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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]-2*H*-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 derivatives **2** (R^1=OH, R^4=H) or other benzaldehyde derivatives (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

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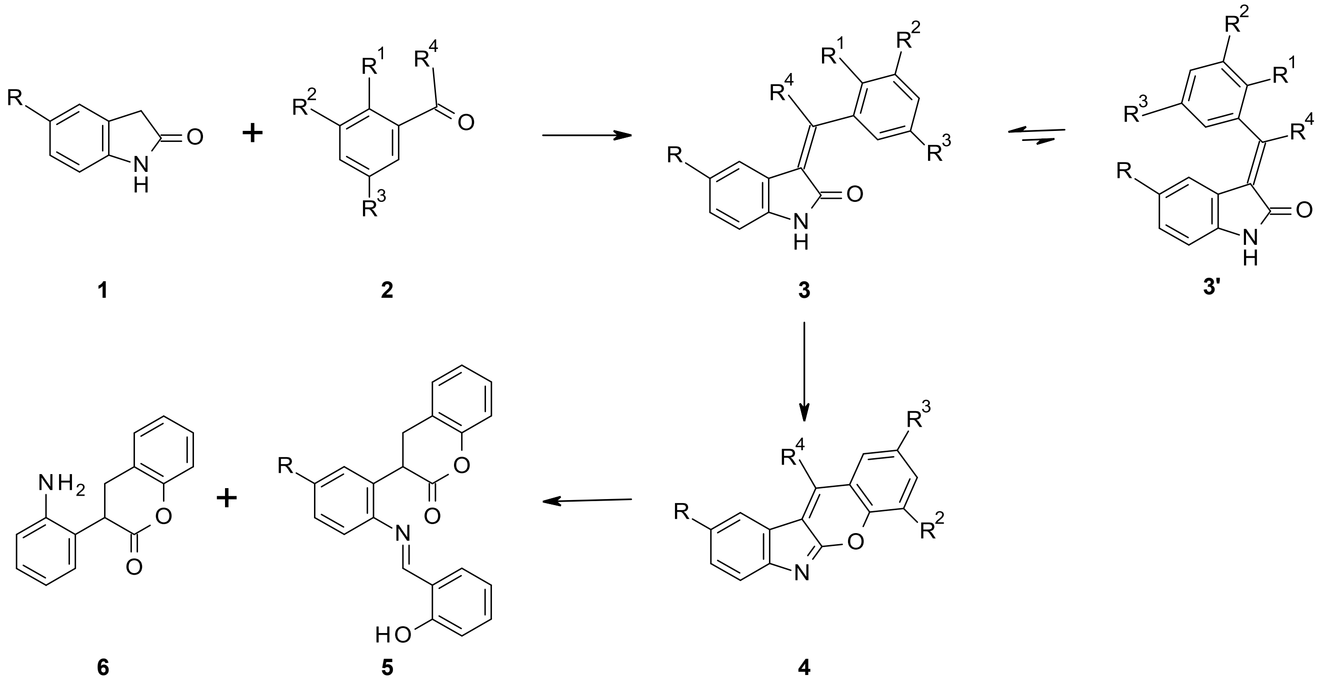
[#] Dedicated to Professor László Tőke on the occasion of his 80th birthday.

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=Me) **1ab** with salicylaldehyde (R^2=R^3=R^4=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

Entry	R	R^1	R^2	R^3	R^4	Method[a]	3 (%)[b]	4% (%)[b]
1	Br	OH	H	Cl	H	**A**	**3a** (76)	-
2	Br	Br	H	Cl	H	**A**	**3b** (53)	-
3	Ph	Br	H	OH	H	**A**	**3c** (60)	-
4	H	OH	H	OMe	Me	**B**	-	**4d** 85 (39)[d]
5	Me	OH	H	OMe	Me	**B**	-	**4e** 79 (15)[c]
6	Me	OH	H	OH	Me	**B**	-	**4f** 94 (72)[c]
7	Me	OH	H	Br	Me	**B**	-	**4g** 63 (28)[c]
8	Ph	OH	H	OMe	Me	**B**	-	**4h** 86 (45)[d]
9	Ph	OH	H	Br	Et	**B**	-	**4i** 47 (9)[e]
10	Br	OH	H	OMe	Me	**B**	-	**4j** 71 (48)[c]
11	Br	OH	H	OH	Me	**B**	-	**4k** 73 (64)[c]
12	Br	OH	Br	Cl	Me	**B**	-	**4l** 24 (10)[c]
13	Br	OH	H	Br	Me	**B**	-	**4m** 64 (38)[d]
14	CN	OH	H	OMe	Me	**B**	-	**4n** 80 (79)[c]
15	CN	OH	H	OH	Me	**B**	-	**4o** 87 (63)[c]
16	CN	OH	H	Br	Me	**B**	-	**4p** 70 (57)[c]
17	CF_3	OH	H	OMe	Me	**B**	-	**4q** 84 (29)[c]
18	CF_3	OH	H	OH	Me	**B**	-	**4r** 94 (49)[c]
19	CF_3	OH	Br	Cl	Me	**B**	-	**4s** 36 (21)[c]
20	CF_3	OH	H	Br	Me	**B**	-	**4t** 55 (21)[c]
21	CF_3	OH	H	Br	Et	**B**	-	**4u** 62 (13)[d]
22	CO_2Me	OH	H	OMe	Me	**B**	-	**4v** 74 (56)[d]
23	CO_2Me	OH	H	OH	Me	**B**	-	**4w** 96 (74)[c]
24	CO_2Me	OH	Br	Cl	Me	**B**	-	**4x** 53 (35)[d]
25	CO_2Me	OH	H	Br	Me	**B**	-	**4y** 62 (55)[d]
26	CO_2Me	OH	H	Br	Et	**B**	-	**4z** 27 (5)[e]

[a]***Method A:*** *cat. piperidine in ethanol, reflux, 1 h;* ***Method B****: 1-butylamine, acetic acid in mesitylene, 140 °C, 24 h*
[b]*HPLC yield (isolated yield)*^{method}*;* [c]*after recrystallization;* [d]*after chromatography ;*[e]*after preparative HPLC.*

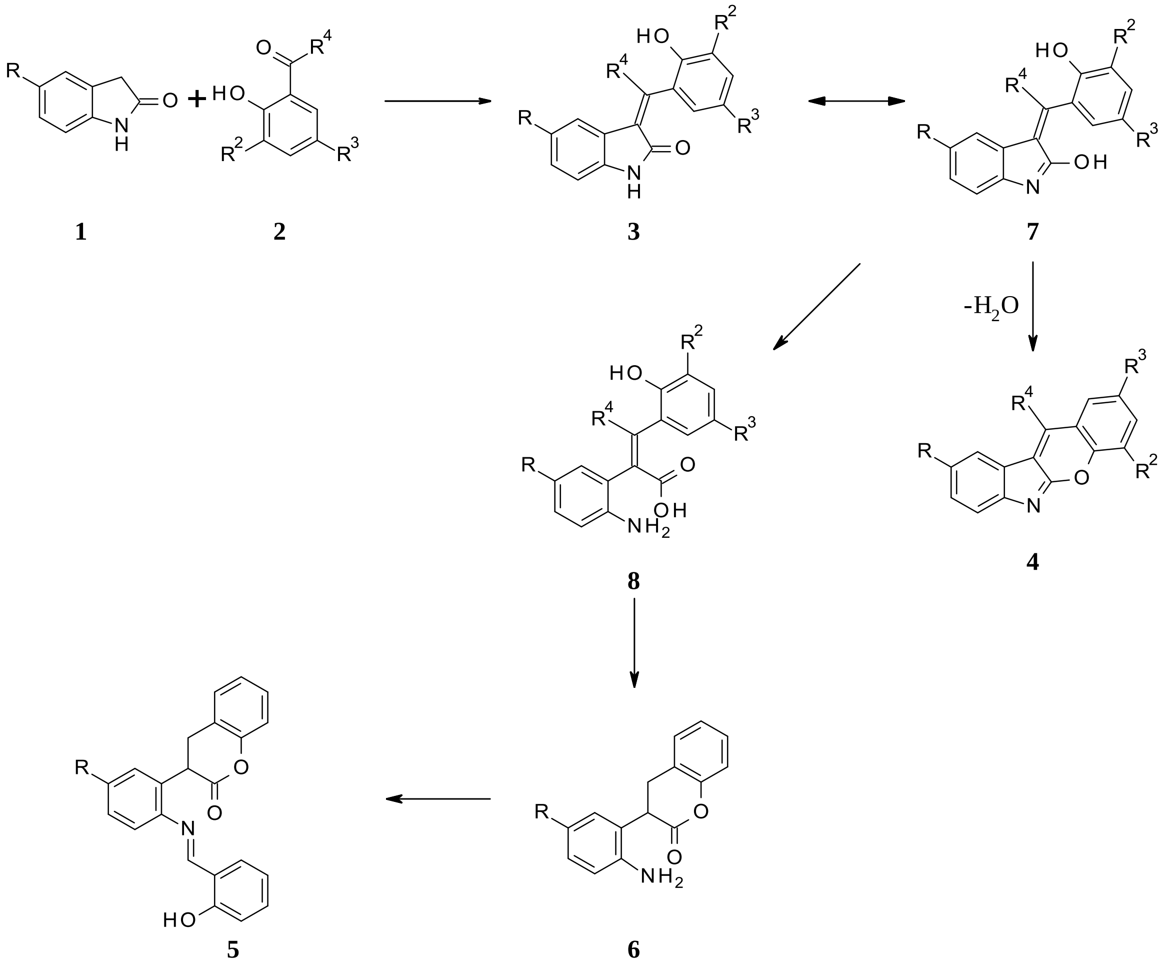
In these cases other by-products, **5ac** and **6**, were also identified. Using 2'-hydroxybenzophenone instead of acetophenones did not result in reaction, only the decomposition of the starting materials was observed (Table 2, Entry 9).

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

Entry	R	R^1	R^4	Method[a]	3% (%)[b]	4% (%)[b]	5 or 6% (%)[b]
1	H	OH	H	**B**	**3aa** 30 (26)[d]	20	-
2	H	OH	H	**C**	**3aa** 52 (35)[d]	**4aa** 37 (7)[d]	**6aa** 2 (2)
3	Me	OH	H	**B**	**3ab** 45 (40)[c]	**4ab** 21 (15)[d]	**5ab** 13 (6)[d]
4	Br	OH	H	**B**	**3ab** 8 (8)[d]	**4ac** 30 (28)[d]	-
5	Br	OH	H	**C**	39	28	**5ac** 32 (5)[d]
6	CN	OH	H	**B**	**3ad** 61 (58)[d]	**4ad** 20 (16)[d]	-
7	CF_3	OH	H	**B**	**3ae** 17 (15)[d]	**4ae** 10 (10)[d]	-
8	CO_2Me	OH	H	**B**	**3af** 37 (26)[d]	2	-
9	CO_2Me	OH	H	**C**	28	**4af** 13 (3.4)[d]	-
10	H	OH	Ph	**B**	-	-	-

*$R^2 = R^3 = H$; [a]**Method B**: 1-butylamine, acetic acid in mesitylene, 140 °C, 2 h; **Method C:** diisopropylethylamine, acetic acid in mesitylene; 140 °C, [b]HPLC yield (isolated yield)^{method}; [c]after recrystallization; [d]after chromatography; [e]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 °C 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 salicilaldehyde (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 °C for 24 h (in case of the salicilaldehyde for 2 h). After cooling, the product was precipitated, collected by filtration, washed with cold EtOAc, and dried *in vacuo* at 50 °C 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 salicylaldehyde 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 °C for 2 h. After cooling the product was precipitated, collected by filtration, washed with iso-propanol and dried *in vacuo* at 50 °C 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 °C. IR (KBr, cm^{-1}): 1694 (>C=O), 1605 (C=C). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 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): δ = 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=*C*H), 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 $C_{15}H_9BrClNO_2$: 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). ^{1}H NMR (500 MHz, DMSO-d_6): 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, J_1 = 8.3 Hz, J_2 = 1.9 Hz, Ar-H), 7.51 (1H, s, >C=C*H*), 7.55 (1H, dd, J_1 = 8.6 Hz, J_2 = 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). ^{13}C NMR (125 MHz, DMSO-d_6): 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=*C*H), 135.2, 136.9, (*C*-Cl), 142.9, 167.9 (NH-*C*=O). HRMS *m/z* calcd for $C_{15}H_9Br_2ClNO$ $(M+H)^+$ 411.8661, found 411.8733. Anal. Calcd for $C_{15}H_8Br_2ClNO$: 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). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.86 (1H, dd, J_1 = 8.6 Hz, J_2 = 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=C*H*), 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). ^{13}C NMR (125 MHz, DMSO-d_6): 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=*C*H), 135.6, 140.5, 143.1, 157.4 (*C*-OH), 168.7 (NH-*C*=O). HRMS *m/z* calcd for $C_{21}H_{15}NO_2Br$ $(M+H)^+$ 392.0208, found 392.0274. Anal. Calcd for $C_{21}H_{14}NO_2Br$: C, 64.30; H, 3.60; N, 3.57%. Found C, 63.56; H, 3.57; N, 3.28%.

3-(2-Hydroxybenzylidene)-1,3-dihydroindol-2-one (3aa): 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). ^{1}H NMR (500 MHz, DMSO-d_6): 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, J_1 = 8.0 Hz, J_2 = 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). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 110.4 (Ar-C), 116.4, 119.3, 121.5, 121.7, 121.8, 122.8, 126.9 (>*C*=CH), 130.0, 130.2, 132.1, 132.9 (>C=*C*H), 143.1, 157.0 (*C*-OH), 169.2 (NH-*C*=O). HRMS *m/z* calcd for $C_{15}H_{12}NO_2$ $(M+H)^+$ 238.0790, found 238.0866. Anal. calcd for $C_{15}H_{11}NO_2$: 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. 201 mg (40%); yellow crystals, mp 173 °C. IR (KBr, cm^{-1}): 3187 (NH or OH), 1679 (>C=O). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.15 (3H, s, CH_3), 6.75 (1H, d, J = 8.0 Hz, Ar-H), 6.93

(1H, t, *J* = 8.0 Hz, Ar-H), 6.97 (1H, dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, Ar-H), 7.02 (1H, bd, *J* = 8.0 Hz, Ar-H), 7.31 (1H, td, J_1 = 7.5 Hz, J_2 = 2.0 Hz, Ar-H), 7.33 (1H, d, *J* = 1.0 Hz, Ar-H), 7.63 (1H, dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, Ar-H), 7.65 (1H, s, =C-H), 10.16 (1H, br OH), 10.44 (1H, s, NH). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 21.3 (CH_3) , 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=*C*H), 140.8, 157.0 (*C*-OH), 169.3 (NH-*C*=O). HRMS calcd for $C_{16}H_{14}NO_2$ (M+H)$^+$ 252.1024, found 252.1020. Anal. Calcd for $C_{16}H_{13}NO_2$: 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). ^{1}H NMR (500 MHz, DMSO-d_6): 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). ^{13}C NMR (125 MHz, DMSO-d_6): 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=*C*H), 142.2, 157.1 (*C*-OH), 168.8 (NH-*C*=O). HRMS *m/z* calcd for $C_{15}H_{11}BrNO_2$ (M+H)$^+$ 315.9973, found 315.9970. Anal. Calcd for $C_{15}H_{10}BrNO_2$: 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). ^{1}H NMR (500 MHz, DMSO-d_6): 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). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 103.5 (*C*-CN), 111.2 (Ar-C), 116.7, 119.6, 119.9 (C-*C*N), 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 $C_{16}H_{11}N_2O_2$ (M+H)$^+$ 263.0742, found 263.0820. Anal. Calcd for $C_{16}H_{10}N_2O_2$: 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), 1691, 1605 (>C=O), 1329, 1104 (CF_3). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.94 (1H, t, *J* = 7.5 Hz, Ar-H), 7.01 (1H, dm, *J* = 8.0 Hz, Ar-H), 7.05 (1H, d, *J* = 8.0 Hz, Ar-H), 7.36 (1H, t, *J* = 7.6 Hz, Ar-H), 7.58 (1H, d, *J* = 8.5 Hz, Ar-H), 7.61 (1H, dm, *J* = 7.5 Hz, Ar-H), 7.69 (1H, bs, Ar-H), 7.80 (1H, s, =C-H), 10.33 (1H, s OH), 10.99 (1H, s, NH). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 110.7, 116.7, 119.1, 119.3, 121.2, 121.9, 122.1, 125.1 (CF_3), 125.8 (>*C*=CH), 127.3, 130.1, 132.8, 135.3 (>C=*C*H), 146.2, 157.1 (*C*-OH), 169.1 (NH-*C*=O). HRMS *m/z* calcd for $C_{16}H_{11}F_3NO_2$ (M+H)$^+$ 300.0741, found 306.0738. Anal. Calcd for $C_{16}H_{10}F_3NO_2$: C, 62.96; H, 3.30; N, 4.59%. Found C, 62.96; H, 2.26; N, 4.05%.

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$_6$*): $\delta = 52.2$ (O*C*H_3), 110.2 (Ar-C), 116.6, 119.3, 121.4, 121.9, 122.7 (*C*CO_2Me), 123.8, 125.9 (*C*=CH), 130.1, 131.8, 132.6, 134.5 (C=*C*H), 147.1, 157.2 (*C*-OH), 166.5 (*C*OOMe), 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 (*C*H_3), 56.4 (O*C*H_3), 109.0 (C_6), 118.9 (C_9), 119.0 (C_1), 120.0 (C_8), 121.3 (C_{5a}), 122.2 (C_{4b}), 122.4 (C_3), 124.0 (C_4), 124.4 (C_{4a}), 129.3 (C_2), 144.4 (*C*CH_3), 145.5 (C_{9a}), 152.6 (C_{11a}), 156.2 (*C*OCH_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_5-*C*H_3), 21.2 (C_3-*C*H_3), 55.7 (O*C*H_3), 108.6 (C_6), 118.4 (C_9), 118.8 (C_8), 119.0 (C_1), 121.4 (C_{5a}), 123.4 (C_{4b}), 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_{9a}), 151.6 (C_{11a}), 156.2 (*C*OCH_3), 163.7 (C=N, 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_8-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_5-CH$_3$), 21.3 (C_3-CH$_3$), 110.7 (C_6), 118.3 (C_9), 118.9 (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). ^{1}H NMR (500 MHz, pyridine-d_5): $\delta = 2.51$ (3H, s, C_3-CH$_3$), 2.82 (3H, s, C_5-CH$_3$), 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, $J_1 = 8.8$ Hz, $J_2 = 2.1$ 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). ^{13}C NMR (125 MHz, pyridine-d_5): $\delta = 14.5$ (C_5-CH$_3$), 21.2 (C_3-CH$_3$), 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_{4a}), 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); ^{1}H NMR (500 MHz, DMSO-d_6): $\delta = 3.10$ (3H, s, CH$_3$), 3.93 (3H, s, OCH$_3$), 7.39-7.35 (1H, m, p-Ar-H), 7.41 (1H, dd, $J_1 = 9.1$ Hz, $J_2 = 2.9$ Hz, C_8-H), 7.52-7.47 (2H, m, m-Ar-H), 7.61 (1H, d, $J = 2.9$ Hz, C_6-H), 7.63 (1H, d, $J = 8.2$ Hz, C_1-H), 7.77 (1H, dd, $J_1 = 9.0$ Hz, $J_2 = 3.8$ Hz, C_2-H), 7.79 (1H, d, $J = 2.9$ Hz, C_9-H), 7.80-7.78 (2H, m, o-Ar-H), 8.35 (1H, d, $J = 1.7$ Hz, C_4-H). ^{13}C NMR (125 MHz, DMSO-d_6): $\delta = 15.8$ (CH$_3$), 56.4 (OCH$_3$), 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 (CCH$_3$), 145.6 (C_{9a}), 152.1 (C_{11a}), 156.3 (COCH$_3$), 164.0 (C_{10a}). HRMS *m/z* calcd for $C_{23}H_{18}NO_2$ $(M+H)^+$ 340.1259, found = 340.1325. Anal. Calcd for $C_{23}H_{17}NO_2$: 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). ^{1}H NMR (500 MHz, DMSO-d_6): $\delta = 1.41$ (3H, t, $J = 7.6$ Hz, CH$_2$$CH_3$), 3.57 (2H, q, $J = 7.6$ Hz, CH_2CH$_3$), 7.38 (1H, t, $J = 7.4$ Hz, p-Ar-H), 7.51 (1H, t, $J = 7.4$ Hz, m-Ar-H), 7.67 (1H, d, $J = 8.2$ Hz, C_1-H), 7.78 (1H, d, $J = 7.4$ Hz, o-Ar-H), 7.81 (1H, dd, $J_1 = 8.2$ Hz, $J_2 = 1.6$ Hz, C_2-H), 7.82 (1H, d, $J = 8.8$ Hz, C_9-H), 7.97 (1H, dd, $J_1 = 8.8$ Hz, $J_2 = 2.2$ Hz, C_8-H), 8.26 (1H, d, $J = 1.6$ Hz, C_4-H), 8.42 (1H, d, $J = 2.2$ Hz, C_6-H). ^{13}C NMR (125 MHz, DMSO-d_6): $\delta = 13.7$ (CH$_2$$CH_3$), 21.8 ($CH_2CH_3$), 117.4 ($C_7$-Br), 119.7 ($C_1$), 120.5 ($C_9$), 121.5 ($C_{5a}$), 122.1 ($C_4$), 122.3 ($C_{4b}$), 124.5 ($C_{4a}$), 127.5 (p-Ar-C), 127.5 (o-Ar-C), 128.4 (C_6), 128.6 (C_2), 129.5 (m-Ar-C), 135.1 (C_8), 135.5 (C_3), 141.1 (C_3-C), 149.3 (CCH$_2$CH$_3$), 150.6 (C_{9a}), 152.1 (C_{11a}), 163.9 (C_{10a}). HRMS *m/z* calcd for $C_{23}H_{17}BrNO$ $(M+H)^+$ 402.0415, found 402.0498. Anal. Calcd for $C_{23}H_{16}BrNO$: C, 68.67; H, 4.01; N, 3.48%. Found C, 67.79; H, 4.03; N, 3.22%.

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, $J_1 = 9.1$ Hz, $J_2 = 2.9$ Hz, C_8-H), 7.51 (1H, d, $J = 8.4$ Hz, C_1-H), 7.62 (1H, d, $J = 2.9$ Hz, C_6-H), 7.64 (1H, d, $J = 8.4$ Hz, C_2-H), 7.78 (1H, d, $J = 9.1$ Hz, C_9-H), 8.31 (1H, brs, C_4-H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): $\delta = 15.9$ (C_5-CH$_3$), 56.4 (OCH$_3$), 109.0 (C_6), 114.4 (C_3-Br), 119.1 (C_9), 120.8 (C_1), 120.9 (C_8), 121.2 (C_{4b}), 121.3 (C_{5a}), 126.3 (C_4), 126.3 (C_{4a}), 131.7 (C_2), 145.8 (C_{9a}), 146.8 (C_5-CH$_3$), 151.5 (C_{11a}), 156.4 (COCH$_3$), 163.8 (C=N, C_{10a}). 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, $J_1 = 8.9$ Hz, $J_2 = 2.8$ Hz, C_8-H), 7.44 (1H, d, $J = 2.8$ Hz, C_6-H), 7.49 (1H, d, $J = 8.4$ Hz, C_1-H), 7.61 (1H, dd, $J_1 = 8.4$ Hz, $J_2 = 1.9$ Hz, C_2-H), 7.66 (1H, d, $J = 8.9$ Hz, C_9-H), 8.25 (1H, d, $J = 1.9$ Hz, C_4-H), 9.98 (1H, s, OH). ^{13}C NMR (125 MHz, DMSO-d_6): $\delta = 15.7$ (C_5-CH$_3$), 110.6 (C_6), 114.3 (C_3), 118.9 (C_9), 120.7 (C_1), 121.1 (C_{4b}), 121.3 (C_{5a}), 121.4 (C_8), 126.1 (C_4), 126.3 (C_{4a}), 131.5 (C_2), 144.7 (C_{9a}), 146.6 (C_5-CH$_3$), 151.5 (C_{11a}), 154.6 (C_7-OH), 163.9 (C=N, C_{10a}). 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, $J = 8.4$ Hz, C_1-H), 7.70 (1H, dd, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, C_2-H), 8.30 (1H, d, $J = 2.3$ Hz, C_8-H), 8.33 (1H, d, $J = 2.3$ Hz, C_6-H), 8.36 (1H, d, $J = 2.0$ Hz, C_4-H). ^{13}C NMR (125 MHz, DMSO-d_6): $\delta = 16.0$ (C_5-CH$_3$), 112.3 (C_9-Br), 115.3 (C_3-Br), 121.3 (C_1), 121.5 (C_{5a}), 122.0 (C_{4b}), 126.1 (C_6), 126.3 (C_{4a}), 126.7 (C_4), 129.5 (C_7-Cl), 132.5 (C_2), 135.0 (C_8), 145.4 (C_5-CH$_3$), 146.7 (C_{9a}), 151.2 (C_{11a}), 164.7 (C=N, C_{10a}). HRMS *m/z* calcd for $C_{16}H_9Br_2ClNO$ $(M+H)^+$ 423.8661, found 425.8722. Anal. Calcd for $C_{16}H_8Br_2ClNO$: 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}): 1544 (aromatic), 1077 (Ar-Br). ^{1}H NMR (500 MHz, DMSO-d_6): $\delta = 3.05$ (3H, s, CH_3), 7.56 (1H, d, $J = 8.4$ Hz, C_1-H), 7.68 (1H, dd, $J_1 = 8.4$ Hz, $J_2 = 1.9$ Hz, C_2-H), 7.82 (1H, d, $J = 8.9$ Hz, C_9-H), 8.00 (1H, dd, $J_1 = 8.9$ Hz, $J_2 = 2.3$ Hz, C_8-H), 8.34 (1H, d, $J = 1.9$ Hz, C_4-H), 8.42 (1H, d, $J = 2.3$ Hz, C_6-H). ^{13}C NMR (125 MHz, DMSO-d_6): $\delta =$ 15.8 (C_5-CH$_3$), 115.0 (C_3), 117.3 (C_7), 120.3 (C_9), 121.1 (C_1), 122.1 (C_{4b}), 122.6 (C_{5a}), 126.4 (C_{4a}), 126.5 (C_4), 129.2 (C_6), 132.1 (C_2), 135.4 (C_8), 145.8 (C_5-CH$_3$), 150.3 (C_{9a}), 151.4 (C_{11a}), 163.5 (C=N, C_{10a}).

HRMS *m/z* calcd for $C_{16}H_{10}Br_2NO$ $(M+H)^+$ 389.9051, found 391.9104. Anal. Calcd for $C_{16}H_9Br_2NO$: C, 49.14; H, 2.32; N, 3.58%. Found C, 48.76; H, 2.26; N, 3.37%.

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=N), 1233 (C-O-C). ^1H NMR (500 MHz, pyridine-d_5): $\delta = 2.95$ (3H, s, C_5-CH_3), 3.90 (3H, s, OCH_3), 7.42 (1H, dd, $J_1 = 9.1$ Hz, $J_2 = 2.9$ Hz, C_8-H), 7.55 (1H, d, $J = 2.9$ Hz, C_6-H), 7.66 (1H, d, $J = 9.1$ Hz, C_9-H), 7.88 (1H, dd, $J_1 = 8.2$ Hz, $J_2 = 1.2$ Hz, C_2-H), 7.90 (1H, d, $J = 8.2$ Hz, C_1-H), 8.50 (1H, brs, C_4-H). ^{13}C NMR (125 MHz, pyridine-d_5): $\delta = 15.0$ (C_5-$\mathit{C}H_3$), 55.8 ($O\mathit{C}H_3$), 104.8 ($\mathit{C_3}$-CN), 108.6 (C_6), 118.8 (C_9), 119.8 (C_1), 120.3 (C_3-$\mathit{C}N$), 120.5 (C_8), 121.2 (C_{5a}), 121.5 (C_{4b}), 125.0 (C_{4a}), 127.3 (C_4), 132.5 (C_2), 146.0 (C_{9a}), 146.4 ($\mathit{C_5}$-CH_3), 156.5 (C_{11a}), 156.7 ($\mathit{C}OCH_3$), 163.9 (C=N, C_{10a}). HRMS *m/z* calcd for $C_{18}H_{13}N_2O_2$ $(M+H)^+$ 289.0898, found 289.0973. Anal. Calcd for $C_{18}H_{12}N_2O_2$: 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=N), 1527 (C=C). ^1H NMR (500 MHz, DMSO-d_6): $\delta = 3.05$ (3H, s, C_5-CH_3), 7.33 (1H, dd, $J_1 = 9.0$ Hz, $J_2 = 2.8$ Hz, C_8-H), 7.51 (1H, d, $J = 2.8$ Hz, C_6-H), 7.70 (1H, d, $J = 8.2$ Hz, C_1-H), 7.75 (1H, d, $J = 9.0$ Hz, C_9-H), 7.90 (1H, dd, $J_1 = 8.2$ Hz, $J_2 = 1.5$ Hz, C_2-H), 8.68 (1H, d, $J = 1.5$ Hz, C_4-H), 10.11 (1H, brs, OH). ^{13}C NMR (125 MHz, DMSO-d_6): $\delta = 15.9$ (C_5-$\mathit{C}H_3$), 104.0 ($\mathit{C_3}$-CN), 110.7 (C_6), 119.2 (C_9), 119.7 (C_1), 120.4 (C_3-$\mathit{C}N$), 120.5 (C_{4b}), 121.4 (C_{5a}), 122.0 (C_8), 124.9 (C_{4a}), 127.9 (C_4), 132.8 (C_2), 144.9 (C_{9a}), 148.4 ($\mathit{C_5}$-CH_3), 154.9 ($\mathit{C_7}$-OH), 155.8 (C_{11a}), 163.9 (C=N, C_{10a}). HRMS *m/z* calcd for $C_{17}H_{11}N_2O_2$ $(M+H)^+$ 275.0742, found 275.0822. Anal. Calcd for $C_{17}H_{10}N_2O_2$: 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=N). ^1H NMR (500 MHz, pyridine-d_5): $\delta = 2.91$ (3H, s, C_5-CH_3), 7.59 (1H, d, $J = 8.8$ Hz, C_9-H), 7.87 (1H, dd, $J_1 = 8.8$ Hz, $J_2 = 2.3$ Hz, C_8-H), 7.88-7.90 (1H, m, C_1-H), 7.88-7.90 (1H, m, C_2-H), 8.28 (1H, d, $J = 2.3$ Hz, C_6-H), 8.49 (1H, s, C_4-H). ^{13}C NMR (125 MHz, pyridine-d_5): $\delta = 14.9$ (C_5-$\mathit{C}H_3$), 105.4 ($\mathit{C_3}$-CN), 117.6 ($\mathit{C_7}$-Br), 119.7 (C_9), 120.0 (C_3-$\mathit{C}N$), 120.1 (C_1), 122.2 (C_{4b}), 122.3 (C_{5a}), 125.0 (C_{4a}), 127.5 (C_4), 128.6 (C_6), 133.0 (C_2), 135.2 (C_8), 145.2 ($\mathit{C_5}$-CH_3), 150.3 (C_{9a}), 156.4 (C_{11a}), 165.4 (C=N, C_{10a}). HRMS *m/z* calcd for $C_{17}H_{10}BrN_2O$ $(M+H)^+$ 336.9898, found 336.9981. Anal. Calcd for $C_{17}H_9BrN_2O$: C, 60.56; H, 2.69; N, 8.31%. Found C, 60.96; H, 2.72; N, 8.59%.

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 (CF_3). ^1H NMR (500 MHz, pyridine-d_5): $\delta = 2.97$ (3H, s, C_5-CH_3), 3.88 (3H, s,

OCH_3), 7.39 (1H, dd, J_1 = 9.0 Hz, J_2 = 2.9 Hz, C_8-H), 7.54 (1H, d, J = 2.9 Hz, C_6-H), 7.65 (1H, d, J = 9.0 Hz, C_9-H), 7.91 (1H, dd, J_1 = 8.2 Hz, J_2 = 1.2 Hz, C_2-H), 7.99 (1H, d, J = 8.2 Hz, C_1-H), 8.46 (1H, brs, C_4-H). ^{13}C NMR (125 MHz, pyridine-d_5): δ = 14.9 (C_5-$C$$H_3$), 55.8 (O$C$$H_3$), 108.7 ($C_6$), 118.7 ($C_9$), 119.4 ($C_1$), 120.1 ($C_8$), 120.3 ($C_4$), 121.2 ($C_{5a}$), 122.1 ($C_{4b}$), 123.4 ($C_3$-$CF_3$), 124.7 ($C_{4a}$), 125.6 ($C_3$-$C$$F_3$), 125.8 ($C_2$), 145.6 ($C_5$-$CH_3$), 146.0 ($C_{9a}$), 156.2 ($C_{11a}$), 156.6 ($C$$OCH_3$), 165.5 (C=N, C_{10a}). HRMS *m/z* calcd for $C_{18}H_{13}F_3NO_2$ $(M+H)^+$ 332.0820, found 332.0881. Anal. Calcd for $C_{18}H_{12}F_3NO_2$: 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 (CF_3). ^{1}H NMR (500 MHz, pyridine-d_5): δ = 2.88 (3H, s, CH_3), 7.52 (1H, dd, J_1 = 8.9 Hz, J_2 = 2.8 Hz, C_8-H), 7.64 (1H, d, J = 8.9 Hz, C_9-H), 7.70 (1H, d, J = 2.8 Hz, C_6-H), 7.90 (1H, dd, J_1 = 8.3 Hz, J_2 = 1.1 Hz, C_2-H), 7.98 (1H, d, J = 8.3 Hz, C_1-H), 8.43 (1H, brs, C_4-H), 11.97 (1H, brs, OH). ^{13}C NMR (125 MHz, pyridine-d_5): δ = 14.8 (C_5-$C$$H_3$), 110.8 ($C_6$), 118.6 ($C_9$), 119.3 ($C_1$), 120.2 ($C_4$), 121.5 ($C_8$), 121.5 ($C_{5a}$), 121.8 ($C_{4b}$), 123.1 ($C_3$), 124.8 ($C_{4a}$), 125.7 ($C_2$), 125.7 ($C_3$-$C$$F_3$), 145.1 ($C_{9a}$), 145.7 ($C_5$-$CH_3$), 155.5 ($C_7$-OH), 156.2 ($C_{11a}$), 165.7 (C=N, C_{10a}). HRMS *m/z* calcd for $C_{17}H_{11}F_3NO_2$ $(M+H)^+$ 318.0664, found 318.0726. Anal. Calcd for $C_{17}H_{10}F_3NO_2$: 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 (CF_3). ^{1}H NMR (500 MHz, pyridine-d_5): δ = 2.97 (3H, s, CH_3), 7.94 (1H, dd, J_1 = 8.3 Hz, J_2 = 1.2 Hz, C_2-H), 7.98 (1H, d, J = 8.3 Hz, C_1-H), 8.09 (1H, d, J = 2.4 Hz, C_8-H), 8.13 (1H, d, J = 2.4 Hz, C_6-H), 8.45 (1H, brs, C_4-H). ^{13}C NMR (125 MHz, pyridine-d_5): δ = 15.0 (C_5-$C$$H_3$), 112.3 ($C_9$-Br), 120.0 ($C_1$), 120.7 ($C_4$), 121.5 ($C_{5a}$), 122.0 ($C_{4b}$), 123.3 ($C_3$-$CF_3$), 124.5 ($C_{4a}$), 125.1 ($C_6$), 125.3 ($C_3$-$C$$F_3$), 126.7 ($C_2$), 129.9 ($C_7$-Cl), 135.1 ($C_8$), 143.9 ($C_5$-$CH_3$), 146.7 ($C_{9a}$), 156.0 ($C_{11a}$), 164.7 (C=N, C_{10a}). HRMS *m/z* calcd for $C_{17}H_9BrClF_3NO$ $(M+H)^+$ 413.9430, found 413.9500. Anal. Calcd for $C_{17}H_8BrClF_3NO$: 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 (CF_3). ^{1}H NMR (500 MHz, pyridine-d_5): δ = 2.94 (3H, s, C_5-CH_3), 7.58 (1H, d, J = 8.8 Hz, C_9-H), 7.85 (1H, dd, J_1 = 8.8 Hz, J_2 = 2.3 Hz, C_8-H), 7.92 (1H, dd, J_1 = 8.2 Hz, J_2 = 1.0 Hz, C_2-H), 7.98 (1H, d, J = 8.2 Hz, C_1-H), 8.28 (1H, d, J = 2.3 Hz, C_6-H), 8.44 (1H, brs, C_4-H). ^{13}C NMR (125 MHz, pyridine-d_5): δ = 14.8 (C_5-$C$$H_3$), 117.4 ($C_7$-Br), 119.6 ($C_9$), 119.7 ($C_1$), 120.5 ($C_4$), 122.3 ($C_{5a}$), 123.0 ($C_8$), 123.0 ($C_{4b}$), 124.2 ($C_3$-$CF_3$), 124.7 ($C_{4a}$), 125.5 ($C_3$-$C$$F_3$), 126.3 ($C_2$), 128.5 ($C_6$), 144.4 ($C_5$-$CH_3$), 150.3 ($C_{9a}$), 156.1 ($C_{11a}$), 165.0 (C=N, C_{10a}). HRMS *m/z* calcd for $C_{17}H_{10}BrF_3NO$ $(M+H)^+$

379.9820, found 379.9888. Anal. Calcd for $C_{17}H_9BrF_3NO$: 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): δ = 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): δ = 13.8 (C_5-CH_2*C*H_3), 22.0 (C_5-*C*H_2CH_3), 117.7 (C_7-Br), 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-*C*F_3), 126.5 (C_2), 128.7 (C_6), 135.8 (C_8), 150.7 (C_{9a}), 151.8 (*C_5*-CH_2CH_3), 155.4 (C_{11a}), 165.3 (C=N, C_{10a}). HRMS *m/z* calcd for $C_{18}H_{12}BrF_3NO$ $(M+H)^+$ 393.9976, found 394.0059. Anal. Calcd for $C_{18}H_{11}BrF_3NO$: 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): δ = 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_1 = 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): δ = 14.9 (C_5-*C*H_3), 51.8 (C_3-COO*C*H_3), 55.7 (C_7-O*C*H_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-*C*OOMe). 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): δ = 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): δ = 14.7 (C_5-*C*H_3), 51.6 (C_3-COO*C*H_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-*C*OOMe). HRMS *m/z* calcd for $C_{18}H_{14}NO_4$ $(M+H)^+$ 308.0845, found 308.0914. Anal. Calcd for $C_{18}H_{13}NO_4$: 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): δ = 2.91 (3H, s, C$_5$-CH$_3$), 3.98 (3H, s, COOCH$_3$), 7.95 (1H, d, J = 8.3 Hz, C$_1$-H), 8.08 (1H, d, J = 2.3 Hz, C$_8$-H), 8.09 (1H, d, J = 2.3 Hz, C$_6$-H), 8.46 (1H, dd, J_1 = 8.3 Hz, J_2 = 1.3 Hz, C$_2$-H), 8.91 (1H, d, J = 1.3 Hz, C$_4$-H). ^{13}C NMR (125 MHz, pyridine-d_5): δ = 14.8 (C$_5$-*C*H$_3$), 51.8 (C$_3$-COO*C*H$_3$), 112.3 (C$_9$-Br), 119.5 (C$_1$), 123.0 (C$_{5a}$), 123.7 (C$_{4b}$), 124.0 (*C$_3$*-COOMe), 124.9 (C$_6$), 125.0 (C$_{4a}$), 125.3 (C$_4$), 129.9 (C$_7$-Cl), 131.4 (C$_2$), 134.8 (C$_8$), 143.0 (*C$_5$*-CH$_3$), 146.7 (C$_{9a}$), 157.2 (C$_{11a}$), 165.6 (C=N, C$_{10a}$), 166.9 (C$_3$-*C*OOMe). HRMS *m/z* calcd for $C_{18}H_{12}BrClNO_3$ (M+H)$^+$ 403.9611, found 403.9683. Anal. Calcd for $C_{18}H_{11}BrClNO_3$: 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). ^{1}H NMR (500 MHz, pyridine-d_5): δ = 2.89 (3H, s, C$_5$-CH$_3$, d, J = 8.8 Hz, C$_9$-H), 7.83 (1H, dd, J_1 = 8.8 Hz, J_2 = 2.3 Hz, C$_8$-H), 7.95 (1H, d, J = 8.2 Hz, C$_1$-H), 8.24 (1H, d, J = 2.3 Hz, C$_6$-H), 8.45 (1H, dd, J_1 = 8.2 Hz, J_2 = 1.5 Hz, C$_2$-H), 8.91 (1H, d, J = 1.5 Hz, C$_4$-H). ^{13}C NMR (125 MHz, pyridine-d_5): δ = 14.7 (C$_5$-*C*H$_3$), 51.7 (C$_3$-COO*C*H$_3$), 117.4 (C$_7$-Br), 119.2 (C$_1$), 119.6 (C$_9$), 122.5 (C$_{5a}$), 123.0 (C$_{4b}$), 124.5 (*C$_3$*-COOMe), 124.6 (C$_{4a}$), 125.1 (C$_4$), 128.4 (C$_6$), 131.1 (C$_2$), 134.7 (C$_8$), 143.5 (*C$_5$*-CH$_3$), 150.2 (C$_{9a}$), 157.3 (C$_{11a}$), 165.3 (C=N, C$_{10a}$), 167.0 (C$_3$-*C*OOMe). HRMS *m/z* calcd for $C_{18}H_{13}BrNO_3$ (M+H)$^+$ 370.0001, found 370.0070. Anal. Calcd for $C_{18}H_{12}BrNO_3$: 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), 1643 (C=N), 1541 (C=C); ^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.40 (3H, t, J = 7.6 Hz, C$_5$-CH$_2$*CH$_3$*), 3.51 (2H, q, J = 7.6 Hz, C$_5$-C*H$_2$*CH$_3$), 3.91 (3H, s, COOCH$_3$), 7.69 (1H, d, J = 8.3 Hz, C$_1$-H), 7.85 (1H, d, J = 8.8 Hz, C$_9$-H), 8.00 (1H, dd, J_1 = 8.8 Hz, J_2 = 2.1 Hz, C$_8$-H), 8.13 (1H, dd, J_1 = 8.3 Hz, J_2 = 1.2 Hz, C$_2$-H), 8.45 (1H, d, J = 2.1 Hz, C$_6$-H), 8.55 (1H, d, J = 1.2 Hz, C$_4$-H);^{13}C NMR (125 MHz, DMSO-d_6): δ = 13.7 (C$_5$-CH$_2$*C*H$_3$), 22.0 (C$_5$-*C*H$_2$CH$_3$), 52.6 (C$_3$-COO*C*H$_3$), 117.4 (C$_7$-Br), 119.3 (C$_1$), 120.7 (C$_9$), 121.4 (C$_{5a}$), 121.5 (C$_{4b}$), 123.8 (*C$_3$*-COOMe), 124.1 (C$_{4a}$), 124.6 (C$_4$), 128.6 (C$_6$), 130.9 (C$_2$), 135.6 (C$_8$), 150.7 (C$_{9a}$), 150.9 (*C$_5$*-CH$_2$CH$_3$), 156.5(C$_{11a}$), 165.6 (C=N, C$_{10a}$), 166.8 (C$_3$-*C*OOMe). HRMS *m/z* calcd for $C_{19}H_{15}BrNO_3$ (M+H)$^+$ 384.0157, found 384.0237. Anal. Calcd for $C_{19}H_{14}BrNO_3$: C, 59.39; H, 3.67; N, 3.65%. Found C, 59.22; H, 3.48; N, 3.56%.

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=N), 1544 (aromatic). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.32 (1H, t, J = 7.5 Hz, C$_3$-H), 7.52 (1H, t, J = 7.5 Hz, C$_2$-H), 7.56 (1H, t, J = 8.0 Hz, C$_7$-H), 7.59 (1H, d, J = 7.5 Hz, C$_1$-H), 7.80 (1H, t, J = 8.0 Hz, C$_8$-H), 7.84 (1H, d, J = 8.0 Hz, C$_9$-H), 8.04 (1H, d, J = 8.0 Hz, C$_6$-H), 8.08 (1H, d, J = 7.5 Hz, C$_4$-H), 8.85 (1H, s, C$_5$-H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6):

δ = 117.9 (C$_9$), 119.1 (C$_1$), 119.8 (C$_{5a}$), 122.6 (C$_4$), 123.0 (C$_3$), 123.9 (C$_{4a}$), 125.2 (C$_{4b}$), 125.4 (C$_7$), 130.3 (C$_2$), 130.3 (C$_6$), 132.3 (C$_5$), 132.7 (C$_8$), 151.6 (C$_{9a}$), 152.3 (C$_{11a}$), 164.3 (C=N, C$_{10a}$) ppm. HRMS *m/z* calcd for $C_{15}H_{10}NO$ $(M+H)^+$ 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). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.45 (3H, s, CH$_3$), 7.33 (1H, dm, J = 8.0 Hz, C$_2$-H), 7.46 (1H, d, J = 8.0 Hz, C$_1$-H), 7.53 (1H, ddd, J_1 = 7.8, J_2 = 6.8 J_3 = 1.5 Hz, C$_7$-H), 7.78 (1H, ddd, J_1 = 8.4, J_2 = 6.8 J_3 = 1.6 Hz, C$_8$-H), 7.81 (1H, dm, J = 8.4 Hz, C$_9$-H), 7.87 (1H, m, C$_4$-H), 8.08 (1H, dd, J_1 = 7.8, J_2 = 1.6 Hz, C$_6$-H), 8.75 (1H, s, C$_5$-H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 21.5 (CH$_3$), 117.8 (C$_9$), 118.8 (C$_1$), 119.8 (C$_{5a}$), 122.8 (C$_4$), 124.0 (C$_{4a}$), 125.4 (C$_{4b}$), 125.2 (C$_7$), 131.1 (C$_2$), 130.2 (C$_6$), 131.6 (C$_5$), 132.5 (C$_8$), 150.5 (C$_{11a}$), 151.5 (C$_{9a}$), 164.0 (C=N, C$_{10a}$). HRMS *m/z* calcd for $C_{16}H_{12}NO$ $(M+H)^+$ 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). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.54 (1H, d, J = 8.4 Hz, C$_1$-H), 7.57 (1H, ddd, J_1 = 7.9 Hz, J_2 = 6.6 Hz, J_3 = 1.8 Hz, C$_7$-H), 7.66 (1H, dd, J_1 = 8.4 Hz, J_2 = 2.1 Hz, C$_2$-H), 7.83 (1H, ddd, J_1 = 8.4 Hz, J_2 = 6.6 Hz, J_3 = 1.5 Hz, C$_8$-H), 7.86 (1H, dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, C$_9$-H), 8.03 (1H, dd, J_1 = 7.9 Hz, J_2 = 1.5 Hz, C$_6$-H), 8.33 (1H, d, J = 2.1 Hz, C$_4$-H), 8.92 (1H, s, C$_5$-H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 114.8 (C_3-Br), 118.0 (C$_9$), 119.7 (C$_{5a}$), 121.0 (C$_1$), 124.4 (C$_{4b}$), 125.3 (C$_4$), 125.5 (C$_7$), 126.1 (C$_{4a}$), 130.6 (C$_6$), 132.5 (C$_2$), 133.2 (C$_8$), 134.1 (C$_5$), 151.7 (C$_{9a}$), 151.8 (C$_{11a}$), 164.6 (C=N, C$_{10a}$). HRMS *m/z* calcd for $C_{15}H_9BrNO$ $(M+H)^+$ 297.9789, found 297.9868. Anal. Calcd for $C_{15}H_8BrNO$: 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). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.62 (1H, m, C$_7$-H), 7.76 (1H, d, J = 8.2 Hz, C$_1$-H), 7.89 (1H, m, C$_8$-H), 7.93 (1H, dm, J = 8.0 Hz, C$_9$-H), 7.95 (1H, dd, J_1 = 8.2 Hz, J_2 = 1.7 Hz, C$_2$-H), 8.12 (1H, dm, J = 7.8 Hz, C$_6$-H), 8.62 (1H, d, J = 1.7 Hz, C$_4$-H), 9.05 (1H, s, C$_5$-H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 104.5 (C_3-CN), 118.1 (C$_9$), 119.7 (C$_{5a}$), 120.1 (C$_1$), 120.2 (CN), 123.7 (C$_{4b}$), 124.6 (C$_{4a}$), 125.8 (C$_7$), 126.8 (C$_4$), 130.8 (C$_6$), 133.7 (C$_8$), 133.8 (C$_2$), 135.5 (C$_5$), 151.9 (C$_{9a}$), 156.1 (C$_{11a}$), 166.7 (C=N, C$_{10a}$). HRMS *m/z* calcd for $C_{16}H_9N_2O$ $(M+H)^+$ 245.0714, found 245.0710. Anal. Calcd for $C_{16}H_8N_2O$: C, 78.68; H, 3.30; N, 11.47%. Found C, 78.34; 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 (CF$_3$). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.61 (1H, ddd, J_1 = 7.8 Hz, J_2 = 7.5 Hz, J_3 = 1.2 Hz, C$_7$-H), 7.77 (1H, d, J

= 8.2 Hz, C_1-H), 7.85 (1H, d, *J* = 8.2 Hz, C_2-H), 7.87 (1H, ddd, J_1 = 8.0 Hz, J_2 = 7.5 Hz, J_3 = 1.2 Hz, C_8-H), 7.91 (1H, dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, C_9-H), 8.07 (1H, dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, C_6-H), 8.55 (1H, brs, C_4-H), 9.09 (1H, s, C_5-H). ^{13}C NMR (125 MHz, DMSO-*d_6*): δ = 118.1 (C_9), 119.6 (C_1), 119.7 (C_{5a}), 119.9 (C_4), 123.2 (*C_3*-CF_3), 124.3 (C_{4a}), 124.3 (C_{4b}), 125.7 (C_7), 125.8 (C_3-*C*F_3), 126.8 (C_2), 130.7 (C_6), 133.4 (C_8), 135.0 (C_5), 151.9 (C_{9a}), 155.6 (C_{11a}), 166.2 (C=N, C_{10a}). HRMS *m/z* calcd for $C_{16}H_9F_3NO$ $(M+H)^+$ 288.0558, found 288.0629. Anal. Calcd for $C_{16}H_8F_3NO$: 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). ^{1}H NMR (500 MHz, DMSO-*d_6*): δ = 3.91 (3H, s, O*CH_3*), 7.60 (1H, dd, J_1 = 7.8 Hz, J_2 = 7.0 Hz, C_7-H), 7.69 (1H, d, *J* = 8.1 Hz, C_1-H), 7.85 (1H, ddd, J_1 = 8.1 Hz, J_2 = 7.0 Hz, J_3 = 1.4 Hz, C_8-H), 7.89 (1H, dm, *J* = 8.1 Hz, C_9-H), 8.14 (1H, dd, J_1 = 8.1, J_2 = 1.7 Hz, C_2-H), 8.04 (1H, dd, J_1 = 7.8, J_2 = 1.4 Hz, C_6-H), 8.75 (1H, d, *J* = 1.7 Hz, C_4-H), 9.11 (1H, s, C_5-H). ^{13}C NMR (125 MHz, DMSO-*d_6*): δ = 52.6 (O*C*H_3), 118.1 (C_9), 119.1 (C_1), 119.8 (C_{5a}), 123.9 (C_4), 124.1 (C_{4a}), 124.5 (C_{4b}), 125.7 (C_7), 130.6 (C_6), 131.3 (C_2), 133.2 (C_8), 134.4 (C_5), 151.8 (C_{9a}), 156.7 (C_{11a}), 166.5 (C=N, C_{10a}), 166.9 (C_3-*C*OOMe). HRMS *m/z* calcd for $C_{17}H_{12}NO_3$ $(M+H)^+$ 278.0739, found 278.0810.

3-(2-Aminophenyl)chromen-2-one (6): Compound was synthesized according to the General Method C. ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ_H 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), 7.38 (1H, t, *J* = 7.8 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. ^{13}C NMR (500 MHz, $(CD_3)_2SO$): δ_C 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*-NH_2), 143.3, 153.8 (>C-O-), 160.2 (>C=O) ppm. HRMS *m/z* calcd for $C_{15}H_{12}NO_2$ $(M+H)^+$ 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). ^{1}H NMR (500 MHz, DMSO-*d_6*): δ = 2.39 (3H, s, CH_3), 6.82 (1H, d, *J* = 8.0 Hz, Ar-H), 6.94 (1H, t, *J* = 8.0 Hz), 7.32 (1H, d, *J* = 1.5 Hz, Ar-H), 7.35 (1H, t, *J* = 8.0 Hz, Ar-H), 7.38 (1H, dd, J_1 = 8.1, J_2 = 1.5 Hz, Ar-H), 7.39 (1H, td, J_1 = 7.7, J_2 = 1.5 Hz, Ar-H), 7.46 (1H, d, *J* = 8.1 Hz, Ar-H), 7.48 (1H, dd, J_1 = 8.2, J_2 = 1.5 Hz, Ar-H), 7.61 (1H, d, *J* = 8.0 Hz), 7.65 (1H, ddd, J_1 = 8.2, J_2 = 7.7 Hz, J_3 = 1.5 Hz, Ar-H), 7.75 (1H, dd, J_1 = 7.7 Hz, J_2 = 1.5 Hz, Ar-H), 8.13 (1H, s, (C=O)C=C*H*-)), 8.93 (1H, s, N=C*H*), 12.85 (1H, s, OH). ^{13}C NMR (125 MHz, DMSO-*d_6*): δ = 21.0 (C-*C*H_3), 116.6, 117.0, 118.5, 119.5, 119.5, 119.8, 125.2, 127.6, 129.1, 131.0, 131.1, 131.6, 132.4, 133.1, 133.7, 137.0 (*C*-CH_3), 143.0, 144.7 (>*C*-N), 153.8 (*C*-O-), 159.7 (*C*=O), 160.7 (*C*-OH), 163.4 (*C*=N). HRMS *m/z* calcd for $C_{23}H_{18}NO_3$

$(M+H)^+$ 356.1290, found 356.3820. Anal. Calcd for $C_{23}H_{17}NO_3$: 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). ^{1}H NMR (500 MHz, DMSO-d_6): $\delta = 6.84$ (1H, d, $J = 8.0$ Hz, Ar-H), 6.95 (1H, t, $J = 8.0$ Hz, Ar-H), 7.37 (1H, t, $J = 8.0$ Hz, Ar-H), 7.40 (1H, td, $J_1 = 7.7$, $J_2 = 1.5$ Hz, Ar-H), 7.48 (1H, dd, $J_1 = 8.2$, $J_2 = 1.5$ 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, $J_1 = 8.2$, $J_2 = 7.7$ Hz, $J_3 = 1.5$ Hz), 7.75 (1H, dd, $J_1 = 7.7$, $J_2 = 1.5$ Hz, Ar-H), 7.75 (1H, d, $J = 2.3$ Hz), 7.77 (1H, dd, $J_1 = 8.6$, $J_2 = 2.3$ Hz, Ar-H, Ar-H), 8.20 (1H, s, (C=O)C=C*H*-)), 8.95 (1H, s, N=C*H*), 12.52 (1H, brs, OH). ^{13}C NMR (125 MHz, DMSO-d_6): $\delta = 116.7$, 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, 132.7, 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 $C_{22}H_{15}BrNO_3$ $(M+H)^+$ 420.0157, found 420.0226. Anal. Calcd for $C_{22}H_{14}BrNO_3$: C, 62.88; H, 3.36; N, 3.33%. Found C, 62.78; H, 3.29; N, 3.10%.

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