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Note

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Synthesis of Chromeno[2,3-*b*]indol-11(6*H*)-one via $PhI(OAc)_2$-Mediated Intramolecular Oxidative $C(sp^2)$–$N(H_2)$ Bond Formation

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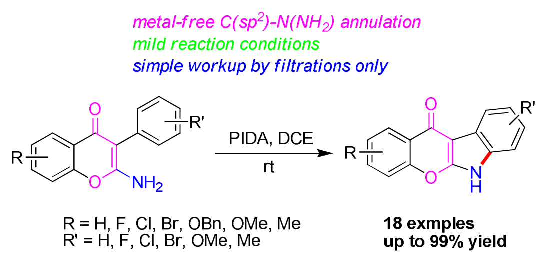
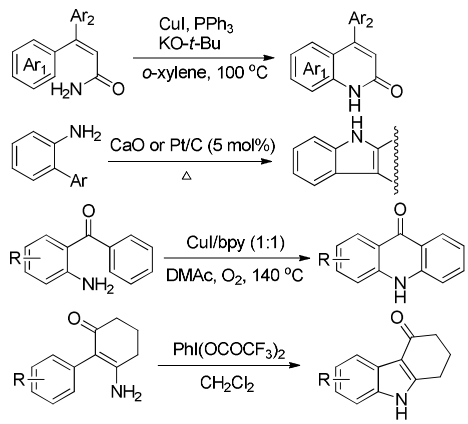


Abstract: Various chromeno[2,3-*b*]indol-11(6*H*)-ones were conveniently constructed via phenyliodine(III) diacetate (PIDA)-mediated intramolecular oxidative annulation. This method, while realizing a direct oxidative C–N bond formation between an aromatic ring and a pendent free-NH_2 moiety, features a metal-free protocol, mild reaction conditions, simple workup, and the readily availability of the starting substrates.

Constructing intramolecular aromatic C–N bonds is one of the most robust approaches for the assembly of the N-containing heterocycles. In addition to the most common strategies such as via transition metal-catalyzed oxidative C–halogen or C–B bond activation,[1] an alternative straightforward approach is the intramolecular aromatic amination of unfunctionalized C–H bond carried out through transition metal-catalyzed direct oxidative C–N bond formation. However, most of the reported examples seem to suggest that a substituted nitrogen atom is indispensable for such transformations.[2]

To our knowledge, there are less than a handful of examples describing the direct oxidative C–N bond formations between unactived arenes and a pendant free NH_2-moiety. Cacchi and co-workers realized the synthesis of 4-aryl-2-quinolones from 3,3-diarylacrylamides bearing a free NH_2-moiety through CuI-mediated oxidative C–N bond formation (Scheme **1a**).[3a] Horaguchi reported an intramolecular annulation of *N*-alkylated 2-aminobiphenyls leading to carbazoles in the presence of CaO and under high temperature (Scheme **1b**).[3b-c] Later on, Matsubara also realized the same oxidative C–N(H_2) bond formation but by using Pt/C at high temperature (Scheme **1b**).[3d] In 2013, Cheng and co-workers reported a CuI/bpy-catalyzed synthesis of acridone derivatives through C–H functionalization and C–N bond formation within 2-aminobenzophenone, containing a nonsubstituted N atom (Scheme **1c**).[3e] In our previous work, we also achieved the synthesis of carbazolones from phenyliodine bis(trifluoroacetate) (PIFA)-mediated direct oxidative annulation of the free NH_2-moiety on the side-chain to the phenyl ring (Scheme **1d**).[4]



Scheme 1. Direct oxidative C–N bond formation between arenes and a free NH_2-moiety

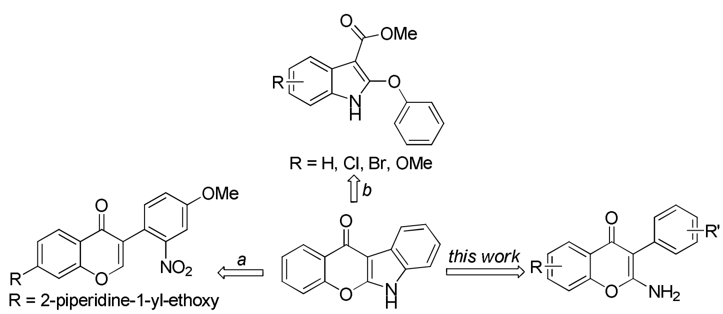


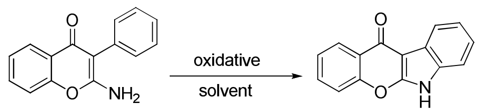
Figure 1. Known synthetic routes to chromeno[2,3-*b*]indol-11(6*H*)-ones

In this note, we report a new application of the protocol that we developed in our previous work, which gave rise to an alternative approach to forming a class of biologically meaningful compounds, namely, chromeno[2,3-*b*]indol-11(6*H*)-ones.

Even though the chromeno[2,3-*b*]indol-11(6*H*)-one skeleton has been identified as a key intermediate in the synthesis of the chromeno[2,3-*b*]indole derivatives, which have shown potent antitumor activities,[5] only a few synthetic approaches have been reported until just about a decade ago. Löwe and co-workers found that these compounds could be obtained from reduction of 7-(2-piperidin-1-ylethoxy)-isoflavone derivatives with zinc dust in acetic acid followed by oxidation with oxygen (Figure. 1, path ***a***).[6] Bergman *et al* reported the building of this skeleton through cyclization of 2-phenoxyindole-3-carboxylates, made available from the coupling of indole-3-carboxylate and phenols (Figure. 1, path ***b***).[7-9] Our work reported here adds to the list of methods.

2-Amino-3-phenyl-4*H*-chromen-4-one, readily prepared via condensation of benzyl cyanide with methyl salicylate,[10] was chosen as the model substrate to probe the feasibility of the proposed conversion. By applying the conditions developed in our previous work, substrate **1a** was successfully converted to the desired chromeno[2,3-*b*]indol-11(6*H*)-one **2a**, albeit in a mere 13% of yield (Table 1, entry 1).

Table 1. Optimization of reaction conditions for the synthesis of chromeno[2,3-*b*] indol-11(6*H*)-one[a]



1a **2a**

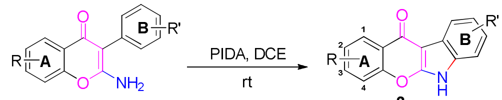
Entry	Oxidant (1.0 equiv)	Solvent	T (° C)	Additive (equiv)	Time (h)	Yield (%)[b]
1	PIFA	DCE	rt	none	4	13
2	PIDA	DCE	rt	none	4	87
3	IBX	EtOAc	rt - reflux	none	24	NR[c]
4	DMP	DCE	rt - reflux	none	24	NR
5	PIDA	CH_3CN	rt	none	4	64
6	PIDA	TFE	rt	none	4	45
7	PIDA	DCE	60	none	3	68
8	PIDA	DCE	0	none	72	81
9[d]	PIDA	DCE	rt	none	4	85
10	PIDA	DCE	rt	$BF_3 \cdot Et_2O$ (0.1)	24	61
11	PIDA	DCE	rt	Na_2CO_3 (1.0)	24	67

[a] Concentrations of **1a** were 0.1 mol/L unless otherwise stated. [b] Isolated yields. [c] No reaction occurred. [d] The concentration of **1a** was 0.01 mol/L.

At the switching of PIFA to the less potent PIDA, another commonly used hypervalent iodine(III) oxidant, we were pleased to witness a near-complete conversion of **1a** into **2a** within 4 h with a 87% yield in 1,2-dichloroethane as solvent (Table 1, entries 2–6). When the reaction was allowed to take place at 60 °C, it took shorter time to completion, but accompanied by a much lower yield of 68%, due to the formation of more byproducts (Table 1, entry 7). On the other hand, lowering reaction temperature to 0 ^{o}C rendered the reaction very sluggish and eventually it took 72 h for the reaction to go completion (Table 1, entry 8). Further study showed that when **1a** was diluted from 0.10 mol/L (supersaturated solution) to 0.01 mol/L, the yield of the product **2a** was insignificantly affected (Table 1, entry 9). Attempts to further improve the yield by adding additives such as $BF_3{\cdot}Et_2O$ or Na_2CO_3 were shown to be unsuccessful (Table 1, entries 10 and 11).

To explore the scope and limitation of this newly developed method, various substituted 2-amino-3-phenyl-4*H*-chromen-4-ones were examined under the optimized reaction conditions. As shown in Table 2, a wide range of substituents on either of the two phenyl rings could be well tolerated for the application of the method. Concerning the substituent effect of R′ (Table 2, entries 2–9), the electron-withdrawing halogen groups at the *para*-position gave the expected product in good to excellent yields (Table 2, entries 2, 4, and 6). The low yields of 38% and 45% (Table 2, entries 3 and 9) from the *ortho*-substituted R′, be it electron-withdrawing or electron-donating, could be ascribed to the steric repulsion of the *ortho*-substituent and the reduced number of available coupling carbon atoms. Yields from substrates bearing an electron-donating substituent, R′ = OMe, at either *para* or *meta* position, were reasonably high (Table 2, entries 7 and 8), with the latter giving two separable regioisomeric products (**2h:2h′** in a ratio of 1:3) (Table 2, entry 8). It is worth noting that only one regioisomeric product **2e** was isolated by filtration from the reaction of the *meta*-substituted substrate **1e**, with R′ = Cl (Table 2, entry 5), although crude ^{1}H NMR analysis showed that the other regioisomeric product **2e′** was also formed. Studies on the substituent effect of R on the reaction show very minor impact on the yield. To our delight, all substrates with the various substituents on the A ring are extremely well tolerated and the cyclized products were obtained in consistently high yields, including that where the A ring was switched to naphthalene (Table 2, entries 10–15). Yield values from doubly substituted substrates shadow the observations of the substitution effect of R and R′, such that the extent of influence of R is small (Table 2, entries 16–18). In these reactions except entries 5 and 8, no column chromatography was needed during the workup, as the desired product could be obtained by simple filtrations.

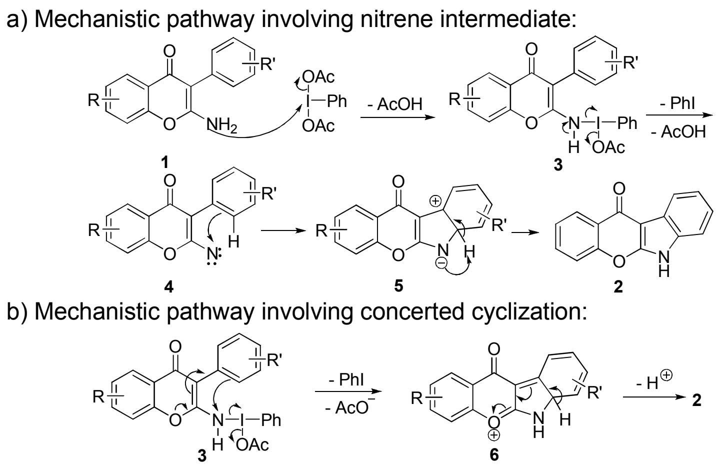
Table 2. Synthesis of chromeno[2,3-*b*]indol-11(6*H*)-ones mediated by PIDA[a]



Entry	Substrate	Product	Time (h)	Yield (%)[b]	Entry	Substrate	Product	Time (h)	Yield (%)
1	1a	2a	4	87%	10	1j	2j	36	80%
2	1b	2b	24	89%	11	1k	2k	6	80%
3	1c	2c	120	38%[c]	12	1l	2l	3	86%
4	1d	2d	24	92%	13	1m	2m	24	99%
5	1e	2e: R^1= H, R^2= Cl; 2e': R^1= Cl, R^2= H	4	50%[d]	14	1n	2n	24	79%
6	1f	2f	4	65%	15	1o	2o	14	95%
7	1g	2g	5	69%	16	1p	2p	12	86%
8	1h	2h: R^1= OMe, R^2= H; 2h': R^1= H, R^2= OMe	4	76%[e]	17	1q	2q	48	88%
9	1i	2i	6	48%[c]	18	1r	2r	14	43%

[a] General conditions: 1 (1.0 equiv), PIDA (1.0 equiv) in DCE at rt. [b] Isolated yield unless otherwise stated. [c] Some unidentified byproducts were formed. [d] Overall yield of two regioisomeric products, **2e**/**2e'** = 3:1. [e] Overall yield of two regioisomeric products, **2h**/**2h'** = 1:3.

Two mechanistic pathways were possible for this transformation. As shown in Scheme 2, path a, the intermolecular reaction of enamine **1** and PIDA generated the *N*-iodo intermediate **3** after losing one molecule of acetic acid. Afterwards, the nitrene intermediate **4**, formed through cleavage of the N–I bond at the release of a molecule of PhI and acetic acid, was inserted into the aromatic ring through electrophilic substitution reaction, and led to the final product **2**. Alternatively, the *N*-iodo intermediate **3** might undergo a concerted cyclization process to give oxonium ion **6**, with the release of a molecule of PhI and acetic acid. Finally, rearomatizaiton of **6** by loss of a proton would give the compound **2**. In order to testify which pathway is more preferable, we carried out a control experiment and found that the reaction was inhibited by the presence of the radical inhibitor, i.e., TEMPO. This result might suggest that the reaction proceeds via a non-ionic mechanism.



Scheme 2. Proposed Mechanism

Conclusion

In summary, we have developed a novel method for the synthesis of biologically important chromeno[2,3-*b*]indol-11(6*H*)-one derivatives from enamines, mediated by the hypervalent iodine(III) reagents. Other than the metal-free advantage, the reported method also bears desirable features such as the readily availability of the substrates, mild reaction conditions and remarkably simple workup procedure.

Experimental Section

I. General Information ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz or

600 MHz (100 MHz or 150 MHz for ^{13}C NMR) spectrometer at 25 °C. Chemical shift values are given in ppm and referred as the internal standard to TMS (tetramethylsilane). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; dd, doublet of doublets and br s, broad singlet. The coupling constants (*J*) are reported in Hertz (Hz). High resolution mass spectrometry (HRMS) was obtained on a Q-TOF microspectrometer. Melting points were determined with a micromelting point apparatus without corrections. Infrared spectra were measured on a FT/IR instrument. Tetrahydrofuran (THF), 1,1-dichloroethane (DCE) and *N*,*N*-dimethylformamide (DMF) were dried by CaH_2 before use.

II. Preparation of 2-Amino-3-phenyl-4*H*-chromen-4-ones 1. General procedure:[10] To a suspension of 60% sodium hydride (40 mmol, 4.0 equiv) in THF (30 mL) was added methyl salicylate (11 mmol, 1.1 equiv) and benzyl cyanide (10 mmol, 1.0 equiv). The mixture was stirred at 60 °C until TLC indicated the total consumption of the benzyl cyanide. After cooling, hydrochloric acid (2 N, 20 mL) was added, and the formed precipitate was filtered and washed with EtOAc (3 × 30 mL), air dried.

Following general procedure, 2-amino-3-phenyl-4*H*-chromen-4-ones **1** were prepared in 7% - 90% yields. The spectral and physical data of known **1a, 1d, 1g, 1p, 1r** were reported in the published literature.[10] The novel 2-amino-3-phenyl-4*H*-chromen-4-ones were characterized as follows:

2-Amino-3-(4-fluorophenyl)-4*H*-chromen-4-one (1b). Following the general procedure for 4 h, **1b** was isolated as a white solid. Yield: 1.38 g, 54%, mp 244–246 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.96 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.67 – 7.62 (m, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.22 (t, *J* = 9.0 Hz, 2H), 7.18 (s, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 172.5, 162.3, 161.1 (d, *J* = 241.1 Hz), 152.5, 133.2 (d, *J* = 8.0 Hz), 132.2, 129.4 (d, *J* = 3.0 Hz), 125.1, 124.4, 122.7, 116.3, 115.1 (d, *J* = 21.0 Hz), 97.9. HRMS (ESI) calcd for $C_{15}H_{11}FNO_2^+$ [M + H$^+$] 256.0768, found 256.0770. IR (KBr, neat) 3279, 3009, 1642, 1603, 1536, 1510, 1451, 1282, 1220, 753 cm^{-1}.

2-Amino-3-(2-fluorophenyl)-4*H*-chromen-4-one (1c). Following the general procedure for 2 h, **1c** was isolated as a white solid. Yield: 1.82 g, 71%, mp 204–206 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.49 – 7.35 (m, 3H), 7.35 – 7.27 (m, 3H), 7.24 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 172.3, 162.1, 160.7 (d, *J* = 243.3 Hz), 152. 7, 133.9 (d, *J* = 3.5 Hz), 132.3, 129.3 (d, *J* = 8.1 Hz), 125.1, 124.5, 124.3 (d, J = 3.0 Hz), 122.4, 120.6 (d, *J* = 16.5 Hz), 116.4, 115.6 (d, *J* = 22.1 Hz), 92.9. HRMS (ESI) calcd for $C_{15}H_{11}FNO_2^+$ [M + H$^+$] 256.0768, found 256.0772. IR (KBr, neat) 3470, 3117, 1649, 1602, 1578, 1540, 1494, 1293, 752 cm^{-1}.

2-Amino-3-(3-chlorophenyl)-4*H*-chromen-4-one (1e). Following the general procedure for 4 h, **1e** was isolated as a light gray solid. Yield: 1.64 g, 60%, mp 238–240 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.97 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.36 (s, 2H), 7.34 (s, 2H), 7.29 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 172.3, 162.2, 152.5, 135.5, 132.7, 132.3, 131.1, 130.0, 129.9, 126.6, 125.1, 124.4, 122.6, 116.4, 97.7.

HRMS (ESI) calcd for $C_{15}H_{11}{}^{35}ClNO_2^+$ [M + H$^+$] 272.0473, found 272.0476. IR (KBr, neat) 3298, 3141, 1634, 1605, 1568, 1536, 1486, 1461, 1410, 750, 679 cm^{-1}.

2-Amino-3-(4-bromophenyl)-4*H*-chromen-4-one (1f). Following the general procedure for 6 h, **1f** was isolated as a light gray solid. Yield: 1.30 g, 41%, mp 272–274 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.97 (d, *J* = 7.2 Hz, 1H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.44 – 7.35 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 4H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 172.3, 162.1, 152.5, 133.4, 132.6, 132.2, 131.2, 125.1, 124.4, 122.6, 119.8, 116.3, 97.7. HRMS (ESI) calcd for $C_{15}H_{11}{}^{79}BrNO_2^+$ [M + H$^+$] 315.9968, found 315.9966. IR (KBr, neat) 3284, 3108, 1641, 1603, 1533, 1492, 1460, 1448, 1004, 753 cm^{-1}.

2-Amino-3-(3-methoxyphenyl)-4*H*-chromen-4-one (1h). Following the general procedure for 4 h, **1h** was isolated as a light yellow solid. Yield: 0.80 g, 30%, mp 180–182 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.97 (d, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.38 (dd, *J* = 18.0, 8.1 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.18 (s, 2H), 6.93 – 6.83 (m, 3H), 3.77 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 172.4, 162.1, 159.2, 152.5, 134.5, 132.1, 129.2, 125.2, 124.3, 123.4, 122.8, 116.5, 116.3, 112.4, 98.8, 54.8. HRMS (ESI) calcd for $C_{16}H_{14}NO_3^+$ [M + H$^+$] 268.0968, found 268.0968. IR (KBr, neat) 3430, 3060, 1649, 1608, 1537, 1489, 1462, 1413, 1033, 754, 702 cm^{-1}.

2-Amino-3-(o-tolyl)-4*H*-chromen-4-one (1i). Following the general procedure for 2 h, **1i** was isolated as a white solid. Yield: 0.70 g, 28%, mp 192–194 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.19 (d, *J* = 6.4 Hz, 1H), 7.17 – 7.08 (m, 3H), 5.11

(s, 2H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 161.7, 153.3, 139.0, 132.0, 131.8, 131.5, 130.5, 128.3, 126.4, 126.0, 124.5, 123.1, 116.5, 100.0, 19.4. HRMS (ESI) calcd for $C_{16}H_{14}NO_2^+$ [M + H$^+$] 252.1019, found 252.1015. IR (KBr, neat) 3465, 3130, 1638, 1602, 1574, 1533, 1475, 1442, 764, 751 cm^{-1}.

2-Amino-7-fluoro-3-phenyl-4*H*-chromen-4-one (1j). Following the general procedure for 4 h, **1j** was isolated as a light yellow solid. Yield: 0.59 g, 23%, mp 232–234 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.02 (t, J = 6.9 Hz, 1H), 7.43 (t, J = 6.9 Hz, 2H), 7.37 – 7.29 (m, 4H), 7.25 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 172.3, 164.3 (d, J = 247.4 Hz), 162.9, 153.8 (d, J = 13.4 Hz), 133.4, 131.6, 128.8, 128.1 (d, J = 10.4 Hz), 127.2, 120.3, 112.9 (d, J = 22.1 Hz), 104.0 (d, J = 25.7 Hz), 98.9. HRMS (ESI) calcd for $C_{15}H_{11}FNO_2^+$ [M + H$^+$] 256.0768, found 256.0772. IR (KBr, neat) 3279, 3108, 1644, 1619, 1533, 1493, 1451, 1437, 1148, 844, 689 cm^{-1}.

2-Amino-5-chloro-3-phenyl-4*H*-chromen-4-one (1k). Following the general procedure for 4 h, **1k** was isolated as a light yellow solid. Yield: 0.46 g, 17%, mp 235–237 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.56 (t, J = 8.4 Hz, 1H), 7.41 (t, J = 7.2 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.30 (dd, J = 13.8, 7.2 Hz, 3H), 7.10 (s, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 171.6, 160.8, 154.3, 133.0, 131.8, 131.7, 131.2, 128.3, 127.5, 126.7, 119.2, 116.2, 99.6. HRMS (ESI) calcd for $C_{15}H_{11}{}^{35}ClNO_2^+$ [M + H$^+$] 272.0473, found 272.0471. IR (KBr, neat) 3311, 3142, 1640, 1593, 1534, 1498, 1457, 1434, 928 cm^{-1}.

2-Amino-7-bromo-3-phenyl-4*H*-chromen-4-one (1l). Following the general procedure for 4 h, **1l** was isolated as a white solid. Yield: 1.08 g, 34%, mp > 300 ºC;

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.01 (s, 1H), 7.79 (d, *J* = 9.0 Hz, 1H), 7.45 – 7.38 (m, 3H), 7.37 – 7.28 (m, 5H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 170.9, 162.3, 151.4, 134.6, 132.8, 131.1, 128.3, 127.3, 126.8, 124.6, 119.0, 116.6, 98.9. HRMS (ESI) calcd for $C_{15}H_{11}{}^{79}BrNO_2^+$ [M + H$^+$] 315.9968, found 315.9962. IR (KBr, neat) 3473, 3104, 1634, 1595, 1585, 1523, 1494, 1460, 1434, 1270, 810 cm^{-1}.

2-Amino-7-(benzyloxy)-3-phenyl-4*H*-chromen-4-one (1m). Following the general procedure for 3 h, **1m** was isolated as a light gray solid. Yield: 3.10 g, 90%, mp 252–254 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.87 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 7.2 Hz, 2H), 7.45 – 7.38 (m, 4H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.29 (dd, *J* = 14.7, 7.2 Hz, 3H), 7.07 – 6.97 (m, 3H), 6.93 (d, *J* = 1.2 Hz, 1H), 5.25 (s, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 172.4, 162.0, 161.3, 153.8, 136.4, 133.3, 131.2, 128.5, 128.2, 128.0, 127.8, 126.5, 126.5, 116.4, 113.1, 100.8, 98.1, 69.8. HRMS (ESI) calcd for $C_{22}H_{18}NO_3^+$ [M + H$^+$] 344.1281, found 344.1284. IR (KBr, neat) 3490, 3089, 1637, 1606, 1587, 1529, 1494, 1460, 1421, 1259, 1183, 1022, 774, 742, 701 cm^{-1}.

2-Amino-8-methyl-3-phenyl-4*H*-chromen-4-one (1n). Following the general procedure for 4 h, **1n** was isolated as a white solid. Yield: 1.24 g, 49%, mp 276-278 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.79 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.31 (dd, *J* = 20.1, 7.6 Hz, 3H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.13 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 172.8, 161.9, 150.8, 133.3, 132.9, 131.1, 128.3, 126.6, 125.4, 123.7, 122.7, 122.6, 98.6, 14.7. HRMS (ESI) calcd for $C_{16}H_{14}NO_2^+$ [M + H$^+$] 252.1019, found 252.1026. IR (KBr, neat) 3477, 3166, 1635, 1606, 1574, 1536, 1496, 1454, 1434, 764 cm^{-1}.

2-Amino-3-phenyl-4*H*-benzo[*g*]chromen-4-one (1o). Following the general procedure for 3 h, **1o** was isolated as a light gray solid. Yield: 1.64 g, 57%, mp 296–298 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.62 (s, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.93 (s, 1H), 7.63 (t, *J* = 6.9 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.41 – 7.28 (m, 5H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 172.5, 162.7, 149.6, 134.5, 133.4, 131.3, 129.7, 129.1, 128.3, 127.9, 127.2, 126.6, 125.6, 125.5, 122.4, 112.1, 98.1. HRMS (ESI) calcd for $C_{19}H_{14}NO_2^+$ [M + H$^+$] 288.1019, found 288.1019. IR (KBr, neat) 3477, 3109, 1629, 1608, 1586, 1551, 1536, 1468, 1447, 1429, 746 cm^{-1}.

2-Amino-3-(4-chlorophenyl)-8-methyl-4*H*-chromen-4-one (1q). Following the general procedure for 5 h, **1q** was isolated as a white solid. Yield: 1.58 g, 55%, mp 300-302 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.78 (d, *J* = 7.2 Hz, 1H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 2.43 (s, 3H). Unfortunately, the poor solubility of **1q** prevented ^{13}C NMR characterization. HRMS (ESI) calcd for $C_{16}H_{13}{}^{35}ClNO_2^+$ [M + H$^+$] 286.0629, found 286.0633. IR (KBr, neat) 3495, 3143, 1637, 1606, 1575, 1535, 1494, 1450, 1428, 758 cm^{-1}.

III. Preparation of Chromeno[2,3-*b*]indol-11(6*H*)-ones 2. General procedure: To a suspension of 2-amino-3-phenyl-4*H*-chromen-4-one **1** (1.0 mmol, 1.0 equiv) in DCE (10 mL) was added PIDA (1.0 mmol, 1.0 equiv). The mixture was stirred at room temperature until TLC indicated the total consumption of the 2-amino-3-phenyl-4*H*-chromen-4-one. Then the formed precipitate was filtered, washed with MeOH (3 × 30 mL), and air dried.

2h and **2h′** were separated by silica gel (200−300 mesh) column chromatography using a mixture of DCM and MeOH (98/3, v/v) as eluent.

The ratio of **2e** and **2e′** was calculated by ^{1}H NMR analysis.

The spectral and physical data of known 3-bromochromeno[2,3-*b*]indol-11(6*H*)-one **2l** was reported in the published literature.[5]

Chromeno[2,3-*b*]indol-11(6*H*)-one (2a). Following the general procedure for 4 h, **2a** was isolated as a white solid. Yield: 205 mg, 87%, mp > 300 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.88 (s, 1H), 8.26 (d, *J* = 7.8 Hz, 1H), 8.12 (d, *J* = 7.8 Hz, 1H), 7.81 (t, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 171.5, 156.2, 153.6, 132.7, 132.4, 125.5, 124.8, 123.5, 123.5, 122.1, 121.8, 120.4, 117.6, 112.0, 98.8. HRMS (ESI) calcd for $C_{15}H_{10}NO_2^+$ [M + H$^+$] 236.0706, found 236.0708. IR (KBr, neat) 3026, 1622, 1604, 1590, 1551, 1522, 1200, 876, 829, 757, 736 cm^{-1}.

8-Fluorochromeno[2,3-*b*]indol-11(6*H*)-one (2b). Following the general procedure for 24 h, **2b** was isolated as a light gray solid. Yield: 226 mg, 89%, mp > 300 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.06 (s, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 8.08 (dd, *J* = 8.7, 5.7 Hz, 1H), 7.81 (t, *J* = 7.2 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.33 (dd, *J* = 9.6, 1.8 Hz, 1H), 7.21 – 7.10 (m, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 171.5, δ 159.5 (d, *J* = 236.0 Hz), 156.1, 153.5, 133.0, 132.3 (d, *J* = 12.6

Hz), 125.5, 125.0, 123.4, 121.5 (d, *J* = 10.1 Hz), 118.4, 117.8, 109.8 (d, *J* = 23.4 Hz), 98.9 (d, *J* = 26.6 Hz), 98.50. HRMS (ESI) calcd for $C_{15}H_9FNO_2^+$ [M + H$^+$] 254.0612, found 254.0619. IR (KBr, neat) 2993, 2841, 1626, 1605, 1557, 1524, 1505, 1198, 1130, 755 cm^{-1}.

10-Fluorochromeno[2,3-*b*]indol-11(6*H*)-one (2c). Following the general procedure for 120 h, **2c** was isolated as a white solid. Yield: 97 mg, 38%, mp > 300 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.23 (s, 1H), 8.26 (d, *J* = 7.8 Hz, 1H), 7.81 (t, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.33 (s, 2H), 7.10 – 7.03 (m, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 170.1, 155.7 (d, *J* = 248.7 Hz), 155.6, 153.2, 134.5 ((d, *J* = 11.0 Hz), 133.1, 125.9, 125.1, 124.8 (d, *J* = 7.4 Hz), 123.4, 117.5, 109.9 (d, *J* = 22.4 Hz), 108.1 (d, *J* = 3.5 Hz), 108.0 (d, *J* = 19.8 Hz), 97.5 (d, *J* = 5.6 Hz). HRMS (ESI) calcd for $C_{15}H_9FNO_2^+$ [M + H$^+$] 254.0612, found 254.0615. IR (KBr, neat) 3041, 1626, 1607, 1594, 1555, 1509, 1458, 787, 750 cm^{-1}.

8-Chlorochromeno[2,3-*b*]indol-11(6*H*)-one (2d). Following the general procedure for 24 h, **2d** was isolated as a light gray solid. Yield: 249 mg, 92%, mp > 300 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.12 (s, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 7.2 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.49 (m, 2H), 7.34 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 171.6, 156.2, 153.6, 133.1, 132.6, 127.8, 125.6, 125.2, 123.3, 122.3, 121.6, 120.7, 117.8, 111.8, 98.6. HRMS (ESI) calcd for $C_{15}H_9{}^{35}ClNO_2^+$ [M + H$^+$] 270.0316, found 270.0323. IR (KBr, neat) 2997, 1625, 1607, 1582, 1551, 1524, 1342, 1195, 1062, 883, 751, 740 cm^{-1}.

9-Chlorochromeno[2,3-*b*]indol-11(6*H*)-one (2e). Following the general procedure for 4 h, **2e** was isolated as a white solid. Yield: 89 mg, 33%, mp > 300 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.09 (s, 1H), 8.25 (d, *J* = 7.2 Hz, 1H), 8.04 (s, 1H), 7.82 (t, *J* = 7.5 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.48 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 1H). Unfortunately, the poor solubility of **2e** prevented ^{13}C NMR characterization. HRMS (ESI) calcd for $C_{15}H_9{}^{35}ClNO_2^+$ [M + H$^+$] 270.0316, found 270.0321. IR (KBr, neat) 3045, 1633, 1607, 1584, 1554, 1526, 1456, 1196, 754 cm^{-1}.

8-Bromochromeno[2,3-*b*]indol-11(6*H*)-one (2f). Following the general procedure for 4 h, **2f** was isolated as a light gray solid. Yield: 205 mg, 65%, mp > 300 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.12 (s, 1H), 8.25 (d, *J* = 7.2 Hz, 1H), 8.03 (d, *J* = 7.2 Hz, 1H), 7.82 (d, *J* = 6.6 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.68 (s, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 171.7, 156.1, 153.6, 133.1, 132.9, 125.6, 125.2, 124.9, 123.3, 122.0, 121.0, 117.8, 115.7, 114.5, 98.6. HRMS (ESI) calcd for $C_{15}H_9{}^{79}BrNO_2^+$ [M + H$^+$] 313.9811, found 313.9811. IR (KBr, neat) 2993, 1623, 1607, 1579, 1550, 1524, 1195, 882, 749, 738 cm^{-1}.

8-Methoxychromeno[2,3-*b*]indol-11(6*H*)-one (2g). Following the general procedure for 5 h, **2g** was isolated as a light gray solid. Yield: 184 mg, 69%, mp > 300 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.75 (s, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.82 – 7.76 (m, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 1.8 Hz, 1H), 6.93 (dd, *J* = 8.4, 1.8 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 171.2, 156.9, 155.5, 153.4, 133.0, 132.6, 125.5, 124.9, 123.5, 121.2, 117.6, 115.4, 110.4, 98.8, 96.3, 55.4. HRMS (ESI) calcd for $C_{16}H_{12}NO_3^+$ [M + H$^+$] 266.0812, found 266.0809. IR (KBr, neat) 2998, 1626, 1604, 1554, 1524, 1509, 1195, 1151, 1101, 784, 755 cm^{-1}.

7-Methoxychromeno[2,3-*b*]indol-11(6*H*)-one (2h). Following the general procedure for 4 h, **2h** was isolated as a white solid. Yield: 51 mg, 19%, mp > 300 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.10 (s, 1H), 8.25 (d, *J* = 7.2 Hz, 1H), 7.84 – 7.77 (m, 1H), 7.72 (dd, *J* = 15.6, 7.8 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 3.98 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 171.8, 155.4, 153.6, 145.8, 133.0, 125.6, 124.9, 123.4, 123.1, 122.8, 121.2, 117.7, 113.0, 105.3, 99.2, 55.5. HRMS (ESI) calcd for $C_{16}H_{12}NO_3^+$ [M + H$^+$] 266.0812, found 266.0806. IR (KBr, neat) 3422, 3117, 1623, 1609, 1545, 1525, 1505, 1214, 1026, 1004 cm^{-1}.

9-Methoxychromeno[2,3-*b*]indol-11(6*H*)-one (2h′). Following the general procedure for 4 h, **2h′** was isolated as a white solid. Yield: 152 mg, 57%, the yield ratio of 2h and 2h' is 1:3,mp > 300 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.78 (s, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.80 (t, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.63 (s, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 9.0 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 171.6, 155.7, 155.3, 153.5, 132.9, 126.2, 125.5, 124.9, 123.3, 122.6, 117.7, 112.6, 112.2, 103.3, 98.9, 55.4. HRMS (ESI) calcd for $C_{16}H_{12}NO_3^+$ [M + H$^+$] 266.0812, found 266.0810. IR (KBr, neat) 3019, 2955, 1623, 1606, 1558, 1524, 1479, 1204, 839, 755, 729 cm^{-1}.

10-Methylchromeno[2,3-*b*]indol-11(6*H*)-one (2i). Following the general procedure for 6 h, **2i** was isolated as a white solid. Yield: 120 mg, 48%, mp > 300 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.90 (s, 1H), 8.26 (d, *J* = 7.2 Hz, 1H), 7.79 (t, *J* =

7.2 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 3.03 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 170.9, 155.9, 152.8, 132.8, 132.3, 131.8, 126.1, 124.8, 124.0, 123.6, 123.5, 121.7, 117.2, 109.0, 99.6, 22.2. HRMS (ESI) calcd for $C_{16}H_{12}NO_2^+$ [M + H$^+$] 250.0863, found 250.0863. IR (KBr, neat) 3035, 1629, 1608, 1578, 1551, 1518, 1501, 1458, 748 cm^{-1}.

3-Fluorochromeno[2,3-*b*]indol-11(6*H*)-one (2j). Following the general procedure for 36 h, **2j** was isolated as a light gray solid. Yield: 203 mg, 80%, mp > 300 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.99 (s, 1H), 8.29 (dd, *J* = 8.7, 6.9 Hz, 1H), 8.10 (d, *J* = 7.2 Hz, 1H), 7.79 – 7.72 (m, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.42 (td, *J* = 8.4, 1.8 Hz, 1H), 7.33 (dt, *J* = 24.6, 7.2 Hz, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 170.9, 164.1 (d, *J* = 248.6 Hz), 155.9, 154.4 (d, *J* = 12.0 Hz), 131.8, 127.9 (d, *J* = 10.5 Hz), 123.8, 122.1, 121.7, 120.5, 120.4, 113.1 (d, *J* = 21.9 Hz), 111.9, 105.0 (d, *J* = 25.7 Hz), 98.6. HRMS (ESI) calcd for $C_{15}H_9FNO_2^+$ [M + H$^+$] 254.0612, found 254.0611. IR (KBr, neat) 3021, 1636, 1608, 1589, 1558, 1524, 1489, 1458, 1255, 784, 774, 741 cm^{-1}.

1-Chlorochromeno[2,3-*b*]indol-11(6*H*)-one (2k). Following the general procedure for 6 h, **2k** was isolated as a gray solid. Yield: 217 mg, 80%, mp > 300 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.86 (s, 1H), 8.12 (d, *J* = 7.2 Hz, 1H), 7.76 – 7.67 (m, 2H), 7.57 – 7.45 (m, 2H), 7.38 – 7.26 (m, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 170.8, 155.4, 154.4, 132.5, 132.3, 131.9, 128.2, 123.7, 122.0, 121.9, 120.3, 120.0, 117.6, 111.8, 99.3. HRMS (ESI) calcd for $C_{15}H_9{}^{35}ClNO_2^+$ [M + H$^+$] 270.0316, found 270.0324. IR (KBr, neat) 3080, 1625, 1592, 1525, 1231, 932, 869, 800, 748 cm^{-1}.

2-Bromochromeno[2,3-*b*]indol-11(6*H*)-one (2l). Following the general procedure for 3 h, **2l** was isolated as a white solid. Yield: 271 mg, 86%, mp > 300 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.03 (s, 1H), 8.29 (d, *J* = 2.4 Hz, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.96 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H).

3-(Benzyloxy)chromeno[2,3-*b*]indol-11(6*H*)-one (2m). Following the general procedure for 24 h, **2m** was isolated as a light gray solid. Yield: 339 mg, 99%, mp > 300 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.85 (s, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 7.2 Hz, 1H), 7.56 – 7.47 (m, 3H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.41 – 7.26 (m, 4H), 7.19 (d, *J* = 8.4 Hz, 1H), 5.29 (s, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 171.5, 161.9, 155.7, 155.0, 136.2, 131.7, 128.5, 128.1, 127.9, 126.8, 123.4, 121.9, 121.9, 120.3, 117.1, 113.7, 111.7, 102.1, 98.3, 70.0. HRMS (ESI) calcd for $C_{22}H_{16}NO_3^+$ [M + H$^+$] 342.1125, found 342.1127. IR (KBr, neat) 3033, 1605, 1551, 1520, 1492, 1460, 1262, 1233, 740 cm^{-1}.

4-Methylchromeno[2,3-*b*]indol-11(6*H*)-one (2n). Following the general procedure for 24 h, **2n** was isolated as a light gray solid. Yield: 198 mg, 79%, mp > 300 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.96 (s, 1H), 8.14 – 8.06 (m, 2H), 7.65 (d, *J* = 6.6 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.31 (dt, *J* = 22.8, 7.2 Hz, 2H), 2.56 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 171.9, 155.7, 152.0, 133.8, 131.9, 126.6, 124.3, 123.6, 123.3, 123.2, 121.9, 121.8, 120.4, 111.8, 98.5, 15.4. HRMS (ESI) calcd for $C_{16}H_{12}NO_2^+$ [M + H$^+$] 250.0863, found 250.0867. IR (KBr, neat) 3004, 1617, 1853, 1555, 1523, 1486, 1478, 1344, 849 cm^{-1}.

Benzo[6,7]chromeno[2,3-*b*]indol-13(5*H*)-one (2o). Following the general procedure for 14 h, **2o** was isolated as a light gray solid. Yield: 272 mg, 95%, mp > 300 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.99 (s, 1H), 8.91 (s, 1H), 8.30 (d, *J* = 9.0 Hz, 2H), 8.14 (d, *J* = 7.2 Hz, 2H), 7.77 – 7.67 (m, 1H), 7.67 – 7.59 (m, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.39 – 7.27 (m, 2H). Unfortunately, the poor solubility of **2o** prevented ^{13}C NMR characterization. HRMS (ESI) calcd for $C_{19}H_{12}NO_2^+$ [M + H$^+$] 286.0863, found 286.0862. IR (KBr, neat) 3047, 1646, 1613, 1589, 1560, 1531, 1196, 1096, 838, 788, 763 cm^{-1}.

8-Chloro-3-methoxychromeno[2,3-*b*]indol-11(6*H*)-one (2p). Following the general procedure for 12 h, **2p** was isolated as a light gray solid. Yield: 259 mg, 86%, mp > 300 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.05 (s, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 1.2 Hz, 1H), 7.32 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.28 (d, *J* = 1.8 Hz, 1H), 7.12 (dd, *J* = 8.7, 2.1 Hz, 1H), 3.93 (s, 3H). Unfortunately, the poor solubility of **2p** prevented ^{13}C NMR characterization. HRMS (ESI) calcd for $C_{16}H_{11}{}^{35}ClNO_3^+$ [M + H$^+$] 300.0422, found 300.0421. IR (KBr, neat) 3064, 1630, 1605, 1578, 1543, 1520, 1486 1264, 1234 cm^{-1}.

8-Chloro-4-methylchromeno[2,3-*b*]indol-11(6*H*)-one (2q). Following the general procedure for 48 h, **2q** was isolated as a white solid. Yield: 251 mg, 88%, mp > 300 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.19 (s, 1H), 8.08 (t, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 1.2 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 7.2 Hz, 1H), 2.56 (s, 3H). Unfortunately, the poor solubility of **2q** prevented ^{13}C NMR characterization. HRMS (ESI) calcd for $C_{16}H_{11}{}^{35}ClNO_2^+$ [M + H$^+$] 284.0473, found

284.0471. IR (KBr, neat) 3065, 1619, 1587, 1556, 1524, 1226, 1187, 762, 746, 665 cm^{-1}.

3,8-Dimethoxychromeno[2,3-*b*]indol-11(6*H*)-one (2r). Following the general procedure for 14 h, **2r** was isolated as a gray solid. Yield: 127 mg, 43%, mp > 300 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.69 (s, 1H), 8.12 (d, *J* = 9.0 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.24 (s, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 6.99 (s, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 3.92 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 171.2, 162.7, 156.6, 155.3, 155.0, 132.8, 126.7, 121.0, 117.0, 115.4, 113.1, 110.4, 101.1, 98.3, 96.1, 56.0, 55.3. HRMS (ESI) calcd for $C_{17}H_{14}NO_4^+$ [M + H^+] 296.0917, found 296.0917. IR (KBr, neat) 3009, 2836, 1635, 1606, 1590, 1519, 1495, 1150, 1100, 825 cm^{-1}.

IV. Preparation of 6-methylchromeno[2,3-*b*]indol-11(6*H*)-one.[9] To a suspension of **2a** (1.0 mmol, 1.0 equiv) in DMF (5 mL) was added NaH (1.2 mmol, 1.2 equiv). The mixture was stirred at room temperature until TLC indicated the total consumption of **2a**. The reaction mixture was treated with water (50 mL), extracted with EtOAc (3 × 20 mL) and then washed with water (2 × 50 mL). The organic phase, after being dried over anhydrous Na_2SO_4, was evaporated under reduced pressure. The residue was purified by flash column chromatography (200−300 mesh silica gel, EtOAc/petroleum ether = 1/4, v/v) to give the desired product. White solid, yield: 237 mg, 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.39 – 8.31 (m, 1H), 7.68 – 7.62 (m, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.41 (m, 1H), 7.39 – 7.28 (m, 3H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 155.1, 153.8, 133.5, 132.3, 126.6, 125.0, 124.1, 123.8, 122.8, 121.9, 117.2, 108.9, 100.0, 99.4, 28.2.

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Supporting Information Available: Spectral data for all new compounds. The material is available free of charge via the Internet at http://pubs.acs.org.

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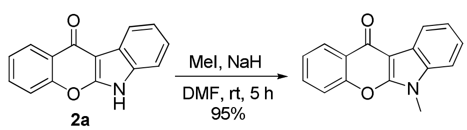
(9) In order to rule out the possibility that the reaction might give the angular isomer of **2a** as product, we prepared the methylated product of **2a** and got it compared with its corresponding angular isomer reported by You. The comparison results clearly indicated that they are not the same product. For You's work, see: Wu, J.; Lan, J.; Guo, S.; You, J. *Org. Lett*. **2014**, *16*, 5862−5865.



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