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**General information:** $^1$H NMR and $^{13}$C NMR spectra were recorded on an Agilent 400 MHz or 600 MHz DD2 spectrometer at ambient temperature. Chemical shifts ($\delta$) are reported in ppm, and coupling constants ($J$) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. NMR yield was determined by $^1$H NMR using mesitylene as an internal standard before working up the reaction.

**Materials:** All reagents were obtained from commercial suppliers, unless noted otherwise. MeCN, DCM and Toluene were distilled under reduced pressure with CaH$_2$. 1,4-Dioxane and THF were distilled with sodium and benzophenone before used.

\[ \text{RS} + \text{Fe} \rightarrow \text{Fe} \rightarrow \text{O} \]

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<th>Base</th>
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<th>Yield (%)b</th>
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</tr>
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*Reaction conditions (unless otherwise specified): 1a (0.3 mmol, 1.0 equiv), O₂ (1 atm), [Fe] (0.03 mmol, 0.1 equiv), disulfide (0.03 mmol, 0.1 equiv), dioxane (0.5 mL), 80 °C, 15 h. bDetermined by ¹H NMR using mesitylene as an internal standard. The isolated yield is shown in parentheses.
Optimization of the Iron-Catalyzed Oxygenation of Isochroman.\textsuperscript{a}

\[
1b + \text{O}_2 \xrightarrow{\text{Fe} \text{RS}^-} 1bb
\]

<table>
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<th>Entry</th>
<th>[Fe]</th>
<th>[Additive 10 mol%]</th>
<th>Temperature</th>
<th>Solvent (0.5 mL)</th>
<th>Yield (%)\textsuperscript{b}</th>
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<tr>
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\textsuperscript{a}Reaction conditions (unless otherwise specified): 1b (0.3 mmol, 1.0 equiv), O\textsubscript{2} (1 atm), [Fe] (0.03 mmol, 0.1 equiv), additive (0.03 mmol, 0.1 equiv), 1,4-dioxane (0.5 mL), 80 °C, 15 h. \textsuperscript{b}Determined by \textsuperscript{1}H NMR using mesitylene as an internal standard. The isolated yield is shown in parentheses.
Synthesis and Characterization data of amine derivatives

**General procedure 1:**

\[
\text{NH}_2 + \text{R}^+ \text{I} \text{CuI (6.5 mol\%)} \quad \text{K}_3\text{PO}_4 (1.3 \text{ equiv})
\]

\[
\text{ethylene glycol (1.3 equiv)} \quad \text{2-Propanol, } 90^\circ\text{C, 24 h}
\]

To a 25 ml of Schlenk tube was added CuI (1.0 mmol) and K$_3$PO$_4$ (20.0 mmol), then 2-propanol (10 mL), ethylene glycol (20.0 mmol), 1,2,3,4-tetrahydroisoquinoline (15.0 mmol), iodobenzene (15.0 mmol) were added under argon atmosphere. The reaction mixture was heated to 90 °C and allowed to react for 24 h. The reaction was quenched with water, and the mixture was extracted with Et$_2$O for three times. The combined organic phase was washed with brine, dried over Na$_2$SO$_4$, filtered and concentrated to give a crude product, and the residue was purified with silica gel chromatography to give product.

**General procedure 2:**

\[
\text{NH}_2 + \text{R}^+ \text{O} \text{TEA (2.5 equiv)} \quad \text{DMAP (0.1 equiv)}
\]

\[
\text{DCM, rt}
\]

To a solution of DMAP (0.5 mmol) in DCM (20 mL) at room temperature under argon atmosphere, was successively added 1,2,3,4-tetrahydroisoquinoline (5.0 mmol), triethylamine (12.5 mmol) and corresponding acyl chloride (5.0 mmol). After stirring for 10 h at room temperature, the reaction was quenched with water, and the mixture was extracted with DCM for three times. The combined organic phase was washed with brine, dried over Na$_2$SO$_4$, filtered and concentrated to give a crude product, and the residue was purified with silica gel chromatography to give product.

**General procedure 3:**

\[
\text{NH}_2 + \text{R}^+ \text{HO} \text{HATU (1.5 equiv)} \quad \text{DIPEA (3 equiv)}
\]

\[
\text{DCM, rt}
\]

To a solution of condensation agent HATU (7.5 mmol), carboxylic acid (5.0 mmol) in DCM (20 mL) at room temperature under argon atmosphere, was successively added
N,N-diisopropylethylamine (15.0 mmol), 1,2,3,4-tetrahydroisoquinoline (5.0 mmol), triethylamine (12.5 mmol) and corresponding carboxylic acid (5.0 mmol). After stirring for 10 h at room temperature, the reaction was quenched with water, and the mixture was extracted with DCM for three times. The combined organic phase was washed with brine, dried over Na₂SO₄, filtered and concentrated to give a crude product, and the residue was purified with silica gel chromatography to give product.

2-Phenyl-1,2,3,4-tetrahydroisoquinoline (1a) The title compound was prepared according to general procedure 1. ¹H NMR (400 MHz, CDCl₃) δ 7.34 (t, J = 8.4 Hz, 2 H), 7.24-7.18 (m, 4 H), 7.03 (d, J = 8.4 Hz, 2 H), 6.88 (t, J = 7.6 Hz, 1H), 4.46 (s, 2 H), 3.61 (t, J = 6.0 Hz, 2 H), 3.03 (t, J = 6.0 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 150.5, 134.9, 134.5, 129.2, 128.5, 126.5, 126.3, 126.0, 118.6, 115.1, 50.7, 46.5, 29.1.

2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (2a) The title compound was prepared according to general procedure 1. ¹H NMR (400 MHz, CDCl₃) δ 7.20-7.13 (m, 4 H), 7.00 (d, J = 8.8 Hz, 2 H), 6.88 (d, J = 8.8 Hz, 2 H), 4.31 (s, 2 H), 3.79 (s, 3 H), 3.46 (t, J = 6.0 Hz, 2 H), 3.00 (t, J = 6.0 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 153.4, 145.3, 134.5, 134.5, 128.7, 126.5, 126.2, 125.9, 118.0, 114.5, 55.6, 52.6, 48.4, 29.1.

2-(4-Chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (3a) The title compound was prepared according to general procedure 1. ¹H NMR (400 MHz, CDCl₃) δ 7.25-7.13 (m, 6 H), 6.87 (d, J = 8.8 Hz, 2 H), 4.37 (s, 2 H), 3.52 (t, J = 6.0 Hz, 2 H), 2.97 (t, J = 6.0 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 149.0, 134.7, 134.1, 129.0, 128.5, 126.5, 126.1, 123.3, 116.1, 50.6, 46.5, 28.9.
2-(4-Bromophenyl)-1,2,3,4-tetrahydroisoquinoline (4a) The title compound was prepared according to general procedure 1. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 (d, $J = 7.2$ Hz, 2 H), 7.21-7.14 (m, 4 H), 6.83 (d, $J = 7.2$ Hz, 2 H), 4.38 (s, 2 H), 3.53 (t, $J = 5.6$ Hz, 2 H), 2.98 (t, $J = 5.6$ Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.4, 134.7, 134.0, 131.9, 128.5, 126.5, 126.1, 116.4, 110.4, 50.4, 46.3, 28.9.

2-(4-Nitrophenyl)-1,2,3,4-tetrahydroisoquinoline (5a) The title compound was prepared according to general procedure 1. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 (d, $J = 8.0$ Hz, 2 H), 7.25-7.20 (m, 4 H), 6.18 (d, $J = 8.0$ Hz, 2 H), 4.56 (s, 2 H), 3.69 (t, $J = 5.6$ Hz, 2 H), 3.02 (t, $J = 5.6$ Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 153.7, 137.4, 134.8, 133.0, 128.0, 127.1, 126.6, 126.4, 126.1, 111.1, 48.7, 44.7, 28.9.

4-(3,4-Dihydroisoquinolin-2(H)-yl)benzonitrile (6a) The title compound was prepared according to general procedure 1. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 (d, $J = 8.8$ Hz, 2 H), 7.25-7.17 (m, 4 H), 6.85 (d, $J = 8.8$ Hz, 2 H), 4.49 (s, 2 H), 3.62 (t, $J = 6.0$ Hz, 2 H), 2.99 (t, $J = 6.0$ Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.1, 134.8, 133.4, 133.3, 128.1, 126.8, 126.4, 126.4, 120.3, 112.5, 98.5, 48.7, 44.5, 28.8.

2-Acetyl-1,2,3,4-tetrahydroisoquinolin-6-yl acetate (7a) The title compound was prepared according to general procedure 2. $^1$H NMR (400 MHz, CDCl$_3$, rotomers seen) $\delta$ 7.11 (dd, $J = 16.0$, 8.0 Hz, 1 H), 6.92-6.87 (m, 2 H), 4.69 (s, 1.2 H), 4.58 (s, 0.8 H), 3.79 (t, $J = 5.6$ Hz, 0.8 H), 3.65 (t, $J = 5.6$ Hz, 1.2 H), 2.88 (t, $J = 5.6$ Hz, 1.2 H), 2.82
(t, $J = 5.6$ Hz, 0.8 H), 2.27 (s, 3.0 H), 2.15 (s, 3.0 H). $^{13}$C NMR (100 MHz, CDCl$_3$, rotomers seen) $\delta$ 169.6, 169.5, 169.3, 149.2, 149.0, 136.5, 135.3, 131.1, 130.1, 127.7, 127.0, 121.8, 121.2, 119.9, 119.7, 47.7, 43.7, 43.6, 39.1, 29.4, 28.5, 21.8, 21.6, 21.0.

**Benzyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (8a)** The title compound was prepared according to general procedure 2. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43-7.32 (m, 5 H), 7.20-7.10 (m, 4 H), 5.21 (s, 2 H), 4.67 (s, 2 H), 3.74 (s (br), 2 H), 2.87 (s (br), 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.4, 136.7, 134.5, 134.4, 133.3, 132.9, 128.7, 128.4, 127.9, 127.9, 126.4, 126.2, 67.1, 45.7, 41.5, 41.3, 28.9, 28.7.

**Benzyl 7-nitro-3,4-dihydroisoquinoline-2(1H)-carboxylate (9a)** The title compound was prepared according to general procedure 2. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.02-7.97 (m, 2 H), 7.38-7.25 (m, 6 H), 5.18 (s, 2 H), 4.73 (s, 2 H), 3.76 (t, $J = 6.0$ Hz, 2 H), 2.94 (s (br), 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.2, 146.5, 142.1, 136.3, 134.6, 129.8, 128.5, 128.2, 128.0, 121.5, 67.5, 45.5, 40.7, 29.0.

**Allyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (10a)** The title compound was prepared according to general procedure 2. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.21-7.11 (m, 4 H), 6.03-6.93 (m, 1 H), 5.33 (d, $J = 17.2$ Hz, 1 H), 5.23 (d, $J = 10.4$ Hz, 1 H), 4.65 (s, 4 H), 3.72 (t, $J = 6.0$ Hz, 2 H), 2.86 (t, $J = 6.0$ Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.2, 134.5, 133.4, 133.0, 128.7, 128.5, 126.4, 126.2, 117.4, 66.0, 45.6, 41.5, 28.9.

**tert-Butyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (11a)** The title compound was prepared according to general procedure 2. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.20-7.10 (m, 4 H), 4.58 (s, 2 H), 3.65 (t, $J = 5.6$ Hz, 2 H), 2.84 (t, $J = 5.6$ Hz, 2 H), 1.50 (s, 9 H).
The title compound was prepared according to general procedure 3. $^1$H NMR (400 MHz, CDCl$_3$, rotomers seen) $\delta$ 7.85 (d, $J = 7.6$ Hz, 2.0 H), 7.50 (t, $J = 7.2$ Hz, 1.0 H), 7.43 (t, $J = 7.2$ Hz, 3.0 H), 7.25-7.11 (m, 4.0 H), 4.77 (s, 1.1 H), 4.62 (s, 0.9 H), 4.35-4.32 (m, 2.0 H), 3.88 (t, $J = 6.0$ Hz, 0.9 H), 3.68 (t, $J = 6.0$ Hz, 1.1 H), 2.94 (t, $J = 6.0$ Hz, 1.1 H), 2.90 (t, $J = 6.0$ Hz, 0.9 H). $^{13}$C NMR (100 MHz, CDCl$_3$, rotomers seen) $\delta$ 167.1, 166.9, 134.5, 133.8, 133.7, 132.6, 131.5, 131.5, 128.8, 128.5, 128.3, 127.2, 127.0, 126.8, 126.7, 126.6, 126.5, 126.1, 45.9, 44.4, 42.1, 41.9, 40.1, 29.0, 28.2.

The title compound was prepared according to general procedure 3. $^1$H NMR (400 MHz, CDCl$_3$, rotomers seen) $\delta$ 7.22-7.08 (m, 4.0 H), 5.33 (t, $J = 9.2$ Hz, 1.0 H), 4.79-4.71 (m, 3.0 H), 3.97-3.79 (m, 1.0 H), 3.74-3.66 (m, 1.0 H), 3.01-2.90 (m, 1.0 H), 2.86 (t, $J = 6.0$ Hz, 1.0 H), 1.77-1.69 (m, 1.0 H), 1.59-1.47 (m, 1.0 H), 1.42 (s, 9.0 H), 1.40-1.31 (m, 1.0 H), 1.02 (d, $J = 3.6$ Hz, 1.8 H), 1.00 (d, $J = 3.6$ Hz, 1.2 H), 0.93 (d, $J = 6.8$ Hz, 1.8 H), 0.89 (d, $J = 6.8$ Hz, 1.2 H). $^{13}$C NMR (100 MHz, CDCl$_3$, rotomers seen) $\delta$ 172.0, 171.8, 155.6, 134.8, 133.9, 133.0, 132.1, 128.8, 128.3, 127.0, 126.6, 126.4, 126.1, 79.5, 49.0, 48.8, 47.0, 44.5, 43.0, 43.0, 42.9, 40.3, 29.4, 28.3, 24.6, 23.4, 21.9, 21.8.

The title compound was prepared according to general procedure 3. $^1$H NMR
(400 MHz, CDCl$_3$, rotomers seen) $\delta$ 7.71-7.64 (m, 3 H), 7.39 (d, $J = 8.4$ Hz, 1 H), 7.15-7.09 (m, 5 H), 6.98 (d, $J = 7.6$ Hz, 0.6 H), 6.86 (d, $J = 7.6$ Hz, 0.4 H), 4.79 (dd, $J = 29.2$, 17.2 Hz, 1.2 H), 4.69 (d, $J = 16.0$ Hz, 0.4 H), 4.35 (d, $J = 16.0$ Hz, 0.4 H), 4.13-4.01 (m, 1.4 H), 3.90 (s, 3 H), 3.73-3.55 (m, 1.6 H), 2.89-2.77 (m, 0.8 H), 2.68-2.61 (m, 0.6 H), 2.38-2.31 (m, 0.6 H), 1.55 (d, $J = 6.8$ Hz, 3.0 H). $^{13}$C NMR (100 MHz, CDCl$_3$, rotomers seen) $\delta$ 172.7, 172.6, 157.5, 137.1, 136.8, 135.0, 134.1, 133.4, 132.6, 129.1, 129.0, 128.6, 128.2, 127.5, 126.7, 126.6, 126.4, 126.3, 126.1, 125.9, 125.5, 119.0, 118.9, 105.6, 55.3, 47.3, 44.6, 43.6, 43.0, 40.2, 29.1, 28.5, 20.8, 20.7.

(S)-1-(3,4-Dihydroisoquinolin-2(1H)-yl)-2-(4-isobutylphenyl)propan-1-one (16a)
The title compound was prepared according to general procedure 3. $^1$H NMR (400 MHz, CDCl$_3$, rotomers seen) $\delta$ 7.18-7.13 (m, 7 H), 7.00 (d, $J = 7.6$ Hz, 0.6 H), 6.87 (d, $J = 7.6$ Hz, 0.4 H), 4.86 (d, $J = 17.2$ Hz, 0.6 H), 4.68 (d, $J = 17.2$ Hz, 0.6 H), 4.62 (d, $J = 16.0$ Hz, 0.4 H), 4.37 (d, $J = 16.0$ Hz, 0.4 H), 3.98-3.90 (m, 1.4 H), 3.76-3.70 (m, 0.4 H), 3.63-3.53 (m, 1.4 H), 2.85-2.80 (m, 0.6 H), 2.66-2.60 (m, 0.6 H), 2.45-2.40 (m, 2.0 H), 2.35-2.27 (m, 0.6 H), 1.89-1.75 (m, 1.0 H), 1.47 (d, $J = 6.0$ Hz, 3.0 H), 0.88 (d, $J = 6.4$ Hz, 3.0 H). $^{13}$C NMR (100 MHz, CDCl$_3$, rotomers seen) $\delta$ 172.7, 140.1, 139.2, 138.9, 135.0, 134.1, 133.5, 132.7, 129.6, 129.5, 128.6, 128.2, 126.9, 126.8, 126.6, 126.3, 126.1, 125.8, 47.2, 44.9, 44.6, 43.3, 43.0, 40.2, 30.1, 30.1, 29.0, 28.4, 22.3, 20.7.

Synthesis and Characterization data of isochroman derivatives
Isochroman derivatives were synthesized according to the methods reported in the literature.1-6

4-Methylisochromane (2b)$^1$ $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.26-7.16 (m, 3 H), 6.99 (d, $J = 7.6$ Hz, 1 H), 4.80 (dd, $J = 20.8$, 15.2 Hz, 2 H), 3.99 (dd, $J = 11.2$, 4.4 Hz, 1 H),
3.69 (dd, $J = 11.2$, 5.6 Hz, 1 H), 2.99-2.92 (m, 1 H), 1.33 (d, $J = 6.8$ Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 138.6, 134.2, 127.7, 126.5, 125.8, 124.1, 71.3, 68.3, 31.8, 19.2.

**3-Methylisochromane (3b)** $^1$H NMR (400 MHz, CDCl$_3$) δ 7.19-7.16 (m, 2 H), 7.13-7.09 (m, 1 H), 7.01 (t, $J = 4.4$ Hz, 2 H), 4.89-4.81 (m, 2 H), 3.88-3.79 (m, 1 H), 2.73 (d, $J = 6.8$ Hz, 2 H), 1.38 (d, $J = 6.4$ Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 134.6, 133.4, 128.6, 126.3, 125.9, 124.1, 70.9, 68.1, 35.7, 21.6.

**7-Methylisochromane (4b)** $^1$H NMR (400 MHz, CDCl$_3$) δ 7.05 (d, $J = 8.0$ Hz, 1 H), 7.02 (d, $J = 8.0$ Hz, 1 H), 6.83 (s, 1 H), 4.78 (s, 2 H), 4.00 (t, $J = 6.0$ Hz, 2 H), 2.85 (t, $J = 6.0$ Hz, 2 H), 2.34 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 135.4, 134.6, 130.0, 128.7, 127.1, 124.8, 67.9, 65.4, 27.9, 21.0.

**7-(tert-Butyl)isochromane (5b)** $^2$H NMR (400 MHz, CDCl$_3$) δ 7.23 (d, $J = 8.0$ Hz, 1 H), 7.09 (d, $J = 8.0$ Hz, 1 H), 7.02 (s, 1 H), 4.80 (s, 2 H), 3.99 (t, $J = 5.6$ Hz, 2 H), 2.84 (t, $J = 5.6$ Hz, 2 H), 1.33 (s, 9 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 148.9, 134.4, 130.2, 128.5, 123.5, 121.0, 68.2, 65.5, 34.4, 31.3, 27.9.

**7-Methoxyisochromane (6b)** $^1$H NMR (400 MHz, CDCl$_3$) δ 7.04 (d, $J = 8.0$ Hz, 1 H), 6.75 (d, $J = 8.0$ Hz, 1 H), 6.53 (s, 1 H), 4.75 (s, 2 H), 3.96 (t, $J = 5.6$ Hz, 2 H), 3.78 (s, 3 H), 2.80 (t, $J = 5.6$ Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.8, 135.8, 129.7, 125.1, 112.6, 109.0, 68.0, 65.6, 55.2, 27.5.
**6.7-Dimethoxyisochromane (7b)** \(^1\) H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.61 (s, 1 H), 6.47 (s, 1 H), 4.70 (s, 2 H), 3.95 (t, \(J = 5.6\) Hz, 2 H), 3.85 (s, 3 H), 3.83 (s, 3 H), 2.77 (t, \(J = 5.6\) Hz, 2 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 147.6, 147.5, 126.6, 125.0, 111.7, 107.3, 67.6, 65.4, 55.9, 27.8.

To a 25 mL two neck round bottom flask was added 8 (200 mg, 1.3 mmol), TBSCI (292 mg, 1.95 mmol), imidazole (176 mg, 2.6 mmol) and 6 mL CH\(_2\)Cl\(_2\) at 0 °C under N\(_2\), the mixture was stirred for 3 h at room temperature, then the mixture was poured into water and extracted with CH\(_2\)Cl\(_2\), the combined organic phases were dried over Na\(_2\)SO\(_4\), concentrated in vacuo, and the residue was purified by silica gel chromatography to give 8b with a quantitative yield.

**tert-Butyl(isochroman-7-yloxy)dimethylsilane (8b)** \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.97 (d, \(J = 8.0\) Hz, 1 H), 6.66 (d, \(J = 8.0\) Hz, 1 H), 6.47 (s, 1 H), 4.71 (s, 2 H), 3.95 (t, \(J = 5.6\) Hz, 2 H), 2.78 (t, \(J = 5.6\) Hz, 2 H), 0.98 (s, 9 H), 0.18 (s, 6 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 153.6, 135.8, 129.7, 125.7, 118.4, 115.5, 67.9, 65.6, 27.6, 25.7, 18.2, -4.4.

A mixture of 4-(2-hydroxyethyl)phenyl acetate (known compound)\(^1\) (2.5 g, 13.9 mmol), DIPEA (4.6 mL, 27.8 mmol), MOMCl (1.6 mL, 20.9 mmol) in dry 30 mL CH\(_2\)Cl\(_2\) was allowed react for 10 h under N\(_2\) at room temperature, then the mixture was poured into water and extracted with CH\(_2\)Cl\(_2\), the combined organic phases were
washed with 30 mL 1 N HCl, dried over Na$_2$SO$_4$, concentrated in vacuo, the crude product can move forward without purification.

b) The residue was dissolved in 30 mL MeCN, then TMSOTf (13.9 mmol, 1.0 equiv) was added at 0 °C and the mixture was stirred at room temperature for 16 h, then the reaction was quenched by saturated NaHCO$_3$ solution and extracted with ethyl acetate, dried over Na$_2$SO$_4$, concentrated in vacuo, the reaction crude was purified with silica gel chromatography to provide the product 9b (1.3 g, 50% yield) and byproduct 8 (416 mg, 20% yield).

Isocroman-7-yl acetate (9b)\textsuperscript{1} \textsuperscript{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 7.11 (d, $J$ = 8.0 Hz, 1 H), 6.87 (d, $J$ = 8.0 Hz, 1 H), 6.71 (s, 1 H), 4.74 (s, 2 H), 3.94 (t, $J$ = 5.2 Hz, 2 H), 2.82 (t, $J$ = 5.2 Hz, 2 H), 2.27 (s, 3 H). \textsuperscript{13}C NMR (100 MHz, CDCl$_3$) $\delta$ 169.6, 148.5, 136.0, 130.7, 129.8, 119.6, 117.2, 67.6, 65.2, 27.7, 21.0.

Isocroman-7-ol (8) \textsuperscript{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 6.96 (d, $J$ = 8.0 Hz, 1 H), 6.66 (d, $J$ = 8.0 Hz, 1 H), 6.43 (s, 1 H), 6.27 (s, 1 H), 4.71 (s, 2 H), 3.98 (t, $J$ = 5.6 Hz, 2 H), 2.78 (t, $J$ = 5.6 Hz, 2 H). \textsuperscript{13}C NMR (100 MHz, CDCl$_3$) $\delta$ 154.0, 135.5, 130.0, 124.7, 114.0, 110.7, 67.8, 65.7, 27.4.

2-(Isocroman-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10b) This compound was synthesized via cross-coupling from 14b according to the literature.\textsuperscript{4} \textsuperscript{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (d, $J$ = 7.6 Hz, 1 H), 7.44 (s, 1 H), 7.12 (d, $J$ = 7.6 Hz, 1 H), 4.78 (s, 2 H), 3.96 (t, $J$ = 5.6 Hz, 2 H), 2.86 (t, $J$ = 5.6 Hz, 2 H), 1.33 (s, 12 H). \textsuperscript{13}C NMR (100 MHz, CDCl$_3$) $\delta$ 136.6, 134.3, 132.6, 130.9, 129.3, 83.7, 67.9, 65.2, 28.6, 24.8. HRMS: Calculated for (M+Na)$^+$:283.1478; Found: 283.1466.

7-Allylisochromane (11b) This compound was synthesized via cross-coupling from 14b according to the literature.\textsuperscript{5} \textsuperscript{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 7.06 (d, $J$ = 7.6 Hz, 1
H), 7.00 (d, \( J = 7.6 \) Hz, 1 H), 6.82 (s, 1 H), 6.00-5.90 (m, 1 H), 5.10-5.05 (m, 2 H), 4.76 (s, 2 H), 3.97 (t, \( J = 5.6 \) Hz, 2 H), 3.34 (d, \( J = 6.8 \) Hz, 2 H), 2.83 (t, \( J = 5.6 \) Hz, 2 H). 
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 137.8, 137.4, 134.9, 130.9, 128.9, 126.7, 124.4, 115.8, 68.0, 65.5, 39.9, 28.0.

7-Fluoroisochromane (12b): \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.06 (t, \( J = 7.2 \) Hz, 1 H), 6.85 (t, \( J = 8.4 \) Hz, 1 H), 6.67 (d, \( J = 9.2 \) Hz, 1 H), 4.72 (s, 2 H), 3.95 (t, \( J = 6.0 \) Hz, 2 H), 2.80 (t, \( J = 6.0 \) Hz, 2 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 161.0 (d, \( J = 243.0 \) Hz), 136.6, 131.6, 131.5, 130.2, 126.5, 124.4, 67.5, 65.2, 27.7.

7-Chloroisochromane (13b): \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.11 (d, \( J = 8.0 \) Hz, 1 H), 7.03 (t, \( J = 8.0 \) Hz, 1 H), 6.96 (s, 1 H), 4.71 (s, 2 H), 3.94 (t, \( J = 6.0 \) Hz, 2 H), 2.80 (t, \( J = 6.0 \) Hz, 2 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 136.6, 131.6, 131.5, 130.2, 126.5, 124.4, 67.5, 65.2, 27.7.

7-Bromoisochromane (14b): \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.26 (d, \( J = 8.0 \) Hz, 1 H), 7.12 (s, 1 H), 6.98 (d, \( J = 8.0 \) Hz, 1 H), 4.71 (s, 2 H), 3.94 (t, \( J = 5.6 \) Hz, 2 H), 2.78 (t, \( J = 5.6 \) Hz, 2 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 137.0, 132.1, 130.5, 129.4, 127.3, 119.5, 67.4, 65.1, 27.8.

1,4-Dihydro-2\(H\)-benzo/[f]isochromene (15b): \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.93 (d, \( J = 8.0 \) Hz, 1 H), 7.85 (d, \( J = 8.0 \) Hz, 1 H), 7.70 (d, \( J = 8.4 \) Hz, 1 H), 7.56 (t, \( J = 8.0 \) Hz, 1 H), 7.50 (t, \( J = 8.0 \) Hz, 1 H), 7.11 (d, \( J = 8.4 \) Hz, 1 H), 4.93 (s, 2 H), 4.16 (t, \( J = 5.6 \) Hz, 1 H), 3.90 (t, \( J = 5.6 \) Hz, 2 H), 3.37 (s, 2 H).
Hz, 2 H), 3.18 (t, \( J = 5.6 \) Hz, 2 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 132.2, 132.0, 132.0, 128.5, 128.2, 126.3, 126.2, 125.3, 122.8, 122.4, 68.2, 65.2, 25.1.

\[
\text{\begin{tikzpicture}
  \node[draw] at (0,0) {\text{S} \text{O}};
\end{tikzpicture}}
\]

4,7-Dihydro-5\(\text{H}\)-thieno[2,3-c]pyran (16b) \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.15 (d, \( J = 5.2 \) Hz, 1 H), 6.83 (d, \( J = 5.2 \) Hz, 1 H), 4.83 (s, 2 H), 3.96 (t, \( J = 5.6 \) Hz, 2 H), 2.76 (t, \( J = 5.6 \) Hz, 2 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 132.7, 126.9, 122.4, 65.6, 65.0, 26.1.

\[
\text{\begin{tikzpicture}
  \node[draw] at (0,0) {\text{O} \text{O}};
\end{tikzpicture}}
\]

7-Benzylisochromane (22b) \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.32-7.27 (m, 2 H), 7.21-7.18 (m, 3 H), 7.07-6.99 (m, 2 H), 6.81 (s, 1 H), 4.73 (s, 2 H), 3.99-3.93 (m, 4 H), 2.83 (t, \( J = 5.6 \) Hz, 2 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 141.1, 138.9, 134.9, 130.9, 129.0, 128.8, 128.4, 127.0, 126.1, 124.7, 68.0, 65.4, 41.6, 28.0. HRMS: Calculated for (M+H)\(^+\):225.1273; Found: 225.1268.

**General procedure for the oxygenation reaction**

To a 25 ml of Schlenk tube was added Fe\(1\) or Fe\(5\) (0.03 mmol, 0.1 equiv) and phenyl disulfide (6.5 mg, 0.03 mmol, 0.1 equiv) under air. The reaction tube was degassed with O\(_2\) (1 atm, 3 times), then substrates (0.30 mmol, 1.0 equiv) and freshly distilled 1,4-dioxane (0.5 mL) were added. The reaction mixture was heated to 80 °C and allowed to react for 15 h. The mixture was concentrated, and the residue was purified with silica gel chromatography to give product.
Characterization data of products

2-Phenyl-3,4-dihydroisoquinolin-1(2H)-one (1aa) The product (44 mg, 66% yield) as a white solid was purified with silica gel chromatography. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 (d, $J = 7.6$ Hz, 2 H), 7.46 (td, $J = 7.6$, 1.6 Hz, 1 H), 7.43-7.35 (m, 5 H), 7.27-7.23 (m, 2 H), 3.99 (t, $J = 6.4$ Hz, 2 H), 3.14 (t, $J = 6.4$ Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.2, 143.1, 138.3, 132.0, 129.7, 128.9, 128.7, 127.2, 126.9, 126.2, 125.3, 49.4, 28.6. HRMS: Calculated for (M+H)$^+$: 224.1069; Found: 224.1073.

2-(4-Methoxyphenyl)-3,4-dihydroisoquinolin-1(2H)-one (2aa) The product (37 mg, 50% yield) as a white solid was purified with silica gel chromatography. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 (d, $J = 7.6$ Hz, 1 H), 7.46 (t, $J = 7.6$ Hz, 1 H), 7.37 (t, $J = 7.6$ Hz, 1 H), 7.30 (d, $J = 8.8$ Hz, 2 H), 7.24 (d, $J = 7.6$ Hz, 1 H), 6.94 (d, $J = 8.8$ Hz, 2 H), 3.95 (t, $J = 6.4$ Hz, 2 H), 3.83 (s, 3 H), 3.14 (t, $J = 6.4$ Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.4, 157.8, 138.3, 136.1, 131.9, 129.8, 128.7, 127.1, 126.9, 126.7, 114.2, 55.5, 49.7, 28.7. HRMS: Calculated for (M+H)$^+$: 254.1175; Found: 254.1178.

2-(4-Chlorophenyl)-3,4-dihydroisoquinolin-1(2H)-one (3aa) The product (49 mg, 63% yield) as a white solid was purified with silica gel chromatography. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 (d, $J = 7.6$ Hz, 1 H), 7.46 (t, $J = 7.6$ Hz, 1 H), 7.37 (t, $J = 7.6$ Hz, 1 H), 7.30 (d, $J = 8.8$ Hz, 2 H), 7.24 (d, $J = 7.6$ Hz, 1 H), 6.94 (d, $J = 8.8$ Hz, 2 H), 3.95 (t, $J = 6.4$ Hz, 2 H), 3.83 (s, 3 H), 3.14 (t, $J = 6.4$ Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.4, 157.8, 138.3, 136.1, 131.9, 129.8, 128.7, 127.1, 126.9, 126.7, 114.2, 55.5, 49.7, 28.7. HRMS: Calculated for (M+H)$^+$: 254.1175; Found: 254.1178.
MHz, CDCl$_3$) $\delta$ 8.06 (d, $J = 8.0$ Hz, 1 H), 7.39 (t, $J = 7.6$ Hz, 1 H), 7.31-7.23 (m, 5 H), 7.16 (d, $J = 7.6$ Hz, 1 H), 3.88 (t, $J = 6.4$ Hz, 2 H), 3.05 (t, $J = 6.4$ Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.1, 141.5, 138.2, 132.2, 131.4, 129.3, 128.9, 128.7, 127.2, 127.0, 126.5, 49.2, 28.5. HRMS: Calculated for (M+Na)$^+$: 280.0499; Found: 280.0502.

2-(4-Bromophenyl)-3,4-dihydroisoquinolin-1(2H)-one (4aa) The product (56 mg, 62% yield) as a white solid was purified with silica gel chromatography. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 (d, $J = 7.6$ Hz, 1 H), 7.53 (d, $J = 8.8$ Hz, 2 H), 7.49 (t, $J = 7.6$ Hz, 1 H), 7.39 (t, $J = 7.6$ Hz, 1 H), 7.29 (d, $J = 8.8$ Hz, 2 H), 7.25 (d, $J = 7.6$ Hz, 1 H), 3.97 (t, $J = 6.4$ Hz, 2 H), 3.15 (t, $J = 6.4$ Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.1, 142.0, 138.2, 131.8, 129.3, 128.7, 127.2, 127.0, 126.8, 119.3, 49.2, 28.5. HRMS: Calculated for (M+H)$^+$: 302.0175; Found: 302.0179.

2-(4-Nitrophenyl)-3,4-dihydroisoquinolin-1(2H)-one (5aa) The product (38 mg, 47% yield) as a white solid was purified with silica gel chromatography. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.27 (d, $J = 9.2$ Hz, 2 H), 8.16 (d, $J = 7.6$ Hz, 1 H), 7.61 (d, $J = 9.2$ Hz, 2 H), 7.51 (td, $J = 7.6$, 1.2 Hz, 1 H), 7.41 (t, $J = 7.6$ Hz, 1 H), 7.28 (d, $J = 7.6$ Hz, 1 H), 4.08 (t, $J = 6.4$ Hz, 2 H), 3.19 (t, $J = 6.4$ Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.2, 148.6, 144.7, 138.2, 132.8, 129.0, 128.9, 127.5, 127.1, 124.8, 124.2, 49.0, 28.4.

4-(1-Oxo-3,4-dihydroisoquinolin-2(1H)-yl)benzonitrile (6aa) The product (56 mg, 75% yield) as a white solid was purified with silica gel chromatography. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 (d, $J = 7.6$ Hz, 1 H), 7.67 (d, $J = 8.4$ Hz, 2 H), 7.53 (d, $J = 8.4$ Hz, 2 H), 7.49 (t, $J = 7.6$ Hz, 1 H), 7.38 (t, $J = 7.6$ Hz, 1 H), 7.25 (d, $J = 7.6$ Hz, 1 H), 4.02 (t, $J = 6.4$ Hz, 2 H), 3.16 (t, $J = 6.4$ Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.0, 146.8, 138.1, 132.6, 128.9, 128.8, 127.3, 127.0, 125.0, 118.6, 108.8, 48.8, 28.3. HRMS: Calculated for (M+H)$^+$: 249.1022; Found: 249.1027.
2-Acetyl-1-oxo-1,2,3,4-tetrahydroisoquinolin-6-yl acetate (7aa) The product (49 mg, 66% yield) as a white solid was purified with silica gel chromatography. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.15 (d, $J = 8.8$ Hz, 1 H), 7.08 (dd, $J = 8.8$ Hz, $J = 2.4$ Hz, 1 H), 7.00 (s, 1 H), 4.09 (t, $J = 6.0$ Hz, 2 H), 2.96 (t, $J = 6.0$ Hz, 2 H), 2.63 (s, 3 H), 2.30 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 173.5, 168.7, 164.9, 154.3, 142.0, 131.4, 126.5, 120.7, 120.3, 41.5, 27.5, 21.1.

Benzyl 1-oxo-3,4-dihydroisoquinoline-2(1H)-carboxylate (8aa) The product (55 mg, 65% yield) as a white solid was purified with silica gel chromatography. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.18 (d, $J = 7.6$ Hz, 1 H), 7.49 (t, $J = 7.6$ Hz, 2 H), 7.41-7.31 (m, 5 H), 7.22 (d, $J = 7.6$ Hz, 1 H), 5.37 (s, 2 H), 4.09 (t, $J = 6.0$ Hz, 2 H), 3.02 (t, $J = 6.0$ Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.7, 154.5, 139.5, 135.4, 133.1, 129.7, 129.0, 128.6, 128.3, 128.1, 127.3, 127.2, 68.7, 44.8, 28.2. HRMS: Calculated for (M+Na)$^+$: 304.0944; Found: 304.0947.

Benzyl 7-nitro-1-oxo-3,4-dihydroisoquinoline-2(1H)-carboxylate (9aa) The product (60 mg, 61% yield) as a white solid was purified with silica gel chromatography. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.00 (d, $J = 2.8$ Hz, 1 H), 8.32 (dd, $J = 8.4$ Hz, $J = 2.4$ Hz, 1 H), 7.50-7.47 (m, 2 H), 7.44-7.34 (m, 4 H), 5.38 (s, 2 H), 4.13 (t, $J = 6.0$ Hz, 2 H), 3.13 (t, $J = 6.0$ Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 161.5, 154.0, 147.6, 145.9, 135.0, 130.4, 128.7, 128.6, 128.5, 128.1, 127.3, 125.0, 69.2, 44.0, 28.3.

Allyl 1-oxo-3,4-dihydroisoquinoline-2(1H)-carboxylate (10aa) The product (42 mg, 60% yield) as a white solid was purified with silica gel chromatography. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.17 (d, $J = 7.6$ Hz, 1 H), 7.49 (t, $J = 7.6$ Hz, 1 H), 7.37 (t, $J = 7.6$ Hz,
1 H), 7.23 (d, J = 7.6 Hz, 1 H), 6.07-5.98 (m, 1 H), 5.49 (d, J = 17.2 Hz, 1 H), 5.31 (d, J = 10.4 Hz, 1 H), 4.82 (d, J = 5.2 Hz, 2 H), 4.09 (t, J = 6.0 Hz, 2 H), 3.03 (t, J = 6.0 Hz, 2 H). 13C NMR (100 MHz, CDCl3) δ 163.7, 154.4, 139.5, 133.1, 131.5, 129.8, 129.0, 127.3, 127.2, 118.9, 67.7, 44.7, 28.3. HRMS: Calculated for (M+Na)+: 254.0787; Found: 254.0793.

**tert-Butyl 1-oxo-3,4-dihydroisoquinoline-2(1H)-carboxylate (11aa)** The product (52 mg, 70% yield) as a white solid was purified with silica gel chromatography. 1H NMR (400 MHz, CDCl3) δ 8.15 (d, J = 7.6 Hz, 1 H), 7.46 (t, J = 7.6 Hz, 1 H), 7.34 (t, J = 7.6 Hz, 1 H), 7.20 (d, J = 7.6 Hz, 1 H), 3.98 (t, J = 6.0 Hz, 2 H), 3.00 (t, J = 6.0 Hz, 2 H), 1.58 (s, 9 H). 13C NMR (100 MHz, CDCl3) δ 163.9, 153.1, 139.5, 132.8, 129.6, 129.3, 127.2, 127.1, 83.2, 44.4, 28.3, 28.1. HRMS: Calculated for (M+Na)+: 270.1100; Found: 270.1105.

N-(2-Oxo-2-(1-oxo-3,4-dihydroisoquinolin-2(1H)-yl)ethyl)benzamide (12aa) The product (58 mg, 63% yield) as a white solid was purified with silica gel chromatography. 1H NMR (400 MHz, CDCl3) δ 8.15 (d, J = 8.0 Hz, 1 H), 7.86 (d, J = 7.6 Hz, 2 H), 7.56-7.49 (m, 2 H), 7.46-7.39 (m, 3 H), 7.27 (d, J = 7.6 Hz, 1 H), 7.17 (t, J = 5.2 Hz, 1 H), 4.95 (d, J = 5.2 Hz, 2 H), 4.16 (t, J = 6.8 Hz, 2 H), 3.04 (t, J = 6.8 Hz, 2 H). 13C NMR (100 MHz, CDCl3) δ 172.9, 167.4, 165.4, 139.9, 134.1, 133.7, 131.5, 129.6, 128.6, 128.5, 127.5, 127.3, 127.1, 47.4, 42.1, 27.9. HRMS: Calculated for (M+Na)+: 331.1053; Found: 331.1057.

**tert-Butyl(S)-(4-Methyl-1-oxo-1-(1-oxo-3,4-dihydroisoquinolin-2(1H)-yl)pentan-2-yl)carbamate (13aa)** The product (71 mg, 71% yield) as a white solid was purified with silica gel chromatography. 1H NMR (400 MHz, CDCl3) δ 7.22-7.08 (m, 4 H), 5.33 (t, J = 9.2 Hz, 1 H), 4.79-4.62 (m, 3 H), 7.31 (d, J = 5.2 Hz, 1 H), 4.82 (t, J = 1.2 Hz, 2 H), 4.48 (t, J = 1.2 Hz, 2 H), 4.19 (s, 5 H), 4.04 (t, J = 4.0 Hz, 2 H), 3.18 (t, J = 4.0 Hz,
2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 177.6, 165.7, 139.9, 133.3, 129.6, 128.7, 127.7, 127.4, 75.9, 71.6, 71.5, 70.4, 45.0, 29.0. HRMS: Calculated for (M+H)$^+$: 361.2121; Found: 361.2124.

![Chemical structure of compound 14aa](image)

**C NMR (100 MHz, CDCl$_3$) δ** 178.9, 165.4, 157.4, 140.1, 136.8, 133.5, 133.2, 129.6, 129.3, 129.0, 128.9, 127.2, 127.0, 126.9, 126.3, 118.6, 105.5, 55.2, 46.8, 42.8, 28.2, 20.0.

**O N O Me**

**H**

(S)-2-(2-(6-Methoxynaphthalen-2-yl)propanoyl)-3,4-dihydroisoquinolin-1(2H)-one (14aa) The product (54 mg, 50% yield) as a white solid was purified with silica gel chromatography. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.11 (d, $J$ = 7.6 Hz, 1 H), 7.71 (s, 1 H), 7.68 (dd, $J$ = 8.4, 3.2 Hz, 2 H), 7.49 (dd, $J$ = 8.4, 2.0 Hz, 1 H), 7.44 (td, $J$ = 7.6, 1.6 Hz, 1 H), 7.33 (t, $J$ = 7.6 Hz, 1 H), 7.16 (d, $J$ = 7.6 Hz, 1 H), 7.11-7.07 (m, 2 H), 5.33 (q, $J$ = 6.8 Hz, 1 H), 4.18-4.12 (m, 1 H), 4.04-3.98 (m, 1 H), 3.88 (s, 3 H), 2.93-2.80 (m, 2 H), 1.62 (d, $J$ = 7.2 Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 178.9, 165.4, 157.4, 140.1, 136.8, 133.5, 133.2, 129.6, 129.3, 129.0, 128.9, 127.2, 127.0, 126.9, 126.3, 118.6, 105.5, 55.2, 46.8, 42.8, 28.2, 20.0.

![Chemical structure of compound 16aa](image)

(S)-2-(2-(4-Isobutylphenyl)propanoyl)-3,4-dihydroisoquinolin-1(2H)-one (16aa) The product (46 mg, 46% yield) as a white solid was purified with silica gel chromatography. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.12 (d, $J$ = 8.0 Hz, 1 H), 7.46 (t, $J$ = 7.6 Hz, 1 H), 7.34 (t, $J$ = 7.6 Hz, 1 H), 7.25 (d, $J$ = 7.6 Hz, 2 H), 7.19 (d, $J$ = 7.6 Hz, 1 H), 7.05 (d, $J$ = 8.0 Hz, 2 H), 5.15 (q, $J$ = 6.8 Hz, 1 H), 4.16-4.10 (m, 1 H), 4.01-3.98 (m, 1 H), 2.89-2.85 (m, 2 H), 2.40 (d, $J$ = 7.2 Hz, 2 H), 1.86-1.76 (m, 1 H), 1.54 (d, $J$ = 6.8 Hz, 3 H), 0.85 (d, $J$ = 6.4 Hz, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 179.1, 165.4, 140.1, 138.7, 133.2, 129.5, 129.1, 129.0, 127.6, 127.2, 46.4, 45.0, 42.9, 30.0, 28.2, 22.3, 19.9.

![Chemical structure of compound 1bb](image)

**Isochroman-1-one (1bb)** The product (33 mg, 75% yield) as a white solid was purified with silica gel chromatography. This compound is known. $^{11}$H NMR (400 MHz, CDCl$_3$) δ 8.08 (d, $J$ = 7.6 Hz, 1 H), 7.52 (t, $J$ = 7.6 Hz, 1 H), 7.38 (t, $J$ = 7.6 Hz, 1 H), 7.25 (d, $J$ = 7.6 Hz, 1 H), 4.52 (t, $J$ = 6.0 Hz, 2 H), 3.05 (t, $J$ = 6.0 Hz, 2 H). $^{13}$C NMR (100
4-Methylisochroman-1-one (2bb) The product (38 mg, 79% yield) as a colorless liquid was purified with silica gel chromatography. This compound is known.\textsuperscript{1} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 8.07 (d, J = 7.6 Hz, 1 H), 7.56 (t, J = 7.6 Hz, 1 H), 7.37 (t, J = 7.6 Hz, 1 H), 7.28 (d, J = 7.6 Hz, 1 H), 4.49 (dd, J = 10.8, 4.0 Hz, 1 H), 4.22 (dd, J = 10.8, 6.8 Hz, 1 H), 3.18-3.10 (m, 1 H), 1.35 (d, J = 6.8 Hz, 3 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 165.1, 144.5, 133.8, 130.4, 127.5, 125.6, 124.3, 72.4, 31.7, 16.6. HRMS: Calculated for C\textsubscript{10}H\textsubscript{10}O\textsubscript{2} (M+Na)\textsuperscript{+}: 185.0573; Found: 185.0575.

3-Methylisochroman-1-one (3bb) The product (39 mg, 80% yield) as a white solid was purified with silica gel chromatography. This compound is known.\textsuperscript{1} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 8.06 (d, J = 7.6 Hz, 1 H), 7.51 (t, J = 7.6 Hz, 1 H), 7.36 (t, J = 7.6 Hz, 1 H), 7.21 (d, J = 7.6 Hz, 1 H), 4.70-4.61 (m, 1 H), 2.98-2.88 (m, 2 H), 1.49 (d, J = 6.0 Hz, 3 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 165.6, 139.0, 133.6, 130.1, 127.5, 127.2, 124.9, 75.0, 34.8, 20.8. HRMS: Calculated for C\textsubscript{10}H\textsubscript{10}O\textsubscript{2} (M+Na)\textsuperscript{+}: 185.0573; Found: 185.0575.

7-Methylisochroman-1-one (4bb) The product (39 mg, 80% yield) as a colorless liquid was purified with silica gel chromatography. This compound is known.\textsuperscript{1} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.88 (s, 1 H), 7.32 (d, J = 7.6 Hz, 1 H), 7.13 (d, J = 7.6 Hz, 1 H), 4.49 (t, J = 6.0 Hz, 1 H), 2.99 (t, J = 6.0 Hz, 1 H), 2.36 (s, 3 H). \textsuperscript{13}C NMR (100 MHz,
CDCl$_3$ δ 165.3, 137.5, 136.5, 134.5, 130.5, 127.0, 125.0, 67.4, 27.4, 20.9. HRMS: Calculated for C$_{10}$H$_{10}$O$_2$ (M+Na)$^+$: 185.0573; Found: 185.0575.

7-(tert-Butyl)isochroman-1-one (5bb) The product (45 mg, 74% yield) as a colorless liquid was purified with silica gel chromatography. This compound is known.$^2$ $^1$H NMR (400 MHz, CDCl$_3$) δ 8.12 (d, $J = 2.0$ Hz, 1 H), 7.57 (dd, $J = 8.0$, $J = 2.0$ Hz, 1 H), 7.20 (d, $J = 8.0$ Hz, 1 H), 4.51 (t, $J = 6.0$ Hz, 2 H), 3.02 (t, $J = 6.0$ Hz, 2 H), 1.33 (s, 9 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.5, 150.9, 136.6, 130.9, 127.04, 127.0, 124.8, 67.3, 34.7, 31.1, 27.3. HRMS: Calculated for C$_{13}$H$_{16}$O$_2$ (M+Na)$^+$: 227.1042; Found: 227.1044.

7-Methoxyisochroman-1-one (6bb) The product (40 mg, 75% yield) as a colorless liquid was purified with silica gel chromatography. This compound is known.$^1$ $^1$H NMR (400 MHz, CDCl$_3$) δ 7.55 (d, $J = 2.8$ Hz, 1 H), 7.15 (d, $J = 8.4$ Hz, 1 H), 7.15 (dd, $J = 8.4$, $J = 2.8$ Hz, 1 H), 4.50 (t, $J = 6.0$ Hz, 2 H), 3.82 (s, 3 H), 2.97 (t, $J = 6.0$ Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.1, 158.9, 131.8, 128.4, 126.0, 121.5, 113.0, 67.6, 55.6, 27.0. HRMS: Calculated for C$_{10}$H$_{10}$O$_3$ (M+Na)$^+$: 201.0522; Found: 201.0524.

6,7-Dimethoxyisochroman-1-one (7bb) The product (41 mg, 66% yield) as a white solid was purified with silica gel chromatography. This compound is known.$^7$ $^1$H NMR (400 MHz, CDCl$_3$) δ 7.53 (s, 1 H), 6.67 (s, 1 H), 4.50 (t, $J = 6.0$ Hz, 2 H), 3.93 (s, 3 H), 3.90 (s, 3 H), 2.97 (t, $J = 6.0$ Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.1, 153.5, 148.4, 133.9, 117.3, 111.7, 109.0, 67.3, 56.16, 56.12, 27.4. HRMS: Calculated for C$_{11}$H$_{12}$O$_4$Na (M+Na)$^+$: 231.0627; Found: 231.0630.
7-((tert-Butyldimethylsilyl)oxy)isochroman-1-one (8bb) The product (52 mg, 62% yield) as a white solid was purified with silica gel chromatography. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51 (d, $J = 2.4$ Hz, 1 H), 7.11 (d, $J = 8.4$ Hz, 1 H), 6.99 (dd, $J = 8.4$, 2.4 Hz, 1 H), 4.48 (t, $J = 6.0$ Hz, 2 H), 2.96 (t, $J = 6.0$ Hz, 2 H), 0.96 (s, 9 H), 0.19 (s, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.0, 155.0, 132.2, 128.3, 126.1, 126.0, 120.9, 67.5, 27.0, 25.6, 25.5, 18.1, -4.5. HRMS: Calculated for (M+NH$_4$)$^+$: 296.1676; Found: 296.1666.

1-Oxoisochroman-7-yl acetate (9bb) The product (43 mg, 70% yield) as a colorless crystal was purified with silica gel chromatography. This compound is known.$^1$ $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.77 (s, 1 H), 7.28-7.23 (m, 2 H), 4.51 (t, $J = 6.0$ Hz, 2 H), 3.02 (t, $J = 6.0$ Hz, 2 H), 2.29 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.2, 164.2, 149.8, 136.9, 128.4, 127.2, 126.3, 123.1, 67.3, 27.2, 20.9. HRMS: Calculated for C$_{11}$H$_{10}$O$_4$Na (M+Na)$^+$: 229.0471; Found: 229.0462.

7-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)isochroman-1-one (10bb) The product (49 mg, 60% yield) as a white solid was purified with silica gel chromatography. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.54 (s, 1 H), 7.92 (d, $J = 7.6$ Hz, 1 H), 7.24 (d, $J = 7.6$ Hz, 1 H), 4.50 (t, $J = 6.0$ Hz, 2 H), 3.05 (t, $J = 6.0$ Hz, 2 H), 1.32 (s, 12 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.0, 142.2, 139.6, 137.0, 126.6, 124.6, 84.1, 67.1, 28.0, 24.8. HRMS: Calculated for (M+H)$^+$: 275.1451; Found: 275.1440.
7-Allylisochroman-1-one (11bb) The product (23 mg, 40% yield) as a colorless liquid was purified with silica gel chromatography. $^1$$H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (s, 1 H), 7.37 (d, $J = 8.0$ Hz, 1 H), 7.19 (d, $J = 8.0$ Hz, 1 H), 5.99-5.89 (m, 1 H), 5.11 (s, 1 H), 5.07 (m, 1 H), 4.52 (t, $J = 6.0$ Hz, 2 H), 3.42 (d, $J = 6.4$ Hz, 2 H), 3.03 (t, $J = 6.0$ Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.3, 139.8, 137.3, 136.4, 134.0, 130.2, 127.3, 125.2, 116.6, 67.4, 39.6, 27.5. HRMS: Calculated for (M+Na)$^+$: 211.0729; Found: 211.0721.

7-Fluoroisochroman-1-one (12bb) The product (35 mg, 71% yield) as a colorless crystal was purified with silica gel chromatography. This compound is known.$^1$ $^1$$H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J = 8.4$ Hz, 1 H), 7.25-7.22 (m, 2 H), 4.52 (t, $J = 6.0$ Hz, 2 H), 3.02 (t, $J = 6.0$ Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.0, 162.0 (d, $J = 245.7$ Hz), 135.3 (d, $J = 3.3$ Hz), 129.1 (d, $J = 7.4$ Hz), 126.9 (d, $J = 7.5$ Hz), 121.0 (d, $J = 21.8$ Hz), 116.7 (d, $J = 23.1$ Hz), 67.4, 27.1. HRMS: Calculated for C$_9$H$_7$FO$_2$ (M+Na)$^+$: 189.0322; Found: 189.0324.

7-Chloroisochroman-1-one (13bb) The product (43 mg, 79% yield) as a white solid was purified with silica gel chromatography. This compound is known.$^1$ $^1$$H$ NMR (400 MHz, CDCl$_3$) $\delta$ 8.05 (s, 1 H), 7.48 (d, $J = 8.0$ Hz, 1 H), 7.21 (d, $J = 8.0$ Hz, 1 H), 4.52 (t, $J = 6.0$ Hz, 2 H), 3.02 (t, $J = 6.0$ Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.8, 137.7, 133.7, 130.1, 128.7, 126.7, 67.2, 27.2. HRMS: Calculated for C$_9$H$_7$ClO$_2$ (M+Na)$^+$: 205.0026; Found: 205.0028.
7-Bromoisochroman-1-one (14bb) The product (54 mg, 80% yield) as a white solid was purified with silica gel chromatography. This compound is known.\(^8\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.20 (s, 1 H), 7.64 (d, \(J = 8.0\) Hz, 1 H), 7.15 (d, \(J = 8.0\) Hz, 1 H), 4.52 (t, \(J = 6.0\) Hz, 2 H), 3.01 (t, \(J = 6.0\) Hz, 2 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.7, 138.2, 136.5, 133.0, 128.9, 126.9, 121.3, 67.2, 27.3. HRMS: Calculated for C\(_9\)H\(_7\)BrO\(_2\) (M+Na\(^+\))\(^\text{\textsuperscript{\textdagger}}\): 248.9521; Found: 248.9523.

1,2-Dihydro-4\(\text{H}\)-benzo[\(f\)]isochromen-4-one (15bb) The product (36 mg, 61% yield) as a white solid was purified with silica gel chromatography. This compound is known.\(^9\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.10 (d, \(J = 8.4\) Hz, 1 H), 8.02-8.00 (m, 1 H), 7.91-7.88 (m, 1 H), 7.82 (d, \(J = 8.4\) Hz, 1 H), 7.66-7.59 (m, 2 H), 4.66 (t, \(J = 6.0\) Hz, 2 H), 3.42 (t, \(J = 6.0\) Hz, 2 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.4, 138.5, 135.5, 129.7, 128.8, 128.6, 127.7, 127.1, 125.1, 124.3, 122.3, 66.6, 24.1. HRMS: Calculated for C\(_{13}\)H\(_{10}\)O\(_2\) (M+Na\(^+\))\(^\text{\textsuperscript{\textdagger}}\): 221.0573; Found: 221.0575.

4,5-Dihydro-7\(\text{H}\)-thieno[2,3-\(c\)]pyran-7-one (16bb) The product (21 mg, 46% yield) as a white solid was purified with silica gel chromatography. This compound is known.\(^1\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.64 (d, \(J = 5.2\) Hz, 1 H), 6.98 (d, \(J = 5.2\) Hz, 1 H), 4.57 (t, \(J = 6.0\) Hz, 1 H), 3.00 (t, \(J = 6.0\) Hz, 1 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 161.2, 147.4, 134.4, 126.6, 126.5, 68.3, 25.1. HRMS: Calculated for C\(_7\)H\(_6\)O\(_2\)S (M+Na\(^+\))\(^\text{\textsuperscript{\textdagger}}\): 176.9980; Found: 176.9983.
1-(4-Fluorophenyl)-3-oxo-1,3-dihydroisobenzofuran-5-carbonitrile (17bb) The product (38 mg, 50% yield) as a light yellow solid was purified with silica gel chromatography. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.98 (s, 1 H), 8.30 (s, 1 H), 7.98 (d, $J$ = 8.0 Hz, 1 H), 7.79 (dd, $J$ = 7.6, 5.6 Hz, 2 H), 7.61 (d, $J$ = 7.6 Hz, 1 H), 7.16 (t, $J$ = 8.0 Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 193.0, 188.2, 166.3 (d, $J$ = 256.4 Hz), 144.4, 136.3, 135.6, 133.8, 132.5 (d, $J$ = 9.7 Hz), 132.4 (d, $J$ = 2.9 Hz), 129.3, 116.8, 116.3 (d, $J$ = 22.0 Hz), 114.9. HRMS: Calculated for (M-H)$^-$: 252.0466; Found: 252.0465.

Isobenzofuran-1(3H)-one (18bb) The product (21 mg, 52% yield) as a white solid was purified with silica gel chromatography. This compound is known.$^1$ $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.92 (d, $J$ = 7.6 Hz, 1 H), 7.68 (t, $J$ = 7.6 Hz, 1 H), 7.54 (t, $J$ = 7.6 Hz, 1 H), 7.51 (d, $J$ = 7.6 Hz, 1 H), 5.32 (s, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.0, 146.5, 134.0, 129.0, 125.7, 69.6.

7-Benzylisochroman-1-one (22bb) The product (31 mg, 44% yield) as a light yellow liquid was purified with silica gel chromatography. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (s, 1 H), 7.35 (d, $J$ = 7.6 Hz, 1 H), 7.39 (t, $J$ = 7.6 Hz, 2 H), 7.23-7.17 (m, 4 H), 4.51 (t, $J$ = 6.0 Hz, 2 H), 4.01 (s, 2 H), 3.01 (t, $J$ = 6.0 Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.2, 141.0, 140.2, 137.3, 134.2, 130.5, 128.8, 128.6, 127.4, 126.3, 125.2, 67.3, 41.4, 27.4. HRMS: Calculated for (M+Na)$^+$: 261.0886; Found: 261.0881.

Radical Inhibition Experiments
To a 25 mL of Schlenk tube were added Fe5 (7.3 mg, 0.03 mmol, 0.1 equiv), phenyl disulfide (6.5 mg, 0.03 mmol, 0.1 equiv), additive (0.1-1.0 equiv) under air. The mixture was then evacuated and backfilled with O2 (3 times), then amine (0.30 mmol, 1 equiv) and freshly distilled 1,4-dioxane (0.5 mL) were added subsequently. The reaction mixture was heated to 80 °C and allowed to react for 15 h. The reaction was cooled to room temperature and mesitylene (0.3 mmol) was added. The yield was determined by 1H NMR.

To a 25 mL of Schlenk tube were added Fe1 (16.6 mg, 0.03 mmol, 0.1 equiv), phenyl disulfide (6.5 mg, 0.03 mmol, 0.1 equiv), additive (0.1-1.0 equiv) under air. The mixture was then evacuated and backfilled with O2 (3 times), then isochroman (0.30 mmol, 1 equiv) and freshly distilled 1,4-dioxane (0.5 mL) were added subsequently. The reaction mixture was heated to 80 °C and allowed to react for 15 h. The reaction
was cooled to room temperature and mesitylene (0.3 mmol) was added. The yield was determined by $^1$H NMR.

**Isotope Labeling Experiments**

1) To a 25 mL of Schlenk tube were added Fe$_5$ (7.3 mg, 0.03 mmol, 0.1 equiv), phenyl disulfide (6.5 mg, 0.03 mmol, 0.1 equiv) under air. The mixture was then evacuated and backfilled with Ar (3 times), then amine (0.30 mmol, 1 equiv), H$_2$O$_{18}$ (0.05 mL) and freshly distilled 1,4-dioxane (0.5 mL) were added subsequently. The reaction mixture was heated to 80 °C and allowed to react for 15 h. The reaction was cooled to room temperature and mesitylene (0.3 mmol) was added. No desired product was detected.

![Chemical structure](image)
2) To a 25 mL of Schlenk tube were added Fe5 (7.3 mg, 0.03 mmol, 0.1 equiv), phenyl disulfide (6.5 mg, 0.03 mmol, 0.1 equiv) under air. The mixture was then evacuated and backfilled with O₂ (3 times), then amine (0.30 mmol, 1 equiv), H₂O¹⁸ (0.05 mL) and freshly distilled 1,4-dioxane (0.5 mL) were added subsequently. The reaction mixture was heated to 80 °C and allowed to react for 15 h. The reaction was cooled to room temperature and mesitylene (0.3 mmol) was added. The yield was determined by ¹H NMR. The ratio of the product was determined by HRMS.

1b

Fe₁ (10 mol%)  S₁ (10 mol%)  1,4-dioxane, 80 °C

1bb

1) Ar, H₂O¹⁸: 0% yield
2) O₂, H₂O¹⁸: 46% yield (O/O¹⁸=6/1)

1) To a 25 mL of Schlenk tube were added dpff (16.6 mg, 0.03 mmol, 0.1 equiv), phenyl disulfide (6.5 mg, 0.03 mmol, 0.1 equiv) under air. The mixture was then...
evacuated and backfilled with Ar (3 times), then isochroman (0.30 mmol, 1 equiv), H$_2$O$_{18}$ (0.05 mL) and freshly distilled 1,4-dioxane (0.5 mL) were added subsequently. The reaction mixture was heated to 80 °C and allowed to react for 15 h. The reaction was cooled to room temperature and mesitylene (0.3 mmol) was added. No desired product was detected.

2) To a 25 mL of Schlenk tube were added dppf (16.6 mg, 0.03 mmol, 0.1 equiv), phenyl disulfide (6.5 mg, 0.03 mmol, 0.1 equiv) under air. The mixture was then evacuated and backfilled with O$_2$ (3 times), then isochroman (0.30 mmol, 1 equiv), H$_2$O$_{18}$ (0.05 mL) and freshly distilled 1,4-dioxane (0.5 mL) were added subsequently. The reaction mixture was heated to 80 °C and allowed to react for 15 h. The reaction was cooled to room temperature and mesitylene (0.3 mmol) was added. The yield was determined by $^1$H NMR. The ratio of the product was determined by HRMS.

Mass Spectrum List Report

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<th>Error (ppm)</th>
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7/4/2018 11:26:54 AM
Some results on iron-catalyzed oxygenation of $^{3}$C-H bonds

**Our work:**

<table>
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<th>Reaction</th>
<th>Product</th>
<th>Yield</th>
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<td>21b, Fe$^{1+}$ (PhS)$_2$</td>
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</table>

Ref 3b: conditions: FeCl$_3$ $\cdot$ 6H$_2$O (2 mol%), TBHP (70%), H$_2$O (3.0 equiv), pyridine, 82 °C, 24 h

<table>
<thead>
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<th>Product</th>
<th>Yield</th>
</tr>
</thead>
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<td>74%</td>
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</table>

Ref 3c: conditions: Fe(NO$_3$)$_3$ $\cdot$ 9H$_2$O (10 mol%), KPF$_6$ (20 mol%), O$_2$, MeCN, 80 ºC, 5 h

<table>
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<th>Yield</th>
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Ref 3f: conditions: FeCl$_3$ $\cdot$ 6H$_2$O (5.0 mol%), LiBr (5.0 mol%), LED, air, MeCN, 25 ºC

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**References:**


2-Phenyl-1,2,3,4-tetrahydroisoquinoline (1a)
2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (2a)
2-(4-Chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (3a)
2-(4-Bromophenyl)-1,2,3,4-tetrahydroisoquinoline (4a)
2-(4-Nitrophenyl)-1,2,3,4-tetrahydroisoquinoline (5a)
4-(3,4-Dihydroisoquinolin-2(1H)-yl)benzonitrile (6a)
2-Acetyl-1,2,3,4-tetrahydroisoquinolin-6-yl acetate (7a)
Benzyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (8a)
Allyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (10a)
tert-Butyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (11a)
N-(2-(3,4-dihydroisoquinolin-2(1H)-yl)-2-oxoethyl)benzamide (12a)
tert-Butyl \((S)-(1-\text{(3,4-dihydroisoquinolin-2(1H)-yl)})-4\text{-methyl-1-oxopentan-2-yl})\) carbamate (13a)
(S)-1-(3,4-dihydroisoquinolin-2(1H)-yl)-2-(6-methoxynaphthalen-2-yl)propan-1-one (14a)
4-Methylisochromane (2b)

\[
\text{O} \quad \text{C} \quad \text{H}_3
\]

\[
\text{O} \quad \text{C} \quad \text{H}_3
\]
3-Methylisochromane (3b)

\[
\begin{align*}
\text{O} & \quad \text{C} \\
\text{H}_3 & \quad \text{CH}_3
\end{align*}
\]
7-Methylisochromane (4b)
7-(*tert*-Butyl)isochromane (5b)

![NMR Spectrum](image)

**Chemical Structure:**

H₃C-CH₃
H₃C

O

C₃H₃

C₃H₃

O
7-Methoxyisochromane (6b)
6.7-Dimethoxyisochromane (7b)

\[
\begin{align*}
\text{H}_2\text{C}^\text{O} & \quad \text{O} \\
\text{H}_2\text{C}^\text{O} & \quad \text{C} \quad \text{H}_3 \\
\end{align*}
\]
tert-Butyl(isochroman-7-yloxy)dimethylsilane (8b)
Isochroman-7-yl acetate (9b)
2-(Isochroman-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10b)
7-Allylisochromane (11b)
7-Fluoroisochromane (12b)
7-Chloroisochromane (13b)

7-Bromoisochromane (14b)
3,4-Dihydro-1H-benzo[h]isochromene (15b)
4,7-Dihydro-5H-thieno[2,3-c]pyran (16b)
7-Benzylisochromane (22b)
2-Phenyl-3,4-dihydroisoquinolin-1(2H)-one (1aa)
2-(4-Methoxyphenyl)-3,4-dihydroisoquinolin-1(2H)-one (2aa)
3-(4-Chlorophenyl)-3,4-dihydroisoquinolin-1(2H)-one (3aa)
2-(4-Bromophenyl)-3,4-dihydroisoquinolin-1(2H)-one (4aa)
2-(4-Nitrophenyl)-3,4-dihydroisoquinolin-1(2H)-one (5aa)
4-(1-Oxo-3,4-dihydroisoquinolin-2(1H)-yl)benzonitrile (6aa)
2-Acetyl-1-oxo-1,2,3,4-tetrahydroisoquinolin-6-yl acetate (7aa)
Benzyl 1-oxo-3,4-dihydroisoquinoline-2(1H)-carboxylate (8aa)
Benzyl 7-nitro-1-oxo-3,4-dihydroisoquinoline-2(1H)-carboxylate (9aa)
Allyl 1-oxo-3,4-dihydroisoquinoline-2(1H)-carboxylate (10aa)
tert-Butyl 1-oxo-3,4-dihydroisoquinoline-2(1\(H\))-carboxylate (11aa)
$N$-(2-oxo-2-(1-oxo-3,4-dihydroisoquinolin-2(1H)-yl)ethyl)benzamide (12aa)
tert-Butyl(S)-(4-Methyl-1-oxo-1-(1-oxo-3,4-dihydroisoquinolin-2(1H)-yl)pentan-2-yl)carbamate (13aa)
(S)-2-(2-(6-Methoxynaphthalen-2-yl)propanoyl)-3,4-dihydroisoquinolin-1(2H)-one (14aa)
(S)-2-(2-(4-Isobutylphenyl)propanoyl)-3,4-dihydroisoquinolin-1(2H)-one (15aa)
Isochroman-1-one (1bb)
4-Methylisochroman-1-one (2bb)
3-Methylisochroman-1-one (3bb)

\[ \text{O} \]
\[ \text{O} \]
\[ \text{C} \]
\[ \text{H}_3 \]

\[ \text{O} \]
\[ \text{O} \]
\[ \text{C} \]
\[ \text{H}_3 \]
7-Methylisochroman-1-one (4bb)

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{O} \\
\end{align*}
\]
7-(tert-Butyl)isochroman-1-one (5bb)

![Chemical Structure](image)

**1H NMR Spectra**

**f1 (ppm)**

- 0.90
- 0.97
- 1.00
- 1.04
- 1.23
- 2.10
- 2.18
- 2.56
- 2.58
- 2.60
- 2.63
- 3.00
- 3.01
- 3.03
- 4.40
- 4.49
- 4.50
- 4.51
- 4.52
- 7.19
- 7.21
- 7.56
- 7.58
- 8.12

**13C NMR Spectra**

**f1 (ppm)**

- 27.40
- 31.18
- 34.74
- 67.37
- 76.72
- 77.04
- 77.36
- 124.80
- 127.00
- 127.04
- 130.98
- 136.61
- 150.96
- 165.58

**Chemical Structure**

- tert-Butyl substituent
- Isochroman ring

**References**

- [Further details](#)
7-Methoxyisochroman-1-one (6bb)
6,7-Dimethoxyisochroman-1-one (7bb)
7-((tert-Butyldimethylsilyl)oxy)isochroman-1-one (8bb)
1-Oxoisochroman-7-yl acetate (9bb)

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{O} \\
\text{O} & \quad \text{C} \\
\text{H}_3 & \quad \text{O}
\end{align*}
\]

\[
\begin{align*}
\text{f1 (ppm)} & \quad 12.5 & 11.5 & 10.5 & 9.5 & 8.5 & 7.5 & 6.5 & 5.5 & 4.5 & 3.5 & 2.5 & 1.5 & 0.5 & -0.1 \\
\text{20.928} & \quad 27.217 & \quad 67.322 & \quad 76.726 & \quad 77.044 & \quad 77.362 & \quad 123.191 & \quad 126.387 & \quad 127.261 & \quad 128.456 & \quad 136.980 & \quad 149.825 & \quad 164.215 & \quad 169.225
\end{align*}
\]
7-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)isochroman-1-one (10bb)
7-Allylochroman-1-one (11bb)
7-Fluoroisochroman-1-one (12bb)
7-Chloroisochroman-1-one (13bb)
7-Bromoisochroman-1-one (14bb)
3,4-Dihydro-1\textit{H}-benzo[\textit{h}]isochromen-1-one (15bb)
4,5-Dihydro-7H-thieno[2,3-c]pyran-7-one (16bb)
1-(4-Fluorophenyl)-3-oxo-1,3-dihydroisobenzofuran-5-carbonitrile (17bb)
Isobenzofuran-1(3H)-one (18bb)
7-Benzylisochroman-1-one (22bb)