Supporting Information

Rh(III)-catalyzed C-H annulation of sulfoxonium ylides with iodonium ylides towards isocoumarins

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1. General information

Unless otherwise noted, all reactions were carried out without exclusion of air or moisture. Commercial solvents and reagents were used without further purification. Analytical thin layer chromatography (TLC) was performed using silica gel GF254 plates. Column chromatography was performed using silica gel (200-300 mesh) eluting with petroleum ether and ethyl acetate. NMR spectra were recorded on 400 MHz or 600 MHz spectrometers in the solvent indicated. Chemical shifts are reported downfield from TMS (δ = 0.00) for $^1$H NMR. For $^{13}$C NMR, chemical shifts are reported in the scale relative to CDCl$_3$ (δ = 77.00). HR-MS spectra were recorded on an electrospray ionization quadrupole time-of-flight (ESI-Q-TOF) mass spectrometer. Melting points were determined using a Büchi B-540 capillary melting point apparatus. $^{1}$a-1s$^{[1]}$, 2a-2h$^{[2]}$, 2i$^{[3]}$, 2j$^{[4]}$, 2K-2m$^{[2]}$ and 2n$^{[5]}$ are known compounds and prepared according to the corresponding literature.

2. Reaction Procedure

2.1 General procedure for the synthesis of products 3

A mixture of 2-(dimethyl(oxy)-λ$_6$-sulfanylidene)-1-phenylethan-1-one 1a (39.2 mg, 0.20 mmol), 5,5-dimethyl-2-(phenyl-λ$_3$-iodanylidene)cyclohexane-1,3-dione 2a (102.6 mg, 0.30 mmol), [Rh*CpCl$_2$]$_2$ (3.1 mg, 2.5 mol %) and NaOPiv (24.8 mg, 0.20 mmol) in HFIP (1.0 mL) was stirred at 40 °C for 12 hours. The resulting mixture was cooled to room temperature, solvent was removed under vacuo and the crude reaction mixture was purified by silica gel (200-300 mesh) column chromatography using hexane/ethyl acetate (6:1) as the eluant to afford 3a as a white solid.

2.2 General Procedure for the gram scale reaction

A mixture of 2-(dimethyl(oxy)-λ$_6$-sulfanylidene)-1-phenylethan-1-one 1a (0.98 g, 5.0 mmol), 2-(phenyl-λ$_3$-iodanylidene)cyclohexane-1,3-dione 2b (2.56 g, 7.5 mmol), [Rh*CpCl$_2$]$_2$ (40.3 mg, 1.3 mol %) and NaOPiv (0.62 g, 5.0 mmol) in HFIP (15.0 mL) was stirred at 40 °C for 12 hours. The resulting mixture was cooled to room temperature, solvent was removed under vacuo and the crude reaction mixture was purified by silica gel (200-300 mesh) column chromatography using hexane/ethyl acetate (5:1) as the eluant to afford 4a as a white solid.
2.3 Further transformation of compound 3a

A mixture of 3a (48.4 mg, 0.2 mmol), methylamine (27.9 mg, 0.3 mmol, 30 wt. % solution in methanol) in THF (2.0 mL) was stirred at 80 °C for 12 hours. Then the resulting mixture was cooled to room temperature, solvent was removed under vacuo and the crude product was purified by silica gel chromatography using PE/EA (3:1) to afford the product 6 in 96% yield.

2.4 Further transformation of compound 4a

A mixture of 4a (42.8 mg, 0.2 mmol), phenylmethanamine (30.2 mg, 0.3 mmol) in DCM (2.0 mL) was stirred at 80 °C for 10 hours. Then the resulting mixture was cooled to room temperature, solvent was removed under vacuo and the crude product was purified by silica gel chromatography using PE/EA (3:1) to afford the product 7 in 69% yield.

A mixture of 4a (42.8 mg, 0.2 mmol) and NH₂NH₂·H₂O (10.1 mg, 0.2 mmol) in THF (2.0 mL) was stirred at 90 °C for 6 hours. After completion of the reaction as indicated by thin-layer chromatography (TLC), solvent was removed under vacuo. The crude reaction mixture was washed with H₂O, extracted with ethyl acetate and purified by silica gel column chromatography using PE/EA (3:1) to afford 8 in 84% yield.
A mixture of 4a (42.8 mg, 0.2 mmol), N-Iodosuccinamide (67.2 mg, 0.3 mmol) in DMSO (2.0 mL) was stirred at 80 °C for 12 hours. After completion of the reaction as indicated by thin-layer chromatography (TLC), the reaction mixture was washed with NH₄Cl solution. The product was extracted with ethyl acetate, dried over sodium sulphate, solvent was removed under vacuo and the crude reaction mixture was purified by silica gel column chromatography using PE/EA (2:1) to afford 9 in 75% yield.

A mixture of 4a (42.8 mg, 0.2 mmol), K₂CO₃ (41.4 mg, 0.3 mmol) and iodine (76.2 mg, 0.3 mmol) in DMF (2.0 mL) was stirred at 100 °C for 12 hours. After completion of the reaction as indicated by thin-layer chromatography (TLC), the reaction mixture was washed with Na₂S₂O₃ solution. The product was extracted with ethyl acetate, solvent was removed under vacuo and the crude reaction mixture was purified by silica gel column chromatography using PE/EA (2:1) to afford 10 in 62% yield.

3. Isotope labeling experiments

3.1 H/D exchange experiment

Ylide 1a (0.20 mmol, 39.2 mg), [Cp*RhCl₂]₂ (2.5 mol %, 3.1 mg), NaOPiv (0.20 mmol, 24.8 mg) and CD₃OD (2.0 mmol, 72.0 mg) were dissolved in HFIP (1.0 mL). The mixture was stirred at 40 °C under air for 1 h. The resulting mixture was cooled
to room temperature and solvent was removed under vacuo. Purification was performed by flash column chromatography on silica gel (5% MeOH in EtOAc) to give the D-1a.

**3.2 Kinetic isotope effect**

Ylide 1a (0.20 mmol, 39.2 mg), 1a-d5 (0.20 mmol, 40.2 mg), 2a (0.3 mmol, 102.6 mg), [Cp*RhCl2]2 (2.5 mol%, 3.1 mg) and NaOPiv (0.20 mmol, 24.8 mg) were dissolved in HFIP (1.0 mL). The mixture was stirred at 40 °C for 1 h. The resulting mixture was cooled to room temperature and solvent was removed under vacuo. Purification was performed by flash column chromatography on silica gel using EtOAc/Hexane (1:6) as the eluant to provide a mixture of 3a and 3a-d4. The ratio of 3a and 3a-d4 was determined to be 4.3:1 by 1H NMR integration method.
In a round bottom flask, a mixture of ylide 1a (0.20 mmol, 39.2 mg), 2a (0.3 mmol, 102.6 mg), [Cp*RhCl₂]₂ (2.5 mol %, 3.1 mg) and NaOPiv (0.20 mmol, 24.8 mg) were dissolved in HFIP (1.0 mL). The mixture was stirred at 40 °C for 1 h. At the same time, in another round bottom flask, a solution of 1a-d₅ (40.2 mg, 0.20 mmol), 2a (102.6 mg, 0.30 mmol), [Cp*RhCl₂]₂ (3.1 mg, 2.5 mol %) and NaOPiv (0.20 mmol, 24.8 mg) in HFIP (1.0 mL) was stirred at 40 °C for 1 h. These two mixtures were rapidly combined, and all the volatiles were rapidly removed under a reduced pressure. The residue was purified by silica gel chromatography using EtOAc/Hexane (1:6) as the eluant to provide a mixture of 3a and 3a-d₄. Upon analyzing the corresponding ^1H NMR spectrum, the KIE (K<sub>H</sub>/K<sub>D</sub>) was about 4.6.
4. Competition experiments

A solution of ylide 1i (45.2 mg, 0.20 mmol) and 1m (52.8 mg, 0.20 mmol), 5,5-dimethyl-2-(phenyl-\(\lambda^3\)-iodanylidene)cyclohexane-1,3-dione 2a (102.6 mg, 0.30 mmol), [Cp*RhCl\(_2\)]\(_2\) (3.1 mg, 2.5 mol %) and NaOPiv (24.8 mg, 0.20 mmol) in HFIP (1.0 mL) was stirred at 40 °C under open air for 12 hours. The solvent was removed under vacuo and the crude reaction mixture was directly loaded on silica gel column chromatography and purified using EtOAc/Hexane (1:4) as the eluant to afford a mixture of compounds 3i and 3m. The ratio of 3i and 3m was determined to be 1.63:1 by \(^1\)H NMR.
5. Analytical data and copies of NMR spectra

5.1 Analytical data for products

3,3-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione

Compound 3a was isolated as a white solid (44.1 mg, 91% yield). M.P.: 140-141 °C. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.03 (d, $J = 8.3$ Hz, 1H), 8.35 - 8.23 (m, 1H), 7.83 - 7.73 (m, 1H), 7.52 (t, $J = 7.6$ Hz, 1H), 2.79 (s, 2H), 2.51 (s, 2H), 1.17 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.9, 167.9, 160.7, 135.6, 133.8, 129.5, 128.3, 125.8, 119.7, 110.5, 52.8, 42.5, 31.9, 28.1. HRMS (ESI) m/z calcd for C$_{15}$H$_{15}$O$_3$ $[M + H^+]$: 243.1016; found: 243.1015.
7-chloro-3,3-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione
Compound 3b was isolated as a white solid (18.3 mg, 33% yield). M.P.: 145-146 °C.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.05 (d, $J = 7.9$ Hz, 1H), 7.64 (t, $J = 8.1$ Hz, 1H), 7.54 (d, $J = 7.4$ Hz, 1H), 2.78 (s, 2H), 2.52 (s, 2H), 1.16 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.4, 168.7, 156.9, 136.8, 136.8, 135.3, 131.4, 124.4, 116.9, 110.0, 53.0, 42.4, 31.8, 28.1. HRMS (ESI) m/z calcd for C$_{15}$H$_{15}$ClO$_3$ $^+$ [M + H$^+$]: 277.0626; found: 277.0630.

3,3,7-trimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione
Compound 3c was isolated as a white solid (10.3 mg, 20% yield). M.P.: 121-123 °C.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.94 (d, $J = 8.3$ Hz, 1H), 7.66 - 7.58 (m, 1H), 7.32 (d, $J = 7.5$ Hz, 1H), 2.79 (s, 3H), 2.76 (s, 2H), 2.50 (s, 2H), 1.16 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.8, 167.9, 159.7, 143.4, 135.3, 134.8, 131.4, 123.6, 118.1, 110.5, 53.1, 42.5, 31.8, 28.1, 23.8. HRMS (ESI) m/z calcd for C$_{16}$H$_{17}$O$_3$ $^+$ [M + H$^+$]: 257.1172; found: 257.1169.

8-methoxy-3,3-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione
Compound 3d was isolated as a white solid (22.3 mg, 41% yield). M.P.: 144-145 °C.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.97 (d, $J = 9.1$ Hz, 1H), 7.68 (d, $J = 2.9$ Hz, 1H), 7.36 (d, $J = 9.1$, 2.9 Hz, 1H), 3.90 (s, 3H), 2.78 (s, 2H), 2.50 (s, 2H), 1.17 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 197.1, 165.8, 160.9, 159.3, 127.6, 127.4, 124.6, 121.1, 110.6, 110.3, 55.6, 52.8, 42.3, 32.0, 28.1. HRMS (ESI) m/z calcd for C$_{16}$H$_{17}$O$_4$ $^+$ [M + H$^+$]: 273.1121; found: 273.1118.
10-methoxy-3,3-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione

Compound 3d’ was isolated as a white solid (6.5 mg, 12% yield). M.P.: 152-153 °C. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 (d, $J = 7.8$ Hz, 1H), 7.48 (t, $J = 8.0$ Hz, 1H), 7.29 (d, $J = 8.2$ Hz, 1H), 3.90 (s, 3H), 2.73 (s, 2H), 2.57 (s, 2H), 1.18 (s, 6H). 

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 193.8, 163.3, 160.8, 155.3, 129.4, 123.0, 122.3, 121.5, 118.0, 113.4, 56.3, 52.6, 42.0, 33.1, 28.7. 

HRMS (ESI) m/z calcd for C$_{16}$H$_{17}$O$_4$ $^+\left[M + H^+\right]$: 273.1121; found: 273.1119.

8-chloro-3,3-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione

Compound 3e was isolated as a white solid (20.5 mg, 37% yield). M.P.: 153-154 °C. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.03 (d, $J = 8.9$ Hz, 1H), 8.24 (d, $J = 2.3$ Hz, 1H), 7.72 (dd, $J = 8.9$, 2.4 Hz, 1H), 2.79 (s, 2H), 2.52 (s, 2H), 1.18 (s, 6H). 

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.7, 168.1, 159.6, 135.8, 134.4, 132.2, 128.9, 127.6, 121.2, 110.1, 52.7, 42.4, 32.0, 28.1. 

HRMS (ESI) m/z calcd for C$_{15}$H$_{14}$ClO$_3$ $^+\left[M + H^+\right]$: 277.0626; found: 277.0621.

10-chloro-3,3-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione

Compound 3e’ was isolated as a white solid (6.6 mg, 12% yield). M.P.: 120-121 °C. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.23 - 8.17 (m, 1H), 7.83 - 7.79 (m, 1H), 7.48 (t, $J = 7.9$ Hz, 1H), 2.78 (s, 2H), 2.61 (s, 2H), 1.22 (s, 6H). 

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 193.4, 165.6, 159.8, 137.5, 131.6, 131.2, 129.0, 128.4, 123.4, 113.7, 52.1, 42.1, 32.8, 28.6. 

HRMS (ESI) m/z calcd for C$_{15}$H$_{14}$ClO$_3$ $^+\left[M + H^+\right]$: 277.0626; found: 277.0620.
3,3,9-trimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione
Compound 3f was isolated as a white solid (47.6 mg, 93% yield). M.P.: 131-132 °C.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.85 (s, 1H), 8.16 (d, $J = 8.1$ Hz, 1H), 7.34 (d, $J = 8.1$ Hz, 1H), 2.78 (s, 2H), 2.53 - 2.47 (m, 5H), 1.17 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 197.1, 168.1, 160.8, 147.0, 133.8, 129.6, 129.6, 125.8, 117.2, 110.5, 52.9, 42.6, 31.9, 28.1, 22.5. HRMS (ESI) m/z calcd for C$_{16}$H$_{17}$O$_3^+$ [M + H$^+$]: 257.1172; found: 257.1175.

9-ethyl-3,3-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione
Compound 3g was isolated as a white solid (49.1 mg, 91% yield). M.P.: 123-124 °C.
$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.90 - 8.85 (m, 1H), 8.17 (d, $J = 8.4$ Hz, 1H), 7.35 (dd, $J = 8.4$, 1.8 Hz, 1H), 2.81-2.75 (m, 4H), 2.50 (s, 2H), 1.28 (t, $J = 7.8$ Hz, 3H), 1.16 (s, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 197.0, 168.0, 160.7, 153.0, 133.9, 129.7, 128.4, 124.8, 117.4, 110.5, 52.9, 42.5, 31.9, 29.6, 28.1, 15.1. HRMS (ESI) m/z calcd for C$_{17}$H$_{19}$O$_3^+$ [M + H$^+$]: 271.1329; found: 271.1326.

9-(tert-butyl)-3,3-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione
Compound 3h was isolated as a white solid (55.8 mg, 94% yield). M.P.: 147-149 °C.
$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 9.13 (d, $J = 1.8$ Hz, 1H), 8.20 (d, $J = 8.4$ Hz, 1H), 7.57 (dd, $J = 8.4$, 1.8 Hz, 1H), 2.79 (s, 2H), 2.51 (s, 2H), 1.39 (s, 9H), 1.17 (s, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 197.2, 168.0, 160.7, 159.8, 133.8, 129.4, 126.1, 122.4, 117.2, 110.7, 53.0, 42.6, 35.8, 31.9, 31.0, 28.1. HRMS (ESI) m/z calcd for C$_{19}$H$_{23}$O$_3^+$ [M + H$^+$]: 299.1642; found: 299.1641.
9-methoxy-3,3-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione
Compound 3i was isolated as a white solid (50.7 mg, 94% yield). M.P.: 143-144 °C. 
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.64 - 8.56 (m, 1H), 8.18 (dd, $J$ = 8.9, 1.6 Hz, 1H), 7.08 - 7.01 (m, 1H), 3.95 (s, 3H), 2.78 (s, 2H), 2.51 (s, 2H), 1.17 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 197.2, 168.9, 165.4, 160.4, 136.3, 131.6, 117.1, 112.6, 110.3, 107.9, 55.7, 52.9, 42.6, 31.9, 28.1. HRMS (ESI) m/z calcd for C$_{16}$H$_{17}$O$_4^+$ [M + H$^+$]: 273.1121; found: 273.1134.

9-fluoro-3,3-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione
Compound 3j was isolated as a white solid (45.0 mg, 87% yield). M.P.: 117-118 °C. 
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.76 (dd, $J$ = 11.3, 2.5 Hz, 1H), 8.27 (dd, $J$ = 8.8, 5.9 Hz, 1H), 7.20 (td, $J$ = 8.7, 2.5 Hz, 1H), 2.79 (s, 2H), 2.51 (s, 2H), 1.17 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.5, 169.1, 167.2 (d, $J$ = 256.1 Hz), 159.7, 136.5 (d, $J$ = 12.3 Hz), 132.7 (d, $J$ = 10.6 Hz), 116.6 (d, $J$ = 23.5 Hz), 116.1 (d, $J$ = 2.2 Hz), 112.4 (d, $J$ = 26.2 Hz), 109.9 (d, $J$ = 3.1 Hz), 52.5, 42.5, 31.9, 28.1. $^{19}$F NMR (396 MHz, CDCl$_3$) $\delta$ -98.84. HRMS (ESI) m/z calcd for C$_{15}$H$_{14}$FO$_3^+$ [M + H$^+$]: 261.0921; found: 261.0924.

9-chloro-3,3-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione
Compound 3k was isolated as a white solid (49.6 mg, 89% yield). M.P.: 155-156 °C. 
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.12 - 9.05 (m, 1H), 8.21 - 8.15 (m, 1H), 7.51 - 7.44 (m, 1H), 2.79 (s, 2H), 2.52 (s, 2H), 1.17 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.5, 169.1, 159.9, 142.7, 135.0, 131.0, 128.9, 125.7, 118.0, 109.7, 52.6, 42.5, 31.9, 28.1. HRMS (ESI) m/z calcd for C$_{15}$H$_{14}$ClO$_3^+$ [M + H$^+$]: 277.0626; found: 277.0638.
9-bromo-3,3-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione
Compound 3l was isolated as a white solid (55.2 mg, 86% yield). M.P.: 159-160 °C. 
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.35 - 9.23 (m, 1H), 8.15 - 8.06 (m, 1H), 7.69 - 7.59 (m, 1H), 2.80 (s, 2H), 2.52 (s, 2H), 1.17 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.5, 169.0, 160.1, 135.0, 131.9, 131.7, 131.0, 128.8, 118.4, 109.6, 52.6, 42.6, 31.9, 28.1. HRMS (ESI) m/z calcd for C$_{15}$H$_{14}$BrO$_3^+$ [M + H$^+$]: 321.0121; found: 321.0136.

3,3-dimethyl-9-(trifluoromethyl)-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione
Compound 3m was isolated as a white solid (35.4 mg, 57% yield). M.P.: 169-170 °C. 
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.42 (s, 1H), 8.45 - 8.34 (m, 1H), 7.75 (d, $J$ = 8.3 Hz, 1H), 2.83 (s, 2H), 2.55 (s, 2H), 1.19 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.5, 169.1, 160.1, 136.8 (d, $J$ = 32.8 Hz), 134.3, 130.3, 124.7 (q, $J$ = 3.5 Hz), 123.3 (q, $J$ = 3.9 Hz), 122.2, 121.9, 109.9, 52.6, 42.5, 32.0, 28.1. $^{19}$F NMR (396 MHz, CDCl$_3$) $\delta$ -63.38. HRMS (ESI) m/z calcd for C$_{16}$H$_{14}$F$_3$O$_3^+$ [M + H$^+$]: 311.0890; found: 311.0904.

3,3-dimethyl-1,6-dioxo-2,3,4,6-tetrahydro-1H-benzo[c]chromene-9-carboxylate
Compound 3n was isolated as a white solid (33.0 mg, 55% yield). M.P.: 156-157 °C. 
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.71 - 9.63 (m, 1H), 8.38 - 8.28 (m, 1H), 8.20 - 8.11 (m, 1H), 3.99 (s, 3H), 2.82 (s, 2H), 2.55 (s, 2H), 1.20 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.5, 168.4, 166.0, 160.0, 136.2, 133.9, 129.7, 128.8, 127.2, 122.6, 110.2, 52.7, 42.4, 31.9, 28.1. HRMS (ESI) m/z calcd for C$_{17}$H$_{17}$O$_5^+$ [M + H$^+$]: 301.1071; found: 301.1083.
3,3-dimethyl-1,6-dioxo-2,3,4,6-tetrahydro-1H-benzo[c]chromene-9-carbonitrile

Compound 3o was isolated as a white solid (16.1 mg, 30% yield). M.P.: 142-143°C. 
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.46 (dd, $J = 0.8$ Hz, 1H), 8.36 (d, $J = 8.4$ Hz, 1H), 7.75 (dd, $J = 8.0, 1.2$ Hz, 1H), 2.84 (s, 2H), 2.56 (s, 2H), 1.20 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.3, 169.5, 159.2, 134.3, 130.7, 130.3, 122.5, 119.0, 117.6, 109.3, 52.5, 42.5, 32.0, 28.1. HRMS (ESI) m/z calcd for C$_{16}$H$_{14}$NO$_3^+$ [M +H$^+$]: 268.0968; found: 268.0963.

7,7-dimethyl-7,8-dihydro-4H-furo[2,3-c]chromene-4,9(6H)-dione

Compound 3p was isolated as a white solid (16.3 mg, 35% yield). M.P.: 143-144 °C. 
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 (d, $J = 1.8$ Hz, 1H), 7.36 (d, $J = 1.8$ Hz, 1H), 2.78 (s, 2H), 2.47 (s, 2H), 1.17 (s, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 195.0, 169.0, 152.0, 151.3, 136.8, 132.5, 110.1, 109.1, 51.0, 41.6, 32.8, 28.2. HRMS (ESI) m/z calcd for C$_{13}$H$_{13}$O$_4^+$ [M +H$^+$]: 233.0808; found: 233.0802.

7,7-dimethyl-7,8-dihydro-4H-thieno[2,3-c]chromene-4,9(6H)-dione

Compound 3q was isolated as a white solid (44.0 mg, 89% yield). M.P.: 128-129 °C. 
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.27 - 8.18 (m, 1H), 7.94 - 7.87 (m, 1H), 7.94 - 7.87 (m, 1H), 2.50 (s, 2H), 1.18 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 195.1, 169.3, 156.8, 143.5, 137.7, 126.0, 122.8, 111.4, 51.5, 41.8, 32.4, 28.2. HRMS (ESI) m/z calcd for C$_{13}$H$_{12}$NaO$_3$S$^+$ [M + Na$^+$]: 271.0399; found: 271.0413.
Compound 3r was isolated as a white solid (45.6 mg, 78% yield). M.P.: 184-185 °C. 
$^1$H NMR (400 MHz, CDCl$_3$) δ 9.51 (s, 1H), 8.89 (s, 1H), 8.04 - 7.95 (m, 2H), 7.69 - 7.62 (m, 1H), 7.60 - 7.53 (m, 1H), 2.81 (s, 2H), 2.56 (s, 2H), 1.20 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 197.3, 166.8, 161.0, 136.8, 132.0, 131.7, 129.5, 129.2, 129.0, 127.7, 127.2, 125.4, 118.0, 110.6, 52.9, 42.5, 31.9, 28.2. HRMS (ESI) m/z calcd for C$_{19}$H$_{17}$O$_3$ + [M + H$^+$]: 293.1172; found: 293.1181.

3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione

Compound 4a was isolated as a white solid (36.8 mg, 86% yield). M.P.: 128-129 °C. 
$^1$H NMR (400 MHz, CDCl$_3$) δ 9.03 (d, $J = 8.3$ Hz, 1H), 8.30 - 8.22 (m, 1H), 7.81 - 7.75 (m, 1H), 7.56 - 7.49 (m, 1H), 2.93 (t, $J = 6.0$ Hz, 2H), 2.65 (t, $J = 6.8$ Hz, 2H), 2.17 (p, $J = 6.4$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 196.9, 169.4, 160.4, 135.6, 134.0, 129.5, 128.4, 126.0, 119.8, 111.5, 38.9, 28.9, 19.9.

3-methyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione

Compound 4b was isolated as a white solid (36.9 mg, 81% yield). M.P.: 123-124 °C. 
$^1$H NMR (600 MHz, CDCl$_3$) δ 9.02 (d, $J = 8.4$ Hz, 1H), 8.25 (dd, $J = 8.4$, 1.2 Hz, 1H), 7.80 - 7.73 (m, 1H), 7.54 - 7.47 (m, 1H), 2.96 - 2.89 (m, 1H), 2.72 - 2.61 (m, 2H), 2.47 - 2.32 (m, 2H), 1.18 (d, $J = 6.6$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 196.8, 168.8, 160.5, 135.5, 133.9, 129.5, 128.3, 125.8, 119.7, 111.1, 47.1, 36.8, 27.6, 20.7.

3-phenyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione

Compound 4c was isolated as a white solid (51.2 mg, 88% yield). M.P.: 168-169 °C. 
$^1$H NMR (600 MHz, CDCl$_3$) δ 9.06 (d, $J = 8.4$ Hz, 1H), 8.27 (dd, $J = 7.8$, 1.2 Hz, 1H), 7.82 - 7.76 (m, 1H), 7.57 - 7.50 (m, 1H), 7.42 - 7.36 (m, 2H), 7.34 - 7.28 (m, 3H), 3.60 - 3.52 (m, 1H), 3.21 - 3.09 (m, 2H), 2.98 - 2.85 (m, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 195.9, 168.5, 160.3, 141.4, 135.6, 133.7, 129.5, 129.0, 128.5, 127.4, 126.5, 125.9, 119.7, 111.2, 45.8, 37.9, 36.3.
3-propyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione
Compound 4d was isolated as a white solid (48.6 mg, 95% yield). M.P.: 113-114 °C.  
$^{1}$H NMR (600 MHz, CDCl$_3$) $\delta$ 9.02 (d, $J$ = 8.4 Hz, 1H), 8.25 (dd, $J$ = 7.8, 1.2 Hz, 1H), 7.79 - 7.74 (m, 1H), 7.53 - 7.48 (m, 1H), 2.98 - 2.90 (m, 1H), 2.76 - 2.69 (m, 1H), 2.68 - 2.60 (m, 1H), 2.40 - 2.23 (m, 2H), 1.50 - 1.36 (m, 4H), 0.94 (t, $J$ = 7.8 Hz, 3H).  
$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 196.9, 169.0, 160.5, 135.5, 133.9, 129.5, 128.3, 125.8, 119.7, 111.2, 45.4, 37.4, 35.1, 32.2, 19.5, 13.9.  
HRMS (ESI) m/z calcd for C$_{16}$H$_{17}$O$_3$+ [M +H$^+$]: 257.1172; found: 257.1164.

4,4-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione
Compound 4e was isolated as a white solid (22.8 mg, 47% yield). M.P.: 119-120 °C.  
$^{1}$H NMR (600 MHz, CDCl$_3$) $\delta$ 9.05 (d, $J$ = 8.4 Hz, 1H), 8.28 (dd, $J$ = 7.8, 1.2 Hz, 1H), 7.80 - 7.75 (m, 1H), 7.56 - 7.48 (m, 1H), 2.70 (t, $J$ = 7.2 Hz, 2H), 2.03 (t, $J$ = 7.2 Hz, 2H), 1.46 (s, 6H).  
$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 197.0, 174.3, 160.6, 135.5, 134.1, 129.4, 128.4, 126.3, 119.8, 110.0, 36.1, 35.8, 34.8, 26.2.

2,2-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione
Compound 4e' was isolated as a white solid (22.8 mg, 47% yield). M.P.: 136-137 °C.  
$^{1}$H NMR (600 MHz, CDCl$_3$) $\delta$ 9.02 (d, $J$ = 8.4 Hz, 1H), 8.27 (dd, $J$ = 8.4, 1.2 Hz, 1H), 7.79 - 7.74 (m, 1H), 7.54 - 7.47 (m, 1H), 2.93 (t, $J$ = 6.6 Hz, 2H), 2.00 (t, $J$ = 6.6 Hz, 2H), 1.23 (s, 6H).  
$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 201.7, 167.4, 160.6, 135.5, 134.4, 129.5, 128.3, 126.1, 120.0, 109.7, 42.0, 33.1, 25.6, 24.5.
2,3-dihydrocyclopenta[c]isochromene-1,5-dione
Compound 4f was isolated as a white solid (37.2 mg, 93% yield). M.P.: 123-124 °C.
$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.48 (d, $J$ = 7.8 Hz, 1H), 8.30 - 8.23 (m, 1H), 7.83 - 7.78 (m, 1H), 7.59 - 7.54 (m, 1H), 7.06 - 2.98 (m, 2H), 2.77 - 2.71 (m, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 200.3, 180.4, 161.0, 135.8, 131.8, 130.4, 129.0, 123.2, 118.6, 114.5, 34.6, 25.8.

7,8,9,10-tetrahydrocyclohepta[c]isochromene-5,11-dione
Compound 4g was isolated as a white solid (11.1 mg, 24% yield). M.P.: 145-146 °C.
$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.28 (dd, $J$ = 8.4, 1.2 Hz, 1H), 8.10 (d, $J$ = 8.4 Hz, 1H), 7.76 - 7.69 (m, 1H), 7.53 - 7.47 (m, 1H), 2.97 - 2.92 (m, 2H), 2.83 - 2.78 (m, 2H), 1.99 - 1.92 (m, 4H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 202.6, 163.5, 161.1, 135.2, 134.5, 129.6, 128.2, 124.6, 119.6, 116.3, 43.0, 32.3, 23.1, 22.4.

5H-dibenzo[c,g]chromene-5,7,12-trione
Compound 4h was isolated as a yellow solid (47.7 mg, 86% yield). M.P.: 251-252 °C.
$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 9.32 (d, $J$ = 7.8 Hz, 1H), 8.44 (dd, $J$ = 7.8, 1.2 Hz, 1H), 8.25 - 8.20 (m, 2H), 7.97 - 7.92 (m, 1H), 7.87 - 7.78 (m, 2H), 7.77 - 7.72 (m, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 183.5, 176.6, 158.7, 150.9, 135.9, 134.9, 134.2, 132.4, 132.1, 131.3, 130.4, 130.3, 128.7, 127.1, 126.7, 122.9, 116.7. HRMS (ESI) m/z calcd for C$_{17}$H$_9$O$_4$$^+$ [M +H$^+$]: 277.0495; found: 277.0487.
6-(dimethyl(o xo)-6-sulfanylidene)tetrathene-5,7,12(6H)-trione

Compound 4h' was isolated as a maroon solid (7.1 mg, 10% yield). M.P.: 263-264 °C.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 9.56 (d, $J = 8.4$ Hz, 1H), 8.41 - 8.36 (m, 1H), 8.20 - 8.16 (m, 1H), 7.97 - 7.93 (m, 1H), 7.77 - 7.70 (m, 2H), 7.68 - 7.62 (m, 1H), 7.59 - 7.51 (m, 1H), 4.01 (s, 6H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 185.9, 182.6, 174.1, 142.2, 134.3, 134.0, 133.8, 133.6, 132.6, 132.5, 132.1, 129.1, 127.9, 126.7, 125.4, 124.9, 119.0, 97.7, 43.8. HRMS (ESI) m/z calcd for C$_{20}$H$_{15}$O$_4$S$^+$ [M +H$^+$]: 351.0686; found: 351.0680.

1,1,1,3,3,3-hexafluoropropan-2-yl-3-oxo-2,3-dihydro-1H-indene-1-carboxylate

Compound 4i was isolated as a white solid (41.3 mg, 63% yield). M.P.: 102-103 °C.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J = 7.8$ Hz, 1H), 7.72 - 7.64 (m, 2H), 7.52 (t, $J = 7.2$ Hz, 1H), 5.86 - 5.76 (m, 1H), 4.50 (dd, $J = 8.4$, 3.6 Hz, 1H), 3.16 (dd, $J = 19.2$, 3.6 Hz, 1H), 2.99 (dd, $J = 19.2$, 8.4 Hz, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 202.4, 169.0, 148.7, 136.3, 135.4, 129.5, 126.3, 124.4, 121.2 - 121.1 (m), 119.4 - 119.2 (m), 67.2 (p, $J = 35.0$ Hz), 42.8, 39.0. $^{19}$F NMR (565 MHz, CDCl$_3$) $\delta$ -72.99 (q, $J = 8.5$ Hz, 3F), -73.17 (q, $J = 8.5$ Hz, 3F). HRMS (ESI) m/z calcd for C$_{13}$H$_9$F$_6$O$_3$+ [M +H$^+$]: 327.0450; found: 327.0453.

3,3,5-trimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione

Compound 6 was isolated as a white solid (49.1 mg, 96% yield). M.P.: 150-151 °C.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 9.23 (d, $J = 8.4$ Hz, 1H), 8.39 (dd, $J = 7.8$, 1.2 Hz, 1H), 7.72 - 7.66 (m, 1H), 7.48 - 7.43 (m, 1H), 3.63 (s, 3H), 2.81 (s, 2H), 2.47 (s, 2H), 1.15 (s, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 196.8, 162.9, 152.2, 133.5, 133.3, 127.6, 126.8, 125.8, 123.7, 110.4, 52.1, 42.6, 31.8, 31.2, 28.3. HRMS (ESI) m/z calcd for C$_{16}$H$_{18}$NO$_2$+ [M +H$^+$]: 256.1332; found: 256.1324.
5-benzyl-3,4-dihydropyridazine-1,6(2H,5H)-dione
Compound 7 was isolated as a white solid (41.8 mg, 69% yield). M.P.: 173-174 °C. 
$^1$H NMR (600 MHz, CDCl$_3$) δ 9.23 (d, $J$ = 7.8 Hz, 1H), 8.47 (dd, $J$ = 8.4, 1.2 Hz, 1H), 7.79 - 7.73 (m, 1H), 7.56 - 7.49 (m, 1H), 7.33 (t, $J$ = 6.6 Hz, 2H), 7.29 - 7.25 (m, 1H), 7.14 (d, $J$ = 7.2 Hz, 2H), 5.51 (s, 2H), 2.93 (t, $J$ = 6.6 Hz, 2H), 2.59 (t, $J$ = 6.0 Hz, 2H), 2.04 (p, $J$ = 6.0 Hz, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 196.7, 162.8, 154.2, 136.0, 134.0, 133.6, 129.0, 128.0, 127.1, 126.3, 126.0, 124.1, 111.9, 47.3, 38.6, 28.4, 20.9.

5-amino-3,4-dihydropyridazine-1,6(2H,5H)-dione
Compound 8 was isolated as a white solid (38.3 mg, 84% yield). M.P.: 187-188 °C. 
$^1$H NMR (600 MHz, CDCl$_3$) δ 9.24 (d, $J$ = 9.0 Hz, 1H), 8.37 (d, $J$ = 8.4 Hz, 1H), 7.48 (t, $J$ = 7.8 Hz, 1H), 5.03 (s, 2H), 3.24 (t, $J$ = 6.6 Hz, 2H), 2.14 (p, $J$ = 6.6 Hz, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 196.8, 161.9, 154.8, 133.7, 133.5, 127.3, 126.8, 126.2, 122.9, 110.4, 38.8, 27.3, 20.6. HRMS (ESI) m/z calcd for C$_{13}$H$_{13}$N$_2$O$_2$ $^+$ [M +H$^+$]: 229.0972; found: 229.0965.

2-hydroxy-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione
Compound 9 was isolated as a white solid (34.5 mg, 75% yield). M.P.: 186-187 °C. 
$^1$H NMR (600 MHz, CDCl$_3$) δ 8.95 (d, $J$ = 8.4 Hz, 1H), 8.30 (dd, $J$ = 8.4, 1.2 Hz, 1H), 7.84 - 7.79 (m, 1H), 7.59 - 7.54 (m, 1H), 4.31 (dd, $J$ = 13.8, 5.4 Hz, 1H), 3.96 (s, 1H), 3.17 - 3.08 (m, 1H), 3.01 - 2.95 (m, 1H), 2.58 - 2.54 (m, 1H), 2.13 - 2.00 (m, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 197.7, 168.9, 160.0, 135.8, 133.3, 129.8, 128.9, 125.3, 119.5, 109.5, 72.0, 28.4, 27.2.
1-hydroxy-6H-benzo[c]chromen-6-one

Compound 10 was isolated as a yellow solid (26.3 mg, 62% yield). M.P.: 241-242 °C. 

$^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ 11.05 (s, 1H), 9.14 (d, $J = 8.4$ Hz, 1H), 8.27 (dd, $J = 7.8$, 1.2 Hz, 1H), 7.93 - 7.89 (m, 1H), 7.62 (t, $J = 7.2$ Hz, 1H), 7.35 (t, $J = 8.4$ Hz, 1H), 6.91 (d, $J = 8.4$ Hz, 1H), 6.87 (d, $J = 8.4$ Hz, 1H). $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$ 160.4, 156.6, 152.1, 135.0, 134.5, 130.2, 129.4, 127.9, 127.1, 120.0, 112.0, 107.7, 106.0.
5.2 Copies of NMR spectra.
S38

-1.0  -0.5  0.0  0.5  1.0  1.5  2.0  2.5  3.0  3.5  4.0  4.5  5.0  5.5  6.0  6.5  7.0  7.5  8.0  8.5  9.0  9.5
f1 (ppm)

2.00 2.01 1.00 1.00 0.97 1.19 2.55 2.82 7.26 7.74 7.74 7.76 7.76 8.35 8.37 9.46 9.46

10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
f1 (ppm)

28.1 32.0 42.5 52.5 76.7 77.0 77.3 109.3 117.6 119.0 122.5 130.3 130.3 130.7 134.3 159.2 169.5 196.3

100 110 120 130 140 150 160 170 180 190 200
f1 (ppm)
6. References.