Supporting Information

Rh(III)-Catalyzed C-H Activation/Annulation of Salicylaldehydes with Sulfoxonium Ylides for the Synthesis of Chromones

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1. General Information

Unless otherwise noted, all chemicals were purchased from commercial suppliers (Adamas, Aladdin, etc) and used without further purification. $^1$H and $^{13}$C NMR spectra were collected on BRUKER (300 or 400 MHz) spectrometer using CDCl$_3$ as solvent. Chemical shifts of $^1$H NMR were recorded in parts per million (ppm, $\delta$) relative to tetramethylsilane ($\delta = 0.00$ ppm) with the solvent resonance as the internal standard (CDCl$_3$: $\delta = 7.26$ ppm). Data are reported as follows: chemical shift in ppm ($\delta$), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz) and integration. Chemical shifts of $^{13}$C NMR were reported in ppm with the solvent as the internal standard (CDCl$_3$: $\delta = 77.0$ ppm). High Resolution Mass measurement was performed on Agilent QTOF 6520 mass spectrometer with electron spray ionization (ESI and APCI) as the ion source. Melting point (m. p.) was measured on a microscopic melting point apparatus. Flash column chromatography was carried out using commercially available 200-300 mesh under pressure unless otherwise indicated. Gradient flash chromatography was conducted eluting with PE/EA, they are listed as volume/volume ratios.
2. Preparation of Starting Materials

Salicylaldehyde substrates were synthesized according to the literature procedure.¹

![](image)

To a mixture of phenol (5.0 mmol), paraformaldehyde (50.0 mmol) and magnesium chloride (13.0 mmol) was added CH₃CN (20.0 mL), followed by triethylamine (23.0 mmol) at room temperature. The sealed tube was heated at 125 °C for 12 h. 2 N HCl (15.0 mL) was added slowly after cooling to room temperature, and then the mixture extracted with diethyl ether (50.0 mL x 2). The extracts were combined, washed with H₂O (50.0 mL x 2), brine (50.0 mL), then dried over Na₂SO₄, filtered and concentrated. The crude product was purified by flash chromatography on silica gel (PE: EA = 100:1) to afford the corresponding salicylaldehyde substrates.

(8S,9R,13R,14R,17R)-2-formyl-3-hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl pentanoate

Pale yellow solid, m. p. 74–75 °C; ^1H NMR (300 MHz, CDCl₃) δ 10.78 (s, 1H), 9.81 (s, 1H), 7.41 (s, 1H), 6.69 (s, 1H), 4.78 – 4.66 (m, 1H), 2.97 – 2.79 (m, 2H), 2.33 (t, J = 7.5 Hz, 3H), 2.27 – 2.13 (m, 2H), 1.98 – 1.84 (m, 2H), 1.83 – 1.69 (m, 1H), 1.67 – 1.22 (m, 11H), 0.94 (t, J = 7.3 Hz, 3H), 0.85 (s, 3H) ppm; ^13C NMR (75 MHz, CDCl₃) δ 196.1, 173.9, 159.2, 147.9, 132.6, 130.6, 119.0, 116.94, 82.2, 49.8, 43.3, 42.9, 38.2, 36.7, 34.3, 30.1, 27.6, 27.2, 26.8, 26.1, 23.2, 22.3, 13.8, 12.1 ppm; HRMS (ESI) m/z Calcd for [C₂₄H₃₂O₄+H]⁺ 385.2373, found 385.2374.
Compounds 2a-m were synthesized according to the literature procedure.\(^2\)

![Reaction Scheme]

To a stirred solution of potassium tert-butoxide (3.0 g, 27.2 mmol) in THF (30.0 mL) was added trimethylsulfoxonium iodide (5.0 g, 20.6 mmol) at room temperature. The resulting mixture was refluxed for 2 h and then cooled to 0 °C, followed by addition of acyl chlorides (7.0 mmol) in THF (5.0 mL). The reaction was allowed to warm to room temperature and stirred for 3 h. Then, the solvent was evaporated and water (15.0 mL) and ethyl acetate (20.0 mL) were added to the resulting mixture. The organic layer was separated and the aqueous layer was washed with ethyl acetate (20 mL x 3) and the organic layers were combined. The organic solution was dried over anhydrous Na\(_2\)SO\(_4\) and then filtered. After removing the solvent under vacuum, the crude product was purified by flash chromatography over silica gel using EtOAc/MeOH (95:5) to afford the corresponding sulfoxonium ylides.

1-(dimethyl(oxo)-l6-sulfanylidene)-3-(4-isobutylphenyl)butan-2-one

Pale yellow solid, m. p. 119–120 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.19 (d, \(J = 8.0\) Hz, 2H), 7.07 (d, \(J = 8.0\) Hz, 2H), 4.28 (s, 1H), 3.50 (q, \(J = 7.1\) Hz, 1H), 3.34 (d, \(J = 11.5\) Hz, 6H), 2.43 (d, \(J = 7.2\) Hz, 2H), 1.89 – 1.77 (m, 1H), 1.43 (d, \(J = 7.2\) Hz, 3H), 0.90 (d, \(J = 6.6\) Hz, 6H) ppm; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 192.3, 140.4, 139.7, 129.1, 127.3, 68.7, 50.1, 45.1, 42.3, 42.1, 30.2, 22.5, 18.4 ppm; HRMS (ESI) \(m/z\) Calcd for \([C_{16}H_{24}O_2S+H]^+\) 281.1570, found 281.1571.
3. General Experimental Procedures

A sealed tube was charged with salicylaldehyde substrates 1 (0.2 mmol), [RhCp*Cl₂]₂ (3.0 mol%), AgOTf (20.0 mol%), PivOH (0.6 mmol), sulfoxonium ylides 2 (0.24 mmol) and 0.5 mL THF. Under an argon atmosphere, the reaction mixture was vigorously stirred at 100 °C (oil temperature) for 7 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a plug of Celite. The filtrate was washed with NaHCO₃ and brine, dried over anhydrous Na₂SO₄. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (PE : EA = 10:1) to afford the desired products 3.
4. Mechanistic Experiments

A sealed tube was charged with salicylaldehyde 1a (0.2 mmol), [RhCp*Cl]₂ (3.0 mol%), AgOTf (20.0 mol%), PivOH (0.6 mmol), sulfoxonium ylide 2a (0.24 mmol) and 0.5 mL THF. Under an argon atmosphere, the reaction mixture was vigorously stirred at 100 °C (oil temperature) for 7 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a plug of Celite. The filtrate was washed with NaHCO₃ and brine, dried over anhydrous Na₂SO₄. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (PE : EA = 10:1) to afford the desired product 3aa.

A sealed tube was charged with salicylaldehyde 1a (0.2 mmol), [RhCp*Cl]₂ (3.0 mol%), AgOTf (20.0 mol%), sulfoxonium ylide 2a (0.24 mmol) and 0.5 mL THF. Under an argon atmosphere, the reaction mixture was vigorously stirred at 100 °C (oil temperature) for 7 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a plug of Celite. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (PE : EA = 10:1) to afford the desired product 3aa.
A sealed tube was charged with salicylaldehyde 1a (0.2 mmol), [RhCp*Cl₂]₂ (3.0 mol%), PivOH (0.6 mmol), sulfoxonium ylide 2a (0.24 mmol) and 0.5 mL THF. Under an argon atmosphere, the reaction mixture was vigorously stirred at 100 °C (oil temperature) for 7 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a plug of Celite. The filtrate was washed with NaHCO₃ and brine, dried over anhydrous Na₂SO₄. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (PE : EA = 10:1) to afford the desired product 3aa.

A sealed tube was charged with 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-dione 16 (0.2 mmol), AgOTf (20.0 mol%) and 0.5 mL THF. Under an argon atmosphere, the reaction mixture was vigorously stirred at 100 °C (oil temperature) for 7 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a plug of Celite. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (PE : EA = 10:1) to afford the desired product 3aa.
A sealed tube was charged with 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-dione 16 (0.2 mmol), PivOH (0.6 mmol) and 0.5 mL THF. Under an argon atmosphere, the reaction mixture was vigorously stirred at 100 °C (oil temperature) for 7 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a plug of Celite. The filtrate was washed with NaHCO₃ and brine, dried over anhydrous Na₂SO₄. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (PE : EA = 100:1) to afford 16.

A sealed tube was charged with 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-dione 16 (0.2 mmol) and 0.5 mL THF. Under an argon atmosphere, the reaction mixture was vigorously stirred at 100 °C (oil temperature) for 7 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a plug of Celite. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (PE : EA = 10:1) to afford the desired product 3aa.
Control experiments

Chromone 3aa was obtained in 8% and 6% yields from the reactions, each carried out in the absence of PivOH or AgOTf, respectively (Scheme 2b and 2c). Notably, diketone 16, a potential reaction intermediate, was formed in 33% yield from the reaction run without AgOTf, which indicated that PivOH took part in the formation of the active Cp*RhX\textsubscript{2} complex and the C-H activation process to generate 16. Treatment of 16 with AgOTf in THF produced 3aa in 95% yield (Scheme 2d). Meanwhile, conversion of 16 to 3aa took place only in 9% yield using PivOH (Scheme 2e). Heating compound 16 directly afforded 3aa in 11% yield (Scheme 2d). These results suggested that AgOTf played an important role...
in the formation of an active Cp*RhX₂ complex and promotion of the intramolecular dehydrative condensation of 16 to yield the desired product 3aa.

**Mechanistic hypothesis**

The active Cp*RhX₂ complex is generated from [RhCp*Cl₂], AgOTf and/or PivOH via ligand exchange. After coordination with salicylaldehydes 1 and aldehydic C–H activation, the rhodium catalyst forms metalacyclic intermediate A. Then, sulfoxonium ylide 2 attacks the metal center of intermediate A to deliver intermediate B, which undergoes α-elimination of DMSO to afford the carbene species C. Subsequently, migratory insertion of the Rh-C bond into the carbene generates the six-membered rhodacyclic intermediate D. Protonation of D with PivOH provides intermediate E and regenerates the active Cp*RhX₂ species for the next catalytic cycle. Finally, the silver salt promotes the intramolecular dehydrative condensation of E to chromone 3.
5. Gram-Scale Experiment and Further Transformations

5.1 A gram scale experiment of 3aa

A sealed tube was charged with salicylaldehyde 1a (7.0 mmol), [RhCp*Cl₂]₂ (1.5 mol%), AgOTf (20.0 mol%), PivOH (21.0 mmol), sulfoxonium ylide 2a (8.4 mmol) and 17.5 mL THF. Under an argon atmosphere, the reaction mixture was vigorously stirred at 100 °C (oil temperature) for 12 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a plug of Celite. The filtrate was washed with NaHCO₃ and brine, dried over anhydrous Na₂SO₄. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (PE : EA = 10:1) to afford the desired product 3aa (1.12 g, 72% yield).

5.2 Synthetic Transformation of 3aa to 10³

A sealed tube was charged with 3aa (0.2 mmol), NFSI (0.21 mmol) and CuBr (10.0 mol%), 6,6'-Me₂bpy (12.0 mol%) in DCE (1.0 mL). Under an argon atmosphere, the reaction mixture was stirred at 70 °C for 11 h. The mixture was cooled to room temperature and then additional NFSI (0.21 mmol) and CuBr (10.0 mol%), 6,6'-Me₂bpy (12.0 mol%) were added to the mixture. The reaction mixture was heated for another 48 h. The mixture was then cooled to room temperature and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding product 10 (82.8 mg, 80% yield). ¹H NMR (300
MHz, CDCl$_3$ $\delta$ 8.15 -8.13 (m, 1H), 7.91 – 7.89 (m, 2H), 7.90 – 7.81 (m, 4H), 7.75 – 7.72 (m, 1H), 7.55 – 7.52 (m, 3H), 7.46 (t, $J$ = 7.0 Hz, 2H), 7.37 – 7.33 (m, 6H) ppm.

**5.3 Synthetic Transformation of 3aa to 11$^4$**

\[ \text{PhI(OAc)$_2$, TMSCI} \xrightarrow{\text{CH$_2$Cl$_2$, 0 °C}} \text{Cl} \]

A two neck flask was charged with PhI(OAc)$_2$ (0.15 mmol) in anhydrous DCM (0.5 ml), the solution was protected under Ar atmosphere and stirred in 0 °C. Then trimethylsilyl chloride (0.3 mmol) was added dropwise and the mixture was stirred in 0 °C for 30 min. The 3aa (0.1 mmol) in anhydrous DCM (0.5 ml) and pyridine (0.4 mmol) was added. The mixture was stirred in 0 °C for another 3.5 h. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding product 11 (22.3 mg, 87% yield). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.30 (d, $J$ = 7.9 Hz, 1H), 7.97 – 7.83 (m, 2H), 7.78 – 7.66 (m, 1H), 7.61 – 7.40 (m, 5H) ppm.

**5.4 Synthetic Transformation of 3aa to 12$^5$**

\[ \text{CuI, DMF, 80 °C} \]

A sealed tube was charged with Togni reagent (0.15 mmol) and CuI (10.0 mol%) under Ar atmosphere. Then 3aa (0.1 mmol) in DMF (0.5 ml) was added. The mixture was heated to 80 °C and stirred for 26 h until the complete conversion of 3aa by TLC detection. The resulting mixture was concentrated in vacuo and the residue was dissolved by DCM. The organic layer was washed with saturated sodium chloride, dried
by MgSO\textsubscript{4} and concentrated. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding product 12 (14.5 mg, 50 % yield). \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) δ 8.27 (d, J = 7.9 Hz, 1H), 7.78 – 7.69 (m, 1H), 7.64 – 7.43 (m, 7H) ppm.

5.5 Synthetic Transformation of 3aa to 13

A sealed tube was charged with CuI (10.0 mol%) under Ar atmosphere. Then CH\textsubscript{3}CN (0.5 ml), PMDETA (0.38 mmol), 3aa (0.25 mmol) and ethyl bromodifluoroacetate (0.75 mmol) was added in subsequence. The mixture was heated to 80 °C for 12 h and then the reaction was cooled to room temperature. The mixture was diluted with EtOAc and filtered with a pad of celite. The filtrate was concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding product 13 (44.5 mg, 52 % yield). \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) δ 8.21 (d, J = 8.0 Hz, 1H), 7.70 – 7.65 (m, 3H), 7.62 – 7.42 (m, 5H), 4.36 (q, J = 7.2 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H) ppm.

5.6 Synthetic Transformation of 3aa to 14

To a stirred mixture of 3aa (0.1 mmol), diethylphosphite (0.4 mmol) in acetic acid (0.4 mL) was added Mn(OAc)$_3$•2H$_2$O (0.3 mmol) and NaOAc (0.3 mmol) in three portions and the resulting solution was heated at 60 °C for 24 h. Then it was quenched with water and extracted with CH$_2$Cl$_2$. The combined organic layers were washed with Na$_2$CO$_3$ and brine, dried over anhydrous Na$_2$SO$_4$ and concentrated in vacuo. The
residue was purified by column chromatography to afford the desired compound 14 (19.8 mg, 55 % yield). ¹H NMR (400 MHz, CDCl₃) δ 8.26 – 8.19 (m, 1H), 7.80 – 7.74 (m, 2H), 7.73 – 7.67 (m, 1H), 7.59 – 7.41 (m, 5H), 4.17 – 3.98 (m, 4H), 1.10 (t, J = 7.1 Hz, 6H) ppm.

5.7 Synthetic Transformation of 3aa to 15

A sealed tube was charged with 3aa (0.23 mmol, 1.0 equiv), benzamidine hydrochloride (0.29 mmol, 1.25 equiv), sodium t-butoxide (0.75 mmol, 3.25 equiv) in anhydrous DMSO (1.0 mL). Under Ar atmosphere, the reaction mixture was stirred at 50 °C for 15 min then immediately cooled to room temperature. The saturated ammonium chloride solution was added to the reaction mixture and extracted with EtOAc. The combined organic phase was washed with saturated brine and dried over Na₂SO₄. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding product 15 (67.9 mg, 91% yield). Yellow solid, m. p. 159–160 °C; ¹H NMR (300 MHz, CDCl₃) δ 14.26 (s, 1H), 8.47 (s, 2H), 8.24 (s, 2H), 8.04 (s, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.55 (s, 6H), 7.41 (t, J = 7.7 Hz, 1H), 7.09 (d, J = 8.2 Hz, 1H), 6.97 (t, J = 7.5 Hz, 1H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 165.1, 165.0, 162.5, 161.1, 137.0, 136.6, 133.4, 131.3, 131.2, 129.0, 128.8, 128.2, 127.4, 126.9, 119.2, 118.9, 117.4, 108.4 ppm; HRMS (ESI) m/z Calcd for [C₂₂H₁₆N₂O+H]+ 325.1335, found 325.1338.
6. Characterization of the Products

2-phenyl-4H-chromen-4-one (3aa):\(^9\)
36.0 mg, 81\% yield; White solid, \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 8.24 – 8.18\) (m, 1H), 7.94 – 7.84 (m, 2H), 7.72 – 7.62 (m, 1H), 7.59 – 7.44 (m, 4H), 7.43 – 7.35 (m, 1H), 6.80 (s, 1H) ppm.

6-fluoro-2-phenyl-4H-chromen-4-one (3ba):
40.3 mg, 84\% yield; Light yellow solid, m. p. 122–123 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 7.88\) (m, 3H), 7.63 – 7.47 (m, 4H), 7.43 – 7.37 (m, 1H), 6.80 (s, 1H) ppm; \(^1\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 177.5, 163.6, 159.5\) (d, \(J = 246.9\) Hz), 152.4, 131.7, 131.4, 129.0, 126.2, 125.1 (d, \(J = 7.1\) Hz), 121.8 (d, \(J = 25.5\) Hz), 120.1 (d, \(J = 8.1\) Hz), 110.6 (d, \(J = 23.7\) Hz), 106.8 ppm; HRMS (ESI) \(m/z\) Calcd for [C\(_{15}\)H\(_9\)FO\(_2\)+H]\(^+\) 241.0659, found 241.0660.

6-chloro-2-phenyl-4H-chromen-4-one (3ca):
42.4 mg, 83\% yield; White solid, m. p. 178–179 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 8.16\) (s, 1H), 7.89 (d, \(J = 7.3\) Hz, 2H), 7.62 (d, \(J = 8.8\) Hz, 1H), 7.59 – 7.47 (m, 4H), 6.80 (s, 1H) ppm; \(^1\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 177.1, 163.6, 154.5, 133.9, 131.9, 131.3, 131.2, 129.1, 126.3, 125.1, 124.9, 119.8, 107.4\) ppm; HRMS (ESI) \(m/z\) Calcd for [C\(_{15}\)H\(_9\)ClO\(_2\)+H]\(^+\) 257.0364, found 257.0368.
6-bromo-2-phenyl-4H-chromen-4-one (3da):
51.7 mg, 86% yield; White solid, m. p. 187–188 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.32 (d, \(J = 2.5\) Hz, 1H), 7.93 – 7.83 (m, 2H), 7.80 – 7.71 (m, 1H), 7.52 (d, \(J = 7.0\) Hz, 3H), 7.45 (d, \(J = 8.9\) Hz, 1H), 6.81 (s, 1H) ppm; \(^1\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 176.5, 163.1, 154.5, 136.2, 131.4, 130.8, 128.6, 127.8, 125.8, 124.8, 119.5, 118.2, 107.0 ppm; HRMS (ESI) m/z Calcd for \([C_{15}H_{9}BrO_2+H]^+\) 300.9859, found 300.9865.

7-chloro-2-phenyl-4H-chromen-4-one (3ea):
36.3 mg, 71% yield; Light red solid, m. p. 150–151 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.16 (d, \(J = 8.5\) Hz, 1H), 7.95 – 7.82 (m, 2H), 7.63 – 7.47 (m, 4H), 7.37 (d, \(J = 8.6\) Hz, 1H), 6.80 (s, 1H) ppm; \(^1\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 177.5, 163.5, 156.3, 139.8, 131.8, 131.3, 129.1, 127.1, 126.3, 126.1, 122.5, 118.2, 107.8 ppm; HRMS (ESI) m/z Calcd for \([C_{15}H_{9}ClO_2+H]^+\) 257.0364, found 257.0362.

6, 8-dibromo-2-phenyl-4H-chromen-4-one (3fa):
68.3 mg, 90% yield; White solid, m. p. 161–162 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.23 (s, 1H), 8.05 – 7.86 (m, 3H), 7.52 (d, \(J = 6.9\) Hz, 3H), 6.82 (s, 1H) ppm; \(^1\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 175.9, 163.0, 151.2, 138.8, 131.7, 130.2, 128.7, 127.2, 125.9, 125.4, 118.0, 112.6, 106.5 ppm; HRMS (ESI) m/z Calcd for \([C_{15}H_{8}Br_2O_2+H]^+\) 378.8964, found 378.8962.
8-bromo-6-chloro-2-phenyl-4H-chromen-4-one (3ga):

59.2 mg, 88% yield; Light yellow solid, m. p. 174–175 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.14 – 8.04 (m, 1H), 8.01 – 7.91 (m, 2H), 7.90 – 7.81 (m, 1H), 7.53 (d, $J$ = 5.5 Hz, 3H), 6.83 (d, $J$ = 2.1 Hz, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) δ 176.0, 163.0, 150.8, 136.2, 131.7, 130.8, 130.3, 128.7, 125.9, 125.1, 124.1, 112.4, 106.5 ppm; HRMS (ESI) $m/z$ Calcd for [C$_{15}$H$_8$BrClO$_2$+H]$^+$ 334.9469, found 334.9470.

5-bromo-2-phenyl-4H-chromen-4-one (3ha):

23.4 mg, 39% yield; Red brown solid, m. p. 144–145 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.90 (d, $J$ = 5.4 Hz, 2H), 7.64 (d, $J$ = 7.2 Hz, 1H), 7.59 – 7.40 (m, 5H), 6.80 (s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) δ 177.1, 161.7, 157.7, 133.2, 131.9, 131.7, 131.1, 129.1, 126.2, 121.7, 120.4, 118.1, 108.5 ppm; HRMS (ESI) $m/z$ Calcd for [C$_{15}$H$_9$BrO$_2$+H]$^+$ 300.9859, found 300.9864.

6-nitro-2-phenyl-4H-chromen-4-one (3ia):

37.2 mg, 70% yield; Light yellow solid, m. p. 182–183 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 9.09 (s, 1H), 8.53 (d, $J$ = 9.1 Hz, 1H), 7.93 (d, $J$ = 6.9 Hz, 2H), 7.73 (d, $J$ = 9.1 Hz, 1H), 7.57 (d, $J$ = 6.4 Hz, 3H), 6.88 (s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) δ 176.2, 163.7, 158.5, 144.3, 131.9, 130.2, 128.8, 127.6, 125.9, 123.5, 121.9, 119.4, 107.3 ppm; HRMS (ESI) $m/z$ Calcd for [C$_{15}$H$_9$NO$_4$+H]$^+$ 268.0604, found 268.0604.
methyl 4-oxo-2-phenyl-4H-chromene-6-carboxylate (3ja):
44.8 mg, 80% yield; Light red solid, m. p. 184–185 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.88 (s, 1H), 8.34 (d, \(J = 8.5\) Hz, 1H), 7.91 (d, \(J = 7.1\) Hz, 2H), 7.67 – 7.46 (m, 4H), 6.83 (s, 1H), 3.95 (s, 3H) ppm; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 177.6, 165.7, 163.6, 158.6, 134.4, 131.9, 131.2, 129.1, 128.1, 127.2, 126.3, 123.6, 118.5, 107.8, 52.4 ppm; HRMS (ESI) m/z Calcd for [C\(_{17}\)H\(_{12}\)O\(_4\)+H]\(^+\) 281.0808, found 281.0809.

6-methyl-2-phenyl-4H-chromen-4-one (3ka):
31.0 mg, 66% yield; White solid, m. p. 124–125 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.02 (s, 1H), 7.98 – 7.87 (m, 2H), 7.59 – 7.42 (m, 5H), 6.81 (s, 1H), 2.47 (s, 3H) ppm; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 178.6, 163.2, 154.6, 135.2, 135.0, 131.9, 131.5, 129.0, 126.3, 125.1, 123.7, 117.8, 107.5, 20.9 ppm; HRMS (ESI) m/z Calcd for [C\(_{16}\)H\(_{12}\)O\(_2\)+H]\(^+\) 237.0910, found 237.0908.

6-methoxy-2-phenyl-4H-chromen-4-one (3la):
30.9 mg, 61% yield; Light yellow solid, m. p. 154–155 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.92 (d, \(J = 4.2\) Hz, 2H), 7.68 – 7.44 (m, 5H), 7.29 (d, \(J = 9.2\) Hz, 1H), 6.82 (s, 1H), 3.91 (s, 3H) ppm; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 178.3, 163.2, 157.0, 151.1, 131.9, 131.5, 129.0, 126.2, 124.6, 123.8, 119.5, 106.8, 104.8, 55.9 ppm; HRMS (ESI) m/z Calcd for [C\(_{16}\)H\(_{12}\)O\(_3\)+H]\(^+\) 253.0859, found 253.0857.
2, 6-diphenyl-4\(H\)-chromen-4-one (3ma):
50.3 mg, 84% yield; White solid, \textbf{m. p.} 150–151 °C; \textbf{\(^1\text{H NMR}\)} (300 MHz, CDCl\(_3\)) \(\delta\) 8.48 – 8.39 (m, 1H), 7.98 – 7.86 (m, 3H), 7.73 – 7.33 (m, 9H), 7.90 – 7.79 (m, 1H) ppm; \textbf{\(^{13}\text{C NMR}\)} (75 MHz, CDCl\(_3\)) \(\delta\) 178.4, 163.4, 155.6, 139.3, 138.3, 132.6, 131.7, 131.6, 129.1, 129.0, 127.9, 127.2, 126.3, 124.1, 123.5, 118.6, 107.6 ppm; \textbf{HRMS (ESI)} \(m/z\) Calcd for \([\text{C}_{21}\text{H}_{14}\text{O}_2]^+\) 299.1067, found 299.1065.

2-phenyl-6-(thiophen-3-yl)-4\(H\)-chromen-4-one (3na):
46.9 mg, 77% yield; Yellow solid, \textbf{m. p.} 196–197 °C; \textbf{\(^1\text{H NMR}\)} (300 MHz, CDCl\(_3\)) \(\delta\) 8.39 (s, 1H), 7.90 (d, \(J = 7.4\) Hz, 3H), 7.65 – 7.35 (m, 7H), 6.82 (s, 1H) ppm; \textbf{\(^{13}\text{C NMR}\)} (75 MHz, CDCl\(_3\)) \(\delta\) 178.4, 163.4, 155.3, 140.5, 133.1, 131.9, 131.6, 129.1, 126.7, 126.3, 126.2, 124.1, 122.5, 121.2, 118.6, 107.5 ppm; \textbf{HRMS (ESI)} \(m/z\) Calcd for \([\text{C}_{19}\text{H}_{12}\text{O}_2\text{S}^+\text{H}]^+\) 305.0631, found 305.0637.

2-phenyl-4\(H\)-benzo[\(h\)]chromen-4-one (3oa):
45.9 mg, 84% yield; Light yellow solid, \textbf{m. p.} 143–144 °C; \textbf{\(^1\text{H NMR}\)} (300 MHz, CDCl\(_3\)) \(\delta\) 8.57 – 8.47 (m, 1H), 8.17 – 8.08 (m, 1H), 7.98 (s, 2H), 7.92 – 8.84 (m, 1H), 7.78 – 7.62 (m, 3H), 7.61 – 7.49 (m, 3H), 6.92 (d, \(J = 3.4\) Hz, 1H) ppm; \textbf{\(^{13}\text{C NMR}\)} (75 MHz, CDCl\(_3\)) \(\delta\) 178.2, 162.6, 153.5, 136.0, 131.9, 131.5, 129.2, 129.2, 128.2, 127.1, 126.2, 125.3, 124.1, 122.3, 120.7, 120.2, 108.7 ppm; \textbf{HRMS (ESI)} \(m/z\) Calcd for \([\text{C}_{19}\text{H}_{12}\text{O}_2]^+\) 273.0910, found 273.0912.
3-phenyl-1H-benzof[\f]chromen-1-one (3pa):
52.9 mg, 97% yield; White solid, m. p. 152–153 °C; m. p. 152–153 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 10.08 (d, $J$ = 8.6 Hz, 1H), 8.06 (d, $J$ = 9.0 Hz, 1H), 7.97 – 7.82 (m, 3H), 7.80 – 7.69 (m, 1H), 7.64 – 7.46 (m, 5H), 6.96 (s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) δ 180.3, 160.7, 157.3, 135.4, 131.4, 130.6, 130.4, 129.2, 129.0, 128.1, 127.2, 126.6, 126.0, 117.5, 117.2, 110.4 ppm; HRMS (ESI) m/z Calcd for [C$_{19}$H$_{12}$O$_2$+H]$^+$ 273.0910, found 273.0914.

3-(2-methoxyphenyl)-1H-benzof[\f]chromen-1-one (3pb):
57.2 mg, 95% yield; Light yellow solid, m. p. 170–171 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 9.99 (d, $J$ = 8.6 Hz, 1H), 7.92 (d, $J$ = 9.0 Hz, 1H), 7.82 (d, $J$ = 8.1 Hz, 1H), 7.75 (d, $J$ = 8.0 Hz, 1H), 7.69 – 7.57 (m, 1H), 7.52 – 7.39 (m, 2H), 7.38 – 7.27 (m, 1H), 7.21 (s, 1H), 7.03 – 6.94 (m, 1H), 6.90 (d, $J$ = 8.3 Hz, 1H), 3.82 (s, 3H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) δ 180.8, 158.1, 158.0, 157.5, 135.2, 132.3, 130.5, 130.5, 129.1, 129.0, 128.1, 127.2, 126.4, 120.7, 120.2, 117.7, 117.0, 115.6, 111.7, 55.7 ppm; HRMS (ESI) m/z Calcd for [C$_{20}$H$_{14}$O$_3$+H]$^+$ 303.1016, found 303.1016.

3-(3-methoxyphenyl)-1H-benzof[\f]chromen-1-one (3pc):
57.4 mg, 95% yield; Light yellow solid, m. p. 124–125 °C; \(^1H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 10.03 (d, \(J = 8.6\) Hz, 1H), 8.02 (d, \(J = 9.0\) Hz, 1H), 7.83 (d, \(J = 8.0\) Hz, 1H), 7.76 – 7.66 (m, 1H), 7.61 – 6.43 (m, 3H), 7.42 – 7.33 (m, 2H), 7.07 – 6.97 (m, 1H), 6.90 (s, 1H), 3.86 (s, 3H) ppm; \(^{13}C\) NMR (75 MHz, CDCl\(_3\)) \(\delta\) 180.2, 160.5, 160.0, 157.3, 135.4, 132.6, 130.5, 130.4, 130.1, 129.2, 128.1, 127.1, 126.6, 118.4, 117.6, 117.2, 116.9, 111.5, 110.5, 55.5 ppm; HRMS (ESI) \(m/z\) Calcd for \([C_{20}H_{14}O_3+H]^+\) 303.1016, found 303.1017.

3-(\(p\)-tolyl)-1\(H\)-benzo[\(f\)]chromen-1-one (3pd):

55.1 mg, 96% yield; Light yellow solid, m. p. 185–186 °C; \(^1H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 10.04 (d, \(J = 8.6\) Hz, 1H), 8.00 (d, \(J = 9.0\) Hz, 1H), 7.88 – 7.65 (m, 4H), 7.61 – 7.44 (m, 2H), 7.24 (d, \(J = 7.7\) Hz, 2H), 6.86 (s, 1H), 2.36 (s, 3H) ppm; \(^{13}C\) NMR (75 MHz, CDCl\(_3\)) \(\delta\) 180.3, 160.9, 157.2, 141.9, 135.3, 130.5, 130.5, 129.7, 129.1, 128.4, 128.1, 127.2, 126.5, 125.9, 117.6, 117.1, 109.7, 21.5 ppm; HRMS (ESI) \(m/z\) Calcd for \([C_{20}H_{14}O_2+H]^+\) 287.1067, found 287.1065.

3-(4-methoxyphenyl)-1\(H\)-benzo[\(f\)]chromen-1-one (3pe):

56.7 mg, 94% yield; Light yellow solid, m. p. 160–161 °C; \(^1H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 10.05 (d, \(J = 8.6\) Hz, 1H), 8.00 (d, \(J = 9.0\) Hz, 1H), 7.81 (d, \(J = 8.3\) Hz, 3H), 7.75 – 7.66 (m, 1H), 7.61 – 7.44 (m, 2H), 6.95 (d, \(J = 8.4\) Hz, 2H), 6.82 (s, 1H), 3.82 (s, 3H) ppm; \(^{13}C\) NMR (75 MHz, CDCl\(_3\)) \(\delta\) 180.2, 162.1, 160.7, 157.1, 135.2, 130.5, 130.5,
129.0, 128.1, 127.6, 127.2, 126.4, 123.5, 117.5, 117.0, 114.4, 108.9, 55.5 ppm; HRMS (ESI) \( m/z \) Calcd for \([C_{20}H_{14}O_3+H]^+\) 303.1016, found 303.1017.

3-(4-fluorophenyl)-1H-benzo[f]chromen-1-one (3pf):
45.2 mg, 78% yield; White solid, \textit{m. p.} 193–194 °C; \(^1\text{H NMR} (300 MHz, CDCl\textsubscript{3}) \delta 10.05 (s, 1H), 8.15 – 7.99 (m, 1H), 7.89 (s, 3H), 7.73 (s, 1H), 7.65 – 7.47 (m, 2H), 7.19 (s, 2H), 6.86 (s, 1H) ppm; \(^{13}\text{C NMR} (75 MHz, CDCl\textsubscript{3}) \delta 180.1, 164.6 (d, J = 253.0 Hz), 159.8, 157.2, 135.5, 130.6, 130.4, 129.3, 128.3, 128.2, 127.5 (d, J = 3.4 Hz), 127.1, 126.7, 117.4, 117.1, 116.3 (d, J = 22.1 Hz), 110.1 ppm; \textbf{HRMS (ESI)} \( m/z \) Calcd for \([C_{19}H_{11}ClO_2+H]^+\) 307.0520, found 307.0522.

3-(4-bromophenyl)-1H-benzo[f]chromen-1-one (3pg):
41.5 mg, 59% yield; White solid, \textit{m. p.} 219–220 °C; \(^1\text{H NMR} (300 MHz, CDCl\textsubscript{3}) \delta 10.05 (d, J = 8.7 Hz, 1H), 8.11 (d, J = 9.1 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.85 – 7.72 (m, 3H), 7.70 – 7.55 (m, 4H), 6.94 (s, 1H) ppm; \(^{13}\text{C NMR} (75 MHz, CDCl\textsubscript{3}) \delta 180.1, 159.7, 157.3, 135.7, 132.4, 130.6, 130.4, 130.3, 129.4, 128.2, 127.5, 127.1, 126.7, 126.1, 117.5, 117.2, 110.5 ppm; \textbf{HRMS (ESI)} \( m/z \) Calcd for \([C_{19}H_{11}BrO_2+H]^+\) 351.0015, found 351.0015.
3-(naphthalen-1-yl)-1H-benzo[f]chromen-1-one (3ph):
42.9 mg, 67% yield; Light yellow solid, m. p. 144–145 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 10.14 (d, \(J = 8.5\) Hz, 1H), 8.23 – 8.08 (m, 2H), 8.03 (d, \(J = 8.2\) Hz, 1H), 7.98 – 7.88 (m, 2H), 7.85 – 7.74 (m, 2H), 7.70 – 7.51 (m, 5H), 6.87 (s, 1H) ppm; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 180.2, 162.8, 158.0, 135.7, 133.8, 131.5, 130.7, 130.6, 130.5, 130.1, 129.4, 128.8, 128.3, 128.1, 127.5, 127.3, 126.7, 126.6, 125.1, 124.9, 117.7, 117.3, 116.0 ppm; HRMS (ESI) \(m/z\) Calcd for [C\(_{23}\)H\(_{14}\)O\(_2\)+H]\(^+\) 323.1067, found 323.1068.

3-(thiophen-2-yl)-1H-benzo[f]chromen-1-one (3pi):
49.4 mg, 89% yield; Brown solid, m. p. 154–155 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 10.02 (d, \(J = 8.6\) Hz, 1H), 8.01 (d, \(J = 9.0\) Hz, 1H), 7.83 (d, \(J = 8.0\) Hz, 1H), 7.75 – 7.62 (m, 2H), 7.59 – 7.44 (m, 3H), 7.17 – 7.10 (m, 1H), 6.77 (s, 1H) ppm; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 179.8, 156.9, 156.6, 135.4, 134.6, 130.6, 130.4, 129.9, 129.2, 128.5, 128.2, 128.1, 127.1, 126.6, 117.4, 117.2, 109.0 ppm; HRMS (ESI) \(m/z\) Calcd for [C\(_{17}\)H\(_{10}\)O\(_2\)S+H]\(^+\) 279.0474, found 279.0473.

3-(tert-butyl)-1H-benzo[f]chromen-1-one (3pj):
45.8 mg, 91% yield; Brown solid, m. p. 105–106 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 10.04 (d, \(J = 8.7\) Hz, 1H), 8.05 (d, \(J = 9.1\) Hz, 1H), 7.87 (d, \(J = 8.0\) Hz, 1H), 7.78 – 7.70
(m, 1H), 7.62 – 7.55 (m, 1H), 7.50 (d, J = 9.1 Hz, 1H), 6.43 (s, 1H), 1.39 (s, 9H) ppm; 
\[\text{\textsuperscript{13}C NMR (75 MHz, CDCl}_3\text{)} \delta 180.9, 173.2, 157.6, 135.1, 130.5, 130.4, 129.1, 128.1, 127.1, 126.4, 117.6, 116.6, 109.7, 36.0, 27.9 \text{ ppm; HRMS (ESI) m/z Calcd for [C}_{17}H_{16}O_2+H]^+ 253.1223, found 253.1224.}

3-cyclohexyl-1\textit{H}-benzo[f]chromen-1-one (3pk):
51.8 mg, 93% yield; White solid, \textbf{m. p.} 166–167 °C; \[\text{\textsuperscript{1}H NMR (300 MHz, CDCl}_3\text{)} \delta 10.04 (d, J = 8.6 Hz, 1H), 8.02 (d, J = 9.1 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.77 – 7.67 (m, 1H), 7.62 – 7.52 (m, 1H), 7.46 (d, J = 9.0 Hz, 1H), 6.31 (s, 1H), 7.265 – 2.47 (m, 1H), 2.07 (d, J = 11.0 Hz, 2H), 1.89 (d, J = 12.3 Hz, 2H), 1.77 (d, J = 11.6 Hz, 1H), 1.58 – 1.19 (m, 5H) ppm; \[\text{\textsuperscript{13}C NMR (75 MHz, CDCl}_3\text{)} \delta 180.7, 170.5, 157.6, 135.1, 130.5, 130.4, 129.0, 128.1, 127.1, 126.4, 117.6, 116.9, 110.8, 42.1, 30.4, 25.9, 25.8 \text{ ppm; HRMS (ESI) m/z Calcd for [C}_{19}H_{18}O_2+H]^+ 279.1380, found 279.1375.}

3-((3\textit{r},5\textit{r},7\textit{r})-adamantan-1-yl)-1\textit{H}-benzo[f]chromen-1-one (3pl):
61.6 mg, 93% yield; White solid, \textbf{m. p.} 173–174 °C; \[\text{\textsuperscript{1}H NMR (300 MHz, CDCl}_3\text{)} \delta 10.04 (d, J = 8.6 Hz, 1H), 8.03 (d, J = 9.1 Hz, 1H), 7.86 (d, J = 7.9 Hz, 1H), 7.76 – 7.67 (m, 1H), 7.62 – 7.53 (m, 1H), 7.49 (d, J = 9.0 Hz, 1H), 6.35 (s, 1H), 2.13 (s, 3H), 1.99 (d, J = 2.9 Hz, 6H), 1.88 – 1.71 (m, 6H) ppm; \[\text{\textsuperscript{13}C NMR (75 MHz, CDCl}_3\text{)} \delta 181.0, 173.0, 157.6, 135.1, 130.5, 130.4, 129.0, 128.1, 127.1, 126.4, 117.6, 116.7, 109.6, 39.6, 37.7, 36.5, 28.0 \text{ ppm; HRMS (ESI) m/z Calcd for [C}_{23}H_{22}O_2+H]^+ 331.1693, found 331.1692.}
6-((3r,5r,7r)-adamantan-1-yl)-8H-[1,3]dioxolo[4,5-g]chromen-8-one (4):

61.6 mg, 95% yield; White solid, m. p. 203–204 °C; \(^{1}H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.48 (s, 1H), 6.86 (s, 1H), 6.14 (s, 1H), 6.09 (s, 2H), 2.12 (s, 3H), 1.94 (s, 6H), 1.87 – 1.70 (m, 6H) ppm; \(^{13}C\) NMR (75 MHz, CDCl\(_3\)) \(\delta\) 177.6, 174.5, 153.2, 152.0, 145.3, 117.9, 105.4, 101.8, 101.6, 97.3, 39.0, 37.5, 35.9, 27.4 ppm; HRMS (ESI) \(m/z\) Calcd for \([C_{20}H_{20}O_4+H]^+\) 325.1434, found 325.1434.

(1R,3aR,3bS,11bR,13aR)-8-cyclohexyl-13a-methyl-10-oxo-1,2,3,3a,4,5,10,11b,12,13,13a-dodecahydrocyclopenta[5,6]naphtho[1,2-g]chromen-1-yl pentanoate (5):

36.0 mg, 37% yield; White solid, m. p. 113–114 °C; \(^{1}H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.05 (s, 1H), 7.14 (s, 1H), 6.12 (s, 1H), 4.70 (dd, \(J = 9.1, 7.5\) Hz, 1H), 3.09 – 2.87 (m, 2H), 2.57 – 2.41 (m, 2H), 2.38 – 2.14 (m, 4H), 2.07 – 1.97 (m, 2H), 1.96 – 1.82 (m, 4H), 1.81 – 1.70 (m, 2H), 1.69 – 1.51 (m, 4H), 1.49 – 1.23 (m, 12H), 0.93 (t, \(J = 7.3\) Hz, 3H), 0.83 (s, 3H) ppm; \(^{13}C\) NMR (75 MHz, CDCl\(_3\)) \(\delta\) 178.9, 174.0, 173.0, 154.7, 144.0, 138.1, 121.8, 121.5, 117.0, 107.5, 82.3, 49.9, 43.9, 42.9, 42.8, 38.1, 36.7, 34.3, 30.4, 29.8, 27.6, 27.2, 26.8, 26.1, 25.9, 25.8, 23.3, 22.3, 13.8, 12.0 ppm; HRMS (ESI) \(m/z\) Calcd for \([C_{32}H_{42}O_4+H]^+\) 491.3156, found 491.3154.
3-(1-(4-isobutylphenyl)ethyl)-1H-benzo[f]chromen-1-one (6):
55.7 mg, 78% yield; Light yellow solid, m. p. 91–92 °C; ¹H NMR (300 MHz, CDCl₃) δ 10.01 (d, J = 8.6 Hz, 1H), 7.99 (d, J = 9.1 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.76 – 7.65 (m, 1H), 7.62 – 7.51 (m, 1H), 7.42 (d, J = 9.1 Hz, 1H), 7.24 (d, J = 7.0 Hz, 2H), 7.12 (d, J = 7.6 Hz, 2H), 6.38 (s, 1H), 4.10 – 3.98 (m, 1H), 2.45 (d, J = 7.1 Hz, 2H), 1.93 – 1.77 (m, 1H), 1.69 (d, J = 7.2 Hz, 3H), 0.89 (d, J = 6.5 Hz, 6H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 180.5, 169.1, 157.6, 140.9, 138.3, 135.1, 130.5, 129.6, 129.1, 128.0, 127.3, 127.1, 126.4, 117.6, 116.9, 112.1, 45.0, 43.4, 30.2, 22.4, 18.9 ppm; HRMS (ESI) m/z Calcd for [C₂₅H₂₄O₂+H]⁺ 357.1849, found 357.1844.

3-((1S,4R)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptan-1-yl)-1H-benzo[f]chromen-1-one (7):
49.5 mg, 71% yield; Brown solid, m. p. 132–133 °C; ¹H NMR (300 MHz, CDCl₃) δ 10.01 (d, J = 8.5 Hz, 1H), 8.10 (d, J = 9.0 Hz, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.81 – 7.70 (m, 1H), 7.68 – 7.56 (m, 1H), 7.48 (d, J = 9.0 Hz, 1H), 6.72 (s, 1H), 2.78 – 2.63 (m, 1H), 2.20 – 1.98 (m, 2H), 1.91 – 1.77 (m, 1H), 1.18 (d, J = 7.0 Hz, 6H), 0.96 (s, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 179.3, 178.0, 159.6, 157.2, 135.8, 130.7, 130.3, 129.5, 128.2, 127.1, 126.9, 117.3, 117.2, 113.2, 90.3, 55.3, 54.5, 30.7, 28.9, 17.0, 16.8, 10.0 ppm; HRMS (ESI) m/z Calcd for [C₂₃H₂₄O₂+H]⁺ 349.1434, found 349.1435.
methyl (R)-2-(1,3-dioxoisodolin-2-yl)-3-(4-oxo-2-((1S,4R)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptan-1-yl)-4H-chromen-6-yl)propanoate (8):
54.1 mg, 51% yield; Brown solid, m. p. 63–64 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.00 (d, J = 6.8 Hz, 1H), 7.75 (d, J = 21.5 Hz, 4H), 7.58 – 7.48 (m, 1H), 7.33 – 7.25 (m, 1H), 6.48 (s, 1H), 5.16 (dd, J = 10.3, 4.9 Hz, 1H), 3.79 (s, 3H), 3.74 – 3.55 (m, 2H), 2.69 – 2.52 (m, 1H), 2.14 – 1.91 (m, 2H), 1.88 – 1.71 (m, 1H), 1.16 (s, 3H), 1.11 (s, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 177.8, 177.0, 168.9, 167.4, 162.2, 154.9, 134.7, 134.5, 134.3, 131.5, 126.0, 123.9, 123.7, 118.2, 110.2, 90.4, 55.3, 54.5, 53.2, 53.1, 34.3, 30.8, 28.8, 17.0, 16.7, 9.9 ppm; HRMS (ESI) m/z Calcd for [C₃₀H₂₇N₄O₈+H]⁺ 530.1809, found 530.1817.

(3aR,3bS,11bR,13aR)-8-((3R,5R,7R)-adamantan-1-yl)-13a-methyl 2,3,3a,3b,4,5,11b,12,13,13a-decahydrocyclopenta[5,6]naphtho[1,2-g]chromene-1,10-dione (9):
61.0 mg, 67% yield; Light yellow solid, m. p. Carbonization; ¹H NMR (300 MHz, CDCl₃) δ 8.06 (s, 1H), 7.20 (s, 1H), 6.14 (s, 1H), 3.14 – 2.88 (m, 2H), 2.69 – 2.42 (m, 2H), 2.41 – 2.25 (m, 1H), 2.24 – 1.86 (m, 13H), 1.85 – 1.41 (m, 12H), 0.91 (s, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 179.1, 175.4, 154.8, 143.7, 137.5, 121.7, 121.4, 117.1, 106.2, 50.5, 47.9, 44.1, 39.5, 38.1, 37.9, 36.5, 35.8, 31.4, 29.6, 28.0, 26.1, 25.8, 21.6, 13.8 ppm; HRMS (ESI) m/z Calcd for [C₃₁H₃₆O₃+H]⁺ 457.2737, found 457.2746.
7. References

(1) P. Sun, S. Gao, C. Yang, S. Guo, A. Lin and H Yao, Org. Lett., 2016, 18, 6464.
8. $^1$H and $^{13}$C NMR Spectra of Title Compounds

(8S,9R,13R,14R,17R)-2-formyl-3-hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl pentanoate
1-(dimethyl(oxo)-l6-sulfanylidene)-3-(4-isobutylphenyl)butan-2-one
$N$-(4-oxo-2-phenyl-$4\text H$-chromen-3-yl)-$N$-(phenylsulfonyl)benzenesulfonamide (10)

3-chloro-2-phenyl-$4\text H$-chromen-4-one (11)
2-phenyl-3-(trifluoromethyl)-4H-chromen-4-one (12)

ethyl 2,2-difluoro-2-(4-oxo-2-phenyl-4H-chromen-3-yl)acetate (13)
diethyl (4-oxo-2-phenyl-4H-chromen-3-yl)phosphonate (14)
2-(2,6-diphenylpyrimidin-4-yl)phenol (15)
2-phenyl-4H-chromen-4-one (3aa)
6-fluoro-2-phenyl-4H-chromen-4-one (3ba)
6-chloro-2-phenyl-4H-chromen-4-one (3ca)
6-bromo-2-phenyl-4\(H\)-chromen-4-one (3da)
7-chloro-2-phenyl-4H-chromen-4-one (3ea)
6, 8-dibromo-2-phenyl-4H-chromen-4-one (3fa)
8-bromo-6-chloro-2-phenyl-4H-chromen-4-one (3ga)
5-bromo-2-phenyl-4H-chromen-4-one (3ha)
6-nitro-2-phenyl-4H-chromen-4-one (3ia)
methyl 4-oxo-2-phenyl-4H-chromene-6-carboxylate (3ja)
6-methyl-2-phenyl-4H-chromen-4-one (3ka)
6-methoxy-2-phenyl-4H-chromen-4-one (3la)
2, 6-diphenyl-4H-chromen-4-one (3ma)
2-phenyl-6-(thiophen-3-yl)-4H-chromen-4-one (3na)
2-phenyl-4H-benzo[h]chromen-4-one (3oa)
3-phenyl-1H-benzo[f]chromen-1-one (3pa)
3-(2-methoxyphenyl)-1H-benzo[f]chromen-1-one (3pb)
3-(3-methoxyphenyl)-1\textit{H}-benzo[\textit{f}]chromen-1-one (3pc)
3-(p-tolyl)-1H-benzo[f]chromen-1-one (3pd)
3-(4-methoxyphenyl)-1H-benzo[f]chromen-1-one (3pe)
3-(4-fluorophenyl)-1H-benzo[f]chromen-1-one (3pf)
3-(4-bromophenyl)-1H-benzo[f]chromen-1-one (3pg)
3-(naphthalen-1-yl)-1H-benzo[f]chromen-1-one (3ph)
3-(thiophen-2-yl)-1H-benzo[f]chromen-1-one (3pi)
3-(tert-butyl)-1H-benzo[f]chromen-1-one (3pj)
3-cyclohexyl-1H-benzo[f]chromen-1-one (3pk)
3-((3r,5r,7r)-adamantan-1-yl)-1H-benzo[f]chromen-1-one (3pl)
6-((3r,5r,7r)- adamantan-1-yl)-8H-[1,3]dioxolo[4,5-g]chromen-8-one (4)
(1R,3aR,3bS,11bR,13aR)-8-cyclohexyl-13a-methyl-10-oxo-1,2,3,3a,3b,4,5,10,11b,12,13,13a-dodecahydrocyclopenta[5,6]naptho[1,2-g]chromen-1-yl pentanoate (5)
3-(1-(4-isobutylphenyl)ethyl)-1H-benzof[chromen-1-one (6)
3-((1S,4R)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptan-1-yl)-1H-benzo[f]chromen-1-one (7)
methyl (R)-2-(1,3-dioxoisindolin-2-yl)-3-(4-oxo-2-((1S,4R)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptan-1-yl)-4H-chromen-6-yl)propanoate (8)
(3aR,3bS,11bR,13aR)-8-((3R,5R,7R)-adamantan-1-yl)-13a-methyl 2,3,3a,4,5,11b,12,13,13a-decahydrocyclopenta[5,6]naphtho[1,2-g]chromene-1,10-dione (9)