Electronic Supplementary Information

Straightforward synthesis of functionalized chroman-4-ones through cascade radical cyclization-coupling of 2-(allyloxy)arylaldehydes

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General Information:

All reagents purchased from commercial sources were used as received. 2-Hydroxyarylaldehyde derivatives and 3-bromoprop-1-ene were purchased from Adamas-beta. The silica gel for column chromatography was supplied as 300–400 meshes. The $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AVANCE III spectrometer and are referenced to the residual solvent signals (7.26 ppm for $^1$H and 77.0 ppm for $^{13}$C in CDCl$_3$). The HRMS spectra were recorded on a Bruker micrOTOF Q II spectrometer.

General Procedure and Data of 2-Allyloxyarylaldehyde Derivatives:

To a 100 mL round-bottomed flask with a stir bar was added 2-hydroxyarylaldehyde (5 mmol), DMF (15 mL), then was added potassium carbonate (828 mg, 6 mmol), followed by the dropwise addition of allyl bromide (726 mg, 6 mmol). The reaction mixture was then stirred for 12 h at room temperature, poured into brine and extracted with EtOAc. The combined extracts were dried over MgSO$_4$, filtered, and evaporated. The residue was purified by column chromatography (petroleum ether/EtOAc) to afford the desired 2-(allyloxy)arylaldehyde.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.54 (s, 1 H), 7.84 (dd, $J$ = 7.8, 1.8 Hz, 1 H), 7.57–7.49 (m, 1 H), 7.02 (d, $J$ = 7.5 Hz, 1 H), 6.97 (d, $J$ = 8.4 Hz, 1 H), 6.15–6.03 (m, 1 H), 5.45 (dd, $J$ = 17.3, 1.8 Hz, 1 H), 4.66 (d, $J$ = 4.9 Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 189.7, 160.9, 135.8, 132.4, 128.4, 125.1, 120.8, 118.1, 112.8, 69.2.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.50 (s, 1 H), 7.63 (d, $J$ = 2.4 Hz, 1 H), 7.33 (dd, $J$ = 8.5, 2.4 Hz, 1 H), 6.87 (d, $J$ = 8.5 Hz, 1 H), 6.02–6.11 (m, 1 H), 5.46–5.41 (m, 1 H), 5.35–5.30 (m, 1 H), 4.62 (dt, $J$ = 5.2, 1.7 Hz, 2 H), 2.30 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 189.8, 159.0, 136.4, 132.5, 130.1, 128.3, 124.6, 117.8, 112.8, 69.2, 20.2.
$^1$H NMR (400 MHz, CDCl$_3$) δ 10.33 (s, 1 H), 7.79 (dd, $J = 8.7, 0.8$ Hz, 1 H), 6.52 (dd, $J = 8.7, 2.2$ Hz, 1 H), 6.42 (d, $J = 2.2$ Hz, 1 H), 6.09–6.00 (m, 1 H), 5.46–5.41 (m, 1 H), 5.34–5.30 (m, 1 H), 4.65–4.55 (m, 2 H), 3.84 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 188.2, 166.0, 162.6, 132.2, 130.4, 119.1, 118.0, 106.0, 98.9, 69.1, 55.5.

![Diagram of molecule 1d]

$^1$H NMR (400 MHz, CDCl$_3$) δ 10.29 (s, 1 H), 7.67 (dd, $J = 34.5, 2.6$ Hz, 2 H), 6.14–6.05 (m, 1 H), 5.55–5.50 (m, 1 H), 5.34–5.31 (m, 1 H), 4.48 (dt, $J = 5.0, 1.7$ Hz, 2 H), 1.43 (s, 9 H), 1.32 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 190.7, 159.7, 146.4, 143.0, 132.8, 130.8, 129.3, 123.8, 117.3, 79.2, 35.3, 34.7, 31.3, 30.8.

![Diagram of molecule 1e]

$^1$H NMR (400 MHz, CDCl$_3$) δ 10.44 (s, 1 H), 7.92 (d, $J = 2.6$ Hz, 1 H), 7.60 (dd, $J = 8.8, 2.6$ Hz, 1 H), 6.88 (d, $J = 8.9$ Hz, 1 H), 6.10–6.0 (m 1 H), 5.47–5.41 (m, 1 H), 5.37–5.33 (m, 1 H), 4.65 (dt, $J = 5.3, 1.6$ Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 188.3, 159.8, 138.2, 131.9, 131.0, 126.3, 118.5, 114.9, 113.7, 69.5.

![Diagram of molecule 1f]

$^1$H NMR (400 MHz, CDCl$_3$) δ 10.42 (s, 1 H), 7.74 (t, $J = 2.3$ Hz, 1 H), 7.52–7.38 (m, 1 H), 6.91 (d, $J = 8.9$ Hz, 1 H), 6.08–5.99 (m, 1 H), 5.50–5.30 (m, 2 H), 4.63 (d, $J = 5.1$ Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 188.3, 159.3, 135.2, 131.8, 127.8, 126.4, 125.8, 118.4, 114.5, 69.5.

![Diagram of molecule 1g]

$^1$H NMR (400 MHz, CDCl$_3$) δ 10.29 (s, 1 H), 7.71 (d, $J = 2.6$ Hz, 1 H), 7.63 (d, $J = 2.7$ Hz, 1 H), 6.17–6.01 (m, 1 H), 5.43–5.32 (m, 2H), 4.63 (dt, $J = 6.1, 1.2$ Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 188.0, 156.2, 135.7, 131.7, 130.5, 130.0, 126.6, 120.4, 75.6, 66.4.

![Diagram of molecule 1h]
**Table S1 Solvent Screening:**

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<td>DCM:H₂O = 1:1</td>
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*a All reactions were carried out on 1a (0.3 mmol), 2a (1.2 mmol), AgNO₃ (0.06 mmol), K₂S₂O₈ (1.2 mmol) in 3 mL solvent for 5 h.
General Procedure and Data of Phosphonate Chroman-4-ones:

To a 25 mL Schlenk tube equipped with a stir bar was added 2-allyloxyarylaldehyde derivatives 1 (0.3 mmol), 2 (1.2 mmol) and DMSO (3 mL), followed by AgSbF$_6$ (21 mg, 0.06 mmol), K$_2$S$_2$O$_8$ (243 mg, 0.9 mmol). The reaction mixture was stirred under argon atmosphere at 35 ºC for 5 h, cooled to room temperature, poured into brine and extracted with EtOAc. The combined extracts were dried over MgSO$_4$, filtered, and evaporated. The residue was purified by column chromatography (petroleum ether/EtOAc) to afford 3.

1$^H$ NMR (400 MHz, CDCl$_3$) δ 7.88 (d, $J$ = 7.8 Hz, 1 H), 7.49–7.46 (m, 1 H), 7.02 (t, $J$ = 7.4 Hz, 1 H), 4.83 (dd, $J$ = 11.3, 4.3 Hz, 1 H), 4.24 (t, $J$ = 11.7 Hz, 1 H), 4.18–4.06 (m, 4 H), 3.30–3.03 (m, 1 H), 2.64 (t, $J$ = 17.5 Hz, 1 H), 1.72–1.56 (m, 1 H), 1.33 (t, $J$ = 7.0 Hz, 6 H);

13$^C$ NMR (100 MHz, CDCl$_3$) δ 192.1 (d, $J_{CP}$ = 15.3 Hz), 161.7, 136.1, 127.5, 121.5, 120.1, 117.8, 70.3 (d, $J_{CP}$ = 2.2 Hz), 62.0 (dd, $J_{CP}$ = 13.8, 6.5 Hz), 40.9 (d, $J_{CP}$ = 3.3 Hz), 21.2 (d, $J_{CP}$ = 145.6 Hz), 16.4 (d, $J_{CP}$ = 6.1 Hz);

31$^P$ NMR (162 MHz, CDCl$_3$) δ 29.39; HRMS (ESI) calcd for C$_{14}$H$_{19}$NaO$_5$P [M+Na]$^+$ 321.0862, found 321.0873.

1$^H$ NMR (400 MHz, CDCl$_3$) δ 7.87 (dd, $J$ = 7.9, 1.8 Hz, 1 H), 7.47 (ddd, $J$ = 8.7, 7.2, 1.8 Hz, 1 H), 7.05–6.99 (m, 1 H), 6.96 (dd, $J$ = 8.4, 1.0 Hz, 1 H), 4.79 (dd, $J$ = 11.4, 5.2 Hz, 1 H), 4.23 (t, $J$ = 11.6 Hz, 1 H), 3.77 (dd, $J$ = 10.9, 4.1 Hz, 6 H), 3.22–3.10 (m, 1 H), 2.65 (ddd, $J$ = 19.1, 15.9, 3.1 Hz, 1 H), 1.67 (ddd, $J$ = 17.2, 15.9, 10.1 Hz, 1 H);

13$^C$ NMR (100 MHz, CDCl$_3$) δ 191.9 (d, $J_{CP}$ = 14.9 Hz), 161.6, 136.1, 127.5, 121.5, 120.0, 117.8, 70.3 (d, $J_{CP}$ = 2.8 Hz), 52.6 (dd, $J_{CP}$ = 18.4, 6.6 Hz), 40.7 (d, $J_{CP}$ = 3.4 Hz), 20.2 (d, $J_{CP}$ = 145.8 Hz);

31$^P$ NMR (162 MHz, CDCl$_3$) δ 32.09; HRMS (ESI) calcd for C$_{12}$H$_{16}$O$_5$P [M+H]$^+$ 271.0730, found 271.0732.

1$^H$ NMR (400 MHz, CDCl$_3$) δ 7.86 (dd, $J$ = 7.9, 1.7 Hz, 1 H), 7.45 (ddd, $J$ = 8.7, 7.1, 1.8 Hz, 1 H), 7.06–6.97 (m, 1 H), 6.95 (dd, $J$ = 8.4, 1.0 Hz, 1 H), 4.85 (dd, $J$ = 11.4, 5.2 Hz, 1 H), 4.76–4.67 (m, 2 H), 4.21 (t, $J$ = 11.7 Hz, 1 H), 3.17–3.06 (m, 1 H), 2.61 (ddd, $J$ = 18.9, 15.8, 2.6 Hz, 1 H), 1.57 (ddd, $J$ = 17.0, 15.8, 10.7 Hz, 1 H), 1.40–1.25 (m, 12 H);

13$^C$ NMR (100 MHz,
CDCl\textsubscript{3}) $\delta$ 192.0 (d, $J_{CP} = 15.5$ Hz), 161.7, 136.1, 127.5, 121.5, 120.1, 117.8, 71.9 (dd, $J_{CP} = 10.5, 7.0$ Hz), 70.4 (d, $J_{CP} = 2.2$ Hz), 40.9 (d, $J_{CP} = 3.3$ Hz), 20.9 (d, $J_{CP} = 145.9$ Hz), 18.7; $^{31}$P NMR (162 MHz, CDCl\textsubscript{3}) $\delta$ 27.32. HRMS (ESI) calcd for C\textsubscript{16}H\textsubscript{24}O\textsubscript{5}P [M+H]$^+$ 327.1356, found 327.1365.

$^1$H NMR (400 MHz, CDCl\textsubscript{3}) $\delta$ 7.90–7.84 (m, 1 H), 7.47 (td, $J = 7.8, 2.2$ Hz, 1 H), 7.01 (t, $J = 7.5$ Hz, 1 H), 6.98–6.88 (m, 1 H), 4.82 (ddd, $J = 10.5, 5.0, 2.4$ Hz, 1 H), 4.23 (tt, $J = 11.7, 2.3$ Hz, 1 H), 4.12–3.98 (m, 4 H), 3.17–3.11 (m, 1 H), 2.64 (ddd, $J = 18.8, 16.0, 2.6$ Hz, 1 H), 1.75–1.55 (m, 5 H), 1.44–1.34 (m, 4 H), 0.93 (t, $J = 7.3, 3.6$ Hz, 6 H); $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}) $\delta$ 192.0 (d, $J_{CP} = 14.9$ Hz), 161.7, 136.1, 127.5, 121.5, 120.1, 117.8, 70.4 (d, $J_{CP} = 2.2$ Hz), 65.7 (dd, $J_{CP} = 12.8, 6.7$ Hz), 40.9 (d, $J_{CP} = 3.3$ Hz), 32.5 (dd, $J_{CP} = 6.6, 4.8$ Hz), 41.05 (d, $J_{CP} = 16.0$ Hz), 161.7, 136.0, 127.4, 121.4, 120.1, 117.8, 70.6 (dd, $J_{CP} = 6.6, 4.8$ Hz), 70.3 (d, $J_{CP} = 1.9$ Hz), 40.7 (d, $J_{CP} = 3.5$ Hz), 24.04, 24.0, 23.96, 22.40 (d, $J_{CP} = 146.7$ Hz); $^{31}$P NMR (162 MHz, CDCl\textsubscript{3}) $\delta$ 29.37; HRMS (ESI) calcd for C\textsubscript{18}H\textsubscript{27}NaO\textsubscript{5}P [M+Na]$^+$ 377.1488, found 377.1507.

$^1$H NMR (400 MHz, CDCl\textsubscript{3}) $\delta$ 7.88 (dd, $J = 7.9, 1.8$ Hz, 1 H), 7.47 (dddd, $J = 8.7, 7.2, 1.8$ Hz, 1 H), 7.01 (dddd, $J = 8.0, 7.2, 1.1$ Hz, 1 H), 6.97 (dd, $J = 8.4, 1.0$ Hz, 1 H), 4.85 (dd, $J = 11.4, 5.2$ Hz, 1 H), 4.24 (t, $J = 11.7$ Hz, 1 H), 3.93–3.74 (m, 4 H), 3.21–3.10 (m, 1 H), 2.67 (dddd, $J = 18.9, 15.8, 2.9$ Hz, 1 H), 1.99–1.88 (m, 2 H), 1.67 (dddd, $J = 17.1, 15.9, 10.5$ Hz, 1 H), 1.0–0.88 (m, 12 H); $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}) $\delta$ 192.1 (d, $J_{CP} = 16.0$ Hz), 161.7, 136.0, 127.4, 121.4, 120.1, 117.8, 70.6 (dd, $J_{CP} = 6.6, 4.8$ Hz), 70.3 (d, $J_{CP} = 1.9$ Hz), 40.7 (d, $J_{CP} = 3.5$ Hz), 24.04, 24.0, 23.96, 22.40 (d, $J_{CP} = 146.7$ Hz); $^{31}$P NMR (162 MHz, CDCl\textsubscript{3}) $\delta$ 29.24; HRMS (ESI) calcd for C\textsubscript{18}H\textsubscript{27}NaO\textsubscript{5}P [M+Na]$^+$ 377.1488, found 377.1507.
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.65 (d, $J = 1.5$ Hz, 1 H), 7.28 (dd, $J = 8.5$, 2.2 Hz, 1 H), 6.86 (d, $J = 8.5$ Hz, 1 H), 4.78 (dd, $J = 11.4$, 5.1 Hz, 1 H), 4.25–4.06 (m, 5 H), 3.19–3.06 (m, 1 H), 2.63 (ddd, $J = 18.9$, 15.9, 2.9 Hz, 1 H), 2.29 (s, 3 H), 1.64 (ddd, $J = 16.9$, 16.0, 10.4 Hz, 1 H), 1.33 (td, $J = 7.1$, 1.8 Hz, 6 H); $^13$C NMR (100 MHz, CDCl$_3$) δ 192.3 (d, $J_{CP} = 15.4$ Hz), 159.7, 137.2, 130.9, 127.0, 119.7, 117.6, 70.3 (d, $J_{CP} = 2.3$ Hz), 61.97 (dd, $J_{CP} = 14.6$, 6.5 Hz), 40.9 (d, $J_{CP} = 3.3$ Hz), 21.2 (d, $J_{CP} = 145.6$ Hz), 20.3, 16.4 (d, $J_{CP} = 5.2$ Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) δ 29.53; HRMS (ESI) calcd for C$_{15}$H$_{22}$O$_5$P [M+H]$^+$ 313.1199, found 313.1208.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.65 (s, 1 H), 7.31–7.24 (m, 1 H), 6.86 (d, $J = 8.5$ Hz, 1 H), 4.78 (d, $J = 11.4$, 5.1 Hz, 1 H), 4.19 (t, $J = 11.6$ Hz, 1 H), 4.10–3.92 (m, 4 H), 3.16–3.06 (m, 1 H), 2.67–2.58 (m, 1 H), 2.28 (s, 3 H), 1.43–1.33 (m, 4 H), 0.92 (t, $J = 7.5$ Hz, 6 H); $^13$C NMR (100 MHz, CDCl$_3$) δ 192.2 (d, $J_{CP} = 15.4$ Hz), 159.8, 137.1, 130.9, 127.0, 119.7, 117.6, 70.4 (d, $J_{CP} = 2.2$ Hz), 65.7 (dd, $J_{CP} = 13.5$, 6.7 Hz), 40.9 (d, $J_{CP} = 3.3$ Hz), 32.5 (d, $J_{CP} = 6.2$, 1.7 Hz), 21.8, 20.4, 18.7, 13.6; $^{31}$P NMR (162 MHz, CDCl$_3$) δ 29.52; HRMS (ESI) calcd for C$_{19}$H$_{30}$O$_6$P [M+Na]$^+$ 369.1825, found 369.1837.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.82 (d, $J = 8.8$ Hz, 1 H), 6.59 (dd, $J = 8.9$, 2.4 Hz, 1 H), 6.41 (d, $J = 2.3$ Hz, 1 H), 4.83 (dd, $J = 11.3$, 5.1 Hz, 1 H), 4.25 (t, $J = 11.5$ Hz, 1 H), 4.22–4.06 (m, 4 H), 3.84 (s, 3 H), 3.18–3.04 (m, 1 H), 2.66 (ddd, $J = 18.8$, 15.8, 2.8 Hz, 1 H), 1.73–1.58 (m, 1 H), 1.35 (td, $J = 7.0$, 1.7 Hz, 6 H); $^13$C NMR (100 MHz, CDCl$_3$) δ 190.6 (d, $J_{CP} = 15.4$ Hz), 159.8, 137.1, 130.9, 127.0, 119.7, 117.6, 70.4 (d, $J_{CP} = 2.2$ Hz), 65.7 (dd, $J_{CP} = 13.5$, 6.7 Hz), 40.9 (d, $J_{CP} = 3.3$ Hz), 32.5 (d, $J_{CP} = 6.2$, 1.7 Hz), 21.8, 20.4, 18.7, 13.6; $^{31}$P NMR (162 MHz, CDCl$_3$) δ 29.64; HRMS (ESI) calcd for C$_{15}$H$_{22}$NaO$_6$P [M+Na]$^+$ 351.0968, found 351.0962.
H), 1.41–1.31 (m, 4 H), 0.89 (t, J = 7.4 Hz, 6 H); 13C NMR (100 MHz, CDCl₃) δ 190.6 (d, JCP = 15.6 Hz), 166.0, 163.7, 129.2, 164.9 (d, JCP = 237.0 Hz), 110.2, 100.6, 70.7 (d, JCP = 2.1 Hz), 65.7 (dd, JCP = 13.0, 6.7 Hz), 55.6, 40.5 (d, JCP = 3.3 Hz), 32.5 (dd, JCP = 6.2, 1.5 Hz), 21.1 (d, JCP = 145.4 Hz), 18.7, 13.6; 31P NMR (162 MHz, CDCl₃) δ 29.65; HRMS (ESI) calcd for C₁₉H₃₀O₆P [M+H]+ 385.1775, found 385.1788.

1H NMR (400 MHz, CDCl₃) δ 7.77 (d, J = 2.5 Hz, 1 H), 7.52 (d, J = 2.6 Hz, 1 H), 4.84 (dd, J = 11.2, 5.1 Hz, 1 H), 4.2–4.09 (m, 5 H), 3.22–2.98 (m, 1 H), 2.64 (ddd, J = 18.9, 15.8, 2.9 Hz, 1 H), 1.64 (ddd, J = 16.9, 15.8, 10.5 Hz, 1 H), 1.39 (s, 9 H), 1.33 (td, J = 7.1, 2.4 Hz, 6 H), 1.28 (s, 9 H); 13C NMR (100 MHz, CDCl₃) δ 193.0 (d, JCP = 15.4 Hz), 158.8, 143.4, 138.3, 130.8, 121.4, 120.1 (d, JCP = 1.4 Hz), 69.8 (d, JCP = 2.3 Hz), 61.9 (dd, JCP = 16.1, 6.5 Hz), 40.7 (d, JCP = 3.3 Hz), 35.0, 34.4, 31.2, 29.6, 21.4 (d, JCP = 145.2 Hz), 16.4 (dd, JCP = 6.1, 1.7 Hz); 31P NMR (162 MHz, CDCl₃) δ 29.71; HRMS (ESI) calcd for C₂₂H₃₅NaO₅P [M+Na]+ 433.2114, found 433.2115.

1H NMR (400 MHz, CDCl₃) δ 7.78 (d, J = 2.5 Hz, 1 H), 7.54 (d, J = 2.6 Hz, 1 H), 4.85 (dd, J = 11.3, 5.1 Hz, 1 H), 4.21 (t, J = 11.4 Hz, 1 H), 4.13–4.02 (m, 4 H), 3.20–3.00 (m, 1 H), 1.71–1.63 (ddd, J = 18.8, 15.8, 2.8 Hz, 1 H), 1.67 (dtt, J = 15.2, 6.5, 3.1 Hz, 5 H), 1.46–1.39 (m, 4 H), 1.39 (s, 9 H), 1.30 (s, 9 H), 0.94 (t, J = 7.4 Hz, 6 H); 13C NMR (100 MHz, CDCl₃) δ 193.1 (d, JCP = 15.6 Hz), 158.9, 143.4, 138.3, 130.8, 121.5, 120.1, 69.9 (d, JCP = 2.1 Hz), 65.7 (dd, JCP = 13.8, 6.7 Hz), 40.8 (d, JCP = 3.2 Hz), 35.1, 34.5, 32.5 (dd, JCP = 6.2, 2.2 Hz), 31.3, 29.6, 21.3 (d, JCP = 144.9 Hz), 18.8, 13.6; 31P NMR (162 MHz, CDCl₃) δ 29.71; HRMS (ESI) calcd for C₂₆H₄₄O₅P [M+H]+ 467.2921, found 467.2921.

1H NMR (400 MHz, CDCl₃) δ 7.95 (d, J = 2.4 Hz, 1 H), 7.53 (dd, J = 8.9, 2.5 Hz, 1 H), 6.86 (d, J = 8.9 Hz, 1 H), 4.83 (dd, J = 11.5, 5.2 Hz, 1 H), 4.22 (t, J = 11.7 Hz, 1 H), 4.18–4.05 (m, 4 H), 3.19–3.07 (m, 1 H), 2.60 (ddd, J = 18.9, 15.9, 2.8 Hz, 1 H), 1.63 (td, J = 16.5, 10.3 Hz, 1 H), 1.32 (td, J = 7.0, 1.0 Hz, 6 H); 13C NMR (100 MHz, CDCl₃) δ 190.9 (d, JCP = 15.5 Hz), 160.5, 138.7, 129.8, 121.3, 119.9, 114.1, 70.4 (d, JCP = 2.2 Hz), 62.0 (dd, JCP = 13.3, 6.5 Hz),
40.7 (d, $J_{CP} = 3.2$ Hz), 21.1 (d, $J_{CP} = 145.8$ Hz), 16.4 (d, $J_{CP} = 5.9$ Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 28.95; HRMS (ESI) calcd for C$_{14}$H$_{18}$BrNaO$_5$P $[\text{M+Na}]^+$ 398.9967, found 398.9974.

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J = 2.5$ Hz, 1 H), 7.54 (dd, $J = 8.8, 2.5$ Hz, 1 H), 6.87 (d, $J = 8.8$ Hz, 1 H), 4.80 (dd, $J = 11.6, 5.2$ Hz, 1 H), 4.22 (t, $J = 11.7$ Hz, 1 H), 3.78 (d, $J = 3.8$ Hz, 3 H), 3.76 (d, $J = 3.9$ Hz, 3 H), 3.23–3.06 (m, 1 H), 2.61 (t, $J = 16.5$ Hz, 1 H), 1.71 (d, $J = 10.1$ Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 190.7 (d, $J_{CP} = 15.0$ Hz), 160.5, 138.7, 129.8, 121.3, 119.9, 114.2, 70.4, 52.7 (dd, $J_{CP} = 17.6, 6.6$ Hz), 40.5 (d, $J_{CP} = 2.7$ Hz), 20.1 (d, $J_{CP} = 145.4$ Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 31.74; HRMS (ESI) calcd for C$_{12}$H$_{14}$BrNaO$_5$P $[\text{M+Na}]^+$ 370.9654, found 370.9673.

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95 (d, $J = 2.5$ Hz, 1 H), 7.52 (dd, $J = 8.9, 2.6$ Hz, 1 H), 6.86 (d, $J = 8.8$ Hz, 1 H), 4.85 (dd, $J = 11.5, 5.3$ Hz, 1 H), 4.79–4.63 (m, 2 H), 4.20 (t, $J = 11.7$ Hz, 1 H), 3.16–3.04 (m, 1 H), 2.57 (ddd, $J = 18.9, 15.8, 2.7$ Hz, 1 H), 1.62–1.51 (m, 1 H), 1.38–1.25 (m, 12 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 191.0 (d, $J_{CP} = 16.1$ Hz), 160.6, 138.6, 129.8, 121.4 (d, $J_{CP} = 1.5$ Hz), 119.9, 114.1, 70.7 (dd, $J = 6.7, 4.0$ Hz), 70.4 (d, $J = 1.9$ Hz), 40.9 (d, $J = 3.4$ Hz), 24.0 (d, $J = 3.9$ Hz), 22.4 (d, $J = 146.8$ Hz); HRMS (ESI) calcd for C$_{16}$H$_{23}$BrO$_5$P $[\text{M+H}]^+$ 405.0461, found 405.0451.

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J = 2.5$ Hz, 1 H), 7.53 (dd, $J = 8.8, 2.5$ Hz, 1 H), 6.87 (d, $J = 8.8$ Hz, 1 H), 4.83 (dd, $J = 11.5, 5.2$ Hz, 1 H), 4.22 (t, $J = 11.7$ Hz, 1 H), 4.09–3.99 (m, 4 H), 3.18–3.07 (m, 1 H), 2.60 (ddd, $J = 18.9, 15.8, 2.9$ Hz, 1 H), 1.70–1.60 (m, 5 H), 1.38 (hd, $J = 7.3, 1.4$ Hz, 4 H), 0.92 (t, $J = 7.4$ Hz, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 190.9 (d, $J_{CP} = 15.6$ Hz), 160.6, 138.7, 129.8, 121.3 (d, $J_{CP} = 1.5$ Hz), 119.9, 114.1, 70.4 (d, $J_{CP} = 2.4$ Hz), 65.8 (dd, $J_{CP} = 12.4, 6.7$ Hz), 40.7 (d, $J_{CP} = 3.3$ Hz), 32.5 (dd, $J_{CP} = 6.2, 1.4$ Hz), 21.0 (d, $J_{CP} = 145.8$ Hz), 18.7, 13.6; $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 28.95; HRMS (ESI) calcd for C$_{18}$H$_{26}$BrNaO$_5$P $[\text{M+Na}]^+$ 455.0593, found 455.0602.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J = 2.5$ Hz, 1 H), 7.53 (dd, $J = 8.8$, 2.6 Hz, 1 H), 6.87 (d, $J = 8.9$ Hz, 1 H), 4.84 (dd, $J = 11.5$, 5.2 Hz, 1 H), 4.22 (t, $J = 11.8$ Hz, 1 H), 3.87–3.74 (m, 4 H), 3.18–3.09 (m, 1 H), 2.63 (dd, $J = 18.9$, 15.8, 2.9 Hz, 1 H), 1.96–1.88 (m, 2 H), 1.65 (ddd, $J = 17.1$, 15.8, 10.4 Hz, 1 H), 0.93 (d, $J = 1.4$ Hz, 6 H), 0.92 (d, $J = 1.4$ Hz, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 190.8 (d, $J_{CP} = 15.6$ Hz), 160.6, 138.6, 129.8, 121.3 (d, $J_{CP} = 1.6$ Hz), 119.9, 114.1, 71.9 (dd, $J_{CP} = 10.1$, 6.9 Hz), 70.4 (d, $J_{CP} = 2.3$ Hz), 40.7 (d, $J_{CP} = 3.3$ Hz), 29.2 (dd, $J_{CP} = 6.4$, 2.4 Hz), 20.8 (d, $J_{CP} = 146.0$ Hz), 18.7 (d, $J_{CP} = 1.2$ Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 28.79; HRMS (ESI) calcd for C$_{18}$H$_{28}$BrNaO$_5$P [M+Na]$^+$ 455.0593, found 455.0615.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J = 2.5$ Hz, 1 H), 7.53 (dd, $J = 8.8$, 2.5 Hz, 1 H), 6.87 (d, $J = 8.8$ Hz, 1 H), 4.83 (dd, $J = 11.5$, 5.2 Hz, 1 H), 4.22 (t, $J = 11.7$ Hz, 1 H), 4.09–3.99 (m, 4 H), 3.18–3.07 (m, 1 H), 2.60 (ddd, $J = 18.9$, 15.8, 2.9 Hz, 1 H), 1.70–1.60 (m, 5 H), 1.38 (hd, $J = 7.3$, 1.4 Hz, 4 H), 0.92 (t, $J = 7.4$ Hz, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 191.0 (d, $J_{CP} = 15.5$ Hz), 160.6, 138.7, 129.8, 121.3 (d, $J_{CP} = 1.5$ Hz), 119.9, 114.1, 70.4 (d, $J_{CP} = 2.4$ Hz), 65.8 (dd, $J_{CP} = 12.4$, 6.7 Hz), 40.7 (d, $J_{CP} = 3.3$ Hz), 32.5 (dd, $J_{CP} = 6.2$, 1.4 Hz), 21.0 (d, $J_{CP} = 145.8$ Hz), 18.7, 13.6; $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 28.95; HRMS (ESI) calcd for C$_{18}$H$_{27}$ClNaO$_5$P [M+Na]$^+$ 355.0473, found 355.0486.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J = 2.6$ Hz, 1 H), 7.41 (dd, $J = 8.9$, 2.7 Hz, 1 H), 6.94 (d, $J = 8.8$ Hz, 1 H), 4.84 (dd, $J = 11.5$, 5.2 Hz, 1 H), 4.24 (t, $J = 11.8$ Hz, 1 H), 4.20–4.07 (m, 4 H), 3.22–3.08 (m, 1 H), 2.70–2.55 (m, 1 H), 1.74–1.59 (m, 5 H), 1.47–1.34 (m, 4 H), 0.93 (t, $J = 7.4$ Hz, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 191.0 (d, $J_{CP} = 15.4$ Hz), 160.1, 135.9, 127.1, 126.8, 120.9 (d, $J_{CP} = 1.5$ Hz), 119.6, 70.5 (d, $J_{CP} = 2.4$ Hz), 62.0 (dd, $J_{CP} = 13.2$, 6.6 Hz), 40.8 (d, $J_{CP} = 3.3$ Hz), 21.2 (d, $J_{CP} = 145.9$ Hz), 16.4 (d, $J_{CP} = 6.3$ Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 28.97; HRMS (ESI) calcd for C$_{14}$H$_{18}$ClNaO$_5$P [M+Na]$^+$ 355.0473, found 355.0486.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 (t, $J = 2.1$ Hz, 1 H), 7.41 (ddd, $J = 8.9$, 2.8, 1.4 Hz, 1 H), 6.94 (dd, $J = 8.8$, 1.2 Hz, 1 H), 4.84 (dd, $J = 11.4$, 5.2 Hz, 1 H), 4.23 (t, $J = 11.7$ Hz, 1 H), 4.15–3.99 (m, 4 H), 3.22–3.08 (m, 1 H), 2.70–2.55 (m, 1 H), 1.74–1.59 (m, 5 H), 1.47–1.34 (m, 4 H), 0.93 (t, $J = 7.4$ Hz, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 191.0 (d, $J = 15.5$ Hz), 160.1,
135.9, 127.0, 126.7, 120.9 (d, \(J_{CP} = 1.4\) Hz), 119.6, 70.5 (d, \(J_{CP} = 2.3\) Hz), 65.8 (dd, \(J_{CP} = 12.4, 6.7\) Hz), 40.8 (d, \(J_{CP} = 3.2\) Hz), 32.5 (dd, \(J_{CP} = 6.2, 1.5\) Hz), 21.0 (d, \(J_{CP} = 145.8\) Hz), 18.7, 13.6; \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta = 28.98\); HRMS (ESI) calcd for C\(_{18}\)H\(_{27}\)ClO\(_5\)P [M+H]\(^+\) 389.1279, found 389.1291.

![Diagram 3ga](image)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.83\) (t, \(J = 2.1\) Hz, 1 H), 7.41 (ddd, \(J = 8.9, 2.8, 1.4\) Hz, 1 H), 6.94 (dd, \(J = 8.8, 1.2\) Hz, 1 H), 4.84 (dd, \(J = 11.4, 5.2\) Hz, 1 H), 4.23 (t, \(J = 11.7\) Hz, 1 H), 4.15–3.99 (m, 4 H), 3.22–3.08 (m, 1 H), 2.70–2.55 (m, 1 H), 1.74–1.59 (m, 5 H), 1.47–1.34 (m, 4 H), 0.93 (t, \(J = 7.4\) Hz, 6 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 191.0\) (d, \(J_{CP} = 15.5\) Hz), 160.1, 135.9, 127.0, 126.7, 120.9 (d, \(J_{CP} = 1.4\) Hz), 119.6, 70.5 (d, \(J_{CP} = 2.3\) Hz), 65.8 (dd, \(J_{CP} = 12.4, 6.7\) Hz), 40.8 (d, \(J_{CP} = 3.2\) Hz), 32.5 (dd, \(J_{CP} = 6.2, 1.5\) Hz), 21.0 (d, \(J_{CP} = 145.8\) Hz), 18.7, 13.6; \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta = 28.98\); HRMS (ESI) calcd for C\(_{18}\)H\(_{27}\)ClO\(_5\)P [M+H]\(^+\) 389.1279, found 389.1291.

![Diagram 3gd](image)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.76\) (t, \(J = 2.6\) Hz, 1 H), 7.54 (d, \(J = 2.6\) Hz, 1 H), 4.98 (dd, \(J = 11.5, 5.4\) Hz, 1 H), 4.30 (t, \(J = 11.9\) Hz, 1 H), 4.10–3.92 (m, 4 H), 3.27–3.10 (m, 1 H), 2.61 (ddd, \(J = 19.0, 15.7, 3.1\) Hz, 1 H), 1.72–1.34 (m, 5 H), 1.44–1.34 (m, 4 H), 0.93 (t, \(J = 7.3\) Hz, 6 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 190.2\) (d, \(J_{CP} = 15.4\) Hz), 155.9, 135.6, 126.8, 125.5, 123.8, 121.7, 71.0 (d, \(J_{CP} = 2.5\) Hz), 65.9 (dd, \(J = 14.2, 6.7\) Hz), 40.6 (d, \(J_{CP} = 3.3\) Hz), 32.5 (dd, \(J_{CP} = 6.2, 2.1\) Hz), 21.0 (d, \(J_{CP} = 146.2\) Hz), 18.7, 13.6; \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta = 28.54\); HRMS (ESI) calcd for C\(_{18}\)H\(_{25}\)Cl\(_2\)NaO\(_5\)P [M+Na]\(^+\) 445.0709, found 445.0731.

![Diagram 3ha](image)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 9.40\) (d, \(J = 8.7\) Hz, 1 H), 7.92 (d, \(J = 9.2\) Hz, 1 H), 7.75 (d, \(J = 8.0\) Hz, 1 H), 7.68–7.59 (m, 1 H), 7.43 (t, \(J = 7.5\) Hz, 1 H), 7.09 (d, \(J = 9.0\) Hz, 1 H), 4.91 (dd, \(J = 11.2, 5.1\) Hz, 1 H), 4.39 (t, \(J = 11.4\) Hz, 1 H), 4.21–4.10 (m, 4 H), 3.23 (ddd, \(J = 13.1, 8.9, 4.9\) Hz, 1 H), 2.70 (ddd, \(J = 19.0, 15.6, 3.0\) Hz, 1 H), 1.74 (td, \(J = 16.3, 10.4\) Hz, 1 H), 1.35 (td, \(J = 7.1, 2.8\) Hz, 6 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 192.9\) (d, \(J_{CP} = 15.5\) Hz), 163.6, 137.6, 131.6, 129.7, 129.2, 128.4, 125.6, 124.9, 118.6, 111.6, 70.2 (d, \(J_{CP} = 2.0\) Hz), 62.0 (dd, \(J_{CP} = 13.3, 6.5\) Hz), 41.3, 21.6 (d, \(J_{CP} = 145.1\) Hz), 16.4 (dd, \(J_{CP} = 6.1, 1.1\) Hz); \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta = 29.69\); HRMS (ESI) calcd for C\(_{18}\)H\(_{22}\)O\(_5\)P [M+H]\(^+\) 349.1199, found 349.1202.
\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.06–7.85 (m, 2 H), 7.66–7.61 (m, 2 H), 7.57–7.53 (m, 1 H), 7.25–7.15 (m, 3 H), 4.98 (dd, \(J = 14.3, 5.1\) Hz, 1 H), 4.25–4.04 (m, 4 H), 3.63 (t, \(J = 13.8\) Hz, 1 H), 2.84–2.66 (m, 1 H), 2.65–2.56 (m, 1 H), 2.37 (s, 3 H), 1.59–1.49 (m, 1 H), 1.36 (q, \(J = 7.0, 6\) H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 193.0 (d, \(J_{CP} = 15.1\) Hz), 144.4, 142.3, 136.6, 134.8, 130.0, 128.3, 127.0, 125.2, 124.3 (d, \(J_{CP} = 1.8\) Hz), 123.6, 62.0 (dd, \(J_{CP} = 16.7, 6.5\) Hz), 50.7 (d, \(J_{CP} = 1.8\) Hz), 40.5 (d, \(J_{CP} = 6.0\) Hz); \textsuperscript{31}P NMR (162 MHz, CDCl\textsubscript{3}) \(\delta\) 29.44; HRMS (ESI) calcd for C\textsubscript{21}H\textsubscript{26}N\textsubscript{1}NaO\textsubscript{6}PS [M+Na]\textsuperscript{+} 474.1111, found 474.1118.

**General Procedure for Radical Trapping Experiments:**

To a 25 mL Schlenk tube equipped with a stir bar was added 2-allyloxybenzaldehyde 1a (49 mg, 0.3 mmol), 2a (166 mg, 1.2 mmol) and DMSO (3 mL), followed by AgSbF\textsubscript{6} (21 mg, 0.06 mmol), K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} (243 mg, 0.9 mmol) and TEMPO (2,2,6,6-tetramethylpiperidinooxy, 140 mg, 0.9 mmol) or BHT (butylated hydroxytoluene, 198 mg, 0.9 mmol). The reaction mixture was stirred under argon atmosphere at 35 °C for 5 h, cooled to room temperature. The desired product 3aa was not detected by GC–MS.

To a 25 mL Schlenk tube equipped with a stir bar was added 2-allyloxy benzaldehyde 1a (49 mg, 0.3 mmol), 2a (166 mg, 1.2 mmol) and DMSO (3 mL), followed by AgSbF\textsubscript{6} (21 mg, 0.06 mmol), K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} (243 mg, 0.9 mmol) and 1,1-diphenylethylene (162 mg, 0.9 mmol). The reaction mixture was stirred under argon atmosphere at 35 °C for 5 h, cooled to room temperature. The desired product 3aa was not detected by GC–MS. The coupling product of the phosphorus radical with 1,1-diphenylethylene was detected by GC–MS.

**General Procedure for Control Experiments:**
To a 25 mL Schlenk tube equipped with a stir bar was added allyloxybenzene 1y (40 mg, 0.3 mmol), 2a (166 mg, 1.2 mmol) and DMSO (3 mL), followed by AgSbF₆ (21 mg, 0.06 mmol) and K₂S₂O₈ (243 mg, 0.9 mmol). The reaction mixture was stirred under argon atmosphere at 35 ºC for 5 h, cooled to room temperature. The possible coupling products of 1-(allyloxy)-4-methoxybenzene and 2a were not detected by GC–MS. And 90% of 1y was recovered.

To a 25 mL Schlenk tube equipped with a stir bar was added 2-allyloxybenzaldehyde 1a (49 mg, 0.3 mmol), allyloxybenzene 1y (40 mg, 0.3 mmol), 2a (166 mg, 1.2 mmol) and DMSO (3 mL), followed by AgSbF₆ (21 mg, 0.06 mmol) and K₂S₂O₈ (243 mg, 0.9 mmol). The reaction mixture was stirred under argon atmosphere at 35 ºC for 5 h, cooled to room temperature. The coupling product 3aa was not detected by GC–MS. And 88% of 1a and 92% of 1y was recovered.

To a 25 mL Schlenk tube equipped with a stir bar was added styrene (31 mg, 0.3 mmol), 2a (166 mg, 1.2 mmol) and DMSO (3 mL), followed by AgSbF₆ (21 mg, 0.06 mmol) and K₂S₂O₈ (243 mg, 0.9 mmol). The reaction mixture was stirred under argon atmosphere at 35 ºC for 5 h, cooled to room temperature. The possible coupling products of styrene and 2a were not detected by GC–MS. And the styrene was found to be polymerized.

To a 25 mL Schlenk tube equipped with a stir bar was added 2-allyloxy benzaldehyde 1a (49 mg, 0.3 mmol), styrene (31 mg, 0.3 mmol), 2a (166 mg, 1.2 mmol) and DMSO (3 mL), followed by AgSbF₆ (21 mg, 0.06 mmol) and K₂S₂O₈ (243 mg, 0.9 mmol). The reaction mixture was stirred under argon atmosphere at 35 ºC for 5 h, cooled to room temperature.
The desired product 3aa was not detected by GC–MS. And the 1a didn’t take part in the reaction.

**General Procedure and Data of Azide or Hydroxyl Chroman-4-ones**

To a 15 mL tube equipped with a stir bar was added 2-(allyloxy)benzaldehyde 1a (49 mg, 0.3 mmol), NaN₃ (78 mg, 1.2 mmol) and MeCN (3 mL), followed by PIFA (310 mg, 0.72 mmol). The reaction mixture was stirred at 25 ºC for 1 h, evaporated and the residue was purified by column chromatography (petroleum ether/EtOAc) to afford azide chroman-4-one 5a (31 mg, 51% yield) and by-product 4 (10 mg, 20% yield). 5a: ¹H NMR (400 MHz, CDCl₃) δ 7.90 (dd, J = 7.9, 1.8 Hz, 1 H), 7.50 (ddd, J = 8.6, 7.2, 1.8 Hz, 1 H), 7.05 (d, J = 7.5 Hz, 1 H), 6.98 (d, J = 8.4 Hz, 1 H), 4.61 (dd, J = 11.5, 4.9 Hz, 1 H), 4.39 (t, J = 11.1 Hz, 1 H), 3.81–3.66 (m, 2 H), 3.05–2.95 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 191.3, 161.7, 136.3, 127.3, 121.7, 120.5, 117.9, 68.9, 47.6, 45.6; HRMS (ESI) calcd for C₁₀H₁₀NO₂ [M–N₂+H]+ 176.0706, found 176.0697.

Following the above procedure, Other azide chroman-4-one derivatives 5b, 5c and 5d were prepared:

5b: ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, J = 1.2 Hz, 1 H), 7.31 (dd, J = 8.4, 2.1 Hz, 1 H), 6.88 (d, J = 8.5 Hz, 1 H), 4.57 (dd, J = 11.4, 4.9 Hz, 1 H), 4.36 (t, J = 11.0 Hz, 1 H), 3.79–3.64 (m, 2 H), 3.05–2.90 (m, 1 H), 2.31 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 191.3, 161.7, 136.3, 127.3, 121.7, 120.5, 117.9, 68.9, 47.6, 45.6; HRMS (ESI) calcd for C₁₁H₁₁N₃NaO₂ [M+Na]+ 240.0743, found 240.0749.

5c: ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, J = 8.8 Hz, 1 H), 6.59 (dd, J = 8.9, 2.4 Hz, 1 H), 6.41 (d, J = 2.4 Hz, 1 H), 4.58 (dd, J = 11.4, 4.9 Hz, 1 H), 4.37 (t, J = 11.0 Hz, 1 H), 3.84 (s, 3 H), 3.80–3.59 (m, 2 H), 2.98–2.87 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 189.8, 166.3, 163.7, 129.1, 114.4, 110.4, 100.7, 69.2, 55.7, 47.8, 45.2; HRMS (ESI) calcd for C₁₁H₁₁N₃NaO₃ [M +Na]+ 256.0693, found 256.0693.
To a 15 mL tube equipped with a stir bar was added 2-(allyloxy)benzaldehyde 1a (49 mg, 0.3 mmol), KI (10 mg, 0.06 mmol) and DCE (3 mL), followed by TBHP (0.9 mmol). The reaction mixture was stirred at 100 ºC for 12 h, evaporated and the residue was purified by column chromatography (petroleum ether/EtOAc) to afford hydroxyl chroman-4-one 6a (23 mg, 43% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.89 (dd, \(J = 7.8, 1.8\) Hz, 1 H), 7.50 (ddd, \(J = 8.6, 7.2, 1.8\) Hz, 1 H), 7.09–7.01 (m, 1 H), 6.98 (dd, \(J = 8.4, 1.0\) Hz, 1 H), 4.59 (dd, \(J = 11.4, 5.3\) Hz, 1 H), 4.41 (t, \(J = 11.6\) Hz, 1 H), 4.01 (dd, \(J = 11.4, 7.1, 5.3\) Hz, 1 H), 3.91 (dt, \(J = 11.3, 5.5\) Hz, 1 H), 3.07–2.88 (m, 1 H), 2.49 (s, 1 H), 2.30 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 194.3, 161.9, 131.0, 126.6, 120.4, 117.7, 68.6, 59.5, 47.8, 20.4; HRMS (ESI) calcd for C\(_{10}\)H\(_{10}\)O\(_3\)Na \([\text{M+Na}]^{+}\) 215.0686, found 215.0679.

Following the above procedure, other hydroxyl chroman-4-one derivatives 6b, 6c and 6d were prepared:

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.67 (d, \(J = 1.3\) Hz, 1 H), 7.30 (dd, \(J = 8.4, 2.1\) Hz, 1 H), 6.87 (d, \(J = 8.5\) Hz, 1 H), 4.55 (dd, \(J = 11.4, 5.2\) Hz, 1 H), 4.37 (t, \(J = 11.5\) Hz, 1 H), 4.00-3.87 (m, 2 H), 3.11–2.88 (m, 1 H), 2.49 (s, 1 H), 2.30 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 194.5, 156.0, 137.4, 131.0, 126.6, 120.4, 117.7, 68.6, 59.5, 47.8, 20.4; HRMS (ESI) calcd for C\(_{11}\)H\(_{12}\)NaO\(_3\) \([\text{M+Na}]^{+}\) 215.0686, found 215.0679.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.82 (d, \(J = 8.8\) Hz, 1 H), 6.58 (dd, \(J = 8.9, 2.4\) Hz, 1 H), 6.40 (d, \(J = 2.4\) Hz, 1 H), 4.55 (dd, \(J = 11.3, 5.3\) Hz, 1 H), 4.38 (t, \(J = 11.4\) Hz, 1 H), 4.04–3.85 (m, 2 H), 3.83 (s, 3 H), 3.00-2.93 (m, 1 H), 2.64 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 193.0, 166.3,
163.9, 128.9, 114.7, 110.2, 100.7, 68.9, 59.5, 55.6, 47.2; HRMS (ESI) calcd for C_{11}H_{12}NaO_4 [M+Na]^+ 231.0628, found 231.0632.

1H NMR (400 MHz, CDCl_3) δ 9.42 (d, J = 8.7 Hz, 1 H), 7.93 (d, J = 9.0 Hz, 1 H), 7.74 (t, J = 9.3 Hz, 1 H), 7.66–7.62 (m, 1 H), 7.46–7.40 (m, 1 H), 7.09 (d, J = 9.0 Hz, 1 H), 4.66 (dd, J = 11.3, 5.4 Hz, 1 H), 4.52 (t, J = 11.5 Hz, 1 H), 4.06-3.94 (m, 2 H), 3.14–3.07 (m, 1 H), 2.68 (s, 1 H); 13C NMR (100 MHz, CDCl_3) δ 195.4, 164.0, 137.9, 131.5, 129.8, 129.2, 128.5, 125.6, 124.9, 118.7, 112.4, 68.4, 59.7, 48.0; HRMS (ESI) calcd for C_{14}H_{12}NaO_3 [M+Na]^+ 251.0679, found 251.0683.
Copies of $^1$H, $^{13}$C, and $^{31}$P NMR Spectra