Supporting Information

Site-specific hydroxyalkylation of chromones via alcohol mediated Minisci-type radical conjugate addition

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1. General experimental details

**General Information:** All chemicals were used as received without further purification unless stated otherwise. NMR spectra were recorded at ambient temperature on a 300 or 400 MHz NMR spectrometer. Chemical shifts (δ) are given in ppm relative to TMS, the coupling constants J are given in Hz. HRMS were recorded on a TOF LC/MS equipped with electrospray ionization (ESI) probe operating in positive or negative ion mode.

**Experimental procedure:** Under N₂, the mixture of 1 (0.2 mmol), 2 or 4 (1 mL) and DTBP (0.6 mmol) were added into the sealed tube. The reaction mixture was vigorously stirred at 140 °C for 15h. Then, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the products.

2. Mechanism Studies

**Standard Procedure + BHT (3.0 equiv)**
Kinetic isotope effect experiments

To a sealed tube, the mixture of 1a (0.2 mmol), DTBP (0.6 mmol), CH$_3$OH (0.5 mL) and CD$_3$OD (0.5 mL) were added into the flask. The reaction mixture was vigorously stirred at 140 °C for 15 h. After the completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the products 3aa and [D]-3aa. $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.88 (dd, $J = 7.8$, 1.5 Hz, 1H), 7.51-7.46 (m, 1H), 7.05-6.98 (m, 2H), 4.61-4.55 (m, 1H), 4.01-3.96 (m, 0.84H), 3.87-3.82 (m, 0.84H), 2.98-2.90 (m, 0.84H), 2.65-2.60 (m, 0.84H), 2.25-2.21 (m, 1H).
3. Characterization data of the products

2-(hydroxymethyl)chroman-4-one (3aa)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow liquid (32.1 mg, 90%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.87 (dd, $J = 7.8$, 1.6 Hz, 1H), 7.49-7.45 (m, 1H), 7.02-6.96 (m, 2H), 4.58-4.52 (m, 1H), 3.98-3.94 (m, 1H), 3.85-3.81 (m, 1H), 2.95-2.88 (m, 1H), 2.74 (s, 1H), 2.64-2.59 (m, 1H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 192.3, 161.2, 136.2, 127.0, 121.7, 120.8, 117.8, 78.2, 64.4, 39.0. HRMS (ESI) $m/z$ calcd for C$_{10}$H$_{11}$O$_3$ (M+H)$^+$ 179.0703, found 179.0704.

2-(hydroxymethyl)-6-methylchroman-4-one (3ba)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow liquid (31.5 mg, 82%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.66 (s, 1H), 7.30-7.27 (m, 1H), 6.89 (d, $J = 8.4$ Hz, 1H), 4.57-4.51 (m, 1H), 3.99-3.95 (m, 1H), 3.86-3.82 (m, 1H), 2.95-2.87 (m, 1H), 2.63-2.58 (m, 2H), 2.30 (s, 3H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 192.4, 159.2, 137.3, 131.1 126.6, 120.4, 117.6, 78.2, 64.5, 39.1, 20.4. HRMS (ESI) $m/z$ calcd for C$_{11}$H$_{13}$O$_3$ (M+H)$^+$ 193.0859, found 193.0861.

2-(hydroxymethyl)-7-methylchroman-4-one (3ca)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow liquid (29.2 mg, 76%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.74 (d, $J = 8.0$ Hz, 1H), 6.81 (d, $J = 8.0$ Hz, 1H), 6.77 (s, 1H), 4.56-4.49 (m, 1H), 3.96-3.92 (m, 1H), 3.84-3.79 (m, 1H), 2.91-2.83 (m, 1H), 2.68 (s, 1H), 2.60-2.55 (m, 1H), 2.32 (s, 3H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 191.9, 161.2, 147.8, 126.9, 123.0, 118.6, 117.9, 78.2, 64.4, 38.9, 21.9. HRMS (ESI) $m/z$ calcd for C$_{11}$H$_{13}$O$_3$ (M+H)$^+$ 193.0859, found 193.0860.

2-(hydroxymethyl)-7-methoxychroman-4-one (3da)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 2/1) gave a yellow solid (32.0 mg, 77%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.78 (d, $J = 8.8$ Hz, 1H), 6.55 (dd, $J = 8.8$, 2.4 Hz, 1H), 6.41 (d, $J = 2.3$ Hz, 1H), 4.57-4.50 (m, 1H), 3.95-3.92 (m, 1H), 3.84-3.80 (m, 1H), 3.79 (s, 3H), 2.88-2.81 (m, 1H), 2.72 (s, 1H), 2.57-2.52 (m, 1H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 190.9,
166.2, 163.2, 128.7, 114.7, 110.1, 100.8, 78.6, 64.4, 55.7, 38.6. HRMS (ESI) m/z calcd for C\textsubscript{11}H\textsubscript{13}O\textsubscript{4} (M+H)	extsuperscript{+} 209.0808, found 209.0809.

2-(hydroxymethyl)-5-methoxychroman-4-one (3ea)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 2/1) gave a yellow solid (28.3 mg, 68%). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \( \delta \) 7.35 (d, \( J = 8.4 \) Hz, 1H), 6.57 (d, \( J = 8.3 \) Hz, 1H), 6.49 (d, \( J = 8.3 \) Hz, 1H), 4.53-4.47 (m, 1H), 3.94-3.90 (m, 1H), 3.88 (s, 3H), 3.82-3.78 (m, 1H), 2.91-2.83 (m, 1H), 2.60 (s, 1H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 75 MHz): \( \delta \) 191.0, 162.8, 160.7, 136.1, 111.2, 109.9, 104.0, 77.7, 64.3, 56.2, 40.4.

7-fluoro-2-(hydroxymethyl)chroman-4-one (3fa)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow solid (27.4 mg, 70%). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \( \delta \) 7.91-7.86 (m, 1H), 6.77-6.65 (m, 2H), 4.62-4.54 (m, 1H), 4.01-3.96 (m, 1H), 3.86-3.81 (m, 1H), 2.97-2.87 (m, 1H), 2.65-2.47 (m, 1H), 2.60 (s, 1H). \textsuperscript{13}C NMR (DMSO-d\textsubscript{6}, 75 MHz): \( \delta \) 191.1, 167.1 (d, \( J_{C-F} = 251.2 \) Hz), 163.3 (d, \( J_{C-F} = 13.8 \) Hz), 129.5 (d, \( J_{C-F} = 11.6 \) Hz), 118.3, 109.6 (d, \( J_{C-F} = 22.7 \) Hz), 104.9 (d, \( J_{C-F} = 24.3 \) Hz), 79.6, 63.0, 38.9. HRMS (ESI) m/z calcd for C\textsubscript{10}H\textsubscript{10}FO\textsubscript{3} (M+H)	extsuperscript{+} 197.0608, found 197.0609.

7-chloro-2-(hydroxymethyl)chroman-4-one (3ga)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow solid (33.9 mg, 80%). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \( \delta \) 7.79 (d, \( J = 8.2 \) Hz, 1H), 7.00-6.97 (m, 2H), 4.60-4.54 (m, 1H), 3.99-3.96 (m, 1H), 3.85-3.81 (m, 1H), 2.96-2.88 (m, 1H), 2.65-2.60 (m, 1H), 2.49 (s, 1H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 75 MHz): \( \delta \) 191.1, 161.5, 142.0, 128.3, 122.5, 119.4, 118.0, 78.7, 64.3, 38.8. HRMS (ESI) m/z calcd for C\textsubscript{10}H\textsubscript{10}ClO\textsubscript{3} (M+H)	extsuperscript{+} 213.0313, found 213.0315.

7-bromo-2-(hydroxymethyl)chroman-4-one (3ha)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow solid (37.9 mg, 74%). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \( \delta \) 7.70 (d, \( J = 8.4 \) Hz, 1H), 7.18-7.13 (m, 2H),
4.59-4.53 (m, 1H), 3.99-3.95 (m, 1H), 3.85-3.80 (m, 1H), 2.95-2.88 (m, 1H), 2.65-2.60 (m, 1H), 2.51 (s, 1H). $^{13}$C NMR (CDCl$_3$, 75 MHz): δ 191.3, 161.3, 130.6, 128.3, 125.3, 121.1, 119.7, 78.7, 64.3, 38.8. HRMS (ESI) $m/z$ calcd for C$_{16}$H$_{10}$BrO$_3$ (M+H)$^+$ 256.9808, found 256.9813.

6-fluoro-2-(hydroxymethyl)chroman-4-one (3ia)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow liquid (19.6 mg, 50%). $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.49 (dd, $J = 8.2, 3.2$ Hz, 1H), 7.21-7.16 (m, 1H), 6.96 (d, $J = 9.0$ 4.2 Hz, 1H), 4.57-4.50 (m, 1H), 3.99-3.80 (m, 1H), 2.95-2.87 (m, 1H), 2.64-2.59 (m, 1H), 2.54 (s, 1H). $^{13}$C NMR (CDCl$_3$, 75 MHz): δ 191.3 (d, $J_{CF} = 2.3$ Hz), 157.4 (d, $J_{CF} = 2.3$ Hz), 157.3 (d, $J_{CF} = 32.1$ Hz), 123.7 (d, $J_{CF} = 32.5$ Hz), 121.3 (d, $J_{CF} = 8.6$ Hz), 119.5 (d, $J_{CF} = 9.8$ Hz), 111.9 (d, $J_{CF} = 31.0$ Hz), 78.4, 64.4, 38.8. HRMS (ESI) $m/z$ calcd for C$_{16}$H$_{10}$FO$_3$ (M+H)$^+$ 197.0608, found 197.0609.

6-chloro-2-(hydroxymethyl)chroman-4-one (3ja)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow solid (17.8 mg, 42%). $^1$H NMR (CDCl$_3$, 300 MHz): δ 7.77 (d, $J = 2.5$ Hz, 1H), 7.35 (dd, $J = 8.8, 2.6$ Hz, 1H), 6.90 (d, $J = 8.8$ Hz, 1H), 4.53-4.46 (m, 1H), 3.95-3.75 (m, 1H), 2.92-2.82 (m, 1H), 2.61-2.54 (m, 1H), 2.15 (s, 1H). $^{13}$C NMR (DMSO-d$_6$, 75 MHz): δ 191.5, 160.3, 136.0, 125.6, 125.5, 122.0, 120.6, 79.2, 63.1, 38.9. HRMS (ESI) $m/z$ calcd for C$_{16}$H$_{10}$ClO$_3$ (M+H)$^+$ 213.0313, found 213.0315.

6-bromo-2-(hydroxymethyl)chroman-4-one (3ka)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow solid (21.0 mg, 41%). $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.97 (d, $J = 2.5$ Hz, 1H), 7.55 (d, $J = 8.8, 2.5$ Hz, 1H), 6.90 (d, $J = 8.8$ Hz, 1H), 4.58-4.53 (m, 1H), 4.00-3.98 (m, 1H), 3.85-3.82 (m, 1H), 2.97-2.89 (m, 1H), 2.66-2.61 (m, 1H), 2.77 (s, 1H). $^{13}$C NMR (CDCl$_3$, 75 MHz): δ 190.8, 160.0, 138.8, 129.5, 122.1, 119.9, 114.3, 78.4, 64.3, 38.7. HRMS (ESI) $m/z$ calcd for C$_{16}$H$_{10}$BrO$_3$ (M+H)$^+$ 256.9808, found 256.9811.

8-bromo-6-chloro-2-(hydroxymethyl)chroman-4-one (3la)
Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow solid (20.3 mg, 35%). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.81 (d, \(J = 2.5\) Hz, 1H), 7.71 (d, \(J = 2.5\) Hz, 1H), 4.67-4.59 (m, 1H), 4.08-4.03 (m, 1H), 3.90-3.86 (m, 1H), 3.02-2.92 (m, 1H), 2.72-2.65 (m, 1H), 2.32 (s, 1H). \(^1\)C NMR (DMSO-d\(_6\), 100 MHz): \(\delta\) 190.8, 156.9, 138.1, 125.7, 125.3, 122.8, 112.8, 79.9, 63.1, 38.5. HRMS (ESI) \(m/z\) calcd for C\(_{10}\)H\(_8\)BrClO\(_3\) (M+H\(^+\)) \(229.9418\), found 229.9414.

### 6,8-dichloro-2-(hydroxymethyl)chroman-4-one (3ma)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow solid (20.2 mg, 41%). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.76 (d, \(J = 2.4\) Hz, 1H), 7.54 (d, \(J = 2.4\) Hz, 1H), 4.66-4.59 (m, 1H), 4.08-4.04 (m, 1H), 3.89-3.86 (m, 1H), 3.03-2.92 (m, 1H), 2.72-2.65 (m, 1H), 2.34 (s, 1H). \(^1\)C NMR (DMSO-d\(_6\), 100 MHz): \(\delta\) 190.8, 156.0, 135.3, 125.3, 124.6, 123.5, 123.0, 79.9, 63.0, 38.6. HRMS (ESI) \(m/z\) calcd for C\(_{10}\)H\(_8\)Cl\(_2\)O\(_3\) (M+H\(^+\)) \(246.9923\), found 246.9920.

### 2-(hydroxymethyl)-2,3-dihydro-4H-benzo[h]chromen-4-one (3ma)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow solid (25.1 mg, 55%). \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 8.30 (d, \(J = 8.4\) Hz, 1H), 7.85 (d, \(J = 8.7\) Hz, 1H), 7.77 (d, \(J = 8.2\) Hz, 1H), 7.63-7.58 (m, 1H), 7.53-7.49 (m, 1H), 7.39 (d, \(J = 8.7\) Hz, 1H), 4.78-4.72 (m, 1H), 4.15-4.41 (m, 1H), 3.99-3.95 (m, 1H), 3.08-3.01 (m, 1H), 2.73-2.68 (m, 1H), 2.52 (s, 1H). \(^1\)C NMR (CDCl\(_3\), 75 MHz): \(\delta\) 191.9, 159.4, 137.5, 129.7, 127.9, 126.3, 124.6, 123.4, 121.6, 121.3, 115.4, 79.2, 64.5, 38.4. HRMS (ESI) \(m/z\) calcd for C\(_{14}\)H:\(_{13}\)O\(_3\) (M+H\(^+\)) \(229.0859\), found 229.0860.

### 3-(hydroxymethyl)-2,3-dihydro-1H-benzo[f]chromen-1-one (3oa)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow solid (18.2 mg, 40%). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 9.44 (d, \(J = 8.6\) Hz, 1H), 7.92 (d, \(J = 9.0\) Hz, 1H), 7.74 (d, \(J = 7.9\) Hz, 1H), 7.66-7.60 (m, 1H), 7.45-7.40 (m, 1H), 7.12 (d, \(J = 9.0\) Hz, 1H), 4.73-4.64 (m, 1H), 4.05-3.88 (m, 2H), 3.11-3.01 (m, 1H), 2.73-2.66 (m, 1H), 2.29 (s, 1H). \(^1\)C NMR (DMSO-d\(_6\), 100 MHz): \(\delta\) 193.9, 163.7, 137.9, 131.4, 129.8, 129.2, 129.1, 125.4, 125.0, 119.5, 112.1, 78.9, 62.9, 39.3. HRMS (ESI) \(m/z\) calcd for C\(_{14}\)H:\(_{13}\)O\(_3\) (M+H\(^+\)) \(229.0859\), found 229.0862.
2-(1-hydroxyethyl)chroman-4-one (3ab)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow liquid (36.5 mg, 95%). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.88-7.84 (m, 1H), 7.50-7.43 (m, 1H), 7.04-6.95 (m, 2H), 4.38-4.17 (m, 1.56H), 4.01-3.92 (m, 0.5H), 3.85-3.81 (m, 1H), 2.98-2.80 (m, 1H), 2.69-2.61 (m, 1.47H), 2.49 (s, 0.54H), 1.32 (d, $J$ = 6.5 Hz, 1.46H), 1.27 (d, $J$ = 6.5 Hz, 1.61H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 192.6, 192.1, 161.3, 160.9, 136.2, 136.1, 127.0, 126.9, 121.7, 121.5, 120.93, 120.91, 117.8, 81.5, 81.3, 69.2, 68.4, 39.6, 37.0, 18.5, 17.7. HRMS (ESI) m/z calcd for C$_{11}$H$_{13}$O$_3$ (M+H)$^+$ 193.0859, found 193.0860.

2-(1-hydroxyethyl)-7-methylchroman-4-one (3cb)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow liquid (33.8 mg, 82%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.74-7.72 (m, 1H), 6.82-6.75 (m, 2H), 4.33-4.16 (m, 1H), 4.20-4.19 (m, 1H), 4.18-4.16 (m, 0.54H), 3.98-3.91 (m, 0.49H), 2.92-2.73 (m, 1.48H), 2.65-2.57 (m, 1.56H), 2.32 (d, 3H), 1.30 (d, $J$ = 6.4 Hz, 1.48H), 1.25 (d, $J$ = 6.4 Hz, 1.65H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 192.4, 191.8, 161.3, 161.0, 147.8, 147.7, 128.9, 126.8, 123.0, 122.9, 118.7, 118.6, 117.83, 117.82, 81.5, 81.3, 69.2, 68.4, 39.5, 36.9, 21.9, 18.5, 17.8. HRMS (ESI) m/z calcd for C$_{13}$H$_{16}$O$_3$ (M+H)$^+$ 207.1016, found 207.1018.

7-bromo-2-(1-hydroxyethyl)chroman-4-one (3gb)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow liquid (49.1 mg, 91%). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.70-7.66 (m, 1H), 7.19-7.10 (m, 2H), 4.37-4.24 (m, 1H), 4.20-4.16 (m, 0.55H), 3.98-3.92 (m, 0.5H), 2.95-2.80 (m, 1H), 2.70-2.59 (m, 2H), 1.32 (d, $J$ = 6.5 Hz, 1.47H), 1.25 (d, $J$ = 6.5 Hz, 1.64H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 191.7, 191.3, 161.4, 161.2, 130.5, 130.4, 128.2, 128.1, 125.3, 125.2, 121.1, 121.0, 119.8, 119.7, 81.9, 81.8, 69.0, 68.3, 39.4, 36.8, 18.5, 17.8. HRMS (ESI) m/z calcd for C$_{11}$H$_{13}$BrO$_3$ (M+H)$^+$ 270.9964, found 270.9960.

2-(1-hydroxypropyl)chroman-4-one (3ac)
Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow liquid (31.3 mg, 76%). $^1$H NMR (CDCl$_3$, 300 MHz): δ 7.89-7.86 (m, 1H), 7.51-7.44 (m, 1H), 7.05-6.96 (m, 2H), 4.46-4.35 (m, 1H), 3.98-3.95 (m, 0.54H), 3.67-3.65 (m, 0.48H), 3.04-2.92 (m, 1H), 2.67-2.66 (m, 0.54H), 2.61-2.60 (m, 0.46H), 2.23 (s, 1H), 1.73-1.67 (m, 1H), 1.61-1.51 (m, 1H), 1.08-1.02 (m, 3H). $^{13}$C NMR (CDCl$_3$, 75 MHz): δ 192.7, 192.3, 161.3, 160.1, 136.12, 136.10, 127.0, 121.7, 121.6, 120.9, 117.9, 117.8, 80.4, 79.9, 74.3, 73.9, 39.8, 36.9, 25.8, 24.8, 10.3, 9.9. HRMS (ESI) m/z calc’d for C$_{12}$H$_{13}$O$_3$ (M+H)$^+$ 207.1016, found 207.1018.

2-(1-hydroxypropyl)-7-methoxychroman-4-one (3dc)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 2/1) gave a yellow liquid (34.0 mg, 72%). $^1$H NMR (CDCl$_3$, 300 MHz): δ 7.79-7.75 (m, 1H), 6.57-6.52 (m, 1H), 6.41-6.38 (m, 1H), 4.41-4.30 (m, 1H), 3.94-3.89 (m, 0.2H), 3.80 (d, 3H), 3.67-3.59 (m, 0.8H), 2.95-2.84 (m, 1H), 2.59-2.50 (m, 2H), 1.72-1.61 (m, 1H), 1.56-1.48 (m, 0.41H), 1.05-1.00 (m, 3H). $^{13}$C NMR (CDCl$_3$, 75 MHz): δ 191.4, 191.0, 166.1, 166.0, 163.3, 161.1, 128.7, 114.83, 114.80, 110.1, 109.9, 100.8, 80.8, 80.3, 74.2, 73.8, 55.7, 39.3, 36.6, 25.7, 24.9, 10.3, 9.9. HRMS (ESI) m/z calc’d for C$_{13}$H$_{17}$O$_3$ (M+H)$^+$ 237.1121, found 237.1122.

7-chloro-2-(1-hydroxypropyl)chroman-4-one (3fc)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow liquid (32.2 mg, 67%). $^1$H NMR (CDCl$_3$, 300 MHz): δ 7.79-7.76 (m, 1H), 7.01-6.95 (m, 2H), 4.44-4.35 (m, 1H), 3.98-3.91 (m, 0.21H), 3.68-3.60 (m, 0.82H), 3.02-2.91 (m, 1H), 2.67-2.58 (m, 1H), 2.44-2.36 (m, 1H), 1.74-1.63 (m, 1.64H), 1.57-1.48 (m, 0.42H), 1.06-1.01 (m, 3H). $^{13}$C NMR (CDCl$_3$, 75 MHz): δ 191.6, 191.3, 161.6, 161.4, 141.9, 141.8, 128.2, 122.4, 122.3, 119.5, 118.0, 117.9, 80.9, 80.4, 74.2, 73.7, 39.5, 36.8, 25.8, 24.9, 10.2, 9.9. HRMS (ESI) m/z calc’d for C$_{12}$H$_{14}$ClO$_3$ (M+H)$^+$ 241.0626, found 241.0624.

2-(1-hydroxybutyl)chroman-4-one (3ad)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow liquid (17.6 mg, 40%). $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.87-7.84 (m, 1H), 7.48-7.43 (m, 1H), 7.02-6.94 (m, 2H), 4.41-4.31 (m, 1H), 4.06-4.04 (m, 0.46H), 3.74-3.73 (m, 0.6H), 3.01-2.92 (m, 1H), 2.65-2.60 (m, 1H), 2.41 (s, 1H), 1.69-1.36 (m, 4H), 0.98-0.94 (m, 3H). $^{13}$C NMR (CDCl$_3$, 75 MHz): δ 192.8, 192.4, 161.3, 161.1, 136.1, 136.0, 126.9, 121.6, 121.5, 120.9, 117.9, 117.8, 80.7, 58
Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow liquid (14.0 mg, 30%). $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.87-7.84 (m, 1H), 7.48-7.43 (m, 1H), 7.02-6.94 (m, 2H), 4.41-4.32 (m, 1H), 4.03 (s, 0.5H), 3.72 (s, 0.51H), 3.01-2.92 (m, 1H), 2.65-2.59 (m, 1H), 2.44 (s, 1H), 1.68-1.24 (m, 6H), 0.93-0.89 (m, 3H). $^{13}$C NMR (CDCl$_3$, 75 MHz): δ 192.8, 192.4, 161.3, 161.1, 136.1, 136.0, 126.9, 121.6, 121.5, 120.9, 117.9, 117.8, 80.7, 80.3, 72.9, 72.3, 39.8, 36.9, 32.4, 31.5, 27.9, 27.6, 22.7, 22.6, 14.03, 14.00. HRMS (ESI) m/z calcd for C$_{13}$H$_{17}$O$_3$ (M+H)$^+$ 235.1329, found 235.1330.

2-((1,4-dioxan-2-yl)chroman-4-one (5a)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow liquid (23.4 mg, 50%). $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.87-7.84 (m, 1H), 7.48-7.43 (m, 1H), 7.02-6.94 (m, 2H), 4.46-4.35 (m, 1H), 4.04-4.03 (m, 0.61H), 3.92-3.59 (m, 6H), 3.53-3.48 (m, 0.62H), 3.08-3.00 (m, 0.43H), 2.83-2.81 (m, 1H), 2.59-2.54 (m, 0.43H). $^{13}$C NMR (CDCl$_3$, 75 MHz): δ 191.9, 191.5, 161.0, 160.7, 136.1, 136.0, 126.97, 126.91, 121.7, 121.1, 120.9, 118.1, 117.9, 76.9, 76.8, 75.7, 75.5, 68.2, 67.4, 67.3, 66.7, 66.5, 66.4, 39.1, 38.9. HRMS (ESI) m/z calcd for C$_{13}$H$_{15}$O$_3$ (M+H)$^+$ 235.0965, found 235.0966.

2-(tetrahydrofuran-2-yl)chroman-4-one (5b)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow liquid (37.5 mg, 86%). $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.83 (d, $J$ = 7.8 Hz, 1H), 7.45-7.40 (m, 1H), 7.02-6.94 (m, 2H), 4.39-4.32 (m, 1H), 4.15-4.10 (m, 0.53H), 4.09-4.04 (m, 0.48H), 3.92-3.77 (m, 2H), 2.90-2.59 (m, 2H), 2.10-1.81 (m, 4H). $^{13}$C NMR (CDCl$_3$, 75 MHz): δ 192.1, 192.0, 161.4, 161.3, 136.0, 135.9, 126.9, 126.8, 121.3, 120.0, 120.9, 118.1, 117.9, 79.8, 79.6, 79.4, 68.9, 68.8, 39.8, 39.0, 27.6, 27.5, 25.9, 25.7. HRMS (ESI) m/z calcd for C$_{13}$H$_{13}$O$_3$ (M+H)$^+$ 219.1016, found 219.1018.

2-(tetrahydro-2H-pyran-2-yl)chroman-4-one (5c)

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Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow liquid (33.9 mg, 73%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.86-7.83 (m, 1H), 7.46-7.42 (m, 1H), 7.03-6.96 (m, 2H), 4.38-4.29 (m, 1H), 4.10-4.02 (m, 1H), 3.64-3.59 (m, 0.66H), 3.52-3.44 (m, 1.42H), 3.02-2.84 (m, 1H), 2.76-2.71 (m, 0.63H), 2.61-2.56 (m, 0.40H), 1.96-1.39 (m, 6H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 192.7, 192.6, 161.5, 161.4, 135.9, 126.9, 126.8, 121.3, 121.1, 120.9, 118.2, 118.0, 80.1, 79.6, 78.2, 78.1, 77.5, 77.1, 76.7, 69.1, 68.8, 39.3, 38.5, 27.3, 26.9, 25.9, 25.8, 23.2, 23.0. HRMS (ESI) $m/z$ calcd for C$_{16}$H$_{12}$O$_3$ (M+H)$^+$ 233.1172, found 233.1175.

2-(1,3-dioxolan-2-yl)chroman-4-one (5d)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow liquid (17.6 mg, 40%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.88-7.85 (m, 1H), 7.49-7.45 (m, 1H), 7.04-6.97 (m, 2H), 5.20 (d, $J$ = 3.5 Hz, 1H), 4.54-4.51 (m, 1H), 4.07-3.95 (m, 4H), 2.92-2.85 (m, 1H), 2.79-2.72 (m, 1H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 192.4, 160.7, 136.1, 126.8, 121.6, 121.1, 117.9, 103.0, 77.6, 65.8, 65.5, 37.1. HRMS (ESI) $m/z$ calcd for C$_{12}$H$_{13}$O$_4$ (M+H)$^+$ 221.0808, found 221.0806.

2-(1-ethoxyethyl)chroman-4-one (5e)

Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave a yellow liquid (22.0 mg, 50%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.86-7.83 (m, 1H), 7.47-7.42 (m, 1H), 6.99-6.96 (m, 2H), 4.44-4.38 (m, 0.38H), 4.34-4.29 (m, 0.61H), 3.75-3.61 (m, 2H), 3.58-3.46 (m, 1H), 2.96-2.74 (m, 1.66H), 2.64-2.59 (m, 0.41H), 1.32-1.25 (m, 3H), 1.21-1.16 (m, 3H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 192.8, 192.6, 161.5, 161.3, 135.9, 135.8, 126.9, 126.8, 121.3, 121.1, 121.0, 118.1, 117.9, 80.6, 79.8, 75.9, 75.5, 65.4, 65.2, 38.9, 38.4, 16.2, 15.5, 15.48, 15.40. HRMS (ESI) $m/z$ calcd for C$_{13}$H$_{17}$O$_3$ (M+H)$^+$ 221.1172, found 221.1171.
4. Copies of $^1$H NMR and $^{13}$C NMR spectra of the products