m, 1H), 5.12 – 5.06 (m, 2H), 3.19 – 3.04 (m, 1H), 2.78 (dd, J = 5.2, 2.8 Hz, 2H), 2.46 – 2.39 (m, 1H), 2.32 – 2.25 (m, 1H); (EI): Mass calcd for [M]+ C₁₂H₁₂O₂: 188.1; found 188.0.

3-allyl-6-methyldihydrocoumarin (2b): Prepared according to the general procedure using 1b. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford 2b as a colorless oil. Analytical data for 2b: ¹H NMR (500 MHz, CDCl₃) δ 6.90 (dd, J = 2.1 Hz, 1H), 6.85 (d, J = 8.3 Hz, 1H), 5.80 – 5.73 (m, 1H), 5.08 – 5.04 (m, 2H), 2.87 (dd, J = 14.4, 4.4 Hz, 1H), 2.74 – 2.59 (m, 3H), 2.29 – 2.22 (m, 4H); ¹³C NMR (CDCl₃, 126 MHz) δ 170.7, 149.5, 134.4, 133.9, 128.7, 128.6, 122.2, 118.2, 116.3, 38.8, 33.9, 28.6, 20.8; IR (film) cm⁻¹ 2980, 1739, 1642, 1625, 1499, 1454, 1379, 1268, 1258, 1210, 1159, 1103, 1025, 886, 775; LRMS (EI): Mass calcd for [M]+ C₁₃H₁₄O₂: 202.1; found 202.1.

3-allyl-7-methyldihydrocoumarin (2c): Prepared according to the general procedure using 1c. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford 2c as a colorless oil. Analytical data for 2c: ¹H NMR (500 MHz, CDCl₃) δ 7.04 (d, J = 7.6 Hz, 1H), 6.88 (d, J = 1.4 Hz, 1H), 5.13 – 5.10 (m, 2H), 2.96 – 2.92 (m, 1H), 2.21 – 2.66 (m, 3H), 2.36 – 2.29 (m, 4H); ¹³C NMR (CDCl₃, 126 MHz) δ 170.7, 151.4, 138.5, 134.4, 127.8, 125.1, 119.3, 118.2, 117.0, 38.9, 34.0, 28.3, 21.2; IR (film)
3-allyl-6-tert-butyldihydrocoumarin (2d): Prepared according to the general procedure using 1d. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford 2d as a colorless oil. Analytical data for 2d: ¹H NMR (500 MHz, CDCl₃) δ 7.19 – 7.17 (m, 1H), 7.09 (d, J = 2.4 Hz, 1H), 6.89 (d, J = 8.5 Hz, 1H), 5.82 – 5.73 (m, 1H), 5.08 – 5.08 (m, 2H), 2.90 (dd, J = 15.0, 5.0 Hz, 1H), 2.76 – 2.62 (m, 3H), 2.31 – 2.24 (m, 1H), 1.23 (s, 9H); ¹³C NMR (CDCl₃, 126 MHz) δ 170.7, 149.3, 147.4, 134.5, 125.1, 125.0, 121.9, 118.2, 116.0, 38.8, 34.4, 34.0, 31.5, 29.0; IR (film) cm⁻¹ 2979, 1763, 1707, 1642, 1613, 1498, 1462, 1365, 1272, 1232, 1145, 1125, 1027, 887, 768; LRMS (EI): Mass calcd for [M]+ C₁₃H₁₄O₂: 202.1; found 202.1.

3-allyl-6,7-dimethyldihydrocoumarin (2e): Prepared according to the general procedure using 1e. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford 2e as a colorless oil. Analytical data for 2e: ¹H NMR (500 MHz, CDCl₃) δ 6.91 (s, 1H), 6.81 (s, 1H), 5.87 – 5.78 (m, 1H), 5.14 – 5.10 (m, 2H), 2.93 – 2.87 (m, 1H), 2.78 – 2.65 (m, 3H), 2.35 – 2.28 (m, 1H), 2.23 (s, 3H), 2.20 (s, 3H); ¹³C NMR (CDCl₃, 126 MHz) δ 170.9, 149.5, 136.7, 134.5, 132.5, 128.9, 119.3, 118.1, 117.4, 39.0, 34.0, 28.2, 19.6, 19.1; IR (film) cm⁻¹ 2975, 1759, 1641, 1627, 1503, 1455, 1409, 1275, 1174, 1102, 1021, 866, 771; LRMS (EI): Mass calcd for [M]+ C₁₄H₁₆O₂: 216.1; found 216.1.

3-allyl-4,6,7,8-tetrahydrocyclopenta[g]chromen-2(3H)-one (2f): Prepared according to the general procedure using 1h. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford 2f as a colorless oil. Analytical data for 2f: ¹H NMR (500 MHz, CDCl₃) δ 1.99 (s, 1H), 6.89 (s, 1H), 5.87 – 5.79 (m, 1H), 5.14 – 5.10 (m, 2H), 2.95 – 2.78 (m, 5H), 2.75 – 2.66 (m, 3H), 2.31 – 2.30 (m, 1H), 2.11 – 2.05 (m, 2H); ¹³C NMR (CDCl₃, 126 MHz) δ 171.0, 150.2, 144.5, 140.2, 134.5, 123.5, 120.0, 118.1, 112.5, 38.9, 33.9, 32.8, 32.2, 28.7, 25.8; IR (film) cm⁻¹ 3002, 1750, 1640, 1622, 1477, 1426, 1356, 1263, 1258, 1204, 1148, 1107, 998, 870, 751; LRMS (EI): Mass calcd for [M]+ C₁₅H₁₆O₂: 228.1; found 228.1.
3-allyl-6-phenyldihydrocoumarin (2g): Prepared according to the general procedure using 1g. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford 2g as a colorless solid. Analytical data for 2g: \( ^1H \) NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.58 – 7.56 (m, 2H), 7.51 – 7.45 (m, 3H), 7.42 – 7.36 (m, 2H), 7.14 (d, \( J = 8.4 \) Hz, 1H), 5.93 – 5.85 (m, 1H), 5.21 – 5.17 (m, 2H), 3.09 (dd, \( J = 15.5, 5.6 \) Hz, 1H), 2.93 – 2.74 (m, 3H), 2.44 – 2.37 (m, 1H); \( ^{13}C \) NMR (CDCl\(_3\), 126 MHz) \( \delta \) 170.4, 151.0, 140.1, 137.6, 134.3, 128.9, 127.4, 127.0, 126.9, 126.8, 122.9, 118.4, 116.9, 38.8, 34.0, 28.8; IR (film) cm\(^{-1}\) 2980, 1762, 1706, 1641, 1601, 1507, 1481, 1453, 1354, 1226, 1142, 1120, 1024, 893, 760; LRMS (EI): Mass calcd for [M]\(^+\) C\(_{18}\)H\(_{16}\)O\(_2\): 264.1; found 264.1.

3-allyl-3,4-dihydro-2\(H\)-benzo[g]chromen-2-one (2h): Prepared according to the general procedure using 1h. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford 2h as a colorless solid. Analytical data for 2h: \( ^1H \) NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.79 – 7.76 (m, 2H), 7.65 (br, 1H), 7.48 – 7.41 (m, 3H), 5.90 – 5.81 (m, 1H), 5.17 – 5.13 (m, 2H), 3.21 – 3.16 (m, 1H), 3.01 – 2.95 (m, 1H), 2.82 – 2.81 (m, 1H), 2.73 – 2.70 (m, 1H), 2.39 – 2.33 (m, 1H); \( ^{13}C \) NMR (CDCl\(_3\), 126 MHz) \( \delta \) 170.5, 149.7, 134.2, 133.1, 130.56, 127.4, 127.3, 127.0, 126.5, 125.5, 123.1, 118.41, 112.8, 39.1, 34.0, 29.1; IR (film) cm\(^{-1}\) 2982, 1764, 1708, 1640, 1603, 1508, 1483, 1455, 1357, 1227, 1142, 1121, 1026, 897, 760; LRMS (EI): Mass calcd for [M]\(^+\) C\(_{16}\)H\(_{14}\)O\(_2\): 238.1; found 238.1.

3-allyl-6-trimethylsilyldihydrocoumarin (2i): Prepared according to the general procedure using 1i. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford 2i as a colorless oil. Analytical data for 2i: \( ^1H \) NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.38 – 7.36 (m, 1H), 7.28 (s, 1H), 7.01 (d, \( J = 8.0 \) Hz, 1H), 5.87 – 5.79 (m, 1H), 5.15 – 5.11 (m, 2H), 2.99 (dd, \( J = 15.1, 5.1 \) Hz, 1H), 2.83 – 2.66 (m, 3H), 2.39 – 2.32 (m, 1H); \( ^{13}C \) NMR (CDCl\(_3\), 126 MHz) \( \delta \) 170.5, 152.2, 136.5, 134.4, 133.3, 133.2, 121.9, 118.2, 116.0, 38.9, 34.0, 28.7, -1.0; IR (film) cm\(^{-1}\) 2980, 1767, 1707, 1642, 1600, 1487, 1440, 1352, 1232, 1143, 1094, 1025, 929, 820; LRMS (EI): Mass calcd for [M]\(^+\) C\(_{15}\)H\(_{20}\)O\(_2\)Si: 260.1; found 260.1.

3-allyl-6-methoxydihydrocoumarin (2j): Prepared according to the general procedure using 1j. The unpurified residue was purified by flash chromatography using 10% EtOAc/hexanes to afford 2j as a colorless solid. Analytical data for 2j: \( ^1H \) NMR (500 MHz, CDCl\(_3\)) \( \delta \) 6.99 (d, \( J = 8.8 \) Hz, 1H), 6.79 (dd, \( J = 8.9, 3.0 \) Hz, 1H), 6.71 (d, \( J = 2.9 \) Hz 1H), 5.90 – 5.82 (m, 1H), 5.17 – 5.14 (m, 2H), 3.81 (s, 3H), 2.97 (dd, \( J = 15.1, 5.1 \) Hz, 1H), 2.84 – 2.70 (m, 3H), 2.39 – 2.32 (m,
$^{13}$C NMR (CDCl$_3$, 126 MHz) δ 170.6, 156.1, 145.5, 134.3, 123.5, 118.3, 117.3, 113.2, 113.2, 55.7, 38.7, 33.9, 28.9; IR (film) cm$^{-1}$ 2980, 1757, 1641, 1593, 1493, 1428, 1354, 1277, 1202, 1147, 1030, 885; LRMS (EI): Mass calcd for [M]$^+$ C$_{13}$H$_{14}$O$_3$: 218.1; found 218.1.

3-allyl-6-methylthioldihydrocoumarin (2k): Prepared according to the general procedure using 1k. The unpurified residue was purified by flash chromatography using 10% EtOAc/hexanes to afford 2k as a colorless solid. Analytical data for 2k: $^1$H NMR (500 MHz, CDCl$_3$) δ 7.14 (d, $J$ = 8.4, 2.3, Hz, 1H), 7.08 – 7.07 (m, 1H), 6.97 (d, $J$ = 8.5 Hz, 1H), 5.86 – 5.79 (m, 1H), 5.15 – 5.11 (m, 2H), 2.96 (dd, $J$ = 14.9, 4.8 Hz, 1H), 2.81 – 2.62 (m, 3H), 2.46 (s, 3H), 2.57 – 2.30 (m, 1H); $^{13}$C NMR (CDCl$_3$, 126 MHz) δ 170.2, 149.5, 134.2, 133.9, 127.0, 126.8, 123.3, 118.4, 117.1, 38.6, 33.9, 28.6, 16.7; IR (film) cm$^{-1}$ 3078, 1750, 1641, 1622, 1479, 1427, 1355, 1263, 1200, 1148, 1106, 1032, 860, 766; LRMS (EI): Mass calcd for [M]$^+$ C$_{13}$H$_{14}$O$_3$: 234.1; found 234.1.

3-allyl-7-methyl-6-methylthioldihydrocoumarin (2l): Prepared according to the general procedure using 1l. The unpurified residue was purified by flash chromatography using 10% EtOAc/hexanes to afford 2l as a colorless solid. Analytical data for 2l: $^1$H NMR (500 MHz, CDCl$_3$) δ 6.95 (s, 1H), 6.84 (s, 1H), 5.86 – 5.78 (m, 1H), 5.14 – 5.10 (m, 2H), 2.96 (dd, $J$ = 14.5, 4.6 Hz, 1H), 2.79 – 2.66 (m, 3H), 2.43 (s, 2H), 2.37 – 2.29 (m, 4H); $^{13}$C NMR (CDCl$_3$, 126 MHz) δ 170.5, 149.2, 136.6, 134.3, 133.1, 125.2, 120.5, 118.3, 117.9, 38.9, 33.9, 28.4, 19.9, 16.1; IR (film) cm$^{-1}$ 3078, 1748, 1640, 1501, 1476, 1436, 1397, 1356, 1244, 1157, 1104, 1034, 885, 781; LRMS (EI): Mass calcd for [M]$^+$ C$_{14}$H$_{16}$O$_2$: 248.1; found 248.1.

7-allyl-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]chromen-6-one (2m): Prepared according to the general procedure using 1m. The unpurified residue was purified by flash chromatography using 10% EtOAc/hexanes to afford 2m as solid. Analytical data for 2m: $^1$H NMR (500 MHz, CDCl$_3$) δ 6.59 (s, 1H), 6.57 (s, 1H), 6.57 (s, 1H), 5.95 (s, 2H), 5.86 – 5.77 (m, 1H), 5.14 – 5.10 (m, 2H), 5.86 – 5.77 (m, 1H), 5.42 (s, 3H), 2.34 – 2.28 (m, 1H); $^{13}$C NMR (CDCl$_3$, 126 MHz) δ 170.4, 147.1, 145.9, 144.1, 134.3, 118.3, 114.5, 107.2, 101.6, 98.9, 38.6, 33.8, 28.4; IR (film) cm$^{-1}$ 2980, 1745, 1641, 1616, 1501, 1474, 1355, 1298, 1260, 1233, 1197, 1105, 1033, 887, 781; LRMS (EI): Mass calcd for [M]$^+$ C$_{13}$H$_{12}$O$_4$: 232.1; found 232.0.
3-allyl-6-fluorodihydrocoumarin (2n): Prepared according to the general procedure using 1n. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford 2n as a colorless solid. Analytical data for 2n: \(^1H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.01 – 6.98 (m, 1H), 6.95 – 6.91 (m, 1H), 6.89 – 6.87 (m, 1H), 5.84 – 5.78 (m, 1H), 5.15 – 5.11 (m, 2H), 2.96 (dd, \(J = 15.4, 5.4\) Hz, 1H), 2.83 – 2.67 (m, 3H), 2.37 – 2.30 (m, 1H); \(^13C\) NMR (CDCl\(_3\), 126 MHz) \(\delta\) 170.0, 159.9, 158.0, 147.6 (d, \(J_{CF} = 2.7\) Hz), 134.0, 124.2 (d, \(J_{CF} = 8.1\) Hz), 118.5, 117.8 (d, \(J_{CF} = 8.5\) Hz), 114.8 (d, \(J_{CF} = 23.7, 18.2\) Hz), 38.3, 33.9, 28.6; IR (film) cm\(^{-1}\) 2980, 1739, 1642, 1597, 1491, 1435, 1270, 1257, 1218, 1196, 1164, 1104, 1025, 894, 776; LRMS (EI): Mass calcd for [M]\(^+\) C\(_{12}\)H\(_{11}\)FO\(_2\): 206.1; found 206.1.

3-allyl-6-chlorodihydrocoumarin (2o): Prepared according to the general procedure using 1o. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford 2o as colorless solid. Analytical data for 2o: \(^1H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.19 – 7.06 (m, 2H), 6.91 (d, \(J = 8.6\) Hz, 1H), 5.79 – 5.71 (m, 1H), 5.10 – 5.06 (m, 2H), 2.92 – 2.88 (m, 1H), 2.76 – 2.61 (m, 3H), 2.30 – 2.24 (m, 1H); \(^13C\) NMR (CDCl\(_3\), 126 MHz) \(\delta\) 169.7, 150.1, 133.9, 129.4, 128.3, 128.0, 124.2, 118.6, 117.9, 38.4, 33.8, 28.4; IR (film) cm\(^{-1}\) 2980, 1747, 1642, 1479, 1439, 1356, 1233, 1152, 1104, 1026, 896, 767; LRMS (EI): Mass calcd for [M]\(^+\) C\(_{12}\)H\(_{11}\)ClO\(_2\): 222.0; found 222.0.

1:1 ratio of 3-d2-allyl-drocoumarins (9) and (10): Prepared according to the general procedure using 8. The NMR yield was determined using Me\(_3\)SiPh as internal standard. The unpurified residue was purified by flash chromatography using 5% EtOAc/hexanes to afford 9 and 10 as a colorless oil. Analytical data for 9 and 10 (1:1): \(^1H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.19 – 7.16 (m, 1H), 7.11 – 7.09 (m, 1H), 7.03 – 7.00 (m, 1H), 6.97 – 6.95 (m, 1H), 5.79 – 5.73 (m, 1H), 5.09 – 5.04 (m, 1H), 2.94 – 2.89 (m, 1H), 2.79 – 2.60 (m, 2.5H), 2.30 – 2.24 (m, 0.5H); \(^13C\) NMR (CDCl\(_3\), 126 MHz) \(\delta\) 170.5, 151.6, 134.2, 134.1, 128.3, 128.2, 124.4, 122.6, 118.3, 116.6, 38.74, 38.59, 33.8, 28.6, 28.5; IR (film) cm\(^{-1}\) 2980, 1739, 1642, 1625, 1511, 1499, 1454, 1379, 128, 1258, 1210, 1159, 1013, 1025, 886, 775; LRMS (EI): Mass calcd for [M]\(^+\) C\(_{12}\)H\(_{10}\)D\(_2\)O\(_2\): 190.1; found 190.1.
Mechanistic Studies

Two component reaction of 2-(2-hydroxyphenyl)acrylaldehyde with allyl (2,6-dimethylphenyl)carbonate: 

\[
\begin{align*}
\text{4} & \quad \text{+} \quad \text{6} \\
\text{H} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

\[20 \text{ mol \% N} \text{N} \text{Mes} \quad 20 \text{ mol \% Cl} \quad 4 \text{ mol \% Pd}_{2}(\text{dba})_{3} \quad 3.0 \text{ equiv CsO}_{2}\text{CtBu} \quad 1,4\text{-dioxane, 60 °C} \]

\[\text{w 6} \quad 50\% \quad \text{w/o 6} \quad \text{no} \]

\[2a \quad 31\% \quad 50\% \quad 87\% \]

[a] Follow the General procedure of NHC-catalyzed reaction and yield was determined by \(^1\text{H} \text{NMR (500 MHz).}

Cross over reaction of 1b and 6:

The non cross-over (2b, 9, 10) and cross-over products (9b, 10b, 2a) were observed by \(^1\text{H} \text{NMR in 45\% combined yield. However, the chemical shifts of these products were too close to each other to accurately calculate the ratio of products using \(^1\text{H} \text{NMR. Instead, an alternative cross-over experiment was conducted, which is discussed in the manuscript text.}}\]

\[
\begin{align*}
\text{Me} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{H} \\
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

\[20 \text{ mol \% A} \quad 2 \text{ mol \% Pd}_{2}(\text{dba})_{3} \quad 8 \text{ mol \% dpf} \quad 10 \text{ mol \% K}_{2}\text{CO}_{3} \quad \text{CH}_{2}\text{Cl}_{2}, 25 \text{ °C} \]

\[\text{2b} \quad \text{9} \quad \text{10} \]

\[\text{cross-over products} \]

\[\text{9b} \quad \text{10b} \quad \text{2a} \]
Procedure for monitoring aldehyde 7 using GC-MS:

The reaction was set up under the standard reaction condition (0.2 mmol scale, 0.2 M). Aliquot (5 μL) was taken from the reaction vial using syringe at indicated time and mixed with dodecane (10 μL, 0.1 M in CH₂Cl₂). The mixture was subjected to GC-MS analysis. The conversion of 1a and yield of 2a and 7 was calculated based on the ratio of integrated area relative to dodecane.

Procedure for allylation of dihydrocoumarin 5:

Dihydrocoumarin 5 (1 mmol, 1.0 equiv) was added to freshly prepared LDA in THF (5 mL) at −78 ºC. After 30 min, freshly distilled allylbromide (5.0 equiv) was added dropwise. The reaction mixture was stirred at −78 ºC for 5 h and then allowed to slowly warm to room temperature overnight. Ammonium chloride (5 mL, sat. aqueous) was added to quench the reaction, followed by extraction with Et₂O (3 x 10 mL). The combined organic fractions were washed with brine and dried over anhydrous Na₂SO₄. After filtration and evaporation of the volatiles, the crude residue was purified by column chromatography (Hexane:EtOAc = 10:1) to afford the product, 2a (17%, 31.5 mg).
Selected NMR Spectra:

\(^1\)H NMR Spectra of 1a (500 MHz, CDCl\(_3\)):

\[^{13}\)C NMR Spectra of 1a (126 MHz, CDCl\(_3\)):
$^1$H NMR Spectra of 1b (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectra of 1b (126 MHz, CDCl$_3$):
$^1$H NMR Spectra of $1c$ (126 MHz, CDCl$_3$):

![H NMR Spectra of 1c](Image)

$^{13}$C NMR Spectra of $1c$ (126 MHz, CDCl$_3$):

![C NMR Spectra of 1c](Image)
\(^1\)H NMR Spectra of 1d (126 MHz, CDCl\(_3\)):

\[^{13}\]C NMR Spectra of 1d (126 MHz, CDCl\(_3\)):
**1H NMR Spectra of 1e (126 MHz, CDCl₃):**

![1H NMR Spectrum](image)

**13C NMR Spectra of 1e (126 MHz, CDCl₃):**

![13C NMR Spectrum](image)
$^{1}$H NMR Spectra of 1f (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectra of 1f (126 MHz, CDCl$_3$):
$^{1}$H NMR Spectra of 1g (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectra of 1g (126 MHz, CDCl$_3$):
\(^1\)H NMR Spectra of 1h (500 MHz, CDCl\(_3\)):

\[^{13}\text{C}\] NMR Spectra of 1g (126 MHz, CDCl\(_3\)):
$^1$H NMR Spectra of 1i (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectra of 1i (126 MHz, CDCl$_3$):
$^1$H NMR Spectra of 1j (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectra of 1j (126 MHz, CDCl$_3$):
$^1$H NMR Spectra of 1k (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectra of 1k (126 MHz, CDCl$_3$):
$^{1}$H NMR Spectra of II (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectra of II (126 MHz, CDCl$_3$):
$^1$H NMR Spectra of 1m (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectra of 1m (126 MHz, CDCl$_3$):
$^{1}H$ NMR Spectra of In (500 MHz, CDCl$_3$):

$^{13}C$ NMR Spectra of In (126 MHz, CDCl$_3$):
^1H NMR Spectra of 1o (500 MHz, CDCl₃):

\[
\text{H} \quad \text{NMR} \quad \text{Spectra} \quad \text{of} \quad \text{1o} \quad (500 \text{ MHz}, \text{CDCl}_3):
\]

\[
\begin{align*}
\text{13C NMR Spectra of 1o (126 MHz, CDCl₃):}
\end{align*}
\]
$^1$H NMR Spectra of 8 (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectra of 8 (126 MHz, CDCl$_3$):
\(^1\)H NMR Spectra of 11 (500 MHz, CDCl\(_3\)):

\(13\)C NMR Spectra of 11 (126 MHz, CDCl\(_3\)):
$^{1}$H NMR Spectra of 14 (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectra of 14 (126 MHz, CDCl$_3$):
^1^H NMR Spectra of 6 (500 MHz, CDCl₃):

\[ \text{PROTON CDCl₃ (500 MHz) [Sample] kio31 14} \]

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$^1$H NMR Spectra of 2b (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectra of 2b (126 MHz, CDCl$_3$):
$^1$H NMR Spectra of 2c (500 MHz, CDCl$_3$):

![H NMR Spectrum of 2c](image)

$^{13}$C NMR Spectra of 2c (126 MHz, CDCl$_3$):

![C NMR Spectrum of 2c](image)
$^1$H NMR Spectra of 2d (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectra of 2d (126 MHz, CDCl$_3$):

$^1$H NMR Spectra of 2e (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectra of 2e (126 MHz, CDCl$_3$):
$^1$H NMR Spectra of 2f (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectra of 2f (126 MHz, CDCl$_3$):
$^1$H NMR Spectra of 2g (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectra of 2g (126 MHz, CDCl$_3$):
$^1$H NMR Spectra of 2h (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectra of 2h (126 MHz, CDCl$_3$):
$^1$H NMR Spectra of 2h (500 MHz, CDCl$_3$):

![H NMR Spectrum](image)

$^{13}$C NMR Spectra of 2i (126 MHz, CDCl$_3$):

![C NMR Spectrum](image)
$^{1}$H NMR Spectra of 2j (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectra of 2j (126 MHz, CDCl$_3$):
$^1$H NMR Spectra of 2k (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectra of 2k (126 MHz, CDCl$_3$):
1H NMR Spectra of 2l (500 MHz, CDCl₃):

13C NMR Spectra of 2l (126 MHz, CDCl₃):
$^{1}H$ NMR Spectra of 2m (500 MHz, CDCl$_3$): 

$^{13}C$ NMR Spectra of 2m (126 MHz, CDCl$_3$):
$^1$H NMR Spectra of 2n (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectra of 2n (126 MHz, CDCl$_3$):
$^{1}$H NMR Spectra of 2o (500 MHz, CDCl$_3$):

$^{13}$C NMR Spectra of 2o (126 MHz, CDCl$_3$):
\(^1\)H NMR Spectra of 9 and 10 (500 MHz, CDCl\(_3\)):

\(^{13}\)C NMR Spectra of 9 and 10 (126 MHz, CDCl\(_3\)):
Structure Determination of the dihydrocoumarin by X-ray analysis for \( 2\alpha \):

The relative stereochemistry was determined by the X-ray diffraction. The dihydrocoumarin was recrystallized from CH\(_2\)Cl\(_2\) and hexane.

X-ray crystal structure of 3-allyl-6-chlorodihydrocoumarin:

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 = 1.084 for 136 variables refined to R1 = 0.0267 for 1613 reflections with I>2\(\sigma(I)\). A SADABS-2012/1 multi-scan absorption correction was performed. Further information can be found in the CIF file. This crystal structure was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 969294.