

# Catalyst-free tandem Michael addition/decarboxylation of (thio)coumarin-3-carboxylic acids with indoles: facile synthesis of indole-3-substituted 3,4-dihydro(thio)coumarins.

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## Supporting Information

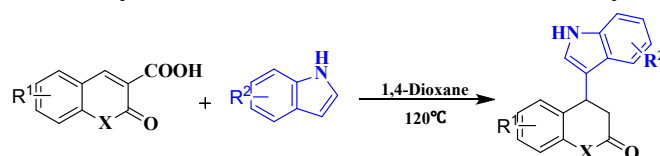
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General experimental details

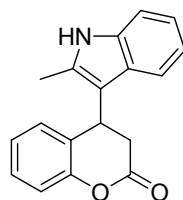
Reagents were purchased from reagent companies. Solvents used in our reactions were dried over appropriate drying agents (Na for THF, dioxane, toluene; CaH<sub>2</sub> for DMF, molecular sieve for DMSO). All reactions were performed in sealed tube and monitored by TLC performed with 0.2 mm silica gel-coated HSGF 254 plates. Gross products were purified on 200-300 mesh silica gel at increased pressure, eluted with the gradient of ethyl acetate and petroleum ether (petroleum ether and ethyl acetate 8-1 to 4-1). Melting point of solids were obtained with a GLO X-5 series micro melting point apparatus and were uncorrected. Proton nuclear magnetic resonance spectra (<sup>1</sup>H NMR) were recorded on a Bruker 500 MHz NMR spectrometer (CDCl<sub>3</sub> or d<sub>6</sub>-DMSO solvent). The chemical shifts are reported in parts per million (ppm), downfield from SiMe<sub>4</sub> (δ 0.0) and relative to the signal of chloroform-d (δ 7.26, singlet) or dimethyl sulfoxide-d<sub>6</sub> (δ 2.54, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet) or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a J value in Hz. Carbon nuclear magnetic resonance spectra (<sup>13</sup>C NMR) are reported as δ in units of parts per million (ppm) downfield from SiMe<sub>4</sub> (δ 0.0) and relative to the signal of chloroform-d (δ 77.00, triplet) or dimethyl sulfoxide-d<sub>6</sub> (δ 40.00, multiplets). Infrared spectra of solids were recorded as KBr pellets on a Thermo Scientific Nicolet IR 200 FT-IR spectrometer. HRMS analyses were performed on a Waters Q-TOF Global mass spectrometer.

### General Procedure for Synthesis of Indole-3-Substituted Dihydrocoumarins



To an 25 mL pressure tube equipped with magnetic bar was added coumarins-3-carboxylic acid (0.3 mmol), indoles (0.75 mmol) and 1,4-dioxane (2 mL), and the solution was stirred at 120°C. The reaction process was monitored by TLC until raw materials were consumed up. Solvent was removed in vacuo and the residue was purified by flash chromatography to give the desired product (eluted with ethyl acetate and petroleum ether 8:1 to 4:1).

#### 4-(2-methyl-1H-indol-3-yl) chroman-2-one (3a)

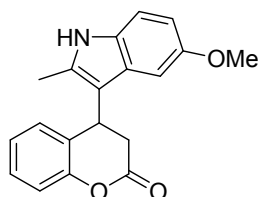


Yellow solid, yield 98%. M. p.:83-85°C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.25 (s, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.14-7.08 (m, 2H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.94-6.89 (m, 3H), 4.61 (dd, *J* = 13.2, 4.8 Hz, 1H), 3.24 (t, *J* = 14.6 Hz, 1H), 2.94 (dd, *J* = 16.1, 5.1 Hz, 1H), 2.32 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 168.9, 151.6, 135.6, 132.9, 128.4, 128.0, 126.2, 125.5, 124.4, 121.1, 119.2, 118.8, 116.7, 110.7, 108.1, 35.7, 31.7, 11.8. HRMS (ESI) calculated for C<sub>18</sub>H<sub>16</sub>NO<sub>2</sub> [M+H]<sup>+</sup>:

278.1176, found: 278.1178. **IR (KBr)**: 3050, 1753, 1637, 1560, 1485, 1458, 1215, 1149, 745  $\text{cm}^{-1}$ .

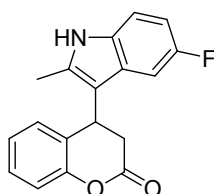
#### 4-(5-methoxy-2-methyl-1H-indol-3-yl) chroman-2-one (3b)



Dark brown solid, yield 90%. M. p.:90-92°C.

**<sup>1</sup>H NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (s, 1H), 7.27 (t,  $J = 7.8$  Hz, 1H), 7.21 (d,  $J = 8.7$  Hz, 1H), 7.14 (d,  $J = 8.1$  Hz, 1H), 7.02-6.91 (m, 2H), 6.77 (dd,  $J = 8.7, 2.1$  Hz, 1H), 6.48 (s, 1H), 4.60 (dd,  $J = 12.9, 5.1$  Hz, 1H), 3.67 (s, 3H), 3.21 (dd,  $J = 16.0, 13.1$  Hz, 1H), 2.95 (dd,  $J = 16.1, 5.3$  Hz, 1H), 2.32 (s, 3H). **<sup>13</sup>C NMR** (125 MHz,  $\text{CDCl}_3$ )  $\delta$  168.7, 153.6, 151.8, 133.6, 130.7, 128.5, 128.1, 126.9, 125.3, 124.4, 116.8, 111.3, 110.5, 108.2, 101.7, 55.8, 35.7, 31.8, 12.0. **HRMS (ESI)** calculated for  $\text{C}_{19}\text{H}_{18}\text{NO}_3$   $[\text{M}+\text{H}]^+$ : 308.1282, found: 308.1280. **IR (KBr)**: 3042, 1762, 1638, 1560, 1485, 1458, 1216, 1149  $\text{cm}^{-1}$ .

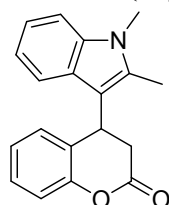
#### 4-(5-fluoro-2-methyl-1H-indol-3-yl) chroman-2-one (3c)



Light Gray solid, yield 73%. M. p.:151-153°C.

**<sup>1</sup>H NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.24 (s, 1H), 7.29 (t,  $J = 7.6$  Hz, 1H), 7.24 (dd,  $J = 8.8, 4.4$  Hz, 1H), 7.15 (d,  $J = 8.1$  Hz, 1H), 7.00 (t,  $J = 7.5$  Hz, 1H), 6.90 (d,  $J = 7.6$  Hz, 1H), 6.87-6.83 (m, 1H), 6.66 (dd,  $J = 9.8, 2.2$  Hz, 1H), 4.59 (dd,  $J = 13.1, 5.1$  Hz, 1H), 3.18 (dd,  $J = 16.0, 13.1$  Hz, 1H), 2.94 (dd,  $J = 16.1, 5.2$  Hz, 1H), 2.36 (s, 3H). **<sup>13</sup>C NMR** (125 MHz,  $\text{CDCl}_3$ )  $\delta$  168.5, 157.4 (d,  $J_F = 234.8$  Hz), 151.8, 134.8, 132.1, 128.6, 127.9, 126.7 (d,  $J_F = 8.2$  Hz), 125.1, 124.5, 116.9, 111.3 (d,  $J_F = 9.4$  Hz), 109.4 (d,  $J_F = 26.0$  Hz), 108.7, 104.0 (d,  $J_F = 23.9$  Hz), 35.7, 31.8, 12.0. **HRMS (ESI)** calculated for  $\text{C}_{18}\text{H}_{15}\text{FNO}_2$   $[\text{M}+\text{H}]^+$ : 296.1082, found: 296.1082. **IR (KBr)**: 3020, 1755, 1637, 1561, 1487, 1458, 1216, 1150, 756  $\text{cm}^{-1}$ .

#### 4-(1,2-dimethyl-1H-indol-3-yl) chroman-2-one (3d)

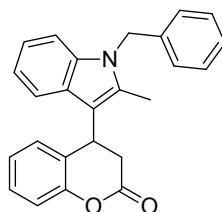


Red-brown solid, yield 69%. M. p.:173-175°C.

**<sup>1</sup>H NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (d,  $J = 8.2$  Hz, 1H), 7.26 (t,  $J = 7.7$  Hz, 1H), 7.18-7.12 (m, 2H), 7.02 (d,  $J = 7.9$  Hz, 1H), 6.98-6.88 (m, 3H), 4.65 (dd,  $J = 13.7, 5.1$  Hz, 1H), 3.71 (s, 3H), 3.24 (dd,  $J = 16.1, 13.7$  Hz, 1H), 2.92 (dd,  $J = 16.1, 5.1$  Hz, 1H), 2.36 (s, 3H). **<sup>13</sup>C NMR** (125

MHz, CDCl<sub>3</sub>)  $\delta$  168.6, 151.7, 145.3, 137.1, 134.5, 128.3, 128.1, 125.7, 125.3, 124.3, 120.8, 119.0, 116.7, 109.0, 107.7, 36.0, 32.1, 29.6, 10.5. **HRMS (ESI)** calculated for C<sub>19</sub>H<sub>18</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 292.1332, found: 292.1330. **IR (KBr)**: 3059, 2928, 1760, 1610, 1581, 1482, 1453, 1371, 1278, 1227, 1151, 920, 763, 738 cm<sup>-1</sup>.

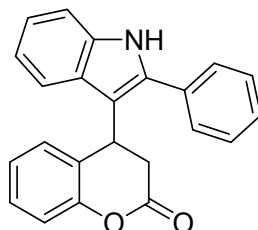
#### 4-(1-benzyl-2-methyl-1H-indol-3-yl) chroman-2-one (3e)



Red-brown solid, yield 53%. M. p.:80-81 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.31-7.27 (m, 3H), 7.16-7.05 (m, 4H), 7.01-6.92 (m, 6H), 5.35 (s, 2H), 4.67 (dd, *J* = 13.7, 5.0 Hz, 1H), 3.28 (dd, *J* = 16.1, 13.8 Hz, 1H), 2.96 (dd, *J* = 16.1, 5.1 Hz, 1H), 2.29 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>)  $\delta$  168.5, 151.7, 137.5, 137.1, 134.5, 128.8, 128.4, 128.0, 127.4, 125.8, 125.6, 125.5, 124.3, 121.2, 119.3, 119.1, 116.8, 109.5, 108.4, 46.6, 35.9, 32.1, 10.5. **HRMS (ESI)** calculated for C<sub>25</sub>H<sub>22</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 368.1646, found: 368.1644. **IR (KBr)**: 3029, 1762, 1638, 1559, 1454, 1416, 1340, 1217, 1149, 741 cm<sup>-1</sup>.

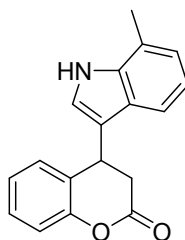
#### 4-(2-phenyl-1H-indol-3-yl) chroman-2-one (3f)



Yellow solid, yield 77%. M. p.:240-241 °C.

**<sup>1</sup>H NMR** (500 MHz, DMSO)  $\delta$  11.51 (s, 1H), 7.57 (d, *J* = 7.4 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.19-7.07 (m, 3H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.86 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 4.84 (dd, *J* = 13.3, 5.2 Hz, 1H), 3.51 (dd, *J* = 15.9, 13.5 Hz, 1H), 2.93 (dd, *J* = 16.1, 5.4 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, DMSO)  $\delta$  168.3, 151.8, 137.5, 137.1, 132.7, 129.3, 129.0, 128.7, 128.5, 128.1, 126.7, 126.2, 124.6, 121.9, 120.4, 119.3, 116.9, 112.2, 108.9, 35.5, 31.9. **HRMS (ESI)** calculated for C<sub>23</sub>H<sub>18</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 340.1333, found: 340.1333. **IR (KBr)**: 3080, 1751, 1638, 1559, 1483, 1455, 1235, 1216, 1156, 762, 747, 701 cm<sup>-1</sup>.

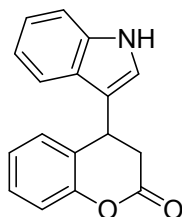
#### 4-(7-methyl-1H-indol-3-yl) chroman-2-one (3g)



Gray solid, yield 94%. M. p.:134-136°C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.11 (s, 1H), 7.36-7.33 (m, 1H), 7.31-7.27 (m, 1H), 7.14 (d, *J* = 7.9 Hz, 2H), 7.08-7.02 (m, 3H), 6.85 (d, *J* = 2.3 Hz, 1H), 4.65 (dd, *J* = 7.4, 5.9 Hz, 1H), 3.25 (dd, *J* = 15.8, 7.9 Hz, 1H), 3.08 (dd, *J* = 15.8, 5.6 Hz, 1H), 2.49 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 168.2, 151.6, 136.3, 128.5, 128.2, 126.0, 125.3, 124.6, 123.1, 121.9, 120.8, 120.1, 117.0, 116.6, 115.6, 36.3, 32.7, 16.5. **HRMS (ESI)** calculated for C<sub>18</sub>H<sub>16</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 278.1176, found: 278.1174. **IR (KBr)**: 2925, 1753, 1638, 1495, 1457, 1218, 1146, 751 cm<sup>-1</sup>.

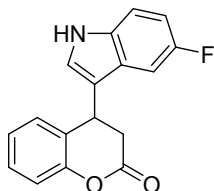
#### 4-(1H-indol-3-yl) chroman-2-one (3h)



Orange red, yield 81%. M. p.:211-213°C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.17 (s, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.31-7.25 (m, 1H), 7.22 (dd, *J* = 13.4, 5.4 Hz, 1H), 7.15-7.09 (m, 3H), 7.08-7.03 (m, 1H), 6.79 (d, *J* = 2.4 Hz, 1H), 4.64 (t, *J* = 6.5 Hz, 1H), 3.24 (dd, *J* = 15.8, 7.6 Hz, 1H), 3.07 (dd, *J* = 15.8, 5.6 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 168.3, 151.5, 136.7, 128.5, 128.2, 125.9, 125.6, 124.6, 122.5, 122.3, 119.8, 118.8, 117.0, 115.0, 111.6, 36.3, 32.5. **HRMS (ESI)** calculated for C<sub>17</sub>H<sub>14</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 264.1020, found: 264.1022. **IR (KBr)**: 3114, 2861, 1744, 1637, 1559, 1484, 1455, 1280, 1248, 1152, 928, 741 cm<sup>-1</sup>.

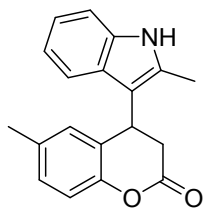
#### 4-(5-fluoro-1H-indol-3-yl) chroman-2-one (3i)



Brown solid, yield 30%. M. p.:76-77°C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.14 (s, 1H), 7.33-7.28 (m, 2H), 7.15-7.08 (m, 4H), 6.99-6.95 (m, 1H), 6.87 (d, *J* = 2.1 Hz, 1H), 4.59 (t, *J* = 6.4 Hz, 1H), 3.21 (dd, *J* = 15.8, 7.3 Hz, 1H), 3.08 (dd, *J* = 15.8, 5.6 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 168.0, 157.8 (d, *J*<sub>F</sub> = 236.2 Hz), 151.6, 133.2, 128.7, 128.1, 126.1 (d, *J*<sub>F</sub> = 9.3 Hz), 125.6, 124.7, 124.0, 117.1, 115.4, 112.3 (d, *J*<sub>F</sub> = 9.4 Hz), 111.1 (d, *J*<sub>F</sub> = 26.3 Hz), 103.8 (d, *J*<sub>F</sub> = 24.0 Hz), 36.2, 32.6. **HRMS (ESI)** calculated for C<sub>17</sub>H<sub>13</sub>FNO<sub>2</sub> [M+H]<sup>+</sup>: 282.0925, found: 282.0927. **IR (KBr)**: 3065, 1755, 1628, 1560, 1486, 1457, 1215, 1140, 801, 760 cm<sup>-1</sup>.

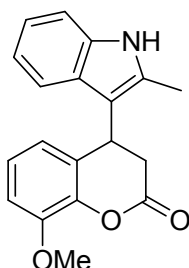
#### 6-methyl-4-(2-methyl-1H-indol-3-yl) chroman-2-one (3j)



Peachblow solid, yield 53%. M. p.:189-190°C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.04 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.15-7.04 (m, 4H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.74 (s, 1H), 4.61 (dd, *J* = 12.8, 5.2 Hz, 1H), 3.24 (dd, *J* = 16.1, 12.9 Hz, 1H), 2.94 (dd, *J* = 16.1, 5.2 Hz, 1H), 2.36 (s, 3H), 2.16 (s, 3H). **<sup>13</sup>C NMR** (125MHz, CDCl<sub>3</sub>) δ 168.9, 149.8, 135.6, 134.0, 132.6, 128.9, 128.3, 126.5, 125.1, 121.3, 119.5, 118.9, 116.5, 110.6, 108.8, 35.9, 31.9, 20.7, 12.0. **HRMS (ESI)** calculated for C<sub>19</sub>H<sub>18</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 292.1333, found: 292.1333. **IR (KBr)**: 3051, 1749, 1638, 1560, 1490, 1460, 1246, 1199, 733 cm<sup>-1</sup>.

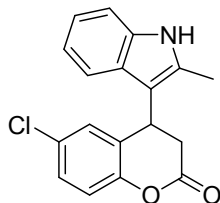
### 8-methoxy-4-(2-methyl-1H-indol-3-yl) chroman-2-one (3k)



Offwhite solid, yield 66%. M. p.:117-118°C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.26 (s, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.9 Hz, 1H), 6.95-6.91 (m, 1H), 6.90-6.85 (m, 2H), 6.51-6.47 (m, 1H), 4.61 (dd, *J* = 13.2, 5.1 Hz, 1H), 3.91 (s, 3H), 3.24 (dd, *J* = 16.0, 13.3 Hz, 1H), 2.92 (dd, *J* = 16.0, 5.1 Hz, 1H), 2.32 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 168.2, 147.5, 140.9, 135.6, 132.8, 126.8, 126.3, 124.1, 121.1, 119.5, 119.2, 118.8, 111.1, 110.7, 108.3, 56.0, 35.6, 31.9, 11.7. **HRMS (ESI)** calculated for C<sub>19</sub>H<sub>18</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 308.1282, found: 308.1282. **IR (KBr)**: 3020, 1762, 1618, 1560, 1481, 1460, 1438, 1277, 1084, 745 cm<sup>-1</sup>.

### 6-chloro-4-(2-methyl-1H-indol-3-yl) chroman-2-one (3l)

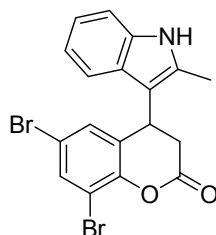


Brown solid, yield 85%. M. p.:170-172°C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.02 (s, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.25-7.23 (m, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.10-7.05 (m, 2H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 1.2 Hz, 1H), 4.60 (dd, *J* = 13.4, 5.2 Hz, 1H), 3.24 (dd, *J* = 16.2, 13.4 Hz, 1H), 2.95 (dd, *J* = 16.2, 5.2 Hz, 1H), 2.38 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 167.8, 150.4, 135.6, 132.8, 129.7, 128.6, 127.8, 127.5, 126.1, 121.6, 119.7, 118.7, 118.2, 110.8, 107.8, 35.4, 31.9, 12.0. **HRMS (ESI)**

calculated for  $C_{18}H_{15}ClNO_2$   $[M+H]^+$ : 312.0786, found: 312.0788. **IR (KBr)**: 3055, 1772, 1638, 1475, 1459, 1221, 738  $cm^{-1}$ .

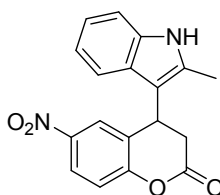
#### 6, 8-dibromo-4-(2-methyl-1H-indol-3-yl) chroman-2-one (3m)



Pink solid, yield 82%. M. p.:149-150°C.

**$^1H$  NMR** (500 MHz,  $CDCl_3$ )  $\delta$  8.09 (s, 1H), 7.66 (d,  $J = 2.2$  Hz, 1H), 7.35 (d,  $J = 8.1$  Hz, 1H), 7.15 (t,  $J = 8.0$  Hz, 1H), 7.05-6.98 (m, 2H), 6.96 (d,  $J = 1.3$  Hz, 1H), 4.61 (dd,  $J = 13.7, 5.1$  Hz, 1H), 3.26 (dd,  $J = 16.2, 13.7$  Hz, 1H), 2.95 (dd,  $J = 16.2, 5.1$  Hz, 1H), 2.38 (s, 3H).  **$^{13}C$  NMR** (125 MHz,  $CDCl_3$ )  $\delta$  166.6, 148.0, 135.7, 134.6, 133.0, 129.9, 129.3, 125.9, 121.7, 119.8, 118.6, 117.2, 111.5, 110.9, 107.1, 35.1, 32.4, 12.0. **HRMS (ESI)** calculated for  $C_{18}H_{14}Br_2NO_2$   $[M+H]^+$ : 433.9386, found: 433.9388.  $C_{18}H_{14}Br^{81}BrNO_2$   $[M+H+2]^+$ : 435.9404, found: 435.9404. **IR (KBr)**: 3067, 1774, 1638, 1560, 1439, 1131, 712  $cm^{-1}$ .

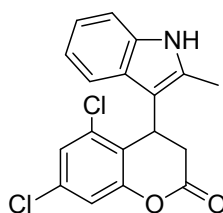
#### 4-(2-methyl-1H-indol-3-yl)-6-nitrochroman-2-one (3n)



Yellow solid, yield 92%. M. p.:286-287°C.

**$^1H$  NMR** (500 MHz,  $CDCl_3$ )  $\delta$  8.19 (dd,  $J = 9.0, 2.5$  Hz, 1H), 8.10 (s, 1H), 7.79 (d,  $J = 1.5$  Hz, 1H), 7.36 (d,  $J = 8.1$  Hz, 1H), 7.28 (d,  $J = 8.9$  Hz, 1H), 7.17-7.12 (m, 1H), 6.97-6.93 (m, 2H), 4.67 (dd,  $J = 13.6, 5.3$  Hz, 1H), 3.30 (dd,  $J = 16.3, 13.7$  Hz, 1H), 3.03 (dd,  $J = 16.3, 5.3$  Hz, 1H), 2.41 (s, 3H).  **$^{13}C$  NMR** (125 MHz,  $CDCl_3$ )  $\delta$  166.5, 144.5, 135.8, 133.1, 127.3, 125.7, 124.5, 124.1, 121.8, 120.0, 118.4, 117.9, 112.5, 111.1, 107.0, 35.0, 31.9, 12.0. **HRMS (ESI)** calculated for  $C_{18}H_{15}N_2O_4$   $[M+H]^+$ : 323.1027, found: 323.1029. **IR (KBr)**: 3057, 1772, 1625, 1592, 1560, 1512, 1460, 1337, 1241, 1214, 1139, 919, 821, 750  $cm^{-1}$ .

#### 5, 7-dichloro-4-(2-methyl-1H-indol-3-yl) chroman-2-one (3o)

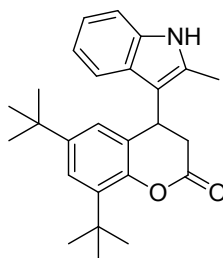


Red solid, yield 70%. M. p.:124-126°C.

**$^1H$  NMR** (500 MHz,  $CDCl_3$ )  $\delta$  7.86 (s, 1H), 7.24 (dd,  $J = 7.9, 3.0$  Hz, 2H), 7.22-7.20 (m, 1H), 7.14 (d,  $J = 2.0$  Hz, 1H), 7.11-7.07 (m, 1H), 7.02 (t,  $J = 7.5$  Hz, 1H), 4.86 (dd,  $J = 6.7, 2.6$  Hz,

1H), 3.06 (t,  $J = 4.9$  Hz, 2H), 2.11 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.4, 153.1, 135.0, 134.8, 134.2, 131.5, 126.8, 125.5, 121.8, 121.5, 119.89, 117.4, 116.2, 110.5, 108.6, 35.9, 30.8, 11.8. **HRMS (ESI)** calculated for  $\text{C}_{18}\text{H}_{14}\text{Cl}_2\text{NO}_2$   $[\text{M}+\text{H}]^+$ : 346.0396, found: 346.0398.  $\text{C}_{18}\text{H}_{14}\text{Cl}^{37}\text{Cl}^{35}\text{NO}_2$   $[\text{M}+\text{H}+2]^+$ : 348.0367, found: 348.0367. **IR (KBr)**: 3083, 1762, 1619, 1572, 1461, 1397, 1131, 745  $\text{cm}^{-1}$ .

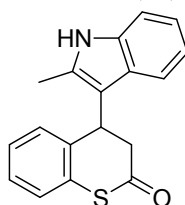
#### 6, 8-di-tert-butyl-4-(2-methyl-1H-indol-3-yl) chroman-2-one (3p)



Red solid, yield 70%. M. p.:174-176°C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (s, 1H), 7.33-7.29 (m, 2H), 7.13-7.08 (m, 2H), 6.98-6.95 (m, 1H), 6.87 (dd,  $J = 2.3, 0.9$  Hz, 1H), 4.61 (dd,  $J = 11.8, 5.0$  Hz, 1H), 3.15 (dd,  $J = 15.9, 11.8$  Hz, 1H), 2.92 (dd,  $J = 15.9, 5.0$  Hz, 1H), 2.26 (s, 3H), 1.49 (s, 9H), 1.13 (s, 9H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  168.8, 148.4, 146.3, 137.1, 135.5, 132.3, 126.8, 125.6, 123.2, 122.7, 121.3, 119.3, 119.0, 110.5, 109.2, 36.2, 35.1, 34.5, 32.6, 31.3, 30.2, 12.0. **HRMS (ESI)** calculated for  $\text{C}_{26}\text{H}_{32}\text{NO}_2$   $[\text{M}+\text{H}]^+$ : 390.2428, found: 390.2428. **IR (KBr)**: 3050, 2962, 1763, 1638, 1560, 1460, 1435, 1216, 1150, 741  $\text{cm}^{-1}$ .

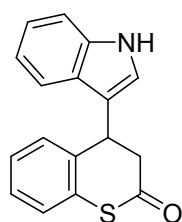
#### 4-(2-methyl-1H-indol-3-yl) thiochroman-2-one (5a)



Pale red solid, yield 75%. M. p.:112-113°C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (s, 1H), 7.33 (dd,  $J = 19.6, 7.9$  Hz, 2H), 7.23 (d,  $J = 7.6$  Hz, 1H), 7.20-7.12 (m, 2H), 7.06 (t,  $J = 7.4$  Hz, 1H), 6.99 (dd,  $J = 12.9, 7.5$  Hz, 2H), 4.62 (dd,  $J = 13.7, 2.3$  Hz, 1H), 3.40 (dd,  $J = 15.8, 14.0$  Hz, 1H), 2.94 (dd,  $J = 15.9, 3.0$  Hz, 1H), 2.38 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  199.8, 195.4, 137.1, 135.7, 132.4, 131.8, 128.2, 127.4, 127.0, 126.9, 121.4, 119.5, 119.4, 110.7, 109.2, 45.9, 36.8, 12.1. **HRMS (ESI)** calculated for  $\text{C}_{18}\text{H}_{16}\text{NOS}$   $[\text{M}+\text{H}]^+$ : 294.0548, found: 294.0547. **IR (KBr)**: 3060, 2930, 1636, 1615, 1458, 1126, 748, 623  $\text{cm}^{-1}$ .

#### 4-(1H-indol-3-yl) thiochroman-2-one (5b)

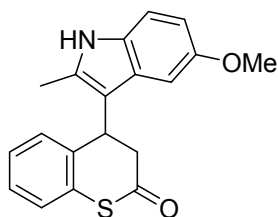




Pale yellow solid, yield 80%. M. p.:75-76°C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.12 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.25-7.23 (m, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.20-7.14 (m, 2H), 7.14-7.09 (m, 1H), 6.93 (d, *J* = 2.3 Hz, 1H), 4.75 (dd, *J* = 8.7, 3.7 Hz, 1H), 3.35 (dd, *J* = 15.7, 8.7 Hz, 1H), 3.11 (dd, *J* = 15.7, 3.8 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 199.1, 136.9, 136.6, 131.5, 128.9, 127.5, 127.2, 127.0, 126.2, 122.6, 122.5, 119.8, 119.2, 114.3, 111.5, 45.6, 37.7. **HRMS (ESI)** calculated for C<sub>17</sub>H<sub>14</sub>NOS [M+H]<sup>+</sup>: 280.0791, found: 280.0791. **IR (KBr)**: 3108, 2867, 1739, 1634, 1562, 1479, 1460, 1277, 1241, 1151, 934, 737 cm<sup>-1</sup>.

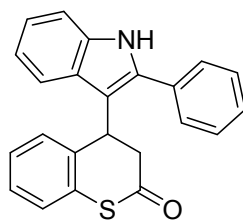
#### 4-(5-methoxy-2-methyl-1H-indol-3-yl)thiochroman-2-one (5c)



Yellow solid, yield 93%. M. p.:84-86°C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.86 (s, 1H), 7.23 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 2H), 7.02-6.97 (m, 1H), 6.92 (d, *J* = 7.7 Hz, 1H), 6.72 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.54 (d, *J* = 2.3 Hz, 1H), 4.52 (dd, *J* = 13.7, 2.9 Hz, 1H), 3.63 (s, 3H), 3.29 (dd, *J* = 15.9, 13.7 Hz, 1H), 2.86 (dd, *J* = 15.9, 3.1 Hz, 1H), 2.26 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 200.1, 153.8, 136.9, 133.3, 131.7, 130.7, 128.8, 128.2, 127.4, 127.0, 126.9, 111.2, 110.7, 108.8, 102.1, 55.9, 45.7, 36.7, 12.0. **HRMS (ESI)** calculated for C<sub>19</sub>H<sub>18</sub>NO<sub>2</sub>S [M+H]<sup>+</sup>: 324.1053, found: 324.1053. **IR (KBr)**: 3062, 2963, 2922, 1686, 1655, 1582, 1439, 1262, 1099, 802, 756, 620 cm<sup>-1</sup>.

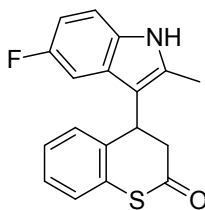
#### 4-(2-phenyl-1H-indol-3-yl)thiochroman-2-one (5d)



Pale yellow solid, yield 78%. M. p.:216-218°C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.21 (s, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.36-7.27 (m, 5H), 7.24 (d, *J* = 6.6 Hz, 1H), 7.20-7.13 (m, 3H), 7.07 (d, *J* = 7.7 Hz, 1H), 7.03-6.99 (m, 1H), 6.98-6.94 (m, 1H), 4.71 (dd, *J* = 14.3, 2.8 Hz, 1H), 3.39 (dd, *J* = 16.0, 14.3 Hz, 1H), 2.82 (dd, *J* = 16.0, 3.0 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 199.9, 137.4, 136.7, 136.5, 132.3, 131.6, 129.1, 129.1, 128.5, 128.4, 127.5, 127.1, 127.0, 122.6, 120.7, 120.0, 111.4, 110.1, 110.0, 45.8, 37.10. **HRMS (ESI)** calculated for C<sub>23</sub>H<sub>18</sub>NOS [M+H]<sup>+</sup>: 356.1104, found: 356.1105. **IR (KBr)**: 3063, 1747, 1642, 1554, 1487, 1450, 1231, 1206, 1149, 759, 706 cm<sup>-1</sup>.

#### 4-(5-fluoro-2-methyl-1H-indol-3-yl)thiochroman-2-one (5e)



Yellow solid, yield 82%. M. p.:79-81 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.00 (s, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.27 (s, 1H), 7.25 (d, *J* = 4.2 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 7.7 Hz, 1H), 6.91-6.85 (m, 1H), 6.81 (d, *J* = 9.8 Hz, 1H), 4.58 (dd, *J* = 13.6, 2.3 Hz, 1H), 3.33 (dd, *J* = 15.5, 14.0 Hz, 1H), 2.91 (dd, *J* = 15.9, 3.0 Hz, 1H), 2.38 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 199.6, 157.6 (d, *JF* = 235.0 Hz), 136.6, 134.3, 132.1, 131.8, 130.9, 128.8, 127.8 (d, *JF* = 55.4 Hz), 127.5, 127.4, 127.1, 111.2 (d, *JF* = 9.4 Hz), 109.6 (d, *JF* = 25.4 Hz), 104.5 (d, *JF* = 24.0 Hz), 45.7, 36.7, 12.3. **HRMS (ESI)** calculated for C<sub>18</sub>H<sub>15</sub>FNOS [M+H]<sup>+</sup>: 312.0853, found: 312.0854. **IR (KBr)**: 3017, 1763, 1646, 1552, 1483, 1462, 1220, 1147, 760 cm<sup>-1</sup>.

# NMR Spectra

