Metal-free Catalytic Cascade to Chromones: Direct Coupling of Salicylaldehydes and Activated Alkynes Triggered by Aryloxy Radical

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# Table of Contents

General experimental procedure ........................................................................................................S2
Decarboxylation of product 3n to 7-hydroxyflavone 4.................................................................S2
General procedure for the syntheses of methyl arylpropiolates....................................................S2
Synthesis of ethyl dimethyl \((E)\)-2-(2-formylphenoxy)-2-butenedioate (5a) ..................S3
Synthesis of ethyl dimethyl \((Z)\)-2-(2-formylphenoxy)-2-butenedioate (5b) ..................S3
General procedure for the synthesis of chromones .....................................................................S4
The spectroscopic data of chromones ..........................................................................................S4
Reference .........................................................................................................................................S11
Copy of the \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra of 7-hydroxyflavone (4) .........................S12
Copy of the \(^1\text{H}\) NMR spectra of \((E)\)-2-(2-formylphenoxy)-2-butenedioate (5a) ......S14
Copy of the \(^1\text{H}\) NMR spectra of \((Z)\)-2-(2-formylphenoxy)-2-butenedioate (5b) ......S15
Copies of the \(^1\text{H},^{13}\text{C}\) and \(^{19}\text{F}\) NMR spectra of chromones \(3\text{a-r}\) .........................S16
General experimental procedure

$^1$H- and $^{13}$C-NMR spectra were recorded on Varian 600 MHz spectrometers in CDCl$_3$ (with tetramethylsilane) solutions and chemical shifts (δ, ppm) were determined with internal solvent signal as reference (7.26 for $^1$H NMR and 77.0 for $^{13}$C NMR). Flash column chromatography was performed on Silica Gel (300-400 mesh) with an appropriate solvent system (see details below).

Decarboxylation of product 3n to 7-hydroxyflavone 4

A mixture of methyl 7-methoxyl-flavone-3-carboxylate (3n, 0.20 mmol) and 48% aqueous hydrobromic acid (3.0 mL) was heated at 110-120 °C under nitrogen atmosphere for 24 h. After completion of the reaction, the excess hydrobromic acid was distilled off under reduced pressure, and the residue was purified by silica gel column with petroleum ether/ethyl acetate (10:1) as the eluent to give the analytically pure 7-hydroxyflavone (4) as a white solid in 92% yield. $^1$H NMR (DMSO-$d_6$, 600 MHz, ppm) δ 10.82 (s, br, 1 H), 8.04 (dd, $J = 8.22$, 1.38 Hz, 2 H), 7.89 (d, $J = 8.64$ Hz, 1 H), 7.59-7.53 (m, 3 H), 7.00 (d, $J = 2.22$ Hz, 1 H), 6.93 (dd, $J = 8.67$, 2.28 Hz, 1 H), 6.88 (s, 1 H). $^{13}$C NMR (DMSO-$d_6$, 150 MHz, ppm) δ 176.8, 163.2, 162.4, 157.9, 131.9, 131.7, 129.5, 127.0, 126.6, 116.6, 115.5, 107.1, 103.0. And the spectra data are in accordance with literature.$^1$

General procedure for the syntheses of methyl arylpropiolates

To a solution of aryl iodide (2.0 mmol) and methyl propiolate (672.6 mg, 8.0 mmol) in anhydrous THF (6.0 mL) were added PdCl$_2$(PPh$_3$)$_2$ (28.1 mg, 2 mol%), CuI (15.3 mg, 4 mol%), and anhydrous K$_2$CO$_3$ (1.104 g, 8.0 mmol) under N$_2$ atmosphere. The obtained mixture was stirred at 65 °C for 10 h. Then THF was evaporated under vacuum and the residue was extracted with EtOAc. After concentration, the crude product was purified by silica gel column chromatography with petroleum
ether/EtOAc (15:1 to 12:1) as the eluent to give the analytically pure methyl arylpropionate. Methyl arylpropiolates 2p-r were obtained according to the above procedures in 70-85% isolated yields.

### Synthesis of ethyl dimethyl (E)-2-(2-formylphenoxy)-2-butenedioate (5a)

\[
\text{OH} \quad + \quad \text{MeO}_2\text{C} \equiv \text{CO}_2\text{Me} \quad \xrightarrow{\text{CH}_2\text{Cl}_2, \text{DABCO (10 mol\%)}} \quad \text{rt, 10 min}
\]

Dimethyl 2-butynedioate (284.2 mg, 2.0 mmol), DABCO (22.4 mg, 0.2 mmol), and salicylaldehyde (244.3 mg, 2.0 mmol) were stirred in CH\(_2\)Cl\(_2\) (16 mL) at room temperature for 10 min. The solvent was evaporated under vacuum and the residue was purified by silica gel column chromatography with petroleum ether/EtOAc (5:1) as the eluent to give 81% total yield (428.1 mg) of the vinyl ethers, with E-isomer 5a as the major product, and Z-isomer 5b as the minor product (E/Z 91:9). \(^1\)H NMR (CDCl\(_3\), 600 MHz, ppm) \(\delta\) 10.53 (s, 0.08 H; Z-isomer) 10.27 (s, 1 H; E-isomer), 7.96 (dd, \(J = 7.80, 1.62\) Hz, 1 H; E-isomer), 7.91 (dd, \(J = 7.74, 1.62\) Hz, 0.09 H; Z-isomer), 7.66 (td, \(J = 7.80, 1.74\) Hz, 1 H; E-isomer), 7.48 (td, \(J = 7.80, 1.74\) Hz, 0.11 H; Z-isomer), 7.39 (t, \(J = 7.59\) Hz, 1 H; E-isomer), 7.19 (d, \(J = 8.22\) Hz, 1 H; E-isomer), 7.17 (d, \(J = 7.38\) Hz, 0.09 H; Z-isomer), 6.82 (d, \(J = 8.28\) Hz, 0.10 H; Z-isomer), 6.74 (s, 0.08 H; Z-isomer), 5.23 (s, 1 H; E-isomer), 3.91 (s, 3 H; E-isomer), 3.76 (s, 0.26 H; Z-isomer), 3.70 (s, 0.27 H; Z-isomer), 3.68 (s, 3 H; E-isomer).

### Synthesis of ethyl dimethyl (Z)-2-(2-formylphenoxy)-2-butenedioate (5b)

\[
\text{OH} \quad + \quad \text{MeO}_2\text{C} \equiv \text{CO}_2\text{Me} \quad \xrightarrow{\text{H}_2\text{O, rt, 5 min}}
\]

Salicylaldehyde (244.3 mg, 2.0 mmol) was dissolved in aqueous solution of K\(_2\)CO\(_3\) (0.276 g, 2.0 mmol), and then dimethyl 2-butynedioate (284.2 mg, 2.0 mmol) was added to the resulting solution. The reaction mixture was stirred vigorously at room...
temperature for 5 min., and was extracted with EtOAc (20 mL × 3). After concentration, the crude product was purified by silica gel column chromatography with petroleum ether/EtOAc (5:1) as the eluent to give 67% total yield (354.1 mg) of vinyl ethers, with Z-isomer 5b as the major product, and E-isomer 5a as the minor product (E/Z 4:96). 1H NMR (CDCl3, 600 MHz, ppm) δ 10.54 (s, 1 H; Z-isomer), 10.28 (s, 0.03 H; E-isomer), 7.96 (dd, J = 7.74, 1.68 Hz, 0.04 H; E-isomer), 7.91 (dd, J = 7.74, 1.74 Hz, 1 H; Z-isomer), 7.66 (td, J = 7.80, 1.74 Hz, 0.05 H; E-isomer), 7.49 (td, J = 7.82, 1.80 Hz, 1 H; Z-isomer), 7.40 (t, J = 7.56 Hz, 0.05 H; E-isomer), 7.18 (t, J = 7.53 Hz, 1 H; Z-isomer), 6.83 (dd, J = 8.22, 0.36 Hz, 1 H; Z-isomer), 6.74 (s, 1 H; Z-isomer), 5.23 (s, 0.04 H), 3.92 (s, 0.09 H; E-isomer), 3.76 (s, 3 H; Z-isomer), 3.71 (s, 3 H; Z-isomer), 3.69 (s, 0.13 H; E-isomer).

General procedure for the synthesis of chromones

To an oven-dried reaction vessel was charged with trimethylphenylammonium iodide (5.3 mg, 0.02 mmol, 10 mol%), salicylaldehydes (0.20 mmol, 1.0 equiv.), anhydrous acetonitrile (2.0 mL), alkynes (0.30 mmol, 1.5 equiv.), and tert-butyl hydroperoxide (90 uL, 5.0-6.0 M in decane, 2.5 equiv.) sequentially. Then the flask was sealed directly, placed into an oil bath, and stirred at 120 °C. After 24 h, the resulting mixture was cooled to room temperature, filtered through a short silica gel pad, and washed with ethyl acetate. After concentrated under vacuum, the residue was purified by silica gel column with petroleum ether/ethyl acetate as the eluent to give the analytically pure chromones.

The spectroscopic data of chromones
Dimethyl chromone-2,3-dicarboxylate (3a). Pale yellow solid. Isolated yield 71% (37.6 mg, from 24.5 mg of 1a), eluent: petroleum ether/EtOAc 6:1. $^1$H NMR (CDCl$_3$, 600 MHz, ppm) δ 8.21 (d, $J = 7.98$ Hz, 1 H), 7.77 (t, $J = 7.83$ Hz, 1 H), 7.58 (d, $J = 8.52$ Hz, 1 H), 7.47 (t, $J = 7.53$ Hz, 1 H), 4.00 (s, 3 H), 3.96 (s, 3 H). $^{13}$C NMR (CDCl$_3$, 150 MHz, ppm) δ 174.9, 163.7, 160.2, 155.1, 149.5, 135.3, 126.4, 126.1, 123.6, 122.4, 118.6, 53.9, 53.2. HR-ESI-MS: [M+Na]$^+$ m/z calcd. for C$_{13}$H$_{10}$O$_6$Na: 285.0375; found 285.0374.

![3b]

Dimethyl 8-methylchromone-2,3-dicarboxylate (3b). Pale yellow solid. Isolated yield 63% (35.5 mg, from 27.8 mg of 1b), eluent: petroleum ether/EtOAc 6:1. $^1$H NMR (CDCl$_3$, 600 MHz, ppm) δ 8.01 (d, $J = 7.92$ Hz, 1 H), 7.57 (d, $J = 7.26$ Hz, 1 H), 7.33 (t, $J = 7.65$ Hz, 1 H), 4.00 (s, 3 H), 3.95 (s, 3 H), 2.51 (s, 3 H). $^{13}$C NMR (CDCl$_3$, 150 MHz, ppm) δ 175.2, 163.7, 160.3, 153.6, 149.2, 136.1, 128.2, 125.9, 123.53, 123.47, 122.0, 53.8, 53.1, 15.3. HR-ESI-MS: [M+H]$^+$ m/z calcd. for C$_{14}$H$_{13}$O$_6$: 277.0712; found 277.0710.

![3c]

Dimethyl 7-methylchromone-2,3-carboxylate (3c). Pale yellow solid. Isolated yield 73% (40.9 mg, from 27.6 mg of 1c), eluent: petroleum ether/EtOAc 6:1. $^1$H NMR (CDCl$_3$, 600 MHz, ppm) δ 8.09 (d, $J = 8.16$ Hz, 1 H), 7.38 (s, 1 H), 7.28 (dd, $J = 8.16$, 0.84 Hz, 1 H), 4.00 (s, 3 H), 3.96 (s, 3 H), 2.51 (s, 3 H). $^{13}$C NMR (CDCl$_3$, 150 MHz, ppm) δ 174.7, 163.8, 160.3, 155.3, 149.1, 147.0, 128.0, 125.8, 122.4, 121.4, 118.2, 53.8, 53.1, 21.9. HR-ESI-MS: [M+Na]$^+$ m/z calcd. for C$_{14}$H$_{12}$O$_6$Na: 299.0532; found 299.0527.

![3d]
**Dimethyl 6-methylchromone-2,3-dicarboxylate (3d).** Pale yellow solid. Isolated yield 75% (41.9 mg, from 27.5 mg of 1d), eluent: petroleum ether/EtOAc 6:1. $^1$H NMR (CDCl$_3$, 600 MHz, ppm) δ 7.96 (s, 1 H), 7.56 (dd, $J = 8.61$, 2.04 Hz, 1 H), 7.46 (d, $J = 8.64$ Hz, 1 H), 3.99 (s, 3 H), 3.95 (s, 3 H), 2.45 (s, 3 H). $^{13}$C NMR (CDCl$_3$, 150 MHz, ppm) δ 174.9, 163.8, 160.3, 153.4, 149.2, 136.7, 136.5, 125.2, 123.3, 122.2, 118.3, 53.8, 53.1, 20.9. HR-ESI-MS: [M+H]$^+$ m/z cald. for C$_{14}$H$_{13}$O$_6$: 277.0712; found 277.0709.

![Dimethyl 6-methylchromone-2,3-dicarboxylate](image)

**Dimethyl 7-methoxychromone-2,3-dicarboxylate (3e).** Pale yellow solid. Isolated yield 80% (47.1 mg, from 30.7 mg of 1e), eluent: petroleum ether/EtOAc 40:1. $^1$H NMR (CDCl$_3$, 400 MHz, ppm) δ 8.08 (d, $J = 8.94$ Hz, 1 H), 7.00 (dd, $J = 8.91$, 2.40 Hz, 1 H), 6.93 (d, $J = 2.34$ Hz, 1 H), 3.98 (s, 3 H), 3.94 (s, 3 H), 3.90 (s, 3 H). $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm) δ 173.9, 165.3, 163.8, 160.2, 157.0, 148.8, 127.3, 122.7, 117.4, 116.1, 100.4, 56.0, 53.8, 53.1. HR-ESI-MS: [M+H]$^+$ m/z cald. for C$_{14}$H$_{13}$O$_7$: 293.0661; found 293.0658.

![Dimethyl 7-methoxychromone-2,3-dicarboxylate](image)

**Dimethyl-6-methoxychromone-2,3-dicarboxylate (3f).** Pale yellow solid. Isolated yield 78% (45.4 mg, from 30.2 mg of 1f), eluent: petroleum ether/EtOAc 5:1. $^1$H NMR (CDCl$_3$, 600 MHz, ppm) δ 7.51-7.49 (m, 2 H), 7.33 (dt, $J = 9.24$, 2.61 Hz, 1 H), 3.98 (s, 3 H), 3.95 (s, 3 H), 3.88 (s, 3 H). $^{13}$C NMR (CDCl$_3$, 150 MHz, ppm) δ 174.7, 163.9, 160.3, 157.8, 149.9, 149.0, 125.4, 124.4, 121.5, 120.0, 104.9, 56.0, 53.8, 53.1. HR-ESI-MS: [M+Na]$^+$ m/z cald. for C$_{14}$H$_{12}$O$_7$Na: 315.0481; found 315.0478.

![Dimethyl-6-methoxychromone-2,3-dicarboxylate](image)

**Dimethyl 7-benzylkoxychromone-2,3-dicarboxylate (3g).** White solid. Isolated yield 63% (46.4 mg, from 45.5 mg of 1g), eluent: petroleum ether/EtOAc 8:1. $^1$H NMR
(CDCl₃, 600 MHz, ppm) δ 8.12 (dd, J = 8.94, 1.92 Hz, 1 H), 7.44-7.40 (m, 4 H), 7.39-7.36 (m, 1 H), 7.11-7.09 (m, 1 H), 7.03 (d, J = 2.22 Hz, 1 H), 5.17 (s, 2 H), 3.99 (s, 3 H), 3.96 (s, 3 H). \(^{13}\)C NMR (CDCl₃, 150 MHz, ppm) δ 174.0, 164.3, 163.8, 160.2, 157.0, 148.9, 135.2, 128.8, 128.5, 127.51, 127.49, 122.7, 117.7, 116.6, 101.5, 70.8, 53.8, 53.1. HR-ESI-MS: [M+H]^+ m/z calcd. for C₂₀H₁₇O₇: 369.0974; found 369.0974.

**Dimethyl 6-chlorochromone-2,3-dicarboxylate (3h).** White solid. Isolated yield 52% (30.8 mg, from 31.2 mg of 1h), eluent: petroleum ether/EtOAc 6:1. \(^{1}\)H NMR (CDCl₃, 600 MHz, ppm) δ 8.17 (d, J = 2.58 Hz, 1 H), 7.71 (dd, J = 8.97, 2.64 Hz, 1 H), 7.55 (d, J = 8.94 Hz, 1 H), 4.01 (s, 3 H), 3.97 (s, 3 H). \(^{13}\)C NMR (CDCl₃, 150 MHz, ppm) δ 173.8, 163.3, 159.9, 153.4, 149.6, 135.5, 132.6, 125.4, 124.5, 122.3, 120.3, 54.0, 53.3. HR-ESI-MS: [M+Na]^+ m/z calcd. for C₁₃H₉ClO₆Na: 318.9985; found 318.9984.

**Dimethyl 6-bromochromone-2,3-dicarboxylate (3i).** White solid. Isolated yield 57% (38.9 mg, from 40.2 mg of 1i), eluent: petroleum ether/EtOAc 5:1. \(^{1}\)H NMR (CDCl₃, 600 MHz, ppm) δ 8.33 (d, J = 2.40 Hz, 1 H), 7.85 (dd, J = 8.91, 2.46 Hz, 1 H), 7.49 (d, J = 8.94 Hz, 1 H), 4.00 (s, 3 H), 3.97 (s, 3 H). \(^{13}\)C NMR (CDCl₃, 150 MHz, ppm) δ 173.6, 163.3, 159.9, 153.9, 148.3, 149.6, 138.3, 128.6, 124.8, 122.4, 120.5, 120.1, 54.0, 53.3. HR-ESI-MS: [M+Na]^+ m/z calcd. for C₁₃H₉BrO₆Na: 362.9480, 364.9460; found 362.9476, 364.9459.

**Diethyl 6-methylchromone-2,3-dicarboxylate (3j).** Pale yellow solid. Isolated yield 69% (42.4 mg, from 27.4 mg of 1d), eluent: petroleum ether/EtOAc 6:1. \(^{1}\)H NMR (CDCl₃, 600 MHz, ppm) δ 7.92 (s, 1 H), 7.52 (d, J = 8.49, 2.16 Hz, 1 H), 7.44 (td, J = 8.64, 2.76 Hz, 1 H), 4.43-4.39 (m, 4 H), 2.42 (s, 3 H), 1.40-1.35 (m, 6 H). \(^{13}\)C NMR
Diethyl chromone-2,3-dicarboxylate (3k). White solid. Isolated yield 65% (38.2 mg, from 24.6 mg of 1a), eluent: petroleum ether/EtOAc 6:1. $^{1}$H NMR (CDCl$_3$, 600 MHz, ppm) δ 8.19-8.18 (m, 1 H), 7.76-7.73 (m, 1 H), 7.57 (d, $J = 8.04$ Hz, 1 H), 7.45 (td, $J = 7.56$, 0.96 Hz, 1 H), 4.45-4.41 (m, 4 H), 1.40-1.38 (m, 6 H). $^{13}$C NMR (CDCl$_3$, 150 MHz, ppm) δ 175.1, 163.2, 159.7, 155.2, 149.5, 135.2, 126.3, 126.0, 123.6, 122.5, 118.6, 63.4, 62.3, 14.0, 13.9. HR-ESI-MS: [M+H]$^+$ m/z calcd. for C$_{16}$H$_{17}$O$_6$: 305.1025; found 305.1023.

Diethyl 6-methoxychromone-2,3-dicarboxylate (3l). Very viscous yellow oil. Isolated yield 69% (44.3 mg, from 30.5 mg of 1f), eluent: petroleum ether/EtOAc 6:1. $^{1}$H NMR (CDCl$_3$, 600 MHz, ppm) δ 7.50-7.48 (m, 2 H), 7.32-7.29 (m, 1 H), 4.43-4.00 (m, 4 H), 1.40-1.35 (m, 6 H). $^{13}$C NMR (CDCl$_3$, 150 MHz, ppm) δ 174.9, 163.4, 159.7, 157.7, 149.1, 125.3, 124.4, 121.6, 120.1, 104.8, 63.3, 62.2, 55.9, 14.0, 13.9. HR-ESI-MS: [M+H]$^+$ m/z calcd. for C$_{16}$H$_{17}$O$_7$: 321.0974; found 321.0971.

(4-Oxo-4H-chromene-2,3-diyl)bis(phenylmethanone) (3m). White solid. Isolated yield 70% (52.0 mg, from 25.6 mg of 1a), eluent: petroleum ether/EtOAc 5:1. $^{1}$H NMR (CDCl$_3$, 600 MHz, ppm) δ 8.27 (d, $J = 7.92$ Hz, 1 H), 7.95 (d, $J = 7.44$ Hz, 2 H), 7.89 (dd, $J = 8.22$, 1.02 Hz, 2 H), 7.79 (td, $J = 7.82$, 1.32 Hz, 1 H), 7.65 (t, $J = 7.44$ Hz, 1 H), 7.58-7.49 (m, 5 H), 7.44 (t, $J = 7.77$ Hz, 2 H). $^{13}$C NMR (CDCl$_3$, 150 MHz, 150 MHz, ppm) δ 174.9, 163.4, 159.7, 157.7, 150.0, 149.1, 125.3, 124.4, 121.6, 120.1, 104.8, 63.3, 62.2, 55.9, 14.0, 13.9. HR-ESI-MS: [M+H]$^+$ m/z calcd. for C$_{16}$H$_{17}$O$_7$: 321.0974; found 321.0971.
ppm) δ 191.6, 187.3, 175.9, 158.5, 155.1, 136.8, 135.1, 134.7, 134.2, 133.7, 130.1, 129.2, 128.8, 128.6, 126.5, 126.3, 126.0, 124.2, 118.5. HR-ESI-MS: [M+H]^+ m/z calcd. for C_{23}H_{15}O_4: 355.0970; found 355.0967.

**Methyl 7-methoxy-flavone-3-carboxylate (3n).** Pale yellow solid. Isolated yield 47% (29.4 mg, from 30.5 mg of 1e), eluent: petroleum ether/EtOAc 8:1. $^1$H NMR (CDCl₃, 600 MHz, ppm) δ 8.16 (d, J = 8.94 Hz, 1 H), 7.72 (dd, J = 7.92, 1.44 Hz, 2 H), 7.55 (td, J = 7.38, 2.28 Hz, 1 H), 7.50 (td, J = 7.41, 1.44 Hz, 2 H), 7.01 (dd, J = 8.91, 2.40 Hz, 1 H), 6.91 (d, J = 2.34 Hz, 1 H), 3.92 (s, 3 H), 3.79 (s, 3 H). $^{13}$C NMR (CDCl₃, 150 MHz, ppm) δ 174.3, 165.7, 164.6, 162.6, 157.6, 132.0, 131.5, 128.8, 127.9, 127.5, 118.0, 116.9, 115.0, 100.3, 55.9, 52.7. HR-ESI-MS: [M+H]^+ m/z calcd. for C_{18}H_{15}O_5: 311.0919; found 311.0917.

**Ethyl 7-methoxy-flavone-3-carboxylate (3o).** Very viscous yellow oil. Isolated yield 49% (32.4 mg, from 30.9 mg of 1e), eluent: petroleum ether/EtOAc 8:1. $^1$H NMR (CDCl₃, 600 MHz, ppm) δ 8.16 (d, J = 8.88 Hz, 1 H), 7.74 (d, J = 7.32 Hz, 2 H), 7.54 (t, J = 7.38 Hz, 1 H), 7.49 (t, J = 7.50 Hz, 2 H), 7.00 (dd, J = 8.88, 2.28 Hz, 1 H), 6.91 (d, J = 2.28 Hz, 1 H), 4.26 (q, J = 7.14 Hz, 2 H), 3.92 (s, 3 H), 1.16 (t, J = 7.14 Hz, 3 H). $^{13}$C NMR (CDCl₃, 150 MHz, ppm) δ 174.3, 165.1, 164.5, 162.6, 157.6, 132.0, 131.4, 128.7, 128.0, 127.5, 118.3, 117.0, 114.9, 100.3, 61.8, 55.9, 13.8. HR-ESI-MS: [M+Na]^+ m/z calcd. for C_{19}H_{16}O_5Na: 347.0895; found 347.0890.
Methyl 4′-cyano-7-methoxy-flavone-3-carboxylate (3p). White solid. Isolated yield 55% (36.7 mg, from 30.3 mg of 1e), eluent: petroleum ether/EtOAc 3:1. \(^1\)H NMR (CDCl\(_3\), 600 MHz, ppm) δ 8.15 (d, \(J = 8.94\) Hz, 1 H), 7.84 (d, \(J = 8.46\) Hz, 2 H), 7.79 (d, \(J = 8.46\) Hz, 2 H), 7.03 (dd, \(J = 8.94, 2.34\) Hz, 1 H), 6.91 (d, \(J = 2.28\) Hz, 1 H), 3.92 (s, 3 H), 3.80 (s, 3 H). \(^{13}\)C NMR (CDCl\(_3\), 150 MHz, ppm) δ 173.8, 165.1, 164.9, 160.2, 157.5, 136.1, 132.5, 128.7, 127.6, 119.0, 117.7, 116.8, 115.4, 115.1, 100.3, 56.0. HR-ESI-MS: [M+H]^+ m/z calcd. for C\(_{19}\)H\(_{14}\)NO\(_5\): 336.0872; found 336.0869.

Methyl 4′-chloro-7-methoxy-flavone-3-carboxylate (3q). Pale yellow solid. Isolated yield 47% (32.8 mg, from 30.7 mg of 1e), eluent: petroleum ether/EtOAc 7:1. \(^1\)H NMR (CDCl\(_3\), 600 MHz, ppm) δ 8.14 (d, \(J = 8.88\) Hz, 1 H), 7.67 (d, \(J = 8.58\) Hz, 2 H), 7.48 (d, \(J = 8.52\) Hz, 2 H), 7.01 (dd, \(J = 8.91, 2.34\) Hz, 1 H), 6.90 (d, \(J = 2.28\) Hz, 1 H), 3.92 (s, 3 H), 3.80 (s, 3 H). \(^{13}\)C NMR (CDCl\(_3\), 150 MHz, ppm) δ 174.1, 165.5, 164.7, 161.3, 157.5, 137.9, 130.3, 129.3, 129.1, 127.5, 118.1, 116.8, 115.1, 100.3, 55.9, 52.9. HR-ESI-MS: [M+H]^+ m/z calcd. for C\(_{18}\)H\(_{14}\)ClO\(_5\): 345.0530; found 345.0528.

Methyl 4′-trifluoromethyl-7-methoxy-flavone-3-carboxylate (3r). Yellow solid. Isolated yield 51% (38.9 mg, from 30.6 mg of 1e), eluent: petroleum ether/EtOAc 7:1. \(^1\)H NMR (CDCl\(_3\), 600 MHz, ppm) δ 8.15 (d, \(J = 8.94\) Hz, 1 H), 7.85 (d, \(J = 8.22\) Hz, 2 H), 7.76 (d, \(J = 8.28\) Hz, 2 H), 7.02 (dd, \(J = 8.91, 2.28\) Hz, 1 H), 6.91 (d, \(J = 2.28\) Hz, 1 H), 3.92 (s, 3 H), 3.80 (s, 3 H). \(^{13}\)C NMR (CDCl\(_3\), 150 MHz, ppm) δ 174.0, 165.3, 164.8, 160.8, 157.5, 135.3, 133.1 (q, \(J_{C-F} = 32.8\) Hz), 128.4, 127.6, 125.8 (q, \(J_{C-F} = 3.7\) Hz), 123.5 (q, \(J_{C-F} = 301.6\) Hz), 118.7, 116.8, 115.3, 100.3, 55.9, 52.9. \(^{19}\)F NMR
(CDCl₃, 564.6 MHz, ppm) δ -63.1. HR-ESI-MS: [M+Na]+ m/z calcd. for C₁₉H₁₃F₃O₅Na: 401.0613; found 401.0607.

Reference
Copy of the $^1$H and $^{13}$C NMR spectra of 7-hydroxyflavone (4) (via decarboxylation and demethylation of compound 3n)
Copy of the $^1$H NMR spectra of (E)-2-(2-formylphenoxy)-2-butenedioate (5a)

$\text{CHO}_2\text{CO}_2\text{Me}$

5a, with trace amount of 5b
5a/5b 91:9
Copy of the $^1$H NMR spectra of (Z)-2-(2-formylphenoxy)-2-butenedioate (5b)

5b, with trace amount of 5a
5a/5b 4:96
Copies of the $^1$H, $^{13}$C and $^{19}$F NMR spectra of chromones 3a-r
| 0.5 | 8.0 | 7.5 | 7.0 | 6.5 | 6.0 | 5.5 | 5.0 | 4.5 | 4.0 | 3.5 | 3.0 | 2.5 | 2.0 | 1.5 | 1.0 | 0.5 | 0 |

$\Gamma_1$ (ppm)
3h

[Chemical structure image]

[Graphical representation of a spectrum with various peaks]

S31
3j
43
$3n$