Supporting Information

Ru(II)-Catalyzed C-H Bond Activation/Annulation of N-iminopyridinium Ylides with Sulfoxonium Ylides

Xiang Li,*,a,b Danlu Li,* and Xiaofei Zhang **,a,b

a. College of Chemistry and Chemistry Engineering, Shaanxi Key Laboratory of Chemistry Additives for Industry, Shaanxi University of Science & Technology, Xi’an 710021, China. E-mail: lix@sust.edu.cn; zhangxiaofei@sust.edu.cn

b. Shaanxi Key Laboratory of Chemical Additives for Industry, Shaanxi University of Science and Technology, Xi’an, Shaanxi 710021, China
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I. General Information.

All reagents and all solvents were used directly as obtained commercially unless otherwise noted. $^1$H NMR and $^{13}$C NMR spectra were recorded at 25 °C on a JEOL 400 MHz and 100 MHz NMR spectrometers or Bruker 600 MHz and 150 MHz NMR spectrometers. For $^1$H NMR, tetramethylsilane (TMS) served as internal standard ($\delta=0$) and data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant(s) in Hz. For $^{13}$C NMR, TMS ($\delta=0$) was used as internal standard and spectra were obtained with complete proton decoupling. HPLC/MS analysis was carried out with gradient elution (5% CH$_3$CN to 100% CH$_3$CN) on a Q-Exactive Orbitrap MS (Thermo, MA, USA) mass spectrometer. (also used to produce high resolution mass spectra).

$N$-iminopyridinium ylides, $^1$ and sulfoxonium ylides$^2$, were prepared according to the reported literatures.
II. General procedure for preparation of 3

Representative Synthesis of Product 3: A glass bottle was charged with 1a (39.6 mg, 0.2 mmol), 2a (78.4 mg, 0.4 mmol), [RuCl₂(p-cymene)]₂ (6.1 mg, 5 mol %), CH₃COOH (24 mg, 0.4 mmol), and TFE (2.0 mL). The reaction mixture was stirred at 100 °C for 12 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 20:1 (v/v) to give the corresponding product 3aa (39.2 mg, 88%).

III. Synthesis of thunberginol A and derivatization of 3aa

A glass bottle was charged with 1d (45.6 mg, 0.2 mmol), 2w (102 mg, 0.4 mmol), [RuCl₂(p-cymene)]₂ (6.2 mg, 5 mol %), CH₃COOH (24.0 mg, 0.4 mmol), and TFE (2.0 mL). The reaction mixture was stirred at 100 °C for 12 h, then the solvent was removed and the residue was purified by silica gel chromatography using dichloromethane/methanol 20:1 (v/v) to give 3dw (57 mg, 91%). Then, the mixture of 3dw (35.0 mg, 1.12 mmol) and a 1M dichloromethane solution of BBr₃ (5.2 eq, 5.83
mmol) was stirred at room temperature under nitrogen for 2 hours. The solution was then poured into ice water (10 mL) and the mixture extracted with ethyl acetate (6 × 15 mL). The organic extract was washed with brine (10 mL), dried over magnesium sulphate and reduced in vacuo. The product was purified via flash column chromatography (30:1 Dichloromethane / methanol) to yield the natural product (30.1 mg, 98%) as a pale orange solid.

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Alkenylation of 3aa

Pd(OAc)₂ (10 mol%) + Ag₂CO₃ (3.0 equiv) + Cu(OAc)₂ (3.0 equiv)

OMe

O

Ph

Pd(OAc)₂

Ag₂CO₃

Cu(OAc)₂

OMe

Ph

3aa, 0.2 mmol + 4, 0.4 mmol → 5, 47% yield
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A Schlenk tube was charged with 3aa (44.6 mg, 0.2 mmol), Pd(OAc)₂ (4.5 mg, 10 mol %), Cu(OAc)₂ (119.8 mg, 3 eq) and Ag₂CO₃ (165.4 mg, 3 eq) were combined in PivOH (2 ml) under N₂. The alkene 4 (34.4 mg, 0.4 mmol) was added slowly and the reaction mixture was heated to 120 °C. The reaction mixture was diluted with CH₂Cl₂ and the excess NaHCO₃ was added to neutralize PivOH. After stirring the mixture for 10 min, the residue was washed with sequentially aqueous NaHCO₃ and NH₄Cl. The organic layer was dried over MgSO₄. Then the solvent was removed and the residue was purified by silica gel chromatography using dichloromethane/methanol 50:1 (v/v) to give 5 (60.4 mg, 47%).

V. Mechanistic Studies

(a) Deuterium Experiments

```
N

O

N

H(D)

[RuCl₂(p-cymene)]₂ (5 mol%)

HOAc (2 equiv), CF₃CH₂OH

D₂O (10 equiv)

100 °C, 1 h

1a, 0.2mmol

15% D

No H/D exchange in the presence of 2a

(15% D)

H(D)

15% D
```

A glass bottle was charged with 1a (39.6 mg, 0.2 mmol), [RuCl₂(p-cymene)]₂ (6.1 mg, 5 mol %), CH₃COOH (24.0 mg, 0.4 mmol), D₂O (32.0 mg, 2mmol) and TFE (2.0 mL). The reaction mixture
was stirred at 100 °C for 1 h, then the solvent was removed and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 20:1 (v/v) to give \( d-1a \) (13 mg). The extent of deuteration was determined on the basis of \(^1\)H NMR analysis.

**H/D Experiment in the absence of 2a**

\[
\begin{array}{c}
\text{1a} + d_5-1a \\
\text{2a (1 equiv)} \quad \text{[RuCl}_2(p\text{-cymene})]_2 (5 \text{ mol%}) \\
\text{HOAc (2 equiv), CF}_3\text{CH}_2\text{OH} \\
100 \degree\text{C, 1 h} \\
\rightarrow \text{3aa + d}_5\text{-3a}
\end{array}
\]

(b) Kinetic isotope effect KIE

A glass bottle was charged with 1a (39.6 mg, 0.2 mmol), 2a (78.4 mg, 0.4 mmol), [RuCl\(_2(p\text{-cymene})\]\(_2\) (6.1 mg, 5 mol %), CH\(_3\)COOH (24 mg, 0.4 mmol), and TFE (2.0 mL). The reaction mixture was stirred at 100 °C for 12 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 20:1 (v/v) to give the corresponding product 3aa (39.2 mg, 88%).

KIE = 2.3
A glass bottle was charged with 1a (19.8 mg, 0.1 mmol), 2a (39.2 mg, 0.2 mmol), [RuCl₂(p-cymene)]₂ (3.1 mg, 5 mol %), CH₃COOH (12.0 mg, 0.2 mmol), and TFE (1.0 mL). The reaction mixture was stirred at 100 °C for 1 h. And to another bottle was added d₅-1a (19.3 mg, 0.1 mmol), 2a (39.2 mg, 0.2 mmol), [Cp*Rh(Cl)]₂ (3.1 mg, 5 mol %), CH₃COOH (12.0 mg, 0.2 mmol), and TFE (1.0 mL). The reaction mixture was stirred at 100 °C for 1 h. After the completion of the reaction, the two reactions were combined, then the solvent was removed and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 20:1 (v/v) to obtain 3aa and d₅-3aa (30 mg). KIE value (kH/kD = 2.3) was determined on the basis of ¹H NMR analysis.

KIE = 2.3
(c) Competitive experiment:

\[
\begin{align*}
1m & \quad (0.1 \text{ mmol}) \\
1n & \quad (0.1 \text{ mmol}) \\
2a & \quad (1 \text{ equiv})
\end{align*}
\]

\[
\begin{align*}
&+ \quad [\text{RuCl}_2(p\text{-cymene})]_2 \quad (5 \text{ mol%}) \\
&\text{HOAc (2 equiv), CF}_3\text{CH}_2\text{OH} \\
&100 \, ^\circ\text{C, 12 h}
\end{align*}
\]

\[
\begin{align*}
3ma & \quad (20.9 \text{ mg}) \\
3na & \quad (18.8 \text{ mg})
\end{align*}
\]

A glass bottle was charged with 1m (26.6 mg, 0.1 mmol), 1n (22.8 mg, 0.1 mmol), 2a (19.6 mg, 0.1 mmol), [RuCl₂(p-cymene)]₂ (3.1 mg, 5 mol%), CH₃COOH (12.0 mg, 0.2 mmol), and TFE (1.0 mL). The reaction mixture was stirred at 100 °C for 12 h, then the solvent was removed and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 20:1 (v/v) to give 3ma (20.9 mg) and 3na (18.8 mg) in 36% and 37% yield, respectively.

(d) Control experiment:

\[
\begin{align*}
3aa & \quad (0.1 \text{ mmol}) \\
2a & \quad (1.5 \text{ equiv})
\end{align*}
\]

\[
\begin{align*}
&+ \quad [\text{RuCl}_2(p\text{-cymene})]_2 \quad (5 \text{ mol%}) \\
&\text{HOAc (2 equiv), CF}_3\text{CH}_2\text{OH} \\
&100 \, ^\circ\text{C, 12 h}
\end{align*}
\]

\[
\begin{align*}
3ab & \quad (0.0 \text{ mg})
\end{align*}
\]

A glass bottle was charged with 3aa (22.3 mg, 0.1 mmol), 2a (29.4 mg, 0.15 mmol), [RuCl₂(p-
cymene)]₂ (3.1 mg, 5 mol %), CH₃COOH (12.0 mg, 0.2 mmol), and TFE (1.0 mL). The reaction mixture was stirred at 100 °C for 12 h. The formation of 3ab was not observed by TLC, and 3aa was fully recovered.

A glass bottle was charged with 1a (19.8 mg, 0.1 mmol), 2a (29.4 mg, 0.3 mmol), [RuCl₂(p-cymene)]₂ (3.1 mg, 5 mol %), CH₃COOH (12.0 mg, 0.2 mmol), and TFE (1.0 mL). The reaction mixture was stirred at 100 °C for 24 h, then the solvent was removed and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 20:1 (v/v) to give 3aa (38.4 mg) and 3ab (6.4 mg) in 83% and 9% yield, respectively. There was no significant increase in 3ab.

V. Characterization data for products

3-phenyl-1H-isochromen-1-one (3aa): white solid (39.2 mg, 88%). (This compound is known.)¹

¹H NMR (400 MHz, CDCl₃) 8.28 (d, 7.9 Hz, 1H), 7.86 (d, 7.1 Hz, 2H), 7.71 – 7.67 (m, 1H), 7.48 – 7.42 (m, 5H), 6.92 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 162.3, 153.6, 137.5, 134.9, 131.9, 130.0, 129.6, 128.8, 128.1, 126.0, 125.2, 120.5, 101.8.

8-chloro-3-phenyl-1H-isochromen-1-one (3ba): white solid (41 mg, 80%). (This compound is known.)³

¹H NMR (400 MHz, CDCl₃) 7.87 – 7.85 (m, 2H), 7.55 (t, 7.8 Hz, 1H), 7.49 – 7.45 (m, 4H), 7.37 (d, 7.6 Hz, 1H), 6.87 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 158.7, 154.3, 140.6, 137.2, 134.5, 131.4, 130.9, 130.3, 128.9, 125.3, 124.9, 117.6, 101.5.
8-bromo-3-phenyl-1H-isochromen-1-one (3ca): white solid (26.8 mg, 44%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 (d, $J = 6.3$ Hz, 2H), 7.73 (d, $J = 7.4$ Hz, 1H), 7.44 (d, $J = 8.4$ Hz, 5H), 6.89 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.0, 154.0, 140.6, 134.7, 134.6, 131.3, 130.3, 128.9, 125.7, 125.3, 125.0, 118.8, 101.6. HRMS (ESI-TOF) (m/z): Calcd for C$_{15}$H$_9$BrNaO$_2^+$ ([M+Na]$^+$) 322.9678, found 322.9675.

8-methoxy-3-phenyl-1H-isochromen-1-one (3da): white solid (34.4 mg, 68%). (This compound is known.) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.92 (d, $J = 6.8$ Hz, 2H), 7.66 (t, $J = 8.0$ Hz, 1H), 7.50 – 7.45 (m, 3H), 7.07 (d, $J = 7.7$ Hz, 1H), 6.98 (d, $J = 8.3$ Hz, 1H), 4.06 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.7, 159.0, 154.0, 140.5, 135.8, 131.9, 130.0, 128.8, 125.3, 118.1, 109.9, 109.3, 101.8, 56.3.

8-methyl-3-phenyl-1H-isochromen-1-one (3ea): white solid (26.2 mg, 55%). (This compound is known.) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 (d, $J = 7.2$ Hz, 2H), 7.55 (t, $J = 7.5$ Hz, 1H), 7.48 – 7.42 (m, 3H), 7.33 – 7.29 (m, 2H), 6.89 (s, 1H), 2.86 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 161.7, 153.2, 143.6, 139.1, 134.0, 132.0, 131.1, 129.8, 128.8, 125.2, 124.2, 119.0, 102.3, 23.2.

3-phenyl-7-(trifluoromethoxy)-1H-isochromen-1-one (3fa): white solid (53.4 mg, 87%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 (s, 1H), 7.89 – 7.86 (m, 2H), 7.56 (s, 2H), 7.48 – 7.45 (m, 3H), 6.96 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.2, 154.2, 148.4, 136.1, 131.5, 130.3, 128.9, 128.1, 127.9, 125.3, 121.7, 121.1, 119.1, 100.8. HRMS (ESI-TOF) (m/z): Calcd for C$_{16}$H$_9$F$_3$NaO$_3^+$ ([M+Na]$^+$) 329.0396, found 329.0391.
7-fluoro-3-phenyl-1H-isochromen-1-one (3ga): light yellow solid (28.2 mg, 59%). (This compound is known.) $^6$ $^1$H NMR (400 MHz, CDCl$_3$) δ 8.11 – 8.10 (m, 1H), 7.90 (d, $J = 6.7$ Hz, 1H), 7.47 – 7.42 (m, 5H), 7.16 (d, $J = 1.1$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 161.0, 157.3 (d, $J = 253.3$ Hz), 154.3, 131.7, 130.3, 128.9, 128.4 (d, $J = 7.7$ Hz), 126.7 (d, $J = 16.8$ Hz), 125.4, 125.3 (d, $J = 4.2$ Hz), 121.9 (d, $J = 3.9$ Hz), 120.2 (d, $J = 19.8$ Hz), 94.2 (d, $J = 4.8$ Hz).

7-chloro-3-phenyl-1H-isochromen-1-one (3ha): light yellow solid (20.0 mg, 39%). (This compound is known.) $^9$ $^1$H NMR (400 MHz, CDCl$_3$) δ 8.23 (d, $J = 7.8$ Hz, 1H), 7.92 (d, $J = 6.6$ Hz, 2H), 7.76 (d, $J = 7.7$ Hz, 1H), 7.48 (d, $J = 6.2$ Hz, 3H), 7.43 – 7.39 (m, 1H), 7.31 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 161.5, 154.6, 135.6, 135.1, 131.7, 130.6, 130.5, 128.9, 128.5, 128.2, 125.6, 122.0, 98.0.

7-bromo-3-phenyl-1H-isochromen-1-one (3ia): white solid (16.2 mg, 27%). (This compound is known.) $^5$ $^1$H NMR (400 MHz, CDCl$_3$) δ 8.28 (d, $J = 7.9$ Hz, 1H), 7.93 (t, $J = 7.6$ Hz, 3H), 7.48 (d, $J = 6.8$ Hz, 3H), 7.35 (t, $J = 7.9$ Hz, 1H), 7.30 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 161.5, 154.7, 138.6, 137.0, 131.7, 130.4, 129.2, 128.9, 128.6, 125.6, 122.1, 120.7, 100.5.

7-methoxy-3-phenyl-1H-isochromen-1-one (3ja): white solid (20.4 mg, 40%). (This compound is known.) $^6$ $^1$H NMR (400 MHz, CDCl$_3$) δ 7.86 (d, $J = 7.6$ Hz, 2H), 7.73 (s, 1H), 7.47 – 7.38 (m, 4H), 7.31 (d, $J = 8.4$ Hz, 1H), 6.93 (s, 1H), 3.92 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.5, 159.6, 151.7, 132.1, 131.2, 129.6, 128.8, 127.6, 124.9, 124.7, 121.7, 110.0, 101.6, 55.8.
7-methyl-3-phenyl-1H-isochromen-1-one (3ka): white solid (44.8 mg, 95%). (This compound is known.\textsuperscript{3}) \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.12 (s, 1H), 7.87 (d, \(J = 6.7\) Hz, 2H), 7.53 (d, \(J = 7.7\) Hz, 1H), 7.45 – 7.39 (m, 4H), 6.93 (s, 1H), 2.47 (s, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 162.5, 152.8, 138.5, 136.2, 135.0, 132.1, 129.7, 129.4, 128.8, 125.9, 125.1, 120.4, 101.8, 21.4.

6-fluoro-3-phenyl-1H-isochromen-1-one (3la): white solid (39.4 mg, 82%). (This compound is known.\textsuperscript{3}) \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.34 – 8.31 (m, 1H), 7.87 (d, \(J = 5.1\) Hz, 2H), 7.46 (s, 3H), 7.20 – 7.13 (m, 2H), 6.91 (s, 1H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 168.0, 165.5, 161.4, 154.9, 140.2 (d, \(J = 10.8\) Hz), 133.0 (d, \(J = 10.5\) Hz), 131.6, 130.4, 128.9, 125.4, 117.0, 116.5 (d, \(J = 23.4\) Hz), 111.5 (d, \(J = 22.7\) Hz) 101.2.

3,6-diphenyl-1H-isochromen-1-one (3ma): yellow solid (54.2 mg, 91%). (This compound is known.\textsuperscript{3}) \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.35 (d, \(J = 8.1\) Hz, 1H), 7.89 (d, \(J = 6.9\) Hz, 2H), 7.71 – 7.66 (m, 4H), 7.52 – 7.45 (m, 6H), 7.00 (s, 1H). \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}) \(\delta\) 162.3, 154.0, 147.7, 139.5, 138.0, 130.3, 130.0, 129.1, 128.9, 128.7, 127.4, 127.2, 125.3, 124.2, 119.3, 102.0

3-phenyl-6-(trifluoromethyl)-1H-isochromen-1-one (3na): white solid (41.8 mg, 72%). (This compound is known.\textsuperscript{3}) \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.41 (d, \(J = 8.2\) Hz, 1H), 7.88 (d, \(J = 5.4\) Hz, 2H), 7.77 (s, 1H), 7.70 (d, \(J = 8.2\) Hz, 1H), 7.47 (s, 3H), 7.00 (s, 1H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 161.1, 155.1, 137.9, 136.3 (q, \(J = 33.1\) Hz), 131.3, 130.6, 130.6, 129.0, 125.4, 124.2 (q, \(J = 3.3\) Hz), 123.1 (q, \(J = 4.0\) Hz), 122.8, 121.9, 101.0.
8-(2-oxo-2-phenylethyl)-3-phenyl-6-(trifluoromethyl)-1H-isochromen-1-one (3na'): white solid (21.1 mg, 26%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.10 (d, $J = 5.8$ Hz, 2H), 7.84 (s, 2H), 7.73 (s, 1H), 7.62 (s, 1H), 7.54 – 7.50 (m, 3H), 7.45 (s, 3H), 7.00 (s, 1H), 4.96 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 196.2, 160.7, 154.8, 141.1, 139.8, 137.0, 135.7, 135.4, 133.2, 131.1, 130.5, 128.9, 128.7, 128.2, 128.0, 125.3, 122.7, 121.5, 101.7, 45.7. HRMS (ESI-TOF) (m/z): Calcd for C$_{24}$H$_{15}$F$_3$NaO$_3$ $^{+}$([M+Na]$^+$) 431.0866, found 431.0861.

6-methoxy-3-phenyl-1H-isochromen-1-one (3oa): white solid (25.3 mg, 50%). (This compound is known.$^*) ^1$H NMR (400 MHz, CDCl$_3$) δ 8.23 (d, $J = 8.8$ Hz, 1H), 7.88 (d, $J = 6.8$ Hz, 2H), 7.45 (d, $J = 7.3$ Hz, 3H), 7.02 (d, $J = 8.7$ Hz, 1H), 6.87 (d, $J = 5.4$ Hz, 2H), 3.92 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 164.7, 162.1, 154.1, 139.8, 132.0, 131.8, 130.0, 128.8, 125.3, 116.5, 113.7, 108.0, 101.8, 55.6.

6-methoxy-8-(2-oxo-2-phenylethyl)-3-phenyl-1H-isochromen-1-one (3oa'): white solid (30.9 mg, 42%). (This compound is known.$^*) ^1$H NMR (400 MHz, CDCl$_3$) δ 8.23 (d, $J = 8.8$ Hz, 1H), 7.88 (d, $J = 6.8$ Hz, 2H), 7.45 (d, $J = 7.3$ Hz, 3H), 7.02 (d, $J = 8.7$ Hz, 1H), 6.87 (d, $J = 5.4$ Hz, 2H), 3.92 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 164.7, 162.1, 154.1, 139.8, 132.0, 131.8, 130.0, 128.8, 125.3, 116.5, 113.7, 108.0, 101.8, 55.6.
6-methyl-3-phenyl-1H-isochromen-1-one (3pa): white solid (28.0 mg, 59%). (This compound is known.5) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.18 (d, \(J = 7.0\) Hz, 1H), 7.87 (d, \(J = 7.0\) Hz, 2H), 7.44 (d, \(J = 8.0\) Hz, 3H), 7.28 (s, 2H), 6.88 (s, 1H), 2.48 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 162.4, 153.7, 146.0, 137.6, 132.1, 129.9, 129.6, 128.8, 126.0, 125.2, 118.2, 101.8, 22.0.

6-methyl-8-(2-oxo-2-phenylethyl)-3-phenyl-1H-isochromen-1-one (3pa'): white solid (21.2 mg, 30%). (This compound is known.5) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.11 (d, \(J = 7.3\) Hz, 2H), 7.82 (d, \(J = 6.6\) Hz, 2H), 7.38 (d, \(J = 6.8\) Hz, 1H), 7.52 – 7.49 (m, 2H), 7.42 (d, \(J = 7.2\) Hz, 3H), 7.13 (s, 1H), 6.89 (s, 1H), 4.86 (s, 2H), 2.47 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 197.4, 161.7, 153.4, 145.3, 139.5, 139.4, 137.4, 133.6, 132.9, 131.9, 129.8, 128.6, 128.3, 125.8, 116.7, 102.3, 45.5, 21.7.

5,7-dichloro-3-phenyl-1H-isochromen-1-one (3qa): white solid (39.6 mg, 68%). (This compound is known.6) \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 8.21 (s, 1H), 8.12 (s, 1H), 7.99 (d, \(J = 3.5\) Hz, 2H), 7.57 (s, 3H), 7.41 (s, 1H). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 197.4, 161.7, 153.4, 145.3, 139.5, 139.4, 137.4, 133.6, 132.9, 131.9, 129.8, 128.6, 128.3, 125.8, 116.7, 102.3, 45.5, 21.7.

6-phenyl-4H-thieno[3,2-c]pyran-4-one (3ra): white solid (18.4 mg, 20%). (This compound is known.5) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.89 – 7.84 (m, 3H), 7.46 (d, \(J = 6.5\) Hz, 3H), 7.26 (d, \(J = 1.8\) Hz, 1H), 7.13 (s, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 158.3, 156.4, 147.5, 136.8, 131.9, 130.1,
3-phenyl-1H-benzo[h]isochromen-1-one (3sa): yellow solid (50.8 mg, 93%). (This compound is known.) \(^7\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.92 (s, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.91 (s, br, 4H), 7.65 – 7.61 (m, 1H), 7.56 – 7.52 (m, 1H), 7.49 – 7.43 (m, 3H), 7.07 (s, 1H). \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 162.6, 152.0, 136.6, 132.4, 132.2, 132.0, 129.8, 129.4, 128.8, 127.7, 126.7, 125.2, 124.3, 119.0, 101.9.

3-(2-chlorophenyl)-1H-isochromen-1-one (3ab): white solid (38.4 mg, 75%). (This compound is known.) \(^8\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.34 (d, J = 7.8 Hz, 1H), 7.77 – 7.73 (m, 2H), 7.57 – 7.49 (m, 3H), 7.37 (s, 2H), 6.99 (s, 1H). \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 162.3, 151.4, 137.0, 134.9, 132.4, 131.6, 130.7, 129.6, 128.7, 127.0, 126.2, 120.7, 107.7.

3-(2-bromophenyl)-1H-isochromen-1-one (3ac): white solid (51.4 mg, 85%). (This compound is known.) \(^7\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.34 (d, J = 7.9 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.31 – 7.27 (m, 1H), 6.87 (s, 1H). \(^1\)C NMR (150 MHz, CDCl\(_3\)) \(\delta 162.3, 153.0, 136.9, 134.9, 133.8, 131.0, 131.0, 129.7, 128.7, 127.5, 126.2, 121.9, 120.7, 107.4.

3-(2-iodophenyl)-1H-isochromen-1-one (3ad): white solid (50.8 mg, 93%). (This compound is known.)
known.\textsuperscript{9} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.35 (d, \(J = 7.9\) Hz, 1H), 7.98 (d, \(J = 7.9\) Hz, 1H), 7.78 – 7.74 (m, 1H), 7.58 – 7.51 (m, 3H), 7.46 – 7.42 (m, 1H), 7.15 – 7.11 (m, 1H), 6.74 (s, 1H). \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}) \(\delta\) 162.3, 155.4, 140.2, 137.9, 136.9, 134.9, 131.1, 130.5, 129.7, 128.7, 128.2, 126.1, 120.7, 107.2, 96.4.

\textbf{3-(p-tolyl)-1H-isochromen-1-one (3ae):} white solid (33.6 mg, 71%). (This compound is known.\textsuperscript{6}) \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.30 (d, \(J = 7.7\) Hz, 1H), 7.77 (d, \(J = 7.4\) Hz, 2H), 7.72 – 7.68 (m, 2H), 7.48 (s, 2H), 7.27 (s, 1H), 6.90 (s, 1H), 2.40 (s, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 162.4, 153.8, 140.3, 137.7, 134.8, 129.6, 129.5, 129.2, 127.9, 125.8, 125.2, 120.4, 101.1, 21.4.

\textbf{3-(1,1'-biphenyl-4-yl)-1H-isochromen-1-one (3af):} white solid (47.0 mg, 79%). (This compound is known.\textsuperscript{6}) \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.29 (d, \(J = 7.8\) Hz, 1H), 7.92 (d, \(J = 7.7\) Hz, 2H), 7.69 – 7.65 (m, 3H), 7.62 (d, \(J = 7.4\) Hz, 2H), 7.48 – 7.43 (m, 4H), 7.39 – 7.35 (m, 1H), 6.96 (s, 1H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 162.3, 153.4, 142.7, 140.0, 137.6, 134.9, 130.8, 129.7, 128.9, 128.2, 127.9, 127.4, 127.1, 126.0, 125.7, 120.6, 101.8.

\textbf{3-(4-methoxyphenyl)-1H-isochromen-1-one (3ag):} white solid (33.9 mg, 67%). (This compound is known.\textsuperscript{6}) \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.28 (d, \(J = 7.8\) Hz, 1H), 7.82 (d, \(J = 8.6\) Hz, 2H), 7.71 – 7.67 (m, 1H), 7.46 – 7.45 (m, 2H), 6.97 (d, \(J = 8.6\) Hz, 2H), 6.82 (s, 1H), 3.86 (s, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 162.5, 161.1, 153.7, 137.9, 134.8, 129.6, 127.7, 126.8, 125.7, 124.5, 120.1, 114.2, 100.2, 55.4.
3-[(4-(trifluoromethyl)phenyl)-1H-isochromen-1-one (3ah): white solid (42.0 mg, 72%). (This compound is known.\textsuperscript{3}) \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.33 (d, \(J = 7.9\) Hz, 1H), 8.00 (d, \(J = 8.0\) Hz, 2H), 7.76 – 7.71 (m, 3H), 7.57 – 7.53 (m, 2H), 7.05 (s, 1H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 161.8, 152.0, 136.9, 135.3, 135.1, 131.8, 129.8, 128.9, 126.3, 125.8 (q, \(J = 3.6\) Hz), 125.5, 120.9, 103.4.

3-[(4-nitrophenyl)-1H-isochromen-1-one (3ai): white solid (15.1 mg, 28%). (This compound is known.\textsuperscript{8}) \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.36 – 8.32 (m, 3H), 8.07 (d, \(J = 8.5\) Hz, 2H), 7.79 (t, \(J = 7.0\) Hz, 1H), 7.62 – 7.57 (m, 2H), 7.14 (s, 1H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 161.5, 151.1, 148.3, 137.8, 136.5, 135.3, 129.9, 129.4, 126.6, 125.9, 124.2, 121.0, 104.9.

3-[(3-fluorophenyl)-1H-isochromen-1-one (3aj): white solid (26.2 mg, 54%). (This compound is known.\textsuperscript{6}) \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.32 (d, \(J = 7.9\) Hz, 1H), 7.75 (t, \(J = 7.6\) Hz, 1H), 7.67 (d, \(J = 7.8\) Hz, 1H), 7.59 (d, \(J = 9.8\) Hz, 1H), 7.55 – 7.51 (m, 2H), 7.46 – 7.41 (m, 1H), 7.13 (t, \(J = 8.2\) Hz, 1H), 6.97 (s, 1H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 164.3, 162.0 (d, \(J = 8.3\) Hz), 152.3, 137.1, 135.0, 134.2 (d, \(J = 8.1\) Hz), 130.5 (d, \(J = 8.3\) Hz), 129.8, 128.6, 126.2, 120.9 (d, \(J = 2.8\) Hz), 120.7, 116.9 (d, \(J = 21.4\) Hz), 112.3 (d, \(J = 24.0\) Hz), 102.6.
3-((1S,2S,5R,7S)-adamantan-2-yl)-1H-isochromen-1-one (3ak): white solid (25.6 mg, 46%).
(This compound is known.\(^3\)) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.25 (d, \(J = 7.8\) Hz, 1H), 7.68 – 7.65 (m, 1H), 7.46 – 7.42 (m, 1H), 7.38 (d, \(J = 7.7\) Hz, 1H), 6.22 (s, 1H), 2.10 (s, 3H), 1.96 (s, 6H), 1.77 (s, 6H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 165.2, 163.2, 137.8, 134.6, 129.4, 127.5, 125.5, 120.3, 99.7, 39.7, 37.2, 36.6, 28.0.

(E)-3-styryl-1H-isochromen-1-one (3al): white solid (42.6 mg, 86%). (This compound is known.\(^10\)) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.29 (d, \(J = 8.0\) Hz, 1H), 7.71 – 7.67 (m, 1H), 7.53 (d, \(J = 7.6\) Hz, 2H), 7.48 – 7.36 (m, 5H), 7.32 (d, \(J = 7.1\) Hz, 1H), 6.71 (d, \(J = 7.6\) Hz, 1H), 6.46 (s, 1H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 162.1, 152.6, 137.6, 135.8, 134.6, 129.4, 128.9, 128.1, 127.1, 125.8, 120.9, 119.4, 105.8.

3-(benzo[b]thiophen-2-yl)-1H-isochromen-1-one (3am): white solid (36.7 mg, 66%). (This compound is known.\(^9\)) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.25 (d, \(J = 7.8\) Hz, 1H), 7.81 (s, 1H), 7.76 (s, 2H), 7.67 (t, \(J = 7.4\) Hz, 1H), 7.47 – 7.41 (m, 2H), 7.35 – 7.33 (m, 2H), 6.78 (s, 1H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 161.5, 149.2, 139.7, 139.6, 137.0, 135.0, 134.9, 129.8, 128.4, 126.0, 125.8, 125.0, 124.5, 123.3, 122.3, 120.6, 102.9.
3-mesityl-1H-isochromen-1-one (3an): white solid (17.6 mg, 33%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.39 (d, $J$ = 8.0 Hz, 1H), 7.80 – 7.77 (m, 1H), 7.58 (t, $J$ = 7.6 Hz, 1H), 7.50 (d, $J$ = 7.8 Hz, 1H), 6.98 (s, 2H), 6.48 (s, 1H), 2.37 (s, 3H), 2.31 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 163.2, 154.3, 139.4, 137.3, 134.8, 130.1, 129.6, 128.4, 128.2, 125.6, 120.4, 107.2, 60.4, 21.2, 20.0. HRMS (ESI-TOF) (m/z): Calcd for C$_{18}$H$_{16}$NaO$_2$ $^+$ ([M+Na]$^+$) 287.1043, found 287.1036.

3-(2-methoxyphenyl)-1H-isochromen-1-one (3ao): white solid (33.7 mg, 67%). (This compound is known.) $^1$H NMR (400 MHz, CDCl$_3$) δ 8.35 (d, $J$ = 7.9 Hz, 1H), 8.03 – 8.01 (m, 1H), 7.77 – 7.73 (m, 1H), 7.55 – 7.51 (m, 2H), 7.45 – 7.41 (m, 2H), 7.14 – 7.05 (m, 2H), 4.01 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.7, 157.2, 150.4, 138.1, 134.7, 130.8, 129.4, 128.8, 128.0, 126.3, 120.9, 120.7, 120.6, 111.4, 107.0, 55.6.

3-(2-methoxyphenyl)-8-(2-(2-methoxyphenyl)-2-oxoethyl)-1H-isochromen-1-one (3ao'): white solid (15.2 mg, 19%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.92 (d, $J$ = 7.6 Hz, 1H), 7.86 (d, $J$ = 7.4 Hz, 1H), 7.65 – 7.62 (m, 1H), 7.49 – 7.42 (m, 2H), 7.37 (s, 2H), 7.30 (d, $J$ = 7.0 Hz, 1H), 7.06 – 6.99 (m, 4H), 4.88 (s, 2H), 3.96 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 198.9, 161.8, 158.5, 157.2, 150.0, 140.0, 139.8, 134.0, 133.2, 132.0, 130.8, 130.6, 128.7, 125.8, 120.8, 120.7, 119.2, 111.4, 111.3, 107.6, 55.6, 55.6, 50.8. HRMS (ESI-TOF) (m/z): Calcd for C$_{25}$H$_{20}$NaO$_5$ $^+$ ([M+Na]$^+$) 423.1203, found 423.1193.
3-(o-tolyl)-1H-isochromen-1-one (3ap): white solid (29.7 mg, 63%). (This compound is known.\(^3\))

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 8.33 (d, \(J = 7.8\) Hz, 1H), 7.75 – 7.72 (m, 1H), 7.54 – 7.47 (m, 3H), 7.37 – 7.33 (m, 1H), 7.29 (s, 1H), 6.61 (s, 1H), 2.51 (s, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta \) 162.6, 155.6, 137.5, 136.8, 134.8, 132.8, 131.1, 129.8, 129.6, 129.2, 126.0, 125.8, 120.3, 105.9, 20.8.

8-(2-oxo-2-(o-tolyl)ethyl)-3-(o-tolyl)-1H-isochromen-1-one (3ap\'): white solid (19.9 mg, 27%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.99 (d, \(J = 7.4\) Hz, 1H), 7.71 – 7.67 (m, 1H), 7.51 (d, \(J = 7.1\) Hz, 1H), 7.44 (d, \(J = 7.6\) Hz, 1H), 7.39 (d, \(J = 7.1\) Hz, 1H), 7.33 (d, \(J = 6.8\) Hz, 3H), 7.28 (s, 1H), 6.61 (s, 1H), 4.84 (s, 2H), 2.50 (d, \(J = 6.8\) Hz, 6H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta \) 200.7, 162.0, 155.3, 139.5, 139.4, 138.5, 138.0, 136.8, 136.0, 134.3, 132.5, 132.3, 131.9, 131.2, 131.1, 129.7, 129.1, 128.7, 126.0, 125.7, 119.0, 106.5, 48.6, 21.2, 20.8. HRMS (ESI-TOF) (m/z): Calcd for C\(_{25}\)H\(_{20}\)NaO\(_3\)\(^+\) ([M+Na\(^+\)]\(^+\)) 391.1305, found 391.1297.

3-(3-bromophenyl)-1H-isochromen-1-one (3aq): white solid (51.4 mg, 85%). (This compound is known.\(^1\)) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 8.29 (d, \(J = 7.8\) Hz, 1H), 8.01 (s, 1H), 7.80 – 7.71 (m, 2H), 7.50 (d, \(J = 8.4\) Hz, 3H), 7.34 – 7.30 (m, 1H), 6.94 (s, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta \) 161.9, 152.0, 137.1, 135.0, 133.9, 132.8, 130.3, 129.7, 128.6, 128.2, 126.2, 123.7, 123.1, 120.7, 102.7.
3-(3-bromophenyl)-8-(2-(3-bromophenyl)-2-oxoethyl)-1H-isochromen-1-one (3aq'): white solid (11.7 mg, 12%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.22 (s, 1H), 8.03 (d, \(J = 7.6\) Hz, 1H), 7.98 (s, 1H), 7.76 – 7.69 (m, 3H), 7.52 (d, \(J = 7.8\) Hz, 1H), 7.48 (d, \(J = 7.8\) Hz, 1H), 7.40 (t, \(J = 7.8\) Hz, 1H), 7.32 (d, \(J = 5.4\) Hz, 2H), 6.96 (s, 1H), 4.83 (s, 2H). \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 195.7, 161.4, 151.8, 139.1, 139.1, 139.0, 135.9, 134.6, 133.6, 132.9, 132.6, 131.3, 130.3, 130.2, 128.1, 126.8, 126.1, 123.6, 123.1, 123.0, 119.1, 103.2, 45.7. HRMS (ESI-TOF) (m/z): Calcd for C\(_{23}\)H\(_{14}\)Br\(_2\)NaO\(_3^+\) ([M+Na\(^+\)]\(^+\)) 518.9202, found 518.9183.

3-(3-methoxyphenyl)-1H-isochromen-1-one (3ar): white solid (37.8 mg, 75%). (This compound is known.\(^6\)) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.35 (d, \(J = 7.9\) Hz, 1H), 7.78 – 7.74 (m, 1H), 7.54 – 7.49 (m, 3H), 7.46 (s, 1H), 7.43 – 7.39 (m, 1H), 7.03 – 6.98 (m, 2H), 3.93 (s, 3H). \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 162.3, 160.0, 153.4, 137.5, 134.9, 133.4, 129.9, 129.7, 128.2, 126.0, 120.6, 117.7, 116.0, 110.5, 102.1, 55.5.

8-(2-oxo-2-(o-tolyl)ethyl)-3-(o-tolyl)-1H-isochromen-1-one (3ar'): white solid (18.4 mg, 23%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.77 (d, \(J = 7.5\) Hz, 1H), 7.72 – 7.66 (m, 2H), 7.50 – 7.44 (m, 3H), 7.40 – 7.30 (m, 3H), 7.18 (d, \(J = 7.9\) Hz, 1H), 6.99 (d, \(J = 6.8\) Hz, 2H), 4.93 (s, 2H), 3.90 (d, \(J = 9.3\) Hz, 6H). \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 196.9, 161.7, 160.0, 159.8, 153.1, 139.5, 139.3, 138.6, 134.3, 133.1, 132.2, 129.8, 129.6, 125.8, 120.9, 119.5, 119.1, 117.6, 116.1, 112.5, 110.2, 102.6,
55.4, 45.8. HRMS (ESI-TOF) (m/z): Calcd for C_{25}H_{20}NaO_5^+ ([M+Na]^+) 423.1203, found 423.1193.

3-[(4-fluorophenyl)-1H-isochromen-1-one (3as): white solid (29.7 mg, 62%). (This compound is known. 6) \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.31 (d, \(J = 7.8\) Hz, 1H), 7.89 – 7.86 (m, 2H), 7.72 (t, \(J = 7.5\) Hz, 1H), 7.52 – 7.48 (m, 2H), 7.15 (t, \(J = 8.7\) Hz, 2H), 6.88 (s, 1H). \(^{13}C\) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 162.5, 162.1, 152.8, 137.4, 134.9, 129.7, 128.3 (d, \(J = 3.1\) Hz), 128.2, 127.3 (d, \(J = 8.5\) Hz), 125.9, 120.4, 116.0 (d, \(J = 22.1\) Hz), 101.5.

3-[(4-fluorophenyl)-8-[(2-[(4-fluorophenyl)-2-oxoethyl)-1H-isochromen-1-one (3as'): white solid (23.3 mg, 31%). \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.20 – 8.17 (m, 2H), 7.88 – 7.85 (m, 2H), 7.72 (t, \(J = 7.7\) Hz, 1H), 7.51 (d, \(J = 7.8\) Hz, 1H), 7.36 (d, \(J = 7.3\) Hz, 1H), 7.25 – 7.16 (m, 4H), 6.94 (s, 1H), 4.91 (s, 2H). \(^{13}C\) NMR (150 MHz, DMSO) \(\delta\) 195.9, 165.4 (d, \(J = 249.9\) Hz), 163.5 (d, \(J = 246.3\) Hz), 161.0, 151.7, 140.0, 139.3, 135.2, 134.2, 133.0, 131.4 (d, \(J = 9.3\) Hz), 128.5 (d, \(J = 2.5\) Hz), 127.7 (d, \(J = 8.6\) Hz), 126.4, 118.8, 116.6 (d, \(J = 21.9\) Hz), 116.2 (d, \(J = 21.7\) Hz), 103.0, 45.7. HRMS (ESI-TOF) (m/z): Calcd for C_{23}H_{14}F_{2}NaO_{3}^+ ([M+Na]^+) 399.0803, found 399.0798.

3-[(4-bromophenyl)-1H-isochromen-1-one (3at): white solid (45.9 mg, 76%). (This compound is known. 3) \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.30 (d, \(J = 7.7\) Hz, 1H), 7.75 – 7.71 (m, 3H), 7.58 (d, \(J = 8.0\) Hz, 2H), 7.53 – 7.48 (m, 2H), 6.94 (s, 1H). \(^{13}C\) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 162.0, 152.6, 137.2, 135.0, 132.1, 130.9, 128.5, 126.7, 126.1, 124.3, 120.6, 102.1.
3-(4-bromophenyl)-8-(2-(4-bromophenyl)-2-oxoethyl)-1H-isochromen-1-one (3at'): white solid (10.5 mg, 11%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97 (d, $J = 8.5$ Hz, 2H), 7.70 – 7.64 (m, 5H), 7.57 (d, $J = 8.6$ Hz, 2H), 7.47 (d, $J = 7.8$ Hz, 1H), 7.32 (d, $J = 7.4$ Hz, 1H), 6.95 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 196.2, 161.5, 152.4, 139.3, 139.2, 136.1, 134.5, 132.5, 132.1, 131.9, 130.6, 129.8, 128.1, 126.6, 126.0, 124.4, 119.0, 102.7, 45.5. HRMS (ESI-TOF) (m/z): Calcd for C$_{23}$H$_{14}$Br$_2$NaO$_3^+$ ([M+Na]$^+$) 518.9202, found 518.9197.

3-cyclohexyl-1H-isochromen-1-one (3au): white solid (32.6 mg, 71%). (This compound is known.$^6$) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.25 (d, $J = 7.9$ Hz, 1H), 7.66 (t, $J = 7.2$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 1H), 7.36 (d, $J = 7.9$ Hz, 1H), 6.23 (s, 1H), 2.48 – 2.41 (m, 1H), 2.04 (d, $J = 12.2$ Hz, 2H), 1.85 (d, $J = 12.6$ Hz, 2H), 1.48 – 1.23 (m, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 163.2, 162.4, 137.8, 134.6, 129.5, 127.5, 125.2, 120.3, 100.9, 41.9, 30.6, 26.0.

3-cyclohexyl-8-(2-cyclohexyl-2-oxoethyl)-1H-isochromen-1-one (3au'): white solid (12.0 mg, 17%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.25 (d, $J = 7.9$ Hz, 1H), 7.56 (t, $J = 7.7$ Hz, 1H), 7.27 – 7.26 (m, 1H), 7.12 (d, $J = 7.3$ Hz, 1H), 6.19 (s, 1H), 4.30 (s, 2H), 2.72 – 2.64 (m, 1H), 2.41 – 2.35 (m, 1H), 2.07 – 1.97 (m, 4H), 1.84 – 1.80 (m, 4H), 1.74 – 1.67 (m, 2H), 1.47 – 1.21 (m, 10H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 210.7, 162.5, 161.9, 139.5, 139.4, 134.0, 131.5, 124.8, 118.6, 101.5, 50.9, 47.8, 41.7, 30.5, 28.6, 26.0, 25.8. HRMS (ESI-TOF) (m/z): Calcd for C$_{23}$H$_{28}$NaO$_3^+$ ([M+Na]$^+$)
375.1931, found 375.1923.

3-(furan-2-yl)-1H-isochromen-1-one (3av): white solid (20.8mg, 49%). (This compound is known.\textsuperscript{7}) \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \textit{\delta} 8.27 (d, \textit{J} = 8.1 Hz, 1H), 7.69 (t, \textit{J} = 7.6 Hz, 1H), 7.51 (s, 1H), 7.48 – 7.45 (m, 2H), 6.94 (d, \textit{J} = 2.8 Hz, 1H), 6.86 (s, 1H), 6.54 – 6.53 (m, 1H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \textit{\delta} 161.6, 146.9, 146.1, 144.0, 137.3, 135.0, 129.8, 128.0, 126.0, 120.5, 112.1, 110.1, 100.0.

3-(furan-2-yl)-8-(2-(furan-2-yl)-2-oxoethyl)-1H-isochromen-1-one (3av\texttextsuperscript{'}): white solid (10.2 mg, 16%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \textit{\delta} 7.66 – 7.62 (m, 2H), 7.49 (s, 1H), 7.42 (d, \textit{J} = 7.8 Hz, 1H), 7.29 (d, \textit{J} = 8.6 Hz, 2H), 6.86 (d, \textit{J} = 4.6 Hz, 2H), 6.57 (s, 1H), 6.50 (s, 1H), 4.75 (s, 2H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \textit{\delta} 185.9, 161.0, 154.6, 152.9, 146.8, 146.1, 146.0, 144.0, 139.2, 138.8, 134.4, 132.3, 125.9, 119.0, 117.0, 112.3, 112.1, 110.1, 100.6, 45.3. HRMS (ESI-TOF) (m/z): Calcd for C\textsubscript{19}H\textsubscript{12}O\textsubscript{5}\textsuperscript{+} ([M+Na\textsuperscript{+}) 343.0577, found 343.0572.

3-(3,4-dimethoxyphenyl)-8-methoxy-1H-isochromen-1-one (3dw): Yellow solid (57 mg, 91%). (This compound is known.\textsuperscript{12}) \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6) \textit{\delta} 7.73 – 7.69 (m, 1H), 7.44 (d, \textit{J} = 7.1 Hz, 1H), 7.38 (s, 1H), 7.27 (s, 1H), 7.13 (d, \textit{J} = 6.9 Hz, 1H), 7.08 – 7.05 (m, 2H), 3.86 (t, \textit{J} = 18.5 Hz, 9H). \textsuperscript{13}C NMR (101 MHz, DMSO-\textit{d}_6) \textit{\delta} 161.5, 158.0, 153.2, 150.9, 149.3, 140.8, 136.8, 124.4, 118.4, 118.4, 112.0, 110.6, 108.4, 100.9, 56.4, 56.1, 56.0.
3-(3,4-dihydroxyphenyl)-8-hydroxy-1H-isochromen-1-one (thunberginol A): Pale orange solid (30.1 mg, 98%). (This compound is known.\textsuperscript{12}) \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6) \delta 10.85 (s, 1H), 9.58 (s, 1H), 9.31 (s, 1H), 7.68 (t, \textit{J} = 7.9 Hz, 1H), 7.28 (s, 1H), 7.23 (d, \textit{J} = 9.0 Hz, 2H), 7.09 (d, \textit{J} = 7.6 Hz, 1H), 6.92 (d, \textit{J} = 8.2 Hz, 1H), 6.86 (d, \textit{J} = 8.3 Hz, 1H). \textsuperscript{13}C NMR (101 MHz, DMSO-\textit{d}_6) \delta 165.6, 160.9, 153.2, 148.3, 146.1, 139.0, 138.1, 122.8, 117.4, 117.0, 116.5, 114.5, 112.6, 105.7, 101.1.

methyl (E)-3-(1-oxo-3-phenyl-1H-isochromen-8-yl)acrylate (5): white solid (20.8mg, 49%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \delta 8.38 (d, \textit{J} = 7.6 Hz, 1H), 8.21 (d, \textit{J} = 15.8 Hz, 1H), 7.96 – 7.93 (m, 3H), 7.54 – 7.48 (m, 4H), 7.25 (d, \textit{J} = 12.2 Hz, 1H), 6.51 (d, \textit{J} = 15.7 Hz, 1H), 3.88 (s, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \delta 166.8, 161.9, 154.4, 139.4, 136.1, 132.8, 131.8, 131.6, 130.4, 128.9, 127.9, 125.6, 121.9, 121.3, 97.5, 52.0. HRMS (ESI-TOF) (m/z): Calcd for C\textsubscript{16}H\textsubscript{14}NaO\textsubscript{4}\textsuperscript{+} ([M+Na]\textsuperscript{+}) 329.0784, found 329.0779.
VI. References


(11) Xiang, Zhang, Xintong, Wan, Ying, Cong, Xiaohua, Zhen, Qiao and Daisy, *J. Org. Chem.*, 2019, **84**, 10402-10411.

VII. 1H NMR and 13C NMR Spectra of New Compound

3aa, CDCl$_3$, 400 MHz

3aa, CDCl$_3$, 100 MHz
3ba, CDCl₃, 400 MHz

3ba, CDCl₃, 100 MHz
3ca, CDCl$_3$, 400 MHz

3ca, CDCl$_3$, 100 MHz
3ea, CDCl₃, 400 MHz

3ea, CDCl₃, 150 MHz
3fa, CDCl₃, 400 MHz

3fa, CDCl₃, 100 MHz
3ga, CDCl₃, 400 MHz

3ga, CDCl₃, 100 MHz
3ha, CDCl₃, 400 MHz

3ha, CDCl₃, 100 MHz
3ia, CDCl₃, 400 MHz

3ia, CDCl₃, 100 MHz
3ja, CDCl₃, 400 MHz

3ja, CDCl₃, 100 MHz
3ka, CDCl₃, 400 MHz

3ka, CDCl₃, 100 MHz
3la, CDCl₃, 400 MHz

3la, CDCl₃, 100 MHz
3ma, CDCl₃, 400 MHz

3ma, CDCl₃, 150 MHz
3na, CDCl₃, 400 MHz

3na, CDCl₃, 100 MHz
3na', CDCl₃, 400 MHz

3na', CDCl₃, 100 MHz
3oa, CDCl₃, 400 MHz

3oa, CDCl₃, 100 MHz
3o′, CDCl₃, 400 MHz

3o′, CDCl₃, 100 MHz
3pa, CDCl₃, 400 MHz

3pa, CDCl₃, 100 MHz
3pa', CDCl₃, 400 MHz

3pa', CDCl₃, 100 MHz
3qa, DMSO, 400 MHz

3qa, DMSO, 150 MHz
3ra, CDCl₃, 400 MHz

3ra, CDCl₃, 100 MHz
3sa, CDCl₃, 400 MHz

3sa, CDCl₃, 100 MHz
3ab, CDCl₃, 400 MHz

3ab, CDCl₃, 100 MHz
3ac, CDCl₃, 400 MHz

3ac, CDCl₃, 150 MHz
3ad, CDCl₃, 400 MHz

3ad, CDCl₃, 150 MHz
3ae, CDCl$_3$, 400 MHz

3ae, CDCl$_3$, 100 MHz
3af, CDCl$_3$, 400 MHz

3af, CDCl$_3$, 100 MHz
3ah, CDCl₃, 400 MHz

3ah, CDCl₃, 100 MHz
3ai, CDCl₃, 400 MHz

3ai, CDCl₃, 100 MHz
3aj, CDCl$_3$, 400 MHz

3aj, CDCl$_3$, 100 MHz
3aI, CDCl₃, 400 MHz

3aI, CDCl₃, 100 MHz
3an, CDCl₃, 400 MHz

3an, CDCl₃, 100 MHz
3ao, CDCl₃, 400 MHz

3ao, CDCl₃, 100 MHz
3ao', CDCl₃, 400 MHz

3ao', CDCl₃, 100 MHz
3ap, CDCl₃, 400 MHz

3ap, CDCl₃, 100 MHz
3ap', CDCl₃, 400 MHz

3ap', CDCl₃, 100 MHz
3aq, CDCl$_3$, 400 MHz

3aq, CDCl$_3$, 150 MHz
3aq', CDCl₃, 400 MHz

3aq', CDCl₃, 100 MHz
3ar, CDCl₃, 400 MHz

3ar, CDCl₃, 100 MHz
3ar', CDCl₃, 400 MHz

3ar', CDCl₃, 100 MHz
3as, CDCl₃, 400 MHz

3as, CDCl₃, 100 MHz
3as', CDCl₃, 400 MHz

3as', CDCl₃, 150 MHz
3at, CDCl₃, 400 MHz

3at, CDCl₃, 150 MHz
3at*, CDCl₃, 400 MHz

3at*, CDCl₃, 100 MHz
3au', CDCl₃, 400 MHz

3au', CDCl₃, 100 MHz
3av, CDCl₃, 400 MHz

3av, CDCl₃, 100 MHz
3av', CDCl₃, 400 MHz

3av', CDCl₃, 100 MHz
Thunberginol A, DMSO-$d_6$, 400MHz

Thunberginol A, DMSO-$d_6$, 100MHz
5, CDCl$_3$, 400MHz

5, CDCl$_3$, 100MHz