Coumarin-3-formylpyrazoles as 3-Carbon Synthons in Cyclocondensation for the Synthesis of Spiro-fused Pentacyclic Spirooxindoles

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Table of Contents

1. General experimental information…………………………………………………………S1
2. General procedure for the synthesis of compounds 1…………………………………….S1
3. General experimental procedures for synthesis of compounds 3 ……………………S3
4. Procedure for the scale-up experiment……………………………………………………S10
5. Synthesis of product 4………………………………………………………………………S10
6. X-ray crystal structure of compound 3a………………………………………………………S10
7. Control experiments (The Scheme 6 and Fig. 3 in manuscript)……………………….S11
8. 1H and 13C NMR spectra for compounds 1, 3, 4, 7, 8 and HPLC of 3a………………S13
1. General experimental information.

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by TLC. $^1$H NMR and $^{13}$C NMR spectra were recorded in CDCl$_3$ and DMSO-d$_6$. $^1$H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard (CDCl$_3$ at 7.26 ppm, DMSO-d$_6$ at 2.50 ppm). Data are reported as follows: chemical shift, multiplicity ($s = $ singlet, $br s = $ broad singlet, $d = $ doublet, $t = $ triplet, $q = $ quartet, $m = $ multiplet), coupling constants (Hz) and integration. $^{13}$C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance employed as the internal standard (CDCl$_3$). Melting points were recorded on a melting point apparatus.

2. General procedure for the synthesis of 1.

To a suspension of the 2-oxo-2H-chromene-3-carboxylic acid (5.0 mmol), HOBt (1.01 g, 7.5 mmol) and pyrazole (0.51 g, 7.5 mmol) in CH$_2$Cl$_2$ (20 mL) was added DCC (1.03 g, 5.0 mmol) at 0 °C and stirred for 15 min. The reaction mixture was warmed to room temperature and stirred for 24-72 h. Upon completion, the mixture was filtered through celite, and washed with CH$_2$Cl$_2$ (approximately 10 mL) and concentrated in vacuo. The desired products were recrystallised from absolute ethanol to give compounds 1a-m as a solid.

3-(1H-pyrazole-1-carbonyl)-2H-chromen-2-one (1a). White solid; 744.1 mg, 62% yield; m.p. 168.5-169.3 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.37 (d, $J = 2.9$ Hz, 1H), 8.18 (s, 1H), 7.75 (s, 1H), 7.69 – 7.58 (m, 2H), 7.42 – 7.32 (m, 2H), 6.54 (dd, $J = 2.9$, 1.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.9, 157.6, 154.9, 146.0, 145.3, 134.1, 129.5, 129.4, 125.2, 122.3, 117.9, 117.3, 110.8; HRMS (ESI) calcd. for C$_{13}$H$_8$N$_2$NaO$_3$ [M + Na]$^+$ 263.0433, found: 263.0427.

6-fluoro-3-(1H-pyrazole-1-carbonyl)-2H-chromen-2-one (1b). White solid; 283.6 mg, 22% yield; m.p. 214.2-215.0 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.37 (d, $J = 2.9$ Hz, 1H), 8.10 (s, 1H), 7.75 (d, $J = 0.9$ Hz, 1H), 7.46 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 6.56 (dd, $J = 2.9$, 1.5 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.5, 159.1 (d, $J = 245.9$ Hz), 157.2, 151.0, 145.4, 144.6 (d, $J = 2.9$ Hz), 129.4, 123.6, 121.6 (d, $J = 24.5$ Hz), 118.9 (d, $J = 8.3$ Hz), 118.5 (d, $J = 9.2$ Hz), 114.5 (d, $J = 24.0$ Hz), 111.0; HRMS (ESI) calcd. for C$_{13}$H$_8$F$_2$NaO$_3$ [M + Na]$^+$ 281.0333, found: 281.0326.

6-bromo-3-(1H-pyrazole-1-carbonyl)-2H-chromen-2-one (1c). White solid; 380.0 mg, 24% yield; m.p. 212.7-214.6 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.36 (d, $J = 2.9$ Hz, 1H), 8.07 (s, 1H), 7.76 – 7.69 (m, 3H), 7.32 – 7.27 (m, 1H), 6.55 (dd, $J = 2.9$, 1.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.4, 156.9, 153.6, 145.4, 144.4, 136.7, 131.5, 129.4, 123.4, 119.8, 119.0, 117.8, 111.0; HRMS (ESI) calcd. for C$_{13}$H$_8$Br$_2$NaO$_3$ [M + Na]$^+$ 340.9532, found: 340.9529.
7-bromo-3-(1H-pyrazole-1-carbonyl)-2H-chromen-2-one (1d). White solid; 396.3 mg, 25% yield; m.p. 200.1-201.1 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.36 (d, \(J = 2.9\) Hz, 1H), 8.13 (s, 1H), 7.75 (s, 1H), 7.58 (s, 1H), 7.53 – 7.41 (m, 2H), 6.55 (dd, \(J = 2.9\), 1.4 Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 162.4, 156.6, 154.8, 145.1, 145.1, 130.1, 129.2, 128.6, 128.3, 122.2, 120.4, 116.6, 110.8; HRMS (ESI) calcd. for C\(_{13}\)H\(_8\)BrN\(_2\)O\(_3\) [M + Na]\(^+\) 340.9532, found: 340.9547.

8-bromo-3-(1H-pyrazole-1-carbonyl)-2H-chromen-2-one (1e). White solid; 301.0 mg, 19% yield; m.p. 196.9-197.8 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.36 (d, \(J = 2.9\) Hz, 1H), 8.13 (s, 1H), 7.87 (dd, \(J = 7.9\), 1.4 Hz, 1H), 7.76 (s, 1H), 7.61 – 7.51 (m, 1H), 7.25 (d, \(J = 5.8\) Hz, 1H), 6.56 (dd, \(J = 2.9\), 1.5 Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 162.5, 156.6, 151.6, 145.4, 145.3, 137.4, 129.4, 128.6, 125.8, 123.2, 119.2, 111.0, 110.8; HRMS (ESI) calcd. for C\(_{13}\)H\(_8\)BrN\(_2\)O\(_3\) [M + Na]\(^+\) 340.9532, found: 340.9522.

7-chloro-3-(1H-pyrazole-1-carbonyl)-2H-chromen-2-one (1f). White solid; 301.1 mg, 22% yield; m.p. 213.1-214.7 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.36 (d, \(J = 2.9\) Hz, 1H), 8.14 (s, 1H), 7.75 (s, 1H), 7.54 (d, \(J = 8.3\) Hz, 1H), 7.41 (d, \(J = 1.9\) Hz, 1H), 7.33 (dd, \(J = 8.3\), 1.9 Hz, 1H), 6.55 (dd, \(J = 2.9\), 1.4 Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 162.5, 156.8, 151.5, 145.3, 145.1, 140.3, 130.2, 129.4, 125.9, 122.2, 117.6, 116.5, 110.9; HRMS (ESI) calcd. for C\(_{13}\)H\(_8\)ClN\(_2\)O\(_3\) [M + Na]\(^+\) 297.0037, found: 297.0048.

6-methyl-3-(1H-pyrazole-1-carbonyl)-2H-chromen-2-one (1g). White solid; 825.7 mg, 65% yield; m.p. 172.1-173.9 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.36 (d, \(J = 2.9\) Hz, 1H), 8.12 (s, 1H), 7.74 (d, \(J = 1.7\) Hz, 1H), 7.45 (dd, \(J = 8.6\), 1.7, 1H), 7.38 (s, 1H), 7.28 (d, \(J = 8.6\) Hz, 1H), 6.54 (dd, \(J = 2.9\), 1.5 Hz, 1H), 2.42 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.0, 157.8, 153.1, 146.2, 145.2, 135.2, 135.1, 129.4, 129.1, 122.0, 117.6, 116.9, 110.7, 20.9; HRMS (ESI) calcd. for C\(_{14}\)H\(_{10}\)N\(_2\)O\(_3\) [M + Na]\(^+\) 277.0584, found: 277.0572.

8-methyl-3-(1H-pyrazole-1-carbonyl)-2H-chromen-2-one (1h): White solid; 558.6 mg, 44% yield; m.p. 165.3-167.2 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.41 (d, \(J = 2.9\) Hz, 1H), 8.21 (s, 1H), 7.80 (s, 1H), 7.54 (d, \(J = 7.7\) Hz, 1H), 7.48 (d, \(J = 7.7\) Hz, 1H), 7.30 (d, \(J = 7.7\) Hz, 1H), 6.58 (dd, \(J = 2.9\), 1.4 Hz, 1H), 2.52 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 163.0, 157.7, 153.2, 146.5, 145.1, 135.4, 129.4, 127.2, 126.8, 124.8, 121.9, 117.6, 110.7, 15.6; HRMS (ESI) calcd. for C\(_{14}\)H\(_{10}\)N\(_2\)O\(_3\) [M + Na]\(^+\) 277.0584, found: 277.0576.

7-methoxy-3-(1H-pyrazole-1-carbonyl)-2H-chromen-2-one (1i). White solid; 891.1 mg, 66% yield; m.p. 164.9-166.7 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.41 (d, \(J = 2.9\) Hz, 1H), 8.12 (s, 1H), 7.80 (s, 1H), 7.49 (d, \(J = 7.7\) Hz, 1H), 7.39 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.1, 163.0, 157.9, 157.2, 147.1, 144.9, 130.8, 129.6, 118.7, 113.8, 111.6, 110.5, 100.9, 56.2; HRMS (ESI) calcd. for C\(_{14}\)H\(_{10}\)N\(_2\)O\(_3\) [M + Na]\(^+\) 293.0533, found: 293.0532.

8-ethoxy-3-(1H-pyrazole-1-carbonyl)-2H-chromen-2-one (1j). White solid; 894.1 mg, 63% yield; m.p. 185.0-186.8 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.34 (d, \(J = 2.9\) Hz, 1H), 8.13 (s, 1H), 7.76 – 7.68 (m, 1H), 7.26 –
7.20 (m, 1H), 7.19 – 7.10 (m, 2H), 6.52 (dd, J = 2.9, 1.4 Hz, 1H), 4.19 (q, J = 7.0 Hz, 2H), 1.49 (t, J = 7.0 Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) δ 163.0, 157.3, 146.8, 146.2, 145.1, 144.8, 129.6, 125.0, 122.4, 120.6, 118.6, 117.1, 110.8, 65.4, 14.9; HRMS (ESI) calcd. for C\(_{15}\)H\(_{12}\)N\(_2\)O\(_4\) [M + Na]\(^{+}\) 307.0689, found: 307.0688.

6-(tert-butyl)-3-(1H-pyrazole-1-carbonyl)-2H-chromen-2-one (1k). White solid; 591.6 mg, 40% yield; m.p. 162.0 – 163.7 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 8.37 (d, J = 2.9 Hz, 1H), 8.19 (s, 1H), 7.75 (s, 1H), 7.69 (dd, J = 8.8, 2.3 Hz, 1H), 7.55 (d, J = 2.3 Hz, 1H), 7.33 (d, J = 8.8 Hz, 1H), 6.54 (dd, J = 2.9, 1.5 Hz, 1H), 1.35 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 162.9, 157.9, 152.9, 148.5, 146.7, 145.2, 132.0, 129.5, 125.7, 121.8, 117.3, 116.8, 110.7, 34.8, 31.5; HRMS (ESI) calcd. for C\(_{17}\)H\(_{16}\)N\(_2\)O\(_3\) [M + Na]\(^{+}\) 319.1053, found: 319.1044.

2-(1H-pyrazole-1-carbonyl)-3H-benzo[f]chromen-3-one (1l). Yellow solid; 376.8 mg, 26% yield; m.p. 174.6 – 176.5 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 9.00 (s, 1H), 8.41 (d, J = 2.5 Hz, 1H), 8.22 (d, J = 8.3 Hz, 1H), 8.09 (d, J = 9.0 Hz, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.79 (s, 1H), 7.77 – 7.68 (m, 1H), 7.65 – 7.57 (m, 1H), 7.48 (d, J = 9.0 Hz, 1H), 6.57 (dd, J = 2.9, 1.5 Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 163.2, 157.9, 152.4, 151.8, 145.2, 141.4, 135.8, 130.5, 129.5, 129.4, 129.2, 126.8, 121.6, 120.6, 117.0, 112.4, 110.8; HRMS (ESI) calcd. for C\(_{17}\)H\(_{10}\)N\(_2\)O\(_3\) [M + Na]\(^{+}\) 321.0584, found: 321.0584.

6-bromo-8-methoxy-3-(1H-pyrazole-1-carbonyl)-2H-chromen-2-one (1m). White solid; 365.1 mg, 21% yield; m.p. 226.4-228.3 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 8.35 (d, J = 2.9 Hz, 1H), 8.03 (s, 1H), 7.73 (d, J = 1.9 Hz, 1H), 7.30 (d, J = 1.9 Hz, 1H), 7.26 (s, 1H), 6.54 (dd, J = 2.9, 1.4 Hz, 1H), 3.98 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 162.4, 156.5, 148.2, 145.4, 144.6, 143.7, 129.4, 123.7, 122.6, 119.5, 118.8, 117.5, 111.0, 56.9; HRMS (ESI) calcd. for C\(_{14}\)H\(_{9}\)N\(_2\)O\(_4\) [M + Na]\(^{+}\) 370.9638, found: 370.9625.


In an ordinary glass tube equipped with a magnetic stirring bar, coumarin-3-formylpyrazoles 1 (0.1 mmol, 1.0 equiv.), 3-hydroxyoxindoles 2 (0.12 mmol, 1.2 equiv.) and DABCO (20 mol %, 0.02 mmol) were placed in 0.5 mL of DCM at room temperature, and the mixture was stirred at this temperature until the reaction completed (monitored by TLC). Then, the resulting mixture was purified by column chromatography (dichloromethane/ethyl acetate = 100/1 to 20/1) to give the desired product 3. The diastereomeric ratio (dr) was determined by \(^1\)H NMR.
1'-methylspirol[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3aH,9bH)-trione (3a). White solid; 33.3 mg, 99% yield; > 20:1 dr; m.p. 267.8-269.5 °C; 1H NMR (300 MHz, DMSO-<sup>d6</sup>) δ 7.87 (dd, J = 7.5, 1.3 Hz, 1H), 7.55 (td, J = 7.8, 1.3 Hz, 1H), 7.37 – 7.28 (m, 2H), 7.13 – 7.03 (m, 2H), 6.93 (td, J = 7.6, 1.2 Hz, 1H), 6.30 (dd, J = 7.6, 1.6 Hz, 1H), 4.67 (s, 2H), 2.78 (s, 3H); 13C NMR (100 MHz, DMSO-<sup>d6</sup>) δ 172.3, 168.9, 158.5, 150.8, 144.4, 132.21, 130.2, 127.2, 125.5, 124.5, 124.0, 123.1, 117.1, 114.4, 109.8, 85.4, 43.2, 42.7, 25.9; HRMS (ESI) calcd. for C<sub>19</sub>H<sub>13</sub>NNaO<sub>3</sub> [M + Na]<sup>+</sup> 358.0691, found: 358.0691. The ee of compound 3a was determined by HPLC analysis using a Chiralpak AD-H column (60/40 hexane/EtOH; flow rate: 1.0 mL/min; λ = 254 nm; t<sub>major</sub> = 11.8 min, t<sub>minor</sub> = 10.3 min).

8-fluoro-1'-methylspirol[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3aH,9bH)-trione (3b). White solid; 27.2 mg, 77% yield; > 20:1 dr; m.p. 274.1-276.0 °C; 1H NMR (300 MHz, DMSO-<sup>d6</sup>) δ 7.86 (d, J = 7.4 Hz, 1H), 7.57 (dd, J = 8.3, 7.2 Hz, 1H), 7.33 (t, J = 7.7 Hz, 1H), 7.25 – 7.13 (m, 2H), 7.10 (d, J = 7.7 Hz, 1H), 6.20 – 5.92 (m, 1H), 4.84 – 4.56 (m, 2H), 2.83 (s, 3H); 13C NMR (100 MHz, DMSO-<sup>d6</sup>) δ 172.1, 168.6, 158.2, 157.9 (d, J = 240.3 Hz), 147.2 (d, J = 2.3 Hz), 144.3, 132.3, 125.6, 124.1, 122.6, 118.9 (d, J = 8.7 Hz), 117.0 (d, J = 23.4 Hz), 116.1 (d, J = 8.2 Hz), 113.3 (d, J = 24.2 Hz), 109.8, 85.2, 43.1, 42.2, 26.0; HRMS (ESI) calcd. for C<sub>19</sub>H<sub>12</sub>FNNaO<sub>3</sub> [M + Na]<sup>+</sup> 376.0592, found: 376.0578.

8-bromo-1'-methylspirol[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3aH,9bH)-trione (3c). White solid; 34.6 mg, 84% yield; > 20:1 dr; m.p. 289.2-291.1 °C; 1H NMR (300 MHz, DMSO-<sup>d6</sup>) δ 7.86 (d, J = 7.2 Hz, 1H), 7.64 – 7.46 (m, 2H), 7.34 (t, J = 7.7 Hz, 1H), 7.11 (dd, J = 8.3, 5.3 Hz, 2H), 6.37 (d, J = 2.4 Hz, 1H), 4.68 (s, 2H), 2.83 (s, 3H); 13C NMR (100 MHz, DMSO-<sup>d6</sup>) δ 172.1, 168.5, 158.0, 150.2, 144.3, 132.9, 132.3, 129.6, 125.6, 124.1, 122.6, 119.3, 117.0, 115.6, 109.8, 85.2, 42.8, 42.3, 26.0; HRMS (ESI) calcd. for C<sub>19</sub>H<sub>12</sub>BrNNaO<sub>3</sub> [M + Na]<sup>+</sup> 435.9791, found: 435.9782.

7-bromo-1'-methylspirol[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3aH,9bH)-trione (3d). White solid; 33.4 mg, 81% yield; > 20:1 dr; m.p. 256.6-257.9 °C; 1H NMR (300 MHz, DMSO-<sup>d6</sup>) δ 7.86 (d, J = 7.1 Hz, 1H), 7.55 (td, J = 7.8, 1.3 Hz, 1H), 7.43 (d, J = 2.0 Hz, 1H), 7.38 – 7.25 (m, 1H), 7.17 (dd, J = 8.2, 2.0 Hz, 1H), 7.09 (d, J = 7.8 Hz, 1H), 6.25 (d, J = 8.2 Hz, 1H), 4.67 (s, 2H), 2.84 (s, 3H); 13C NMR (100 MHz, DMSO-<sup>d6</sup>) δ 172.2, 168.5, 158.1, 151.5, 144.4, 132.3, 128.9, 127.4, 125.6, 124.1, 122.8, 122.1, 120.0, 114.1, 109.9, 85.1, 42.6, 42.5, 26.0; HRMS (ESI) calcd. for C<sub>19</sub>H<sub>12</sub>BrNNaO<sub>3</sub> [M + Na]<sup>+</sup> 435.9791, found: 435.9793.

6-bromo-1'-methylspirol[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3aH,9bH)-trione (3e). White solid; 40.0 mg, 97% yield; > 20:1 dr; m.p. 267.9-269.4 °C; 1H NMR (300 MHz, DMSO-<sup>d6</sup>) δ 7.88 (d, J = 7.3 Hz, 1H), 7.62 (d, J = 7.7 Hz, 1H), 7.55 (t, J = 7.7 Hz, 1H), 7.32 (t, J = 7.3 Hz, 1H), 7.08 (d, J = 7.7 Hz, 1H), 6.89 (t, J = 7.7 Hz, 1H), 6.30 (d, J = 7.3 Hz, 1H), 4.84 – 4.62 (m, 2H), 2.83 (s, 3H); 13C NMR (100 MHz, DMSO-<sup>d6</sup>) δ 172.1, 168.5, 158.0, 147.6, 144.4, 133.6, 132.3, 126.7, 125.6, 125.5, 124.1, 122.9, 116.7, 109.9, 109.7, 85.3, 43.1, 42.8, 26.0; HRMS
7-chloro-1'-methylspiro[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3aH,9bH)-trione (3f). White solid; 29.5 mg, 80% yield; > 20:1 dr; m.p. 296.6-297.9 °C; 1H NMR (300 MHz, DMSO-d6) δ 7.86 (d, J = 7.3 Hz, 1H), 7.55 (t, J = 7.8 Hz, 1H), 7.37 – 7.27 (m, 2H), 7.13 – 6.99 (m, 2H), 6.31 (d, J = 8.3 Hz, 1H), 4.87 – 4.54 (m, 2H), 2.83 (s, 3H); 13C NMR (100 MHz, DMSO-d6) δ 172.2, 168.6, 158.1, 151.5, 144.4, 134.0, 132.3, 128.7, 125.5, 124.6, 124.1, 122.8, 117.2, 113.7, 109.9, 85.2, 42.5, 42.5, 26.0; HRMS (ESI) calcd. for C19H12BrNNaO5 [M + Na]^+ 392.0296, found: 392.0297.

1',8-dimethylspiro[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3aH,9bH)-trione (3g). White solid; 34.3 mg, 98% yield; > 20:1 dr; m.p. 253.4-254.9 °C; 1H NMR (300 MHz, DMSO-d6) δ 7.86 (d, J = 7.4 Hz, 1H), 7.56 (td, J = 7.8, 1.3 Hz, 1H), 7.40 – 7.23 (m, 1H), 7.20 – 7.04 (m, 2H), 6.97 (td, J = 8.4 Hz, 1H), 6.05 (d, J = 2.2 Hz, 1H), 4.66 – 4.56 (m, 2H), 2.79 (s, 3H), 1.99 (s, 3H); 13C NMR (100 MHz, DMSO-d6) δ 172.2, 168.8, 158.5, 148.7, 144.4, 133.4, 132.1, 130.5, 127.2, 125.3, 123.9, 123.1, 116.7, 114.0, 109.6, 85.3, 43.2, 42.6, 25.9, 20.0; HRMS (ESI) calcd. for C20H15NNaO5 [M + Na]^+ 372.0842, found: 372.0842.

1',6-dimethylspiro[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3aH,9bH)-trione (3h). White solid; 33.8 mg, 97% yield; > 20:1 dr; m.p. 276.9-278.3 °C; 1H NMR (300 MHz, DMSO-d6) δ 7.87 (d, J = 7.4 Hz, 1H), 7.64 – 7.47 (m, 1H), 7.31 (t, J = 7.5 Hz, 1H), 7.18 (d, J = 7.5 Hz, 1H), 7.06 (d, J = 7.9 Hz, 1H), 6.82 (t, J = 7.6 Hz, 1H), 6.12 (d, J = 7.6 Hz, 1H), 4.73 – 4.54 (m, 2H), 2.80 (s, 3H), 2.21 (s, 3H); 13C NMR (100 MHz, DMSO-d6) δ 172.2, 168.9, 158.5, 149.1, 144.4, 132.1, 131.3, 125.5, 125.4, 124.7, 123.9, 123.8, 123.2, 114.1, 109.7, 85.4, 43.1, 42.6, 25.9, 15.5; HRMS (ESI) calcd. for C20H15NNaO5 [M + Na]^+ 372.0842, found: 372.0835.

7-methoxy-1'-methylspiro[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3aH,9bH)-trione (3i). White solid; 36.1 mg, 99% yield; > 20:1 dr; m.p. 265.1-266.7 °C; 1H NMR (300 MHz, DMSO-d6) δ 7.84 (d, J = 6.9 Hz, 1H), 7.53 (td, J = 7.8, 1.1 Hz, 1H), 7.30 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 7.8 Hz, 1H), 6.68 (d, J = 2.5 Hz, 1H), 6.53 (dd, J = 8.5, 2.5 Hz, 1H), 6.20 (d, J = 8.5 Hz, 1H), 4.68 – 4.54 (m, 2H), 3.70 (s, 3H), 2.82 (s, 3H); 13C NMR (100 MHz, DMSO-d6) δ 172.4, 168.9, 160.4, 158.6, 151.8, 144.4, 132.2, 128.0, 125.5, 124.0, 123.2, 111.0, 109.8, 106.0, 102.2, 85.4, 55.6, 42.7, 42.7, 26.0; HRMS (ESI) calcd. for C20H15NNaO6 [M + Na]^+ 388.0792, found: 388.0787.

6-ethoxy-1'-methylspiro[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3aH,9bH)-trione (3j). White solid; 36.8 mg, 97% yield; > 20:1 dr; m.p. 233.3-234.7 °C; 1H NMR (300 MHz, DMSO-d6) δ 7.86 (d, J = 7.6 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.06 (d, J = 7.8 Hz, 1H), 6.99 (d, J = 8.1 Hz, 1H), 6.85 (t, J = 7.9 Hz, 1H), 5.82 (d, J = 7.6 Hz, 1H), 4.71 – 4.57 (m, 2H), 4.11 – 3.96 (q, J = 7.0 Hz, 2H), 2.82 (s, 3H), 1.36 (t, J = 7.0 Hz, 3H); 13C NMR (100 MHz, DMSO-d6) δ 172.2, 168.9, 158.4, 146.2, 144.5, 140.0, 132.2, 125.4, 124.4, 124.0, 123.3, 118.1, 115.1, 113.6, 109.8, 85.3, 64.1, 43.2, 42.5, 26.0, 14.6; HRMS (ESI) calcd. for C21H17NNaO6 [M +
8-(tert-butyl)-1'-methylspiro[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3\(\text{a}f\)9\(\text{b}\)f)trione (3k). White solid; 27.4 mg, 70% yield; > 20:1 dr; m.p. 255.6-257.2 °C; \(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 7.87 (d, \(J = 7.4\) Hz, 1H), 7.56 (t, \(J = 7.8\) Hz, 1H), 7.41 - 7.28 (m, 2H), 7.07 (d, \(J = 7.8\) Hz, 1H), 6.99 (d, \(J = 8.6\) Hz, 1H), 6.13 (d, \(J = 2.2\) Hz, 1H), 4.65 - 4.55 (m, 2H), 2.71 (s, 3H), 0.96 (s, 9H); \(^1\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 172.3, 169.0, 158.5, 148.4, 146.7, 144.3, 132.0, 126.8, 125.5, 124.0, 123.3, 116.4, 113.6, 109.6, 85.6, 44.0, 42.4, 33.7, 30.7, 25.7; HRMS (ESI) calcd. for C\(_{23}\)H\(_{21}\)NNaO\(_5\) [M + Na]\(^+\) 414.1312, found: 414.1325.

1'-methylspiro[benzo\(f\)[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3\(\text{a}f\)9\(\text{b}\)f)trione (3l). Yellow solid; 33.1 mg, 86% yield; > 20:1 dr; m.p. 268.3-270.1°C; \(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 8.09 (dd, \(J = 7.4, 1.4\) Hz, 1H), 7.93 (d, \(J = 9.0\) Hz, 1H), 7.84 (d, \(J = 8.2\) Hz, 1H), 7.46 (td, \(J = 7.6, 1.4\) Hz, 1H), 7.37 (td, \(J = 7.6, 1.1\) Hz, 1H), 7.32 - 7.23 (m, 2H), 6.99 (d, \(J = 3.9\) Hz, 2H), 6.77 (d, \(J = 7.8\) Hz, 1H), 5.41 (d, \(J = 10.5\) Hz, 1H), 4.74 (d, \(J = 10.5\) Hz, 1H), 2.58 (s, 3H); \(^1\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 172.3, 169.0, 158.9, 149.4, 144.1, 132.0, 131.0, 130.5, 130.3, 128.5, 126.4, 125.5, 125.1, 124.1, 123.8, 122.5, 117.5, 109.8, 108.0, 86.0, 43.3, 40.7, 25.8; HRMS (ESI) calcd. for C\(_{23}\)H\(_{21}\)NNaO\(_5\) [M + Na]\(^+\) 408.0842, found: 408.0848.

8-bromo-6-methoxy-1'-methylspiro[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3\(\text{a}f\)9\(\text{b}\)f)trione (3m). White solid; 34.0 mg, 77% yield; > 20:1 dr; m.p. 236.9-238.7 °C; \(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 7.85 (d, \(J = 7.4\) Hz, 1H), 7.57 (td, \(J = 7.8, 1.2\) Hz, 1H), 7.33 (t, \(J = 7.4\) Hz, 1H), 7.23 (d, \(J = 2.2\) Hz, 1H), 7.12 (d, \(J = 7.8\) Hz, 1H), 5.92 (d, \(J = 2.0\) Hz, 1H), 4.74 - 4.57 (m, 2H), 3.83 (s, 3H), 2.86 (s, 3H); \(^1\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 172.0, 168.4, 157.7, 147.8, 144.4, 139.4, 132.3, 125.5, 124.0, 122.8, 120.4, 116.9, 115.8, 115.6, 109.7, 85.1, 56.4, 42.8, 42.2, 26.0; HRMS (ESI) calcd. for C\(_{20}\)H\(_{15}\)BrNaO\(_6\) [M + Na]\(^+\) 465.9902, found: 465.9880.

1'-ethylspiro[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3\(\text{a}f\)9\(\text{b}\)f)trione (3n). White solid; 33.9 mg, 97% yield; > 20:1 dr; m.p. 229.1-231.0 °C; \(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 7.86 (d, \(J = 7.5\) Hz, 1H), 7.53 (td, \(J = 7.8, 1.2\) Hz, 1H), 7.38 - 7.26 (m, 2H), 7.16 - 7.06 (m, 2H), 6.92 (td, \(J = 7.5, 1.1\) Hz, 1H), 6.32 - 6.20 (m, 1H), 4.79 - 4.48 (m, 2H), 3.52 - 3.40 (m, 1H), 3.32 - 3.21 (m, 1H), 0.49 (t, \(J = 7.1\) Hz, 3H); \(^1\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 172.0, 168.9, 158.4, 150.9, 143.2, 132.1, 130.1, 127.3, 125.6, 124.4, 123.8, 123.2, 116.9, 114.3, 109.7, 85.3, 43.7, 42.6, 34.0, 11.6; HRMS (ESI) calcd. for C\(_{24}\)H\(_{23}\)NNaO\(_5\) [M + Na]\(^+\) 372.0842, found: 372.0834.

1'-isopropylspiro[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3\(\text{a}f\)9\(\text{b}\)f)trione (3o). White solid; 34.8 mg, 96% yield; > 20:1 dr; m.p. 338.6-340.1 °C; \(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 7.85 (d, \(J = 6.6\) Hz, 1H), 7.50 (dd, \(J = 12.3, 4.5\) Hz, 1H), 7.37 - 7.24 (m, 2H), 7.19 (d, \(J = 8.0\) Hz, 1H), 7.10 (d, \(J = 8.2\) Hz, 1H), 6.93 (t, \(J = 7.5\) Hz, 1H), 6.23 (d, \(J = 6.5\) Hz, 1H), 4.61 (q, \(J = 11.0\) Hz, 2H), 4.12 - 3.93 (m, 1H), 0.99 (d, \(J = 6.9\) Hz, 3H), 0.86 (d, \(J = 6.9\) Hz, 3H); \(^1\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 172.2, 168.9, 158.3, 150.9, 143.1, 132.0, 130.0, 127.2, 125.7, 124.3, 123.6, 123.4, 116.9, 114.4,
1'-isobutylspiro[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3aH,9bH)-trione (3p). White solid; 33.2 mg, 88% yield; > 20:1 dr; m.p. 261.4-263.1 °C; 1H NMR (300 MHz, DMSO-d6) δ 7.88 (d, J = 7.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 1H), 7.30 (t, J = 7.7 Hz, 2H), 7.13 - 7.05 (m, 2H), 6.94 (t, J = 7.5 Hz, 1H), 6.37 (d, J = 7.7 Hz, 1H), 4.75 - 4.62 (m, 2H), 3.26 (dd, J = 13.9, 7.8 Hz, 1H), 3.13 (dd, J = 13.9, 6.6 Hz, 1H), 1.49 (dt, J = 13.6, 6.7 Hz, 1H), 0.58 (d, J = 6.7 Hz, 3H), 0.25 (d, J = 6.6 Hz, 3H); 13C NMR (100 MHz, DMSO-d6) δ 172.7, 168.9, 158.5, 151.0, 144.4, 132.1, 130.2, 127.6, 125.6, 124.6, 123.7, 123.0, 117.0, 114.4, 110.2, 85.2, 46.8, 43.1, 42.7, 26.5, 19.8, 18.9; HRMS (ESI) calcd. for C21H17NNaO5 [M + Na]+ 386.0999, found: 386.0985.

1'-allylspiro[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3aH,9bH)-trione (3q). White solid; 31.4 mg, 87% yield; > 20:1 dr; m.p. 252.2-253.9 °C; 1H NMR (300 MHz, DMSO-d6) δ 7.89 (d, J = 6.7 Hz, 1H), 7.51 (td, J = 7.8, 1.2 Hz, 1H), 7.32 (ddd, J = 10.9, 4.7, 2.0 Hz, 2H), 7.14 - 7.04 (m, 1H), 6.95 (ddd, J = 8.7, 5.3, 1.5 Hz, 2H), 6.34 (dd, J = 7.6, 1.4 Hz, 1H), 5.32 - 5.21 (m, 1H), 4.83 - 4.75 (m, 1H), 4.75 - 4.60 (m, 2H), 4.40 (dd, J = 17.0, 1.2 Hz, 1H), 4.18 - 4.04 (m, 1H), 3.91 (dd, J = 17.0, 5.3 Hz, 1H); 13C NMR (100 MHz, DMSO-d6) δ 172.2, 168.9, 158.5, 151.0, 143.5, 132.1, 130.4, 130.2, 127.5, 124.5, 124.0, 123.0, 117.1, 116.3, 114.4, 110.3, 85.4, 43.4, 42.7, 41.4; HRMS (ESI) calcd. for C21H15NNaO5 [M + Na]+ 384.0842, found: 384.0831.

1'-benzylspiro[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3aH,9bH)-trione (3r). White solid; 36.2 mg, 88% yield; > 20:1 dr; m.p. 188.7-190.2 °C; 1H NMR (300 MHz, DMSO-d6) δ 7.91 (d, J = 7.1 Hz, 1H), 7.44 (dd, J = 15.0, 7.1 Hz, 2H), 7.29 (t, J = 7.5 Hz, 1H), 7.21 - 7.03 (m, 4H), 6.97 (t, J = 7.2 Hz, 1H), 6.83 (d, J = 7.8 Hz, 1H), 6.51 (d, J = 7.0 Hz, 2H), 6.37 (d, J = 6.7 Hz, 1H), 4.93 - 4.66 (m, 3H), 4.45 (d, J = 16.0 Hz, 1H); 13C NMR (100 MHz, DMSO-d6) δ 172.6, 168.8, 158.6, 151.0, 143.5, 134.8, 132.1, 130.4, 128.6, 127.8, 127.3, 126.4, 125.8, 124.8, 124.1, 123.0, 117.2, 114.3, 110.3, 85.3, 43.1, 42.8, 42.8; HRMS (ESI) calcd. for C23H19NNaO5 [M + Na]+ 434.0999, found: 434.1009.

1'-phenylspiro[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3aH,9bH)-trione (3s). White solid; 34.6 mg, 87% yield; > 20:1 dr; m.p. 270.1-271.7 °C; 1H NMR (300 MHz, DMSO-d6) δ 7.97 (dd, J = 7.4, 1.4 Hz, 1H), 7.55 - 7.34 (m, 6H), 7.15 (dd, J = 8.3, 1.2 Hz, 1H), 7.02 (td, J = 7.4, 1.4 Hz, 1H), 6.76 - 6.66 (m, 3H), 6.36 (dd, J = 7.7, 1.6 Hz, 1H), 4.73 (s, 2H); 13C NMR (100 MHz, DMSO-d6) δ 172.2, 168.9, 158.3, 150.9, 143.9, 132.4, 132.2, 130.3, 129.8, 128.8, 127.3, 126.0, 125.9, 124.7, 124.5, 123.1, 117.2, 114.4, 109.9, 85.6, 44.4, 42.6; HRMS (ESI) calcd. for C24H13NNaO5 [M + Na]+ 420.0842; found: 420.0826.

spiro[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3aH,9bH)-trione (3t). White solid; 29.6 mg, 92% yield; > 20:1 dr; m.p. 247.1-248.1 °C; 1H NMR (300 MHz, DMSO-d6) δ 10.66 (s, 1H), 7.82 (d, J = 7.3 Hz, 1H), 7.44 (td, J = 7.7, 1.2 Hz, 1H), 7.38 - 7.28 (m, 1H), 7.24 (t, J = 7.6 Hz, 1H), 7.15 - 7.05 (m, 1H), 7.03 - 6.93 (m, 1H), 6.84 (d, J = 7.7 Hz, 1H), 6.36 (dd, J = 7.6, 1.4 Hz, 1H), 4.64 (s,
2H); ¹³C NMR (100 MHz, DMSO-d₆) δ 174.0, 168.8, 158.4, 150.9, 143.0, 132.0, 127.4, 125.8, 124.5, 123.6, 123.3, 116.9, 114.7, 110.7, 85.7, 43.1, 42.6; HRMS (ESI) calcd. for C₁₈H₁₂NNaO₅ [M + Na]⁺ 344.0529, found: 344.0527.

4'-bromo-1'-methylspiropiro[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3aH,9bH)
-trione (3u). White solid; 30.1 mg, 73% yield; > 20:1 dr; m.p. 288.1-290.0 °C; ¹H NMR (300 MHz, DMSO-d₆) δ 7.58 – 7.44 (m, 2H), 7.36 (td, J = 7.9, 7.3, 1.6 Hz, 1H), 7.19 – 7.07 (m, 2H), 7.00 (td, J = 7.5, 1.2 Hz, 1H), 6.39 (dd, J = 7.7, 1.6 Hz, 1H), 4.94 (d, J = 11.2 Hz, 1H), 4.84 (d, J = 11.2 Hz, 1H), 2.77 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆) δ 171.5, 168.3, 158.0, 150.7, 146.4, 134.2, 130.5, 127.7, 127.4, 124.8, 120.3, 119.2, 117.2, 113.8, 109.6, 85.9, 41.7, 40.2, 26.1; HRMS (ESI) calcd. for C₁₉H₁₂BrNNaO₅ [M + Na]⁺ 435.9812, found: 435.9797.

5'-fluoro-1'-methylspiropiro[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3aH,9bH)
-H-trione (3v). White solid; 31.0 mg, 88% yield; > 20:1 dr; m.p. 206.4-208.2 °C; ¹H NMR (300 MHz, DMSO-d₆) δ 7.84 (dd, J = 7.9, 2.7 Hz, 1H), 7.42 (td, J = 9.3, 2.7 Hz, 1H), 7.32 (dd, J = 11.3, 4.2 Hz, 1H), 7.17 – 7.06 (m, 2H), 6.96 (t, J = 7.0 Hz, 1H), 6.40 (d, J = 6.3 Hz, 1H), 4.70 (s, 2H), 2.78 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆) δ 172.1, 168.6, 150.1 (d, J = 237.8 Hz), 157.9, 150.8, 140.6 (d, J = 1.7 Hz), 130.2, 127.4, 124.8 (d, J = 8.6 Hz), 124.5, 118.5 (d, J = 23.5 Hz), 117.0, 114.2, 113.6 (d, J = 25.9 Hz), 111.1 (d, J = 8.1 Hz), 85.2, 43.1, 42.5, 26.1; HRMS (ESI) calcd. for C₁₉H₁₂FNNaO₅ [M + Na]⁺ 376.0592, found: 376.0596.

5'-chloro-1'-methylspiropiro[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3aH,9bH)
-H-trione (3w). White solid; 31.7 mg, 86% yield; > 20:1 dr; m.p. 261.5-262.9 °C; ¹H NMR (300 MHz, DMSO-d₆) δ 8.03 (d, J = 1.9 Hz, 1H), 7.62 (dd, J = 8.4, 1.9 Hz, 1H), 7.33 (t, J = 7.2 Hz, 1H), 7.15 – 7.04 (m, 2H), 6.97 (t, J = 7.2 Hz, 1H), 6.41 (d, J = 6.9 Hz, 1H), 4.89 – 4.34 (m, 2H), 2.78 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆) δ 172.0, 168.5, 158.4, 150.7, 143.2, 131.9, 130.2, 128.0, 127.3, 125.8, 125.1, 124.5, 117.0, 114.2, 111.4, 85.0, 43.0, 42.5, 26.0; HRMS (ESI) calcd. for C₁₉H₁₂ClNNaO₅ [M + Na]⁺ 392.0296, found: 392.0301.

5'-bromo-1'-methylspiropiro[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3aH,9bH)
-H-trione (3x). White solid; 36.7 mg, 89% yield; > 20:1 dr; m.p. 265.9-267.8 °C; ¹H NMR (300 MHz, DMSO-d₆) δ 8.15 (d, J = 1.9 Hz, 1H), 7.75 (dd, J = 8.4, 2.0 Hz, 1H), 7.33 (t, J = 7.7 Hz, 1H), 7.08 (dd, J = 10.4, 8.5 Hz, 2H), 6.97 (t, J = 7.2 Hz, 1H), 6.41 (d, J = 6.5 Hz, 1H), 4.78 – 4.63 (m, 2H), 2.78 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆) δ 171.9, 168.6, 158.4, 150.8, 143.7, 134.8, 130.2, 128.5, 127.3, 125.5, 124.6, 117.0, 115.6, 114.2, 111.9, 84.9, 43.0, 42.5, 26.1; HRMS (ESI) calcd. for C₁₉H₁₂BrNNaO₅ [M + Na]⁺ 435.9791, found: 435.9771.

7'-fluoro-1'-methylspiropiro[furo[3,4-c]chromene-1,3'-indoline]-2',3,4(3aH,9bH)
-H-trione (3y). White solid; 33.2 mg, 94% yield; > 20:1 dr; m.p. 277.2-278.5 °C; ¹H NMR (300 MHz, DMSO-d₆) δ 7.75 (dd, J = 7.4, 0.9 Hz, 1H), 7.52 – 7.40 (m, 1H), 7.40 – 7.29 (m, 2H), 7.11 (d, J = 8.2 Hz, 1H), 7.00 (td, J = 7.5, 1.1 Hz, 1H), 6.35 (dd, J = 7.6, 1.4 Hz, 1H), 4.82 – 4.45 (m, 2H), 2.94 (d, J = 2.7 Hz, 3H); ¹³C NMR (100 MHz, DMSO-d₆) δ 172.1, 168.6, 158.4, 150.8, 147.0 (d, J = 244.0
Hz), 130.6 (d, J = 8.9 Hz), 130.3, 127.2, 126.1 (d, J = 3.1 Hz), 125.3 (d, J = 6.4), 124.6, 121.9 (d, J = 3.1 Hz), 120.1 (d, J = 19.9 Hz), 117.1, 114.1, 85.1, 43.5, 42.6, 28.3 (d, J = 5.4 Hz); HRMS (ESI) calcd. for C_{19}H_{12}FNNaO_5 [M + Na]^+ 376.0592, found: 376.0578.

**6'-chloro-1'-methylspiro[furo[3,4-c]chromene-1,3'-indoline]-2',3',4(3aH,9bH)-trione (3z).** White solid; 23.6 mg 64% yield; > 20:1 dr; m.p. 248.5-249.9 °C; 1H NMR (300 MHz, DMSO-d_6) δ 7.89 (d, J = 8.0 Hz, 1H), 7.45 – 7.28 (m, 2H), 7.27 (d, J = 1.8 Hz, 1H), 7.15 – 7.03 (m, 1H), 7.03 – 6.89 (m, 1H), 6.50 – 6.31 (m, 1H), 4.68 (s, 2H), 2.79 (s, 3H); 13C NMR (100 MHz, DMSO-d_6) δ 172.4, 168.7, 158.5, 150.8, 145.9, 136.7, 130.2, 127.3, 127.1, 124.6, 123.8, 122.0, 117.1, 114.2, 110.5, 84.9, 43.0, 42.6, 26.2; HRMS (ESI) calcd. for C_{19}H_{12}ClNNaO_5 [M + Na]^+ 392.0302, found: 392.0302.

**7'-chloro-1'-methylspiro[furo[3,4-c]chromene-1,3'-indoline]-2',3',4(3aH,9bH)-trione (3a').** White solid; 31.7 mg, 86% yield; > 20:1 dr; m.p. 260.0-261.6 °C; 1H NMR (400 MHz, DMSO-d_6) δ 7.88 (dd, J = 7.4, 1.0 Hz, 1H), 7.57 (dd, J = 8.3, 1.0 Hz, 1H), 7.39 – 7.27 (m, 2H), 7.11 (d, J = 7.6 Hz, 1H), 7.01 (td, J = 7.5, 1.0 Hz, 1H), 6.36 (dd, J = 7.6, 1.2 Hz, 1H), 4.75 – 4.54 (m, 2H), 3.07 (s, 3H); 13C NMR (100 MHz, DMSO-d_6) δ 172.8, 168.6, 158.4, 150.8, 139.9, 134.0, 130.3, 127.2, 126.3, 125.4, 124.7, 124.6, 117.1, 115.3, 114.1, 84.6, 43.5, 42.6, 29.2; HRMS (ESI) calcd. for C_{19}H_{12}ClNNaO_5 [M + Na]^+ 392.0319, found: 392.0302.

**1',5'-dimethylspiro[furo[3,4-c]chromene-1,3'-indoline]-2',3',4(3aH,9bH)-trione (3b').** White solid; 30.0 mg, 86% yield; > 20:1 dr; m.p. 247.1-248.5 °C; 1H NMR (300 MHz, DMSO-d_6) δ 7.69 (s, 1H), 7.36 – 7.26 (m, 2H), 7.08 (d, J = 8.0 Hz, 1H), 6.94 (t, J = 7.7 Hz, 2H), 6.33 (d, J = 7.5 Hz, 1H), 4.65 (s, 2H), 2.76 (s, 3H), 2.39 (s, 3H); 13C NMR (100 MHz, DMSO-d_6) δ 172.1, 168.8, 158.4, 150.8, 142.0, 133.2, 132.2, 130.0, 127.3, 126.0, 124.4, 123.1, 117.0, 114.4, 109.5, 85.5, 43.1, 42.6, 25.9, 20.7; HRMS (ESI) calcd. for C_{20}H_{12}ClNNaO_6 [M + Na]^+ 372.0842, found: 372.0856.

**5'-methoxy-1'-methylspiro[furo[3,4-c]chromene-1,3'-indoline]-2',3',4(3aH,9bH)-trione (3c').** White solid; 34.4 mg, 94% yield; > 20:1 dr; m.p. 236.7-238.5 °C; 1H NMR (300 MHz, DMSO-d_6) δ 7.59 (d, J = 2.5 Hz, 1H), 7.31 (dd, J = 11.3, 4.3 Hz, 1H), 7.09 (dd, J = 8.5, 2.5 Hz, 2H), 7.03 – 6.87 (m, 2H), 6.35 (d, J = 6.3 Hz, 1H), 4.87 – 4.31 (m, 2H), 3.82 (s, 3H), 2.75 (s, 3H); 13C NMR (100 MHz, DMSO-d_6) δ 171.9, 168.8, 158.5, 156.5, 150.8, 137.5, 130.1, 127.4, 124.4, 124.3, 117.0, 116.7, 114.5, 112.2, 110.4, 85.6, 55.7, 43.1, 42.6, 25.9; HRMS (ESI) calcd. for C_{20}H_{12}OMNNaO_6 [M + Na]^+ 388.0792, found: 388.0786.

**1',7'-dimethylspiro[furo[3,4-c]chromene-1,3'-indoline]-2',3',4(3aH,9bH)-trione (3d').** White solid; 32.5 mg, 93 % yield; >20:1 dr; m.p. 262.4-264.3 °C; 1H NMR (300 MHz, DMSO-d_6) δ 7.71 (d, J = 6.6 Hz, 1H), 7.38 – 7.25 (m, 2H), 7.20 (t, J = 7.5 Hz, 1H), 7.09 (d, J = 7.5 Hz, 1H), 6.97 (t, J = 7.5 Hz, 1H), 6.36 – 6.26 (m, 1H), 4.89 – 4.48 (m, 2H), 3.04 (s, 3H), 2.45 (s, 3H); 13C NMR (100 MHz, DMSO-d_6) δ 172.9, 168.9, 158.6, 150.8, 142.1, 135.6, 130.1, 127.3, 124.5, 123.9, 123.8, 123.3, 121.1, 117.0, 114.5, 84.9, 43.3, 42.8, 28.9, 18.1; HRMS (ESI) calcd. for C_{20}H_{12}OMNNaO_6 [M + Na]^+ 372.0842, found: 372.0842.
1',5',7'-trimethylspiro[furo[3,4-c]chromene-1,3'-indoline]-2',3',4(3aH,9b
H)-trione (3e'). White solid; 31.3 mg, 86% yield; > 20:1 dr; m.p. 243.6-245.5 °C; 1H NMR (300 MHz, DMSO-d6) δ 7.53 (s, 1H), 7.32 (t, J = 7.2 Hz, 1H), 7.15 – 7.02 (m, 2H), 6.98 (t, J = 7.2 Hz, 1H), 6.35 (d, J = 6.7 Hz, 1H), 4.62 (q, J = 11.0 Hz, 2H), 3.01 (s, 3H), 2.40 (s, 3H), 2.33 (s, 3H); 13C NMR (100 MHz, DMSO-d6) δ 172.8, 168.8, 158.5, 150.8, 139.6, 135.9, 133.0, 130.1, 127.4, 124.4, 123.8, 123.8, 120.8, 116.9, 114.5, 85.0, 43.3, 42.7, 28.8, 20.4, 17.9; HRMS (ESI) calcd. for C21H17NNaO5 [M+Na]+ 386.0999, found: 386.0988.

4. Procedure for the gram-scale experiment.

In a round bottomed flask equipped with a magnetic stirring bar, coumarin-3-formylpyrazole 1a (0.96 g, 4.0 mmol), 3-hydroxyoxindole 2a (0.78 g, 4.8 mmol) and DABCO (20 mol %, 0.8 mmol) were placed in 20 mL of DCM at room temperature, and the reaction mixture was stirred at this temperature until the reaction completed (monitored by TLC). Then, the resulting mixture was concentrated and the residue was purified by column chromatography (dichloromethane/ethyl acetate = 50/1) on silica gel to afford the corresponding product 3a as a white solid; 1.322 g, 99% yield.


To a solution of compound 3a (33.5 mg, 0.1 mmol) in 2.0 mL DCM was added DDQ (33.9 mg, 0.15 mmol). Then the mixture was stirred at room temperature for 4 h. After completion, the reaction mixture was directly purified by flash chromatography on silica gel (dichloromethane/ethyl acetate = 100/1) to afford the corresponding product 4 with 98% yield.

1'-methylspiro[furo[3,4-c]chromene-1,3'-indoline]-2',3',4-trione (4). White solid; 32.6 mg, 98% yield; m.p. 323.9-325.0 °C; 1H NMR (300 MHz, DMSO-d6) δ 7.86 – 7.74 (m, 1H), 7.62 (dd, J = 8.7, 6.4 Hz, 2H), 7.51 (d, J = 7.4 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.28 (t, J = 7.6 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 6.84 (dd, J = 8.0, 1.5 Hz, 1H), 3.37 (s, 3H); 13C NMR (100 MHz, DMSO-d6) δ 168.2, 165.0, 164.4, 155.8, 153.6, 144.1, 136.4, 132.9, 126.1, 126.0, 124.4, 124.2, 122.1, 117.9, 112.9, 112.8, 111.1, 82.6, 27.4; HRMS (ESI) calcd. for C19H11NNaO5 [M + Na]+ 356.0529, found: 356.0517.

6. X-ray crystal structure of compound 3a.

Crystal data and structure refinement for 3a (CCDC 1941065).

Identification code 3a
Empirical formula C10H11NO3
Formula weight 335.30
Temperature/K 293(2)

S10
Crystal system: orthorhombic
Space group: Pnca

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7. Control experiments (The Scheme 6 and Fig. 3 in manuscript).

Scheme 6 Control experiments
Fig. 3 Tracking and monitoring to the reaction of 1a and 2a. (A) The reaction of 1a and 2a under the standard conditions for 10 mins. (B) The 1H NMR spectra of compound 8. (C) The 1H NMR spectra of compounds 1a and 2a.

Synthesis of compound 7.

In an ordinary vial equipped with a magnetic stirring bar, compound 1a (0.1 mmol), compound 6 (0.12 mmol) and DABCO (20 mol %, 0.02 mmol) were placed in 0.5 mL of DCM at room temperature for 60 h. Then, the mixture was by column chromatography (petroleum ether/ethyl acetate = 5:1) to give compound 7.

**2-ethoxy-2-oxo-2H-chromene-3-carboxylic carboxylate (7):**

White solid; 27.2 mg, 95% yield; 1H NMR (400 MHz, CDCl3) δ 8.62 (s, 1H), 7.68 – 7.53 (m, 4H), 7.44 – 7.37 (m, 3H), 7.35 – 7.31 (m, 2H), 6.13 (s, 1H), 4.30 – 4.20 (m, 1H), 4.18 – 4.09 (m, 1H), 1.21 (t, J = 7.2 Hz, 3H);

**13C NMR (100 MHz, CDCl3) δ 168.6, 162.1, 156.5, 155.5, 149.7, 135.0, 133.6, 129.9, 129.5, 129.0, 127.8, 125.1, 117.9, 117.2, 117.0, 75.5, 62.1, 14.2. HRMS (ESI) calcd. for C20H16NaO6 [M + Na]+ 375.0839, found: 375.0824.**

Synthesis of compound 8.

To a 10 mL round bottomed flask was added 2-oxo-2H-chromene-3-carboxylic acids (1.0 mmol), HOBt (1.2. mmol), 3-hydroxy-1-methylindolin-2-one (1.05 mmol) and CH2Cl2 (5 mL). The mixture was added DCC (1.2 mmol) at 0 °C and stirred for 15 min. Then, the reaction system was warmed to room temperature and stirred for 24 h. Upon completion, the mixture was filtered through celite, and washed with CH2Cl2 and concentrated in vacuo. The desired product was recrystallised from absolute ethanol.

**1-methyl-2-oxindolin-3-yl 1H 2-oxo-2H-chromene-3-carboxylate (8).**

White solid, 48.7 mg, 15% yield; 1H NMR (400 MHz, CDCl3) δ 8.61 (s, 1H), 7.64 (dd, J = 8.7, 7.3, 1.6 Hz, 1H), 7.57 (dd, J = 7.8, 1.6 Hz, 1H), 7.45 (d, J = 7.4 Hz, 1H), 7.40 – 7.26 (m, 3H), 7.06 (td, J = 7.6, 1.0 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 6.14 (s, 1H), 3.23 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 172.0, 161.9, 156.5, 155.5, 150.2, 144.8, 135.1, 130.8, 130.0, 126.2, 125.2, 125.0, 123.5, 117.9, 117.1, 116.7, 108.8, 71.0, 26.7; HRMS (ESI) calcd. for C19H13NNaO5 [M + Na]+ 358.0686, found: 358.0683.
8. $^1$H and $^{13}$C NMR spectra for compounds 1, 3 and 4.

$^1$H and $^{13}$C NMR of 1a
$^1$H and $^{13}$C NMR of 1b
$^1$H and $^{13}$C NMR of 1c
$^1$H and $^{13}$C NMR of 1d
$^1$H and $^{13}$C NMR of 1e
$^1$H and $^{13}$C NMR of 1f
$^1$H and $^{13}$C NMR of $1g$
$^1$H and $^{13}$C NMR of 1h
$^1$H and $^{13}$C NMR of 1i
$^1$H and $^{13}$C NMR of 1j
$^1$H and $^{13}$C NMR of 1k

[Chemical structures and spectra]

S23
$^1$H and $^{13}$C NMR of 11

![NMR Spectra of 11](image)

The spectra show the characteristic peaks for the protons and carbon atoms in the molecule, indicating the structure and chemical properties of 11.
$^1$H and $^{13}$C NMR of 1m
$^1$H and $^{13}$C NMR of 3a
$^{1}H$ and $^{13}C$ NMR of 3b

[Diagram of molecular structure]

[Spectroscopic data]

S27
$^1$H and $^{13}$C NMR of 3c
$^1$H and $^{13}$C NMR of 3d
$\text{H and }^{13}\text{C NMR of 3e}$
$^1$H and $^{13}$C NMR of 3f
$^{1}H$ and $^{13}C$ NMR of 3g
$^{1}H$ and $^{13}C$ NMR of 3h
$^1$H and $^{13}$C NMR of 3i
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$^1$H and $^{13}$C NMR of 3k
$^1$H and $^{13}$C NMR of 31
$^1$H and $^{13}$C NMR of 3m
$^1$H and $^{13}$C NMR of 3n

![NMR Spectra of 3n](image-url)
$^1$H and $^{13}$C NMR of 3o

![NMR Spectra](image_url)
$^1$H and $^{13}$C NMR of 3p
$^1$H and $^{13}$C NMR of 3q
$^{1}$H and $^{13}$C NMR of 3r
$^{1}H$ and $^{13}C$ NMR of 3s

![NMR Spectra](image-url)
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$^1$H and $^{13}$C NMR of 3u
$^1$H and $^{13}$C NMR of 3v
$^1$H and $^{13}$C NMR of 3w
$^1$H and $^{13}$C NMR of 3x
$^1$H and $^{13}$C NMR of 3z
\(^1\text{H and }^{13}\text{C NMR of } 3a'\)
$^1$H and $^{13}$C NMR of 3b'}
$^1$H and $^{13}$C NMR of 3c'
$^{1}\text{H}$ and $^{13}\text{C}$ NMR of 3d'
$^1$H and $^{13}$C NMR of 3e'}
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HPLC of 3a with Catalyst B

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