SYNTHESIS OF CHROMENO[2,3-b]INDOLE DERIVATES#

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Abstract – Several new chromeno[2,3-b]indole tetracycles were synthesized by the reaction of 2'-hydroxyacetophenones or 2'-hydroxypropiophenones and salicylaldehyde derivates. Under the harsh reaction conditions, the initially formed Knoevenagel adducts lost water, giving rise to the formation of ring closed tetracyclic products.

During one of our ongoing medicinal chemistry programs we intended to prepare a small library of 1,3-dihydro-[1-(3-hydroxyphenyl)ethylidene]-2H-indol-2-one derivatives 3 using the frequently applied Knoevenagel reaction between the appropriate 2'-hydroxyacetophenones and oxindole derivatives.1 The condensation between 2'-hydroxybenzaldehydes and oxindoles is a well-described and often utilized reaction but to date, there is no example of the use of 2'-hydroxyacetophenones in this process.2

The reactions between oxindole 1 and salicylaldehyde derivates 2 (R^1=OH, R^4=H) or other benzaldehyde derivates (R^1=Br) were performed under the standard conditions for this reaction (EtOH, cat. piperidine, reflux), giving rise the formation of the expected products in good yields (Table 1, Entries 1-3). Under the same conditions, the related 2'-hydroxyacetophenones (2, R^4=Me) or propiophenones (2, R^4=Et) did not react with oxindole 1 and only the starting materials were recovered. After we had investigated several other harsher sets of reaction conditions we found, that using of n-butylamine as a base, in the presence of acetic acid in mesitylene at 140 °C, the starting material disappeared accordingly to HPLC. In most cases a single new product was formed in addition to some decomposition products, arising from the starting

# Dedicated to Professor László Tőke on the occasion of his 80th birthday.
materials. From the mass spectra it was apparent that it was not the expected product 3 which was formed, and a new tetracycle 4 was isolated as revealed by NMR studies (Scheme 1).

The chromeno[2,3-\(b\)]indole ring system has been described only as a by-product in a similar intramolecular cyclization of \(o\)-aminobenzylidene-oxindoles,\(^3\) while a few closely related chromono[2,3-\(b\)]indoles have been prepared from the corresponding 3-(2-hydroxybenzoyl)oxindoles\(^4\) or, in one case, via an aminoisoflavone – salicyloylindole ring transformation.\(^5\)

Scheme 1

The chromeno[2,3-\(b\)]indole derivatives (Table 1, Entries 4-26) were formed, in most cases, in fair to good yields. The nature of the substituent in the aromatic ring of the oxindole 1 or of the acetophenone 2 has little effect on the yields and the progress of the reaction, although a halogen at position 5 of the acetophenone decreases the yield of the condensation. In some cases, however, when the crude product was not pure enough for our purposes (<95%, by HPLC) we could isolate it them after purification (e.g. entries 9 or 26) only in very low yields due to the sparingly soluble nature of these substances.

We have applied the same reaction conditions to aldehydes (Table 2), however the ring-closed products 4 were formed only in low yields, in addition to the 3 ‘normal’ Knoevenagel products in all cases. In the cyclization of the 5-methyloxindole (\(R=\text{Me}\)) 1ab with salicylaldehyde (\(R^2=R^3=R^4=\text{H}\)) 2, a small quantity of dihydrocoumarin-type product 5ab was also separated. When a stronger base, Hünig’s, base, was utilized instead of butylamine (Table 2, Entries 2, 5 and 9) the conversions of the reactions increased, but product 3 still remained the major product.
### Table 1

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<th>R</th>
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<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>R&lt;sup&gt;3&lt;/sup&gt;</th>
<th>R&lt;sup&gt;4&lt;/sup&gt;</th>
<th>Method&lt;sup&gt;a&lt;/sup&gt;</th>
<th>3 (%)&lt;sup&gt;b&lt;/sup&gt;</th>
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<td>-</td>
<td>4z 27 (5)&lt;sup&gt;c&lt;/sup&gt;</td>
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</table>

<sup>a</sup>Method A: cat. piperidine in ethanol, reflux, 1 h; Method B: 1-butylamine, acetic acid in mesitylene, 140 °C, 24 h

<sup>b</sup>HPLC yield (isolated yield)<sup>method</sup>, <sup>c</sup>after recrystallization; <sup>d</sup>after chromatography; <sup>e</sup>after preparative HPLC.

In these cases other by-products, 5ac and 6, were also identified. Using 2'-hydroxybenzophenone instead of acetophenones did not result in reaction, only the decomposition of the starting materials was observed (Table 2, Entry 9).

The formation of the four different isolated products can be explained according to Scheme 2. The initially formed Knoevenagel adduct 3 loses water under the reaction conditions through its tautomeric form 7, giving rise to the formation of the ring closed tetracyclic product 4. However, the ring opening of 7 indolenine can lead to carboxylic acid 8, which can undergo immediate intramolecular O-acylation to product 6, followed by the reaction of the free aniline moiety with an additional molecule of starting aldehyde to give the byproduct 5.
**Table 2**

<table>
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<th>Entry</th>
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<th>( R^1 )</th>
<th>( R^2 )</th>
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<th>3% (%)</th>
<th>4% (%)</th>
<th>5 or 6% (%)</th>
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<td>H</td>
<td>B</td>
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<tr>
<td>2</td>
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<td>OH</td>
<td>H</td>
<td>C</td>
<td>3aa 52 (35)d</td>
<td>4aa 37 (7)d</td>
<td>6aa 2 (2)</td>
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<tr>
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<td>OH</td>
<td>H</td>
<td>B</td>
<td>3ab 45 (40)d</td>
<td>4ab 21 (15)d</td>
<td>5ab 13 (6)d</td>
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<td>OH</td>
<td>H</td>
<td>B</td>
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<td>4ac 30 (28)d</td>
<td>-</td>
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<tr>
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<td>OH</td>
<td>H</td>
<td>C</td>
<td>-</td>
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<tr>
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<td>OH</td>
<td>H</td>
<td>B</td>
<td>3ad 61 (58)d</td>
<td>4ad 20 (16)d</td>
<td>-</td>
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<td>4ae 10 (10)d</td>
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<td>OH</td>
<td>H</td>
<td>B</td>
<td>3af 37 (26)d</td>
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<td>OH</td>
<td>H</td>
<td>C</td>
<td>-</td>
<td>28</td>
<td>4af 13 (3.4)d</td>
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<td>OH</td>
<td>Ph</td>
<td>B</td>
<td>-</td>
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</table>

\( R^2 \) = \( R^3 \) = H; *Method B*: 1-butylamine, acetic acid in mesitylene, 140 °C, 2 h; *Method C*: diisopropylethylamine, acetic acid in mesitylene; 140 °C, HPLC yield (isolated yield)\(^\text{method}\); \(^\text{a}\) after recrystallization; \(^\text{b}\) after chromatography; \(^\text{c}\) after preparative HPLC.

**Scheme 2**
In summary, the reaction described herein represents a simple entry into the synthesis of polyfunctional chromeno[2,3-b]indole derivatives 4 of potential pharmaceutical interest, for which there have been no previously described syntheses. Further investigations of the present method will be required to optimize the yields, and establish its utility and scope.

EXPERIMENTAL

All melting points were obtained on MPA100 Optimelt Automated Melting Point System and are uncorrected. IR spectra were recorded with a Bruker Tensor 27 FT-IR spectrophotometer. $^1$H NMR and $^{13}$C spectra were recorded in DMSO-$d_6$ or in pyridine-$d_5$ using TMS as an internal reference on a Bruker Avance III spectrometer operating at 500 MHz and 125 MHz respectively (1H-, DEPTQ-, HSQC-, HMBC-, NOE-NMR). High-resolution MS spectra were measured on an Agilent 6230 TOF LC/MS spectrometer. Elemental analysis was performed on FlashEA 1112 Elemanalyzer.

**General Method A:** A mixture of 1.0 mmol of oxindole derivate (1), 1.0 mmol of benzaldehyde (2, $R^4=H$), and 20 µL of piperidine in 3 mL of EtOH was refluxed for 1 h. The precipitated product was collected by filtration, washed with cold EtOH, and dried *in vacuo* at 50 ºC to give the corresponding product.

**General Method B:** A mixture of 2.0 mmol of oxindole (1), and 2.0 mmol of 2’-hydroxyacetophenone (2, $R^4=Me$) or 2’-hydroxypropiophenone (2, $R^4=Et$) or salicyaldehyde ($R^4=H$) derivate was dissolved in 8.0 mL of mesitylene. After stirring for 10 min, 0.30 mL of 1-butylamine (3.0 mmol) and 0.17 mL of acetic acid (3.0 mmol) were added to the reaction and the mixture was kept at 140 ºC for 24 h (in case of the salicyaldehyde for 2 h). After cooling, the product was precipitated, collected by filtration, washed with cold EtOAc, and dried *in vacuo* at 50 ºC for overnight. The product obtained was further purified by recrystallization, column chromatography, or preparative HPLC.

**General Method C:** A mixture of 1.0 mmol of oxindole and 1.5 mmol of the salicyaldehyde was dissolved in 4.0 mL of mesitylene. After stirring for 10 min, 0.26 mL of diisopropylethylamine (1.5 mmol) and 0.086 mL of acetic acid (1.5 mmol) were added and the mixture was kept at 140 ºC for 2 h. After cooling the product was precipitated, collected by filtration, washed with iso-propanol and dried *in vacuo* at 50 ºC for overnight.

**5-Bromo-3-[(5-chloro-2-hydroxyphenyl)methylene]indolin-2-one (3a):** Compound was synthesized according to the General Method A. 266.5 mg, (76%); yellow crystals; mp 249 ºC. IR (KBr, cm$^{-1}$): 1694 (>C=O), 1605 (C=C). $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta = 6.84 (1H, d, J = 8.2 Hz, Ar-H), 7.01 (1H, d, J = 8.8 Hz, Ar-H), 7.38 (1H, dd, $J_1 = 8.8$ Hz, $J_2 = 2.9$ Hz, Ar-H), 7.41 (1H, dd, $J_1 = 8.2$ Hz, $J_2 = 1.9$ Hz, Ar-H), 7.43 (1H, d, $J = 1.9$ Hz, Ar-H), 7.60 (1H, d, $J = 2.9$ Hz, Ar-H), 7.61 (1H, s, >C=CH), 10.60 (1H, brs, OH), 10.76 (1H, s, NH). $^{13}$C NMR (125 MHz, DMSO-$d_6$): $\delta = 112.4$ (Ar-C), 113.1 (C-Br), 118.3, 122.8 (C-Cl),
123.0, 123.6, 125.4, 127.4 (>C=CH), 129.3, 131.7, 132.7, 132.8 (>C=CH), 142.4, 155.7 (C-OH), 168.5 (NH-C=O). HRMS m/z calcd for C_{15}H_{10}BrClNO_2 (M+H)^+ 349.9505, found 349.9574. Anal. Calcd for C_{15}H_{9}BrClNO_2: C, 51.39; H, 2.59; N, 4.00%. Found C, 51.47; H, 2.57; N, 3.74%.

5-Bromo-3-[(2-bromo-5-chlorophenyl)methylene]indolin-2-one (3b): Compound was synthesized according to the General Method A. 219.2 mg (53%); yellow crystals, mp 260 °C. IR (KBr, cm⁻¹): 3180 (-NH), 1716 (>C=O), 1612 (C=C). 1H NMR (500 MHz, DMSO-d₆): δ = 6.86 (1H, d, J = 8.3 Hz, Ar-H), 7.05 (1H, d, J = 1.9 Hz, Ar-H), 7.44 (1H, dd, J₁ = 8.3 Hz, J₂ = 1.9 Hz, Ar-H), 7.51 (1H, s, >C=CH), 7.55 (1H, dd, J₁ = 8.6 Hz, J₂ = 2.6 Hz, Ar-H), 7.83 (1H, d, J = 2.6 Hz, Ar-H), 7.86 (1H, d, J = 8.6 Hz, Ar-H), 10.88 (1H, brs, NH). 13C NMR (125 MHz, DMSO-d₆): δ = 112.8 (Ar-C), 113.3 (C-Br), 121.8, (C-Br), 122.9, 125.4, 129.7 (>C=CH), 130.2, 131.7, 133.1, 133.6, 134.3 (>C=CH), 135.2, 136.9, (C-Cl), 142.9, 167.9 (NH-C=O). HRMS m/z calcd for C_{15}H_{9}Br₂ClNO (M+H)^+ 411.8661, found 411.8733. Anal. Calcd for C_{15}H_{8}Br₂ClNO: C, 43.57; H, 1.95; N, 3.39%. Found C, 43.26; H, 1.96; N, 3.16%.

3-[(2-Bromo-5-hydroxyphenyl)methylene]-5-phenylindolin-2-one (3c): Compound was synthesized according to the General Method A. 235.4 mg, (60%); yellow crystals mp 220 °C. IR (KBr, cm⁻¹): 1694 (>C=O), 1615 (C=C). 1H NMR (500 MHz, DMSO-d₆): δ = 6.86 (1H, dd, J₁ = 8.6 Hz, J₂ = 1.9 Hz, Ar-H), 6.97 (1H, d, J = 8.1 Hz, Ar-H), 7.26 (1H, d, J = 1.9 Hz, Ar-H), 7.29-7.43 (5H, m, Ar-H), 7.51 (1H, s, >C=CH), 7.52 (1H, s, Ar-H), 7.55 (1H, d, J = 8.1 Hz, Ar-H), 7.58 (1H, d, J = 8.6 Hz, Ar-H), 10.07 (1H, s, OH), 10.79 (1H, s, NH). 13C NMR (125 MHz, DMSO-d₆): δ = 111.1 (Ar-C), 112.0 (C-Br), 117.2, 119.3, 121.6, 121.6, 126.5, 127.5, 129.4, 129.4 (>C=CH), 129.7, 133.9 (C-Ph), 134.3, 134.8 (>C=CH), 135.6, 140.5, 143.1, 157.4 (C-OH), 168.7 (NH-C=O). HRMS m/z calcd for C_{21}H_{15}NO₂Br (M+H)^+ 411.8661, found 411.8733. Anal. Calcd for C_{21}H_{14}NO₂Br: C, 64.30; H, 3.60; N, 3.57%. Found C, 63.56; H, 3.96; N, 3.16%.

3-(2-Hydroxybenzylidene)-1,3-dihydroindol-2-one (3aa): Compound was synthesized according to the General Method B. 235.4 mg, (60%); yellow crystals; mp 100 °C. IR (KBr, cm⁻¹): 1694 (>C=O), 1615 (C=C). 1H NMR (500 MHz, DMSO-d₆): δ = 6.85 (1H, t, J = 7.7 Hz, Ar-H), 6.86 (1H, d, J = 8.0 Hz, J₂ = 1.9 Hz, Ar-H), 6.92 (1H, t, J = 7.7 Hz, Ar-H), 7.26 (1H, d, J = 1.9 Hz, Ar-H), 7.51 (1H, s, >C=CH), 7.68 (1H, s, OH), 10.79 (1H, s, NH). 13C NMR (125 MHz, DMSO-d₆): δ = 110.4 (Ar-C), 112.0 (C-Br), 117.2, 119.3, 121.6, 121.6, 126.5, 127.5, 129.4, 129.4 (>C=CH), 130.0, 130.2, 132.1, 132.9 (>C=CH), 143.1, 157.0 (C-OH), 169.2 (NH-C=O). HRMS m/z calcd for C_{15}H_{12}NO₂ (M+H)^+ 238.0790, found 238.0866. Anal. Calcd for C_{15}H_{11}NO₂: C, 75.94; H, 4.67; N, 5.90%. Found C, 75.13; H, 4.86; N, 5.64%.

3-[(2-Hydroxyphenyl)methylene]-5-methylindolin-2-one (3ab): Compound was synthesized according to the General Method B. 123.4 mg (26%); yellow crystals; mp 100 °C. IR (KBr, cm⁻¹): 3177 (NH or OH), 1677 (>C=O), 1603 (C=C). 1H NMR (500 MHz, DMSO-d₆): δ = 6.85 (1H, t, J = 7.7 Hz, Ar-H), 6.86 (1H, d, J = 7.7 Hz, Ar-H), 6.92 (1H, t, J = 7.5 Hz, Ar-H), 6.98 (1H, d, J = 8.0 Hz, Ar-H), 7.21 (1H, t, J = 7.7 Hz, Ar-H), 7.31 (1H, dd, J₁ = 8.0 Hz, J₂ = 7.5 Hz, Ar-H), 7.50 (1H, d, J = 7.7 Hz, Ar-H), 7.63 (1H, d, J = 7.5 Hz, Ar-H), 7.68 (1H, s, >C=CH), 10.18 (1H, s, OH), 11.12 (1H, s, NH). 13C NMR (125 MHz, DMSO-d₆): δ = 110.4 (Ar-C), 116.4, 119.3, 121.5, 121.7, 122.8, 126.9 (>C=CH), 130.0, 130.2, 132.1, 132.9 (>C=CH), 143.1, 157.0 (C-OH), 169.2 (NH-C=O). HRMS m/z calcd for C_{15}H_{12}NO₂ (M+H)^+ 238.0790, found 238.0866. Anal. Calcd for C_{15}H_{11}NO₂: C, 75.94; H, 4.67; N, 5.90%. Found C, 75.13; H, 4.86; N, 5.64%.

3-[(2-Hydroxyphenyl)methylene]-5-phenylindolin-2-one (3ab): Compound was synthesized according to the General Method B. 201 mg (40%); yellow crystals, mp 173 °C. IR (KBr, cm⁻¹): 3177 (NH or OH), 1679 (>C=O). 1H NMR (500 MHz, DMSO-d₆): δ = 2.15 (3H, s, CH₃), 6.75 (1H, d, J = 8.0 Hz, Ar-H), 6.93
(1H, t, J = 8.0 Hz, Ar-H), 6.97 (1H, dd, J1 = 8.0 Hz, J2 = 1.0 Hz, Ar-H), 7.02 (1H, bd, J = 8.0 Hz, Ar-H), 7.31 (1H, td, J1 = 7.5 Hz, J2 = 2.0 Hz, Ar-H), 7.33 (1H, d, J = 1.0 Hz, Ar-H), 7.63 (1H, dd, J1 = 7.5 Hz, J2 = 1.5 Hz, Ar-H), 7.65 (1H, s, =C-H), 10.16 (1H, br OH), 10.44 (1H, s, NH). 13C NMR (125 MHz, DMSO-d6): δ = 21.3 (CH3), 110.1, 116.4, 119.2, 121.8, 121.8, 123.3, 127.0 (>C=CH), 130.0, 130.0, 130.6, 132.1, 132.7 (>C=CH), 140.8, 157.0 (C-OH), 169.3 (NH-C=O). HRMS calcd for C16H14NO2 (M+H)+ 252.1024, found 252.1020. Anal. Calcd for C16H13NO2: C, 76.48; H, 5.21; N, 5.57%. Found C, 76.00; H, 5.15; N, 5.33%.

5-Bromo-3-[2-hydroxyphenyl)methylene]indolin-2-one (3ac): Compound was synthesized according to the General Method B. 50.5 mg (8%); yellow crystals, mp 203 °C. IR (KBr, cm−1): 3172 (NH or OH), 1685, 1605 (>C=O). 1H NMR (500 MHz, DMSO-d6): δ = 6.83 (1H, d, J = 8.0 Hz, Ar-H), 6.95 (1H, t, J = 7.8 Hz, Ar-H), 7.00 (1H, d, J = 8.5 Hz, Ar-H), 7.35 (1H, t, J = 7.3 Hz, Ar-H), 7.39 (1H, d, J = 8.0 Hz, Ar-H), 7.52 (1H, bs, Ar-H), 7.58 (1H, d, J = 7.5 Hz, Ar-H), 7.73 (1H, s, =C-H), 10.29 (1H, br OH), 10.72 (1H, s, NH). 13C NMR (125 MHz, DMSO-d6): δ = 112.3, 113.0, 116.6, 119.3, 121.3, 123.9, 125.1, 126.1 (C=CH), 130.1, 132.4, 132.6, 134.8 (>C=CH), 142.2, 157.1 (C-OH), 168.8 (NH-C=O). HRMS m/z calcd for C15H11BrNO2 (M+H)+ 315.9973, found 315.9970. Anal. Calcd for C15H10BrNO2: C, 56.99; H, 3.19; N, 4.43%. Found C, 56.56; H, 3.15; N, 3.99%.

3-[(2-Hydroxyphenyl)methylene]-2-oxoindoline-5-carbonitrile (3ad): Compound was synthesized according to the General Method B. 304.2 mg (58%); yellow crystals, mp 243 °C. IR (KBr, cm−1): 3278 (NH or OH), 2231 (nitrile), 1715 (>C=O), 1603 (C=C). 1H NMR (500 MHz, DMSO-d6): δ = 6.98 (1H, t, J = 7.6 Hz, Ar-H), 7.02 (1H, d, J = 7.6 Hz, Ar-H), 7.02 (1H, d, J = 6.9 Hz, Ar-H), 7.38 (1H, t, J = 7.6 Hz, Ar-H), 7.63 (1H, d, J = 7.6 Hz, Ar-H), 7.68 (1H, s, Ar-H), 7.69 (1H, d, J = 6.9 Hz, Ar-H), 7.83 (1H, s, >C=CH), 10.37 (1H, brs, OH), 11.12 (1H, s, NH). 13C NMR (125 MHz, DMSO-d6): δ = 103.5 (C-CN), 111.2 (Ar-C), 116.7, 119.6, 119.9 (C-CN), 121.2, 122.5, 125.0, 126.0, 130.3, 132.9, 134.6, 135.9, 146.7, 157.2, 169.0. HRMS m/z calcd for C16H11N2O2 (M+H)+ 263.0742, found 263.0820. Anal. Calcd for C16H10N2O2: C, 73.27; H, 3.84; N, 10.68%. Found C, 72.30; H, 3.45; N, 10.43%.

3-[(2-Hydroxyphenyl)methylene]-5-(trifluoromethyl)indolin-2-one (3ae): Compound was synthesized according to the General Method B. 91.6 mg (15%); yellow crystals, mp 202 °C. IR (KBr, cm−1): 3176 (NH or OH), 2231 (nitrile), 1715 (>C=O), 1603 (C=C). 1H NMR (500 MHz, DMSO-d6): δ = 6.98 (1H, t, J = 7.6 Hz, Ar-H), 7.02 (1H, d, J = 7.6 Hz, Ar-H), 7.02 (1H, d, J = 6.9 Hz, Ar-H), 7.38 (1H, t, J = 7.6 Hz, Ar-H), 7.63 (1H, d, J = 7.6 Hz, Ar-H), 7.68 (1H, s, Ar-H), 7.69 (1H, d, J = 6.9 Hz, Ar-H), 7.83 (1H, s, >C=CH), 10.37 (1H, brs, OH), 11.12 (1H, s, NH). 13C NMR (125 MHz, DMSO-d6): δ = 103.5 (C-CN), 111.2 (Ar-C), 116.7, 119.6, 119.9 (C-CN), 121.2, 122.5, 125.0, 126.0, 130.3, 132.9, 134.6, 135.9, 146.7, 157.2, 169.0. HRMS m/z calcd for C16H11BrNO2 (M+H)+ 263.0742, found 263.0820. Anal. Calcd for C16H10BrNO2: C, 56.99; H, 3.19; N, 10.68%. Found C, 56.56; H, 3.15; N, 3.99%.

3-[(2-Hydroxyphenyl)methylene]-2-oxoindoline-5-carbonitrile (3ad): Compound was synthesized according to the General Method B. 304.2 mg (58%); yellow crystals, mp 243 °C. IR (KBr, cm−1): 3278 (NH or OH), 2231 (nitrile), 1715 (>C=O), 1603 (C=C). 1H NMR (500 MHz, DMSO-d6): δ = 6.98 (1H, t, J = 7.6 Hz, Ar-H), 7.02 (1H, d, J = 7.6 Hz, Ar-H), 7.02 (1H, d, J = 6.9 Hz, Ar-H), 7.38 (1H, t, J = 7.6 Hz, Ar-H), 7.63 (1H, d, J = 7.6 Hz, Ar-H), 7.68 (1H, s, Ar-H), 7.69 (1H, d, J = 6.9 Hz, Ar-H), 7.83 (1H, s, >C=CH), 10.37 (1H, brs, OH), 11.12 (1H, s, NH). 13C NMR (125 MHz, DMSO-d6): δ = 103.5 (C-CN), 111.2 (Ar-C), 116.7, 119.6, 119.9 (C-CN), 121.2, 122.5, 125.0, 126.0, 130.3, 132.9, 134.6, 135.9, 146.7, 157.2, 169.0. HRMS m/z calcd for C16H11N2O2 (M+H)+ 263.0742, found 263.0820. Anal. Calcd for C16H10N2O2: C, 73.27; H, 3.84; N, 10.68%. Found C, 72.30; H, 3.45; N, 10.43%.
Methyl 3-[(2-hydroxyphenyl)methylene]-2-oxoindoline-5-carboxylate (3af): Compound was synthesized according to the General Method B. 153.6 mg (26%); yellow crystals, mp 205 °C. IR (KBr, cm\(^{-1}\)): 1704 (>C=O), 1607 (C=C). \(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta = 3.76\) (3H, s, OCH\(_3\)), 6.94 (1H, t, J = 7.6 Hz, Ar-H), 6.97 (1H, d, J = 7.7 Hz, Ar-H), 7.01 (1H, d, J = 7.6 Hz, Ar-H), 7.36 (1H, t, J = 7.6 Hz, Ar-H), 7.64 (1H, d, J = 7.6 Hz, Ar-H), 7.78 (1H, s, >C=CH), 7.86 (1H, dd, J\(_1\) = 7.7 Hz, J\(_2\) = 1.2 Hz, Ar-H), 8.16 (1H, brs, Ar-H), 10.27 (1H, s, OH), 10.97 (1H, s, NH). \(^13\)C NMR (125 MHz, DMSO-\(d_6\)): \(\delta = 52.2\) (OCH\(_3\)), 110.2 (Ar-C), 116.6, 119.3, 121.4, 122.7 (CO\(_2\)Me), 123.8, 125.9 (C=CH), 130.1, 131.8, 132.6, 134.5 (C=H), 147.1, 157.2 (C=O), 166.5 (COOMe), 169.5 (NH-C=O). HRMS m/z calcd for C\(_{17}\)H\(_{14}\)NO\(_4\) (M+H)\(^+\) 296.0845, found 296.0918. Anal. Calcd for C\(_{17}\)H\(_{13}\)NO\(_4\): C, 69.15; H, 4.44; N, 4.74%. Found C, 68.40; H, 4.28; N, 4.66%.

2-Methoxy-11-methylchromeno[2,3-b]indole (4d): Compound was synthesized according to the General Method B. 205.3 mg (39%), orange crystals, mp 166 °C. IR (KBr, cm\(-1\)): 2922 (C-H), 1192 (C-O-C). \(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta = 3.02\) (3H, s, CH\(_3\)), 3.92 (3H, s, OCH\(_3\)), 7.28 (1H, m, C\(_3\)-H), 7.40 (1H, dd, J\(_1\) = 9.1 Hz, J\(_2\) = 2.9 Hz, C\(_8\)-H), 7.48 (1H, m, C\(_2\)-H), 7.55 (1H, d, J = 9.1 Hz, C\(_1\)-H), 7.58 (1H, d, J = 2.9 Hz, C\(_6\)-H), 7.75 (1H, d, J = 9.1 Hz, C\(_9\)-H), 8.16 (1H, d, J = 7.6 Hz, C\(_4\)-H). \(^13\)C NMR (125 MHz, DMSO-\(d_6\)): \(\delta = 15.6\) (CH\(_3\)), 56.4 (OCH\(_3\)), 109.0 (C\(_6\)), 118.9 (C\(_9\)), 119.0 (C\(_1\)), 120.0 (C\(_8\)), 121.3 (C\(_5\)a), 122.2 (C\(_4\)b), 122.4 (C\(_3\)), 124.0 (C\(_4\)), 124.4 (C\(_4a\)), 129.3 (C\(_2\)), 144.4 (CCH\(_3\)), 145.5 (C\(_9\)a), 156.2 (COCH\(_3\)), 163.7 (C\(_{10a}\)). HRMS m/z calcd for C\(_{17}\)H\(_{14}\)NO\(_2\) (M+H)\(^+\) 264.0946, found 264.1009. Anal. Calcd for C\(_{17}\)H\(_{13}\)NO\(_2\): C, 77.55; H, 4.98; N, 5.32%. Found C, 76.46; H, 5.15; N, 4.96%.

2-Methoxy-9,11-dimethylchromeno[2,3-b]indole (4e): Compound was synthesized according to the General Method B. 83.2 mg, (15%); orange crystals; mp 189 °C. IR (KBr, cm\(-1\)): 2916 (C-H), 1644 (C=N), 1201 (C-O-C). \(^1\)H NMR (500 MHz, pyridine-\(d_5\)): \(\delta = 2.51\) (3H, s, C\(_3\)-CH\(_3\)), 2.87 (3H, s, C\(_5\)-CH\(_3\)), 3.86 (3H, s, OCH\(_3\)), 7.30 (1H, dd, J\(_1\) = 9.0 Hz, J\(_2\) = 2.9 Hz, C\(_8\)-H), 7.41 (1H, d, J = 7.9 Hz, C\(_2\)-H), 7.45 (1H, d, J = 2.9 Hz, C\(_6\)-H), 7.58 (1H, d, J = 9.0 Hz, C\(_9\)-H), 7.85 (1H, d, J = 7.9 Hz, C\(_1\)-H), 7.95 (1H, brs, C\(_4\)-H). \(^13\)C NMR (125 MHz, pyridine-\(d_5\)): \(\delta = 14.6\) (C\(_3\)-CH\(_3\)), 21.2 (C\(_3\)-CH\(_3\)), 55.7 (OCH\(_3\)), 108.6 (C\(_6\)), 118.4 (C\(_9\)), 118.8 (C\(_8\)), 119.0 (C\(_1\)), 121.4 (C\(_5\)a), 123.4 (C\(_4\)b), 124.0 (C\(_4\)), 125.0 (C\(_4a\)), 130.0 (C\(_2\)), 131.3 (C\(_3\)-CH\(_3\)), 142.0 (C\(_5\)-CH\(_3\)), 145.8 (C\(_9\)a), 151.6 (C\(_{11a}\)), 156.2 (COCH\(_3\)), 163.7 (C=H, C\(_{10a}\)). HRMS m/z calcd for C\(_{18}\)H\(_{16}\)NO\(_2\) (M+H)\(^+\) 278.1103, found 278.1178. Anal. Calcd for C\(_{18}\)H\(_{15}\)NO\(_2\): C, 77.96; H, 5.45; N, 5.05%. Found C, 77.66; H, 5.36; N, 4.91%.

9,11-Dimethylchromeno[2,3-b]indol-2-ol (4f): Compound was synthesized according to the General Method B. 379.2 mg (72%); mp 278 °C. IR (KBr, cm\(-1\)): 1644 (C=N), 1549 (aromatic). \(^1\)H NMR (500 MHz, pyridine-\(d_5\)): \(\delta = 2.50\) (3H, s, C\(_3\)-CH\(_3\)), 2.82 (3H, s, C\(_5\)-CH\(_3\)), 7.39 (1H, brd, J = 7.9 Hz, C\(_2\)-H), 7.44 (1H, dd, J\(_1\) = 8.9 Hz, J\(_2\) = 2.7 Hz, C\(_9\)-H), 7.58 (1H, d, J = 8.9 Hz, C\(_9\)-H), 7.63 (1H, d, J = 2.7 Hz, C\(_6\)-H), 7.85 (1H, d, J = 7.9 Hz, C\(_1\)-H), 7.94 (1H, brs, C\(_4\)-H), 11.76 (1H, vbrs, OH). \(^13\)C NMR (125 MHz, pyridine-\(d_5\)): \(\delta = 14.5\)
(C_3-CH_3), 21.3 (C_3-CH_3), 110.7 (C_6), 118.3 (C_1), 120.3 (C_8), 121.7 (C_5a), 123.1 (C_4b), 124.0 (C_4), 125.0 (C_4a), 129.9 (C_2), 131.1 (C_3-CH_3), 142.2 (C_5-CH_3), 145.0 (C_9a), 151.6 (C_11a), 155.1 (C_7-OH), 163.9 (C=N, C_10a). HRMS m/z calcd for C_{17}H_{14}NO_2 (M+H)^+ 264.0946, found 264.1022. Anal. Calcd for C_{17}H_{13}NO_2: C, 77.55; H, 4.98; N, 5.32%. Found C, 76.90; H, 4.86; N, 5.12%.

2-Bromo-9,11-dimethylchromeno[2,3-b]indole (4g): Compound was synthesized according to the General Method B. 224.5 mg (28%); orange crystals, mp 243 °C. IR (KBr, cm⁻¹): 1649 (C=N), 1552 (aromatic). ¹H NMR (500 MHz, pyridine-d₅): δ = 2.51 (3H, s, C_3-CH₃), 2.82 (3H, s, C_5-CH₃), 7.41 (1H, brd, J = 7.9 Hz, C_2-H), 7.49 (1H, d, J = 8.8 Hz, C_9-H), 7.75 (1H, dd, J₁ = 8.8 Hz, J₂ = 2.1 Hz, C_8-H), 7.83 (1H, d, J = 7.9 Hz, C_1-H), 7.93 (1H, brs, C_4-H), 8.13 (1H, d, J = 2.1 Hz, C_6-H). ¹³C NMR (125 MHz, pyridine-d₅): δ = 14.5 (C_5-CH₃), 21.3 (C_3-CH₃), 116.7 (C_7-Br), 119.2 (C_1), 119.3 (C_9), 122.6 (C_5a), 124.0 (C_4b), 124.3 (C_4), 124.9 (C_9a), 128.1 (C_6), 130.4 (C_2), 131.9 (C_3-CH_3), 133.9 (C_8), 140.7 (C_5-CH_3), 150.2 (C_9a), 151.4 (C_11a), 163.1 (C=N, C_10a). HRMS m/z calcd for C_{17}H_{13}BrNO (M+H)^+ 326.0102, found 326.0183. Anal. Calcd for C_{17}H_{12}BrNO: C, 62.60; H, 3.71; N, 4.29%. Found C, 61.63; H, 3.58; N, 4.04%.

2-Methoxy-11-methyl-9-phenylchromeno[2,3-b]indole (4h): Compound was synthesized according to the General Method B. 305.5 mg, (45%); mp 174 °C. IR (KBr, cm⁻¹): 1641 (C=N), 1208 (C-O-C); ¹H NMR (500 MHz, DMSO-d₆): δ = 3.10 (3H, s, CH₃), 3.93 (3H, s, OCH₃), 7.39-7.35 (1H, m, p-Ar-H), 7.41 (1H, d, J = 9.1 Hz, C_8-H), 7.52-7.47 (2H, m, m-Ar-H), 7.61 (1H, d, J = 2.9 Hz, C_6-H), 7.75 (1H, d, J = 2.9 Hz, C_9-H), 7.79 (1H, d, J = 8.2 Hz, C_1-H), 7.80-7.78 (2H, m, o-Ar-H), 8.35 (1H, d, J = 1.7 Hz, C_4-H). ¹³C NMR (125 MHz, DMSO-d₆): δ = 15.8 (CH₃), 56.4 (OCH₃), 108.9 (C_6), 119.0 (C_9), 119.3 (C_1), 120.3 (C_8), 121.3 (C_5a), 122.3 (C_4), 122.3 (C_4b), 125.1 (C_4a), 127.3 (p-Ar-C), 127.4 (o-Ar-C), 128.1 (C_2), 129.4 (m-Ar-C), 134.8 (C_3), 141.2 (C_3-C), 145.1 (CH₂C), 145.6 (C_9a), 152.1 (C_11a), 156.3 (COCH₃), 164.0 (C_10a). HRMS m/z calcd for C_{23}H_{18}NO₂ (M+H)^+ 340.1259, found = 340.1325. Anal. Calcd for C_{23}H_{17}NO₂: C, 81.04; H, 5.05; N, 4.13%. Found C, 81.44; H, 5.22; N, 4.14%.

2-Bromo-11-ethyl-9-phenylchromeno[2,3-b]indole (4i): Compound was synthesized according to the General Method B. 72.4 mg (9%); orange crystals, mp 218 °C. IR (KBr, cm⁻¹): 1638 (C=N), 1547 (C=C). ¹H NMR (500 MHz, DMSO-d₆): δ = 1.41 (3H, t, J = 7.6 Hz, CH₂C₃H₃), 3.57 (2H, q, J = 7.6 Hz, CH₂C₃H₃), 7.38 (1H, t, J = 7.4 Hz, p-Ar-H), 7.51 (1H, t, J = 7.4 Hz, m-Ar-H), 7.67 (1H, d, J = 8.2 Hz, C₁-H), 7.78 (1H, d, J = 7.4 Hz, o-Ar-H), 7.81 (1H, dd, J₁ = 8.2 Hz, J₂ = 1.6 Hz, C₃-H), 7.82 (1H, d, J = 8.8 Hz, C₉-H), 7.97 (1H, dd, J₁ = 8.8 Hz, J₂ = 2.2 Hz, C₈-H), 8.26 (1H, d, J = 1.6 Hz, C₄-H), 8.42 (1H, d, J = 2.2 Hz, C₆-H). ¹³C NMR (125 MHz, DMSO-d₆): δ = 13.7 (CH₂C₃H₃), 21.8 (CH₂C₃H₃), 117.4 (C₇-Br), 119.7 (C₁), 120.5 (C₉), 121.5 (C₅a), 122.1 (C₄), 122.3 (C₄b), 124.5 (C₆a), 127.5 (p-Ar-C), 127.5 (o-Ar-C), 128.4 (C₆), 128.6 (C₂), 129.5 (m-Ar-C), 135.1 (C₈), 135.5 (C₃), 141.1 (C₇-C), 149.3 (CH₂C₃H₃), 150.6 (C₉a), 152.1 (C₁₁a), 163.9 (C₁₀a). HRMS m/z calcd for C_{23}H_{18}BrNO (M+H)^+ 402.0415, found 402.0498. Anal. Calcd for C_{23}H_{17}BrNO: C, 68.67; H, 4.01; N, 3.48%. Found C, 67.79; H, 4.03; N, 3.22%. 

[2061]
9-Bromo-2-methoxy-11-methylchromeno[2,3-b]indole (4j): Compound was synthesized according to the General Method B. 328.5 mg, (48%); orange crystals, mp 202 °C. IR (KBr, cm\(^{-1}\)): 1642 (C=C), 1537 (aromatic), 1232 (C-O-C). \(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta\) = 3.05 (3H, s, CH\(_3\)), 3.93 (3H, s, OCH\(_3\)), 7.44 (1H, dd, \(J_1 = 9.1 \text{ Hz, } J_2 = 2.9 \text{ Hz, } C_8\)-H), 7.51 (1H, d, \(J = 8.4 \text{ Hz, } C_1\)-H), 7.62 (1H, d, \(J = 2.9 \text{ Hz, } C_6\)-H), 7.64 (1H, d, \(J = 8.4 \text{ Hz, } C_2\)-H), 7.78 (1H, d, \(J = 9.1 \text{ Hz, } C_9\)-H), 8.31 (1H, brs, C4-H) ppm. \(^13\)C NMR (125 MHz, DMSO-\(d_6\)): \(\delta\) = 15.9 (C5-CH\(_3\)), 56.4 (OCH\(_3\)), 109.0 (C\(_6\)), 114.4 (C3-Br), 119.1 (C9), 120.8 (C1), 120.9 (C8), 121.2 (C4b), 121.3 (C5a), 126.3 (C4a), 131.7 (C2), 145.8 (C9a), 146.8 (C3-CH\(_3\)), 151.5 (C11a), 156.4 (COCH\(_3\)), 163.8 (C=N, C10a). HRMS \(m/z\) calcd for C\(_{17}\)H\(_{13}\)BrNO\(_2\) (M+H\(^+\)) = 342.0051, found 342.0126. Anal. Calcd for C\(_{17}\)H\(_{12}\)BrNO\(_2\): C, 59.67; H, 3.53; N, 4.09%. Found C, 58.86; H, 3.38; N, 3.84%.

9-Bromo-11-methylchromeno[2,3-b]indol-2-ol (4k): Compound was synthesized according to the General Method B. 420.1 mg (64%); orange crystals, mp 302 °C. IR (KBr, cm\(^{-1}\)): 1547 (aromatic), 1061 (Ar-Br). \(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta\) = 2.95 (3H, s, CH\(_3\)), 7.26 (1H, dd, \(J_1 = 8.9 \text{ Hz, } J_2 = 2.8 \text{ Hz, } C_8\)-H), 7.44 (1H, d, \(J = 2.8 \text{ Hz, } C_6\)-H), 7.49 (1H, d, \(J = 8.4 \text{ Hz, } C_1\)-H), 7.61 (1H, dd, \(J_1 = 8.4 \text{ Hz, } J_2 = 1.9 \text{ Hz, } C_2\)-H), 7.66 (1H, d, \(J = 8.9 \text{ Hz, } C_9\)-H), 8.25 (1H, d, \(J = 1.9 \text{ Hz, } C_4\)-H), 9.98 (1H, s, OH). \(^13\)C NMR (125 MHz, DMSO-\(d_6\)): \(\delta\) = 15.7 (C5-CH\(_3\)), 110.6 (C\(_6\)), 114.3 (C3), 118.9 (C9), 120.7 (C1), 121.1 (C4b), 121.3 (C5a), 121.4 (C8), 126.1 (C4), 126.3 (C4a), 131.5 (C2), 144.7 (C9a), 146.6 (C3-CH\(_3\)), 151.5 (C11a), 154.6 (C7-OH), 163.9 (C=N, C10a). HRMS \(m/z\) calcd for C\(_{16}\)H\(_{11}\)BrNO\(_2\) (M+H\(^+\)) = 327.9895, found 327.9970. Anal. Calcd for C\(_{16}\)H\(_{10}\)BrNO\(_2\): C, 58.56; H, 3.07; N, 4.27%. Found C, 58.48; H, 2.98; N, 3.96%.

4,9-Dibromo-2-chloro-11-methylchromeno[2,3-b]indole (4l): Compound was synthesized according to the General Method B. 85.1 mg, (10%); red crystal, mp 284 °C. IR (KBr, cm\(^{-1}\)): 1639 (aromatic), 1063 (Ar-Br). \(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta\) = 3.03 (3H, s, CH\(_3\)), 7.56 (1H, d, \(J = 8.4 \text{ Hz, } C_1\)-H), 7.70 (1H, dd, \(J_1 = 8.4 \text{ Hz, } J_2 = 2.0 \text{ Hz, } C_2\)-H), 8.30 (1H, d, \(J = 2.3 \text{ Hz, } C_8\)-H), 8.33 (1H, d, \(J = 2.3 \text{ Hz, } C_6\)-H), 8.36 (1H, d, \(J = 2.0 \text{ Hz, } C_4\)-H). \(^13\)C NMR (125 MHz, DMSO-\(d_6\)): \(\delta\) = 16.0 (C5-CH\(_3\)), 112.3 (C9-Br), 115.3 (C3-Br), 121.3 (C1), 121.5 (C5a), 122.0 (C4b), 126.1 (C6), 126.3 (C4a), 126.7 (C4), 129.5 (C7-Cl), 132.5 (C2), 135.0 (C8), 145.4 (C3-CH\(_3\)), 146.7 (C9a), 151.2 (C11a), 164.7 (C=N, C10a). HRMS \(m/z\) calcd for C\(_{16}\)H\(_9\)Br\(_2\)ClNO (M+H\(^+\))\(^+\) = 423.8661, found 425.8722. Anal. Calcd for C\(_{16}\)H\(_8\)Br\(_2\)ClNO: C, 45.16; H, 1.89; N, 3.29%. Found C, 45.12; H, 1.87; N, 3.10%.

2,9-Dibromo-11-methylchromeno[2,3-b]indole (4m): Compound was synthesized according to the General Method B. 297.2 mg (38%); orange crystals, mp 234 °C. IR (KBr, cm\(^{-1}\)): 1639 (aromatic), 1063 (Ar-Br). \(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta\) = 3.05 (3H, s, CH\(_3\)), 7.56 (1H, d, \(J = 8.4 \text{ Hz, } C_1\)-H), 7.68 (1H, dd, \(J_1 = 8.4 \text{ Hz, } J_2 = 1.9 \text{ Hz, } C_2\)-H), 7.82 (1H, d, \(J = 8.4 \text{ Hz, } C_9\)-H), 8.00 (1H, dd, \(J_1 = 8.9 \text{ Hz, } J_2 = 2.3 \text{ Hz, } C_8\)-H), 8.34 (1H, d, \(J = 1.9 \text{ Hz, } C_4\)-H), 8.42 (1H, d, \(J = 2.3 \text{ Hz, } C_6\)-H). \(^13\)C NMR (125 MHz, DMSO-\(d_6\)): \(\delta\) = 15.8 (C5-CH\(_3\)), 115.0 (C3), 117.3 (C7), 120.3 (C6), 121.1 (C1), 122.1 (C4b), 122.6 (C5a), 126.4 (C4a), 126.5 (C4), 129.2 (C6), 132.1 (C2), 135.4 (C8), 145.8 (C3-CH\(_3\)), 150.3 (C9a), 151.4 (C11a), 163.5 (C=N, C10a).
2-Methoxy-11-methylchromeno[2,3-b]indole-9-carbonitrile (4n): Compound was synthesized according to the General Method B. 455.5 mg, (79%); yellow crystals, mp 259 °C. IR (KBr, cm⁻¹): 2215 (nitrile), 1644 (C=O-C). ¹H NMR (500 MHz, pyridine-d₅): δ = 2.95 (3H, s, C₅-CH₃), 3.89 (3H, s, OCH₃), 7.42 (1H, dd, J₁ = 9.1 Hz, J₂ = 2.9 Hz, C₈-H), 7.55 (1H, d, J = 2.9 Hz, C₆-H), 7.66 (1H, d, J = 9.1 Hz, C₉-H), 7.88 (1H, dd, J₁ = 8.2 Hz, J₂ = 1.2 Hz, C₂-H), 7.90 (1H, d, J = 8.2 Hz, C₁-H), 8.50 (1H, brs, C₄-H). ¹³C NMR (125 MHz, pyridine-d₅): δ = 15.0 (C₅-CH₃), 55.8 (OCH₃), 104.8 (C₃-CN), 108.6 (C₆), 118.8 (C₉), 119.8 (C₁), 120.3 (C₃-CN), 120.5 (C₈), 121.2 (C₅a), 121.5 (C₄b), 125.0 (C₄a), 127.3 (C₄), 132.5 (C₂), 146.0 (C₅a), 146.4 (C₃-CN), 156.5 (C₁₇a), 156.7 (COCH₃), 163.9 (C=O, C₁₀a). HRMS m/z calcd for C₁₈H₁₃N₂O₂ (M+H)⁺ 289.0898, found 289.0973. Anal. Calcd for C₁₈H₁₂N₂O₂: C, 74.99; H, 4.20; N, 9.72%. Found C, 74.62; H, 4.10; N, 9.59%.

2-Hydroxy-11-methylchromeno[2,3-b]indole-9-carbonitrile (4o): Compound was synthesized according to the General Method B. 345.6 mg, (63%); brown crystals, mp 319 °C. IR (KBr, cm⁻¹): 2216 (nitrile), 1643 (C=O-C), 1527 (C=C). ¹H NMR (500 MHz, DMSO-d₆): δ = 3.05 (3H, s, C₅-CH₃), 7.33 (1H, dd, J₁ = 9.0 Hz, J₂ = 2.8 Hz, C₈-H), 7.51 (1H, d, J = 2.8 Hz, C₆-H), 7.70 (1H, d, J = 8.2 Hz, C₁-H), 7.75 (1H, d, J = 9.0 Hz, C₉-H), 7.90 (1H, dd, J₁ = 8.2 Hz, J₂ = 1.5 Hz, C₂-H), 8.68 (1H, d, J = 1.5 Hz, C₄-H), 10.11 (1H, brs, OH). ¹³C NMR (125 MHz, DMSO-d₆): δ = 15.9 (C₅-CH₃), 104.0 (C₃-CN), 110.7 (C₆), 119.2 (C₉), 119.7 (C₁), 120.4 (C₃-CN), 120.5 (C₄b), 121.4 (C₅a), 122.0 (C₈), 124.9 (C₄a), 127.9 (C₄), 132.8 (C₂), 144.9 (C₅a), 148.4 (C₃-CN), 154.9 (C₇-OH), 155.8 (C₇a), 163.9 (C=O, C₁₀a). HRMS m/z calcd for C₁₇H₁₁N₂O₂ (M+H)⁺ 275.0742, found 275.0822. Anal. Calcd for C₁₇H₁₁O₂N₂: C, 74.45; H, 3.67; N, 10.21%. Found C, 70.64; H, 3.45; N, 9.51%.

2-Bromo-11-methylchromeno[2,3-b]indole-9-carbonitrile (4p): Compound was synthesized according to the General Method B. 384.4 mg (57%); yellow crystals, mp 247 °C. IR (KBr, cm⁻¹): 2216 (nitrile), 1642 (C=O). ¹H NMR (500 MHz, pyridine-d₅): δ = 2.91 (3H, s, C₅-CH₃), 7.59 (1H, d, J = 8.8 Hz, C₉-H), 7.87 (1H, dd, J₁ = 8.8 Hz, J₂ = 2.3 Hz, C₈-H), 7.88-7.90 (1H, m, C₁-H), 7.88-7.90 (1H, m, C₂-H), 8.28 (1H, d, J = 2.3 Hz, C₆-H), 8.49 (1H, s, C₄-H). ¹³C NMR (125 MHz, pyridine-d₅): δ = 14.9 (C₅-CH₃), 105.4 (C₇-CN), 117.6 (C₇-Br), 119.7 (C₀), 120.0 (C₃-CN), 120.1 (C₁), 122.2 (C₄b), 122.3 (C₅a), 125.0 (C₄a), 127.5 (C₄), 128.6 (C₆), 133.0 (C₂), 135.2 (C₈), 145.2 (C₃-CN), 150.3 (C₉a), 156.4 (C₇a), 165.4 (C=O, C₁₀a). HRMS m/z calcd for C₁₇H₁₀BrN₂O₂ (M+H)⁺ 336.9898, found 336.9981. Anal. Calcd for C₁₇H₉BrNO₂: C, 60.56; H, 2.69; N, 8.31%. Found C, 60.96; H, 2.72; N, 8.41%. 2-Methoxy-11-methyl-9-(trifluoromethyl)chromeno[2,3-b]indole (4q): Compound was synthesized according to the General Method B. 192.2 mg, (29%); brown crystals, mp 223 °C. IR (KBr, cm⁻¹): 1541 (aromatic), 1331, 1154 (CF₃). ¹H NMR (500 MHz, pyridine-d₅): δ = 2.97 (3H, s, C₅-CH₃), 3.88 (3H, s,
OCH₃), 7.39 (1H, dd, J₁ = 9.0 Hz, J₂ = 2.9 Hz, C₈-H), 7.54 (1H, d, J = 2.9 Hz, C₆-H), 7.65 (1H, d, J = 9.0 Hz, C₉-H), 7.91 (1H, dd, J₁ = 8.2 Hz, J₂ = 1.2 Hz, C₂-H), 7.99 (1H, d, J = 8.2 Hz, C₁-H), 8.46 (1H, brs, C₄-H).

¹³C NMR (125 MHz, pyridine-d₅): δ = 14.9 (C₅-C₃H₃), 55.8 (O-C₃H₃), 108.7 (C₆), 118.7 (C₉), 119.4 (C₁), 120.1 (C₈), 120.3 (C₄), 121.2 (C₅a), 122.1 (C₄b), 123.4 (C₃-CF₃), 124.7 (C₄a), 125.6 (C₅-CF₃), 125.8 (C₂), 145.6 (C₅-C₇CH₃), 146.0 (C₉a), 156.2 (C₁₁a), 156.6 (COCH₃), 165.5 (C=N, C₁₀a). HRMS m/z calcd for C₁₈H₁₃F₃NO₂ (M+H)⁺ 332.0820, found 332.0881. Anal. Calcd for C₁₈H₁₂F₃NO₂: C, 65.26; H, 3.65; N, 4.23%. Found C, 65.20; H, 3.56; N, 3.98%.

11-Methyl-9-(trifluoromethyl)chromeno[2,3-b]indol-2-ol (4r): Compound was synthesized according to the General Method B. 310.9 mg (49%); yellow crystals, mp 302 °C. IR (KBr, cm⁻¹): 1549 (aromatic), 1329, 1105 (CF₃). ¹H NMR (500 MHz, pyridine-d₅): δ = 2.88 (3H, s, CH₃), 7.52 (1H, dd, J₁ = 8.9 Hz, J₂ = 2.8 Hz, C₈-H), 7.64 (1H, d, J = 8.9 Hz, C₉-H), 7.70 (1H, d, J = 2.8 Hz, C₆-H), 7.90 (1H, dd, J₁ = 8.3 Hz, J₂ = 1.1 Hz, C₂-H), 7.98 (1H, d, J = 8.3 Hz, C₁-H), 8.43 (1H, brs, C₄-H), 11.97 (1H, brs, OH).

¹³C NMR (125 MHz, pyridine-d₅): δ = 14.8 (C₅-C₃H₃), 110.8 (C₆), 118.6 (C₉), 119.3 (C₁), 120.2 (C₄), 121.5 (C₈), 121.5 (C₅a), 121.8 (C₄b), 123.1 (C₃), 124.8 (C₄a), 125.7 (C₅), 125.7 (C₃-CF₃), 145.1 (C₉a), 145.7 (C₅-C₇CH₃), 155.5 (C₃-OH), 156.2 (C₁₁a), 165.7 (C=N, C₁₀a). HRMS m/z calcd for C₁₇H₁₁F₃NO₂ (M+H)⁺ 318.0664, found 318.0726. Anal. Calcd for C₁₇H₁₁F₃NO₂: C, 64.36; H, 3.18; N, 4.41%. Found C, 63.89; H, 3.27; N, 4.16%.

4-Bromo-2-chloro-11-methyl-9-(trifluoromethyl)chromeno[2,3-b]indole (4s): Compound was synthesized according to the General Method B. 174.1 mg (21%), yellow crystals, mp: 263 °C. IR (KBr, cm⁻¹): 1545 (aromatic), 1318, 1116 (CF₃). ¹H NMR (500 MHz, pyridine-d₅): δ = 2.97 (3H, s, CH₃), 7.94 (1H, dd, J₁ = 8.3 Hz, J₂ = 1.2 Hz, C₂-H), 7.98 (1H, d, J = 8.3 Hz, C₁-H), 8.09 (1H, d, J = 2.4 Hz, C₈-H), 8.13 (1H, d, J = 2.4 Hz, C₆-H), 8.45 (1H, brs, C₄-H).

¹³C NMR (125 MHz, pyridine-d₅): δ = 15.0 (C₅-C₃H₃), 112.3 (C₉-Br), 120.0 (C₁), 120.7 (C₄), 121.5 (C₅a), 122.0 (C₄b), 123.3 (C₃-CF₃), 124.5 (C₄a), 125.1 (C₆), 125.3 (C₃-CF₃), 126.7 (C₂), 129.9 (C₇-Cl), 135.1 (C₈), 143.9 (C₅-C₇CH₃), 146.7 (C₉a), 156.0 (C₁₁a), 164.7 (C=N, C₁₀a). HRMS m/z calcd for C₁₇H₉BrClF₃NO (M+H)⁺ 413.9430, found 413.9500. Anal. Calcd for C₁₇H₈BrClF₃NO: C, 49.25; H, 1.94; N, 3.38%. Found C, 49.21; H, 1.94; N, 3.13%.

2-Bromo-11-methyl-9-(trifluoromethyl)chromeno[2,3-b]indole (4t): Compound was synthesized according to the General Method B. 159.7 mg (21%); yellow crystals, mp 244 °C. IR (KBr, cm⁻¹): 1650 (C=N), 1545 (aromatic), 1320, 1154 (CF₃). ¹H NMR (500 MHz, pyridine-d₅): δ = 2.94 (3H, s, C₅-C₃H₃), 7.58 (1H, d, J = 8.8 Hz, C₉-H), 7.85 (1H, dd, J₁ = 6.8 Hz, J₂ = 2.3 Hz, C₆-H), 7.92 (1H, dd, J₁ = 6.8 Hz, J₂ = 1.0 Hz, C₂-H), 7.98 (1H, d, J = 8.2 Hz, C₆-H), 8.28 (1H, d, J = 2.3 Hz, C₂-H), 8.44 (1H, brs, C₄-H).

¹³C NMR (125 MHz, pyridine-d₅): δ = 14.8 (C₅-C₇CH₃), 117.4 (C₇-Br), 119.6 (C₉), 119.7 (C₁), 120.5 (C₄), 122.3 (C₉a), 123.0 (C₈), 123.0 (C₄b), 124.2 (C₃-CF₃), 124.7 (C₄a), 125.5 (C₅-CF₃), 126.3 (C₂), 128.5 (C₆), 144.4 (C₇-CH₃), 150.3 (C₉a), 156.1 (C₁₁a), 165.0 (C=N, C₁₀a). HRMS m/z calcd for C₁₇H₉BrClF₃NO (M+H)⁺ 379.9820, found 379.9888. Anal. Calcd for C₁₇H₉BrClF₃NO: C, 53.71; H, 2.39; N, 3.68%. Found C, 53.38; H,
2.44; N, 3.44%.

2-Bromo-11-ethyl-9-(trifluoromethyl)chromeno[2,3-b]indole (4u): Compound was synthesized according to the General Method B. 102.5 mg (13%), yellow crystals, mp 226 °C. IR (KBr, cm\(^{-1}\)): 1644 (C=N), 1325, 1100 (CF\(_3\)).

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta = 1.39\) (3H, t, \(J = 7.6\) Hz, CH\(_3\)), 3.55 (2H, q, \(J = 7.6\) Hz, CH\(_2\)), 7.77 (1H, d, \(J = 8.8\) Hz, C\(_1\)-H), 7.86 (1H, d, \(J = 8.8\) Hz, C\(_2\)-H), 7.86 (1H, d, \(J = 8.8\) Hz, C\(_9\)-H), 8.01 (1H, dd, \(J_1 = 8.8\) Hz, \(J_2 = 2.3\) Hz, C\(_8\)-H), 8.32 (1H, brs, C\(_4\)-H), 8.47 (1H, d, \(J = 2.3\) Hz, C\(_6\)-H);

\(^13\)C NMR (125 MHz, DMSO-\(d_6\)): \(\delta = 13.8\) (C\(_5\)-CH\(_2\)C\(_6\)H\(_3\)), 22.0 (C\(_5\)-C\(_6\)H\(_2\)CH\(_3\)), 117.7 (C\(_7\)-Br), 117.7 (C\(_5\)-CH\(_2\)CH\(_3\)), 119.8 (C\(_1\)), 120.5 (C\(_4\)), 120.7 (C\(_9\)), 121.2 (C\(_4b\)), 121.4 (C\(_5a\)), 123.3 (C\(_3\)), 124.0 (C\(_4a\)), 125.4 (C\(_3\)-CF\(_3\)), 126.5 (C\(_2\)), 128.7 (C\(_6\)), 135.8 (C\(_8\)), 150.7 (C\(_9a\)), 151.8 (C\(_5\)-CH\(_2\)CH\(_3\)), 155.4 (C\(_11a\)), 165.3 (C=N, C\(_10a\)). HRMS m/z calcd for C\(_{18}\)H\(_{12}\)BrF\(_3\)NO (M+H\(^+\)) 393.9976, found 394.0059. Anal. Calcd for C\(_{18}\)H\(_{11}\)BrF\(_3\)NO: C, 54.85; H, 2.81; N, 3.55%. Found C, 54.68; H, 2.74; N, 3.43%.

Methyl 2-methoxy-11-methylchromeno[2,3-b]indole-9-carboxylate (4v): Compound was synthesized according to the General Method B. 359.9 mg, (56%), yellow crystals, mp 229 °C. IR (KBr, cm\(^{-1}\)): 1704 (>C=O), 1248, 1186 (C-O-C).

\(^1\)H NMR (500 MHz, pyridine-\(d_5\)): \(\delta = 2.89\) (3H, s, C\(_5\)-CH\(_3\)), 3.83 (3H, s, OCH\(_3\)), 3.95 (3H, s, COOCH\(_3\)), 7.37 (1H, dd, \(J_1 = 9.0\) Hz, \(J_2 = 2.8\) Hz, C\(_8\)-H), 7.49 (1H, d, \(J = 2.8\) Hz, C\(_6\)-H), 7.63 (1H, d, \(J = 9.0\) Hz, C\(_9\)-H), 7.99 (1H, d, \(J = 8.3\) Hz, C\(_1\)-H), 8.45 (1H, dd, \(J = 8.3\) Hz, \(J_2 = 0.9\) Hz, C\(_2\)-H), 8.94 (1H, brs, C\(_4\)-H).

\(^13\)C NMR (125 MHz, pyridine-\(d_5\)): \(\delta = 14.9\) (C\(_5\)-CH\(_3\)), 51.8 (C\(_3\)-COOCH\(_3\)), 55.7 (C\(_7\)-OCH\(_3\)), 108.4 (C\(_6\)), 118.7 (C\(_9\)), 118.9 (C\(_1\)), 119.9 (C\(_8\)), 121.3 (C\(_5a\)), 122.3 (C\(_4b\)), 123.8 (C\(_3\)-COOMe), 124.6 (C\(_4a\)), 125.0 (C\(_4\)), 130.7 (C\(_2\)), 145.0 (C\(_5\)-CH\(_3\)), 145.8 (C\(_9a\)), 156.4 (C\(_7\)-OCH\(_3\)), 157.3 (C\(_11a\)), 165.9 (C=N, C\(_10a\)), 167.2 (C\(_3\)-COOMe). HRMS m/z calcd for C\(_{19}\)H\(_{16}\)NO\(_4\) (M+H\(^+\)) 322.1001, found 322.1067. Anal. Calcd for C\(_{19}\)H\(_{15}\)NO\(_4\): C, 71.02; H, 4.70; N, 4.36%. Found C, 69.74; H, 4.42; N, 4.22%.

Methyl 2-hydroxy-11-methylchromeno[2,3-b]indole-9-carboxylate (4w): Compound was synthesized according to the General Method B. 454.8 mg, (74%); brown crystals, mp 283 °C. IR (KBr, cm\(^{-1}\)): 1727 (>C=O), 1225 (C-O-C).

\(^1\)H NMR (500 MHz, pyridine-\(d_5\)): \(\delta = 2.83\) (3H, s, C\(_5\)-CH\(_3\)), 3.97 (3H, s, COOCH\(_3\)), 7.50 (1H, dd, \(J_1 = 8.9\) Hz, \(J_2 = 2.8\) Hz, C\(_8\)-H), 7.62 (1H, d, \(J = 8.9\) Hz, C\(_9\)-H), 7.65 (1H, d, \(J = 2.8\) Hz, C\(_6\)-H), 7.95 (1H, d, \(J = 8.3\) Hz, C\(_1\)-H), 8.44 (1H, dd, \(J_1 = 8.3\) Hz, \(J_2 = 1.5\) Hz, C\(_2\)-H), 8.91 (1H, d, \(J = 1.5\) Hz, C\(_4\)-H), 11.93 (1H, brs, OH).

\(^13\)C NMR (125 MHz, pyridine-\(d_5\)): \(\delta = 14.7\) (C\(_5\)-CH\(_3\)), 51.6 (C\(_3\)-COOCH\(_3\)), 110.7 (C\(_6\)), 118.6 (C\(_9\)), 118.8 (C\(_1\)), 121.2 (C\(_8\)), 121.6 (C\(_5a\)), 122.2 (C\(_4b\)), 123.8 (C\(_3\)-COOMe), 124.6 (C\(_4a\)), 124.9 (C\(_4\)), 130.6 (C\(_2\)), 144.9 (C\(_5\)-CH\(_3\)), 145.1 (C\(_9a\)), 155.5 (C\(_7\)-OH), 157.5 (C\(_11a\)), 166.1 (C=N, C\(_10a\)), 167.2 (C\(_3\)-COOMe). HRMS m/z calcd for C\(_{19}\)H\(_{15}\)NO\(_4\) (M+H\(^+\)) 308.0845, found 308.0914. Anal. Calcd for C\(_{19}\)H\(_{15}\)NO\(_4\): C, 70.35; H, 4.26; N, 4.56%. Found C, 69.74; H, 4.16; N, 4.52%.

Methyl 4-bromo-2-chloro-11-methylchromeno[2,3-b]indole-9-carboxylate (4x): Compound was synthesized according to the General Method B. 283.3 mg (35%), yellow crystals, mp 277 °C. IR (KBr, cm\(^{-1}\)): 1706 (>C=O), 1244 (C-O-C).

\(^1\)H NMR (500 MHz, pyridine-\(d_5\)): \(\delta = 2.91\) (3H, s, C\(_5\)-CH\(_3\)), 3.98 (3H, s, C\(_5\)-CH\(_3\)), 3.98 (3H, s, C\(_5\)-CH\(_3\)).
s, COOCH₃), 7.95 (1H, d, J = 8.3 Hz, C₁-H), 8.08 (1H, d, J = 2.3 Hz, C₈-H), 8.09 (1H, d, J = 2.3 Hz, C₆-H), 8.46 (1H, dd, J₁ = 8.3 Hz, J₂ = 1.3 Hz, C₂-H), 8.91 (1H, d, J = 1.3 Hz, C₄-H). ¹³C NMR (125 MHz, pyridine-d₅): δ = 14.8 (C₅-C₅H₃), 51.8 (C₃-COOCH₃), 112.3 (C₉-Br), 119.5 (C₁), 123.0 (C₅a), 123.7 (C₄b), 124.0 (C₃-COOMe), 124.9 (C₆), 125.0 (C₄a), 125.3 (C₄), 129.9 (C₇-Cl), 131.4 (C₂), 134.8 (C₈), 143.0 (C₂-C₂H₅), 146.7 (C₉a), 157.2 (C₁₁a), 165.6 (C=N, C₁₀a), 166.9 (C₃-COOMe). HRMS m/z calc'd for C₁₈H₁₂BrClNO₃ (M+H)⁺ 403.9611, found 403.9683. Anal. Calcd for C₁₈H₁₁BrClNO₃: C, 53.43; H, 2.74; N, 3.46%. Found C, 53.47; H, 2.73; N, 3.20%.

Methyl 2-bromo-11-methylchromeno[2,3-b]indole-9-carboxylate (4y): Compound was synthesized according to the General Method B. 407.2 mg (55%), yellow crystals, mp 261 °C. IR (KBr, cm⁻¹): 1718 (>C=O), 1252 (C-O-C). ¹H NMR (500 MHz, pyridine-d₅): δ = 2.89 (3H, s, C₅-CH₃), 7.83 (1H, dd, J₁ = 8.8 Hz, J₂ = 2.3 Hz, C₈-H), 7.95 (1H, d, J = 8.2 Hz, C₁-H), 8.24 (1H, d, J = 2.3 Hz, C₆-H), 8.45 (1H, dd, J₁ = 8.2 Hz, J₂ = 1.5 Hz, C₂-H), 8.91 (1H, d, J = 1.5 Hz, C₄-H). ¹³C NMR (125 MHz, pyridine-d₅): δ = 14.7 (C₅-C₅H₃), 51.7 (C₃-COOCH₃), 112.4 (C₇-Br), 119.2 (C₁), 122.5 (C₅a), 123.0 (C₄b), 124.5 (C₃-COOMe), 124.6 (C₄a), 125.1 (C₄), 128.4 (C₆), 131.1 (C₂), 134.7 (C₈), 143.5 (C₂-C₂H₅), 150.2 (C₉a), 157.3 (C₁₁a), 165.3 (C=N, C₁₀a), 167.0 (C₃-COOMe). HRMS m/z calc'd for C₁₈H₁₃BrNO₃ (M+H)⁺ 370.0001, found 370.0070. Anal. Calcd for C₁₈H₁₂BrNO₃: C, 58.40; H, 3.27; N, 3.78%. Found C, 58.32; H, 3.24; N, 3.72%.

Methyl 2-bromo-11-ethylchromeno[2,3-b]indole-9-carboxylate (4z): Compound was synthesized according to the General Method B. 38.4 mg (5%), yellow crystals, mp 220 °C. IR (KBr, cm⁻¹): 1688 (>C=O), 1541 (C=C); ¹H NMR (500 MHz, DMSO-d₆): δ = 1.40 (3H, t, J = 7.6 Hz, C₅-CH₂C₅H₃), 3.51 (2H, q, J = 7.6 Hz, C₅-C₅H₂CH₃), 3.91 (3H, s, COOCH₃), 7.69 (1H, d, J = 8.3 Hz, C₁-H), 7.85 (1H, d, J = 8.8 Hz, C₉-H), 8.00 (1H, dd, J₁ = 8.8 Hz, J₂ = 2.1 Hz, C₈-H), 8.13 (1H, dd, J₁ = 8.3 Hz, J₂ = 1.2 Hz, C₂-H), 8.45 (1H, d, J = 2.1 Hz, C₆-H), 8.55 (1H, d, J = 1.2 Hz, C₄-H); ¹³C NMR (125 MHz, DMSO-d₆): δ = 13.7 (C₅-CH₂C₅H₃), 22.0 (C₅-CH₂C₅H₃), 52.6 (C₃-COOCH₃), 117.4 (C₇-Br), 119.3 (C₁), 120.7 (C₉a), 121.4 (C₅a), 121.5 (C₄b), 123.8 (C₃-COOMe), 124.1 (C₄a), 124.6 (C₄), 128.4 (C₆), 130.9 (C₂), 135.6 (C₈), 150.7 (C₉a), 150.9 (C₅-C₅H₂C₅H₃), 156.5(C₁₁a), 165.6 (C=N, C₁₀a), 166.8 (C₃-COOMe). HRMS m/z calc'd for C₁₉H₁₅BrNO₃ (M+H)⁺ 384.0157, found 384.0237. Anal. Calcd for C₁₉H₁₄BrNO₃: C, 59.40; H, 3.27; N, 3.78%. Found C, 59.32; H, 3.24; N, 3.72%.

Chromeno[2,3-b]indole (4aa): Compound was synthesized according to the General Method C. 53 mg (7%), yellow crystals, mp 115 °C. IR (KBr, cm⁻¹): 1653 (>C=O), 1544 (aromatic). ¹H NMR (500 MHz, DMSO-d₆): δ = 7.32 (1H, t, J = 7.5 Hz, C₃-H), 7.52 (1H, t, J = 7.5 Hz, C₂-H), 7.56 (1H, t, J = 8.0 Hz, C₇-H), 7.59 (1H, d, J = 7.5 Hz, C₁-H), 7.80 (1H, t, J = 8.0 Hz, C₈-H), 7.84 (1H, d, J = 8.0 Hz, C₉-H), 8.04 (1H, d, J = 8.0 Hz, C₆-H), 8.08 (1H, d, J = 7.5 Hz, C₄-H), 8.85 (1H, s, C₅-H) ppm. ¹³C NMR (125 MHz, DMSO-d₆): δ = 117.9 (C₉), 119.1 (C₁), 119.8 (C₅a), 122.6 (C₄), 123.0 (C₃), 123.9 (C₄a), 125.2 (C₄b), 125.4 (C₇), 130.3
(C₃), 130.3 (C₆), 132.3 (C₅), 132.7 (C₈), 151.6 (C₉a), 152.3 (C₁₁a), 164.3 (C=N, C₁₀a) ppm. HRMS m/z calcd for C₁₅H₁₀NO (M+H)+ 220.0684, found 220.0756;

**9-Methylchromeno[2,3-b]indole (4ab):** Compound was synthesized according to the General Method B. 69.9 mg (15%); orange crystals; mp 200 °C. IR (KBr, cm⁻¹): 2915 (C-H), 1655 (aromatic). ¹H NMR (500 MHz, DMSO-d₆): δ = 2.45 (3H, s, CH₃), 7.33 (1H, dm, J = 8.0 Hz, C₂-H), 7.46 (1H, d, J = 8.0 Hz, C₁-H), 7.53 (1H, ddd, J₁ = 7.8, J₂ = 6.8 J₃ = 1.5 Hz, C₇-H), 7.78 (1H, ddd, J₁ = 8.4, J₂ = 6.8 J₃ = 1.6 Hz, C₈-H), 7.81 (1H, dm, J = 8.4 Hz, C₉-H), 7.87 (1H, m, C₄-H), 8.08 (1H, dd, J₁ = 7.8, J₂ = 1.6 Hz, C₆-H), 8.75 (1H, s, C₅-H). ¹³C NMR (125 MHz, DMSO-d₆): δ = 21.5 (CH₃), 117.8 (C₉), 118.8 (C₁), 119.8 (C₉a), 122.8 (C₄), 124.0 (C₄a), 125.4 (C₄b), 125.2 (C₇), 131.1 (C₂), 130.2 (C₆), 131.6 (C₃), 132.5 (C₈), 150.5 (C₁₁a), 151.5 (C₉a), 164.0 (C=N, C₁₀a). HRMS m/z calcd for C₁₆H₁₂NO (M+H)+ 234.0919, found 234.0915.

**9-Bromochromeno[2,3-b]indole (4ac):** Compound was synthesized according to the General Method B. 166.9 mg (28%); orange crystals, mp 210 °C. IR (KBr, cm⁻¹): 1651 (C=N), 1612 (C=C). ¹H NMR (500 MHz, DMSO-d₆): δ = 7.54 (1H, d, J = 8.4 Hz, C₁-H), 7.57 (1H, ddd, J₁ = 7.9 Hz, J₂ = 6.6 Hz, J₃ = 1.8 Hz, C₇-H), 7.66 (1H, dd, J₁ = 8.4 Hz, J₂ = 2.1 Hz, C₂-H), 7.83 (1H, ddd, J₁ = 8.4 Hz, J₂ = 6.6 Hz, J₃ = 1.5 Hz, C₈-H), 7.86 (1H, dd, J₁ = 8.4 Hz, J₂ = 1.8 Hz, C₉-H), 8.03 (1H, dd, J₁ = 7.9 Hz, J₂ = 1.5 Hz, C₆-H), 8.33 (1H, d, J = 2.1 Hz, C₄-H), 8.92 (1H, s, C₅-H). ¹³C NMR (125 MHz, DMSO-d₆): δ = 114.8 (C₃-Br), 118.0 (C₉), 119.7 (C₉a), 121.0 (C₁), 124.4 (C₄b), 125.3 (C₄), 125.5 (C₇), 126.1 (C₄a), 130.6 (C₆), 132.5 (C₂), 133.2 (C₈), 134.1 (C₅), 151.7 (C₉a), 151.8 (C₁₁a), 164.6 (C=N, C₁₀a). HRMS m/z calcd for C₁₅H₉BrNO (M+H)+ 297.9789, found 297.9868. Anal. Calcd for C₁₅H₈BrNO: C, 60.43; H, 2.70; N, 4.70%. Found C, 59.30; H, 2.73; N, 4.55%.

**Chromeno[2,3-b]indole-9-carbonitrile (4ad):** Compound was synthesized according to the General Method B. 78.2 mg (16%); orange crystals; mp 326 °C. IR (KBr, cm⁻¹): 1656 (C=N), 2221 (C≡N). ¹H NMR (500 MHz, DMSO-d₆): δ = 7.62 (1H, m, C₇-H), 7.76 (1H, d, J = 8.2 Hz, C₁-H), 7.89 (1H, m, C₈-H), 7.93 (1H, dm, J = 8.0 Hz, C₉-H), 7.95 (1H, dd, J₁ = 8.2 Hz, J₂ = 1.7 Hz, C₂-H), 8.12 (1H, dm, J = 7.8 Hz, C₆-H), 8.62 (1H, d, J = 1.7 Hz, C₄-H), 9.05 (1H, s, C₅-H). ¹³C NMR (125 MHz, DMSO-d₆): δ = 104.5 (C₃-CN), 118.1 (C₉), 119.7 (C₉a), 120.1 (C₁), 120.2 (CN), 123.7 (C₄b), 124.6 (C₄a), 125.8 (C₇), 126.8 (C₄), 130.8 (C₆), 133.7 (C₈), 133.8 (C₂), 135.5 (C₃), 151.9 (C₉a), 156.1 (C₁₁a), 166.7 (C=N, C₁₀a). HRMS m/z calcd for C₁₆H₉N₂O (M+H)+ 245.0714, found 245.0710. Anal. Calcd for C₁₆H₈N₂O: C, 76.03; H, 3.30; N, 11.47%. Found C, 76.8; H, 2.91; N, 11.21%.

**9-(Trifluoromethyl)chromeno[2,3-b]indole (4ae):** Compound was synthesized according to the General Method B. 57.4 mg (10%); yellow crystals, mp 268 °C. IR (KBr, cm⁻¹): 1655 (C=N), 1323, 1157 (CF₃). ¹H NMR (500 MHz, DMSO-d₆): δ = 7.61 (1H, d, J = 7.8 Hz, C₆-H), 7.77 (1H, d, J = 8.2 Hz, C₁-H), 7.85 (1H, d, J = 8.2 Hz, C₂-H), 7.87 (1H, ddd, J₁ = 8.0 Hz, J₂ = 7.5 Hz, J₃ = 1.2 Hz, C₇-H), 7.97 (1H, d, J = 8.2 Hz, C₁-H), 7.99 (1H, d, J = 8.2 Hz, C₂-H), 8.07 (1H, dd, J₁ = 7.8, J₂ = 1.6 Hz, C₆-H), 8.75 (1H, s, C₅-H).
7.91 (1H, dd, J = 8.0 Hz, J = 1.2 Hz, C9-H), 8.07 (1H, dd, J = 7.8 Hz, J = 1.2 Hz, C6-H), 8.55 (1H, brs, C4-H), 9.09 (1H, s, C5-H). 13C NMR (125 MHz, DMSO-d6): δ = 118.1 (C9), 119.6 (C1), 119.7 (C5a), 119.9 (C4), 123.2 (C3-CF3), 124.3 (C4a), 124.3 (C4b), 125.7 (C7), 125.8 (C3-CF3), 126.8 (C2), 130.7 (C6), 133.4 (C8), 135.0 (C2), 151.9 (C6a), 155.6 (C11a), 166.2 (C=N, C10a). HRMS m/z calcld for C16H9F3NO (M+H)+ 288.0558, found 288.0629. Anal. Calcd for C16H8F3NO: C, 66.90; H, 2.81; N, 4.88%. Found C, 66.80; H, 2.98; N, 4.69%.

**Methyl chromeno[2,3-b]indole-9-carboxylate (4af):** Compound was synthesized according to the General Method C. 9.4 mg (3.4%), orange crystals, mp 220 °C. IR (KBr, cm⁻¹): 1709 (>C=O), 1103 (C-O-C).

1H NMR (500 MHz, DMSO-d6): δ = 3.91 (3H, s, OCH3), 7.60 (1H, dd, J = 7.8 Hz, J = 1.7 Hz, C7-H), 7.69 (1H, d, J = 8.1 Hz, C1-H), 7.85 (1H, ddd, J = 8.1 Hz, J = 7.0 Hz, J = 1.4 Hz, C8-H), 7.89 (1H, dm, J = 8.1 Hz, C9-H), 8.14 (1H, dd, J = 8.1, J = 1.7 Hz, C2-H), 8.04 (1H, dd, J = 7.8, J = 1.4 Hz, C6-H), 8.14 (1H, s, Ar-H) ppm. 13C NMR (125 MHz, DMSO-d6): δ = 52.6 (OCH3), 118.1 (C9), 119.1 (C1), 119.8 (C5a), 123.9 (C4), 124.1 (C4a), 124.5 (C4b), 125.7 (C7), 130.6 (C6), 131.3 (C2), 133.2 (C8), 134.4 (C3), 151.8 (C9a), 156.7 (C11a), 166.5 (C=N, C10a), 166.9 (C3-COOMe). HRMS m/z calcld for C17H12NO3 (M+H)+ 278.0739, found 278.0810.

**3-(2-Aminophenyl)chromen-2-one (6):** Compound was synthesized according to the General Method C. 1H NMR (500 MHz, (CD3)₂SO): δH 6.82 (1H, t, J = 8.0 Hz, Ar-H), 6.89 (1H, d, J = 8.0 Hz, Ar-H), 7.15 (1H, d, J = 8.0 Hz, Ar-H), 7.21 (1H, t, J = 8.0 Hz, Ar-H), 7.32 (1H, d, J = 1.5 Hz, Ar-H), 7.35 (1H, t, J = 8.0 Hz, Ar-H), 7.45 (1H, d, J = 7.8 Hz, Ar-H), 7.63 (1H, t, J = 7.8 Hz, Ar-H), 7.74 (1H, d, J = 7.8 Hz, Ar-H), 8.03 (1H, s, Ar-H) ppm. 13C NMR (500 MHz, (CD3)₂SO): δC 116.4, 117.7, 119.2, 120.0, 122.6, 124.9, 127.2, 128.9, 129.9, 131.4, 132.1, 143.0 (>C-NH2), 143.3, 153.8 (>C-O-), 160.2 (>C=O) ppm. HRMS m/z calcld for C15H12NO2 (M+H)+ 238.0789, found 238.0863;

**3-[2-[(E)-(2-Hydroxyphenyl)methyleneamino]-5-methylphenyl]chroman-2-one (5ab):** Compound was synthesized according to the General Method B. 42.6 mg (6%); yellow crystals, mp 224 °C. IR (KBr, cm⁻¹): 1711 (C=N), 1613 (C=C).

1H NMR (500 MHz, DMSO-d6): δ = 2.39 (3H, s, CH3), 6.82 (1H, t, J = 8.0 Hz, Ar-H), 6.94 (1H, t, J = 8.0 Hz, Ar-H), 7.32 (1H, d, J = 1.5 Hz, Ar-H), 7.35 (1H, t, J = 8.0 Hz, Ar-H), 7.45 (1H, d, J = 7.8 Hz, Ar-H), 7.63 (1H, t, J = 7.8 Hz, Ar-H), 7.74 (1H, d, J = 7.8 Hz, Ar-H), 8.03 (1H, s, Ar-H) ppm. 13C NMR (125 MHz, DMSO-d6): δC 21.0 (C-CH3), 116.6, 117.0, 118.5, 119.5, 119.8, 125.2, 127.6, 129.1, 130.0, 130.1, 131.6, 132.4, 133.0, 133.8, 133.7, 137.0 (C-CH3), 140.7 (>C-N), 153.8 (C-O-), 159.7 (C=O), 160.7 (C-OH), 163.4 (C=N). HRMS m/z calcld for C23H18NO3 (M+H)+ 356.1290, found 356.3820. Anal. Calcd for C23H17NO3: C, 77.73; H, 4.82; N, 3.94%. Found C, 77.24; H, 3.43; N, 3.86%.
3-[5-Bromo-2-[(E)-(2-hydroxyphenyl)methyleneamino]phenyl]chroman-2-one (5ac): Compound was synthesized according to the General Method C. 21 mg, (5%); yellow crystals, mp 232 °C. IR (KBr, cm⁻¹): 1710 (>C=O), 1606 (C=N). ¹H NMR (500 MHz, DMSO-d₆): δ = 6.84 (1H, d, J = 8.0 Hz, Ar-H), 6.95 (1H, t, J = 8.0 Hz, Ar-H), 7.40 (1H, td, J₁ = 7.7, J₂ = 1.5 Hz, Ar-H), 7.48 (1H, dd, J₁ = 8.2, J₂ = 1.5 Hz, Ar-H), 7.50 (1H, d, J = 8.6 Hz, Ar-H), 7.62 (1H, d, J = 8.0 Hz, Ar-H), 7.67 (1H, ddd, J₁ = 8.2, J₂ = 7.7 Hz, J₃ = 1.5 Hz), 7.75 (1H, dd, J₁ = 7.7, J₂ = 1.5 Hz, Ar-H), 7.75 (1H, d, J = 2.3 Hz), 7.77 (1H, dd, J₁ = 8.6, J₂ = 2.3 Hz, Ar-H, Ar-H), 8.20 (1H, s, (C=O)(C=CH₂)), 8.95 (1H, s, N=C), 12.52 (1H, brs, OH). ¹³C NMR (125 MHz, DMSO-d₆): δ = 116.7, 117.1, 119.4, 119.6 (C-Br), 119.7, 121.1, 125.3, 125.9, 129.2, 132.7, 133.1, 133.2, 133.2, 133.6, 134.2, 143.8, 146.8 (>C=N), 153.8 (C-O-), 159.5 (C=O), 160.7 (C-OH), 164.8 (C=N). HRMS m/z calcd for C₂₂H₁₅BrNO₃ (M+H)⁺ 420.0157, found 420.0226. Anal. Calcd for C₂₂H₁₄BrNO₃: C, 62.88; H, 3.36; N, 3.33%. Found C, 62.78; H, 3.29; N, 3.10%.

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