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Base-promoted synthesis of dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridines from 4-chloro-3-substituted coumarins and α-aminomaleimides†

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This paper describes the base-mediated cascade reactions of 4-chloro-3-substituted coumarins with α-aminomaleimides, allowing the efficient synthesis of dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridines with interesting chemoselectivity. These transformations include the domino-style formation of C–C/C–N bonds through a base-mediated nucleophilic substitution, Michael addition, *N*-cyclization, and elimination. The presented synthetic strategy has several advantages: it is simple, uses readily available starting materials and an environmentally friendly solvent, has a highly chemoselective route, and allows the purification of products *via* washing with EtOH (96%), a technique called GAP (Group-Assisted-Purification) chemistry.

Introduction

Maleimides, one of the five members of the family of N-heterocyclic pharmacophores with two carbonyl groups adjacent to the nitrogen atom, are useful building blocks for the synthesis of nitrogen-containing organic compounds. Maleimides also describes a *class* of derivatives of the parent maleimide where the N*H* group is replaced with alkyl or aryl groups such as a methyl or phenyl, respectively. The substituent can also be a small molecule (for example, biotin, a fluorescent dye, an oligosaccharide, or a nucleic acid).[1] These compounds exhibit a variety of interesting pharmaceutical properties, including antiepileptic (ethosuximide), anxiolytic and antidepressant (tandospirone), and antipsychotic (perospirone) properties.[2,3] Also, certain anti-inflammatory compounds contain these targeted heterocycles.[4] In addition, many *N*-substituted maleimides possess activities such as antitumor,[5] antiviral,[6] antimicrobial,[7] anti-fungal,[8] and insecticidal (larvicidal) activities. Maleimides are also important building blocks for the synthesis of high-performance polymers.[9] The most common representatives of this class of chemicals are α-aminomaleimides, which have become increasingly popular in organic synthesis. A notable characteristic of α-aminomaleimides is their highly polarized ethylene system in which electron-donating (amino group) and electron-withdrawing (two carbonyl groups) substituents are found on either end. Thus, reactions of α-aminomaleimides with diverse bis-electrophiles have been extensively studied as methods for constructing nitrogen-containing heterocycles or fused heterocycles. Among them, the syntheses of pyrrolo[3,4-*b*]pyridines,[10] trifluoromethylated pyrazol-4-yl-pyrrole-2,5-diones,[11] pyrrolo[3,4-*d*]tetrahydropyrimidine derivatives,[12] and pyrrolo[3,4-*b*]quinolones[13] are interesting examples. A special property of maleimides is their susceptibility to additions across the double bond *via* Michael additions[11,14] or Diels–Alder reactions.[15]

On the other hand, coumarin is considered a promising scaffold in medicinal and biological chemistry, because it is present as a part of the structure of the nucleus in many medicinally active organic substances.[16] Therefore, one of the most popular areas in synthetic organic chemistry is the development of effective methods for preparing molecules based on coumarin.[17–19]

The literature demonstrates that chromenopyridines and hetero-fused chromenopyridines are effective bioactive cores in diverse synthetic and natural compounds.

Some representative examples of the biological and photophysical properties of chromenopyridines and hetero-fused chromenopyridines are shown in Fig. 1. In a review, Núñez-Vergara and his colleagues have introduced chromenopyridines as privileged skeletons in medicinal and biological chemistry. They have fully described the processes involved in synthesizing these skeletons and their biological properties.[20] So far, many attempts have been made to synthesize hetero-fused chromenopyridines. For example, Magedov *et al.* have reported the synthesis of 2,3-dihydrochromeno[4,3-*d*]pyrazolo[3,4-*b*]pyridin-1,6-diones with antibacterial properties.[21] Similarly, Choudhury *et al.* have reported a three-component

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†Electronic supplementary information (ESI) available: Experimental and computational details; single crystal X-ray diffraction analysis; ^{1}H and ^{13}C NMR spectra. CCDC 2254629. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d3ob00632h

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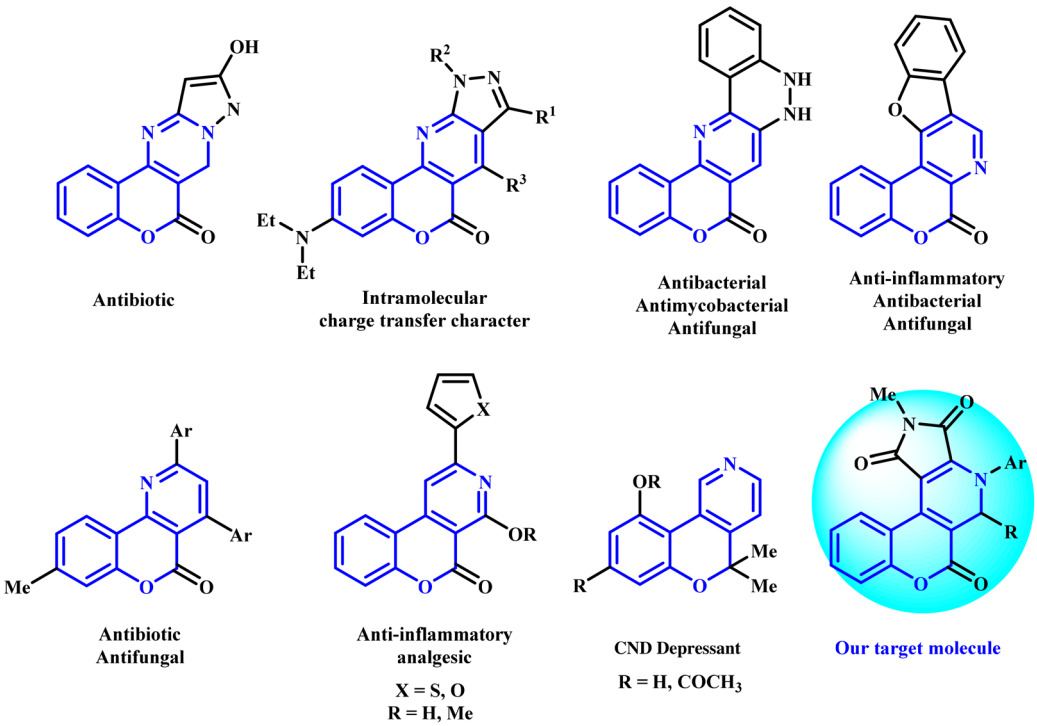

Fig. 1 Examples of biologically active chromenopyridines and hetero-fused chromenopyridines.

reaction for the synthesis of dihydrochromeno[4,3-*b*]pyrazolo[4,3-*e*]pyridin-6(7*H*)-ones using 4-hydroxycoumarin as the key starting material and using iodine as the catalyst.[22] Recently, we also reported the synthesis of dihydro-6*H*-chromeno[4,3-*d*]pyrazolo[1,5-*a*]pyrimidin-6-ones from the reaction of 4-chloro-3-vinyl coumarins and 3-amino pyrazoles under mild conditions with acceptable efficiency.[23] The possibility of a wide range of biological and physical properties makes chromenopyridines interesting synthetic targets.

As a result, the development of straightforward and flexible synthetic methods toward functionalized chromenopyridines has attracted much attention from organic chemists. Perhaps for this reason, it is necessary to develop new methods to increase the structural complexity while reducing the number of synthetic steps to facilitate the construction of new chromenopyridines.

However, there are no reports on the synthesis of tetracyclic dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine derivatives *via* reactions of α-aminomaleimides with 4-chloro-3-substituted coumarins. Herein, we envisioned that the chemical entity tetracyclic dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridines, with a hybrid structure involving chromone, pyridine, and maleimide motifs, may possess significant biological features.

Results and discussion

Recently, 4-chloro-3-substituted coumarins have been attracting the attention of organic chemists as the most reactive electrophiles and the most readily available starting materials for the synthesis of heterocyclic systems based on coumarins.[24] Our group has shown great interest in investigating multicomponent reactions using this targeted heterocycle. Using it, we produced new complex molecular scaffolds containing the coumarin skeleton.[25] Here, we turn our attention to the development of a two-component reaction using 4-chloro-3-formyl (3-vinyl)coumarins with α-aminomaleimides to access novel complex molecular scaffolds containing coumarin with potential bioactivity. In the beginning, α-aminomaleimide was prepared based on a known method.[12] Then, with our previous knowledge, we focused on the preparation of 4-chloro-3-vinyl coumarins **2** and 4-chloro-3-formyl coumarin **2′**.[23] α-Aminomaleimide **1** (1.0 equiv.) and 4-chloro-3-vinyl coumarin **2** or **2′** (1.0 equiv.) in the presence of 50 mol% triethylamine and ethanol as the solvent were stirred at 80 °C in an oil bath for more than 12 h. As a result, **3** or **3′** was formed as a red solid (41–92% yield) and filtered (Scheme 1).

After the confirmation of the structure of **3a**, we tried to find a suitable base and solvent for the model reaction. The results are summarized in Table 1. The reaction was studied in the presence of 10, 20, and 40 mol% of triethylamine as the base in ethanol and the yields obtained were 25, 40, and 60%, respectively (entries 1–3, Table 1).

After changing the ratio of triethylamine to 50 mol%, the yield of the pure product was increased to 88% in ethanol. In the next step, the influence of different bases on the reaction outcome was investigated. The yield of the reaction in the presence of DBU was 30%, which indicated no good signs of **3a** forming.

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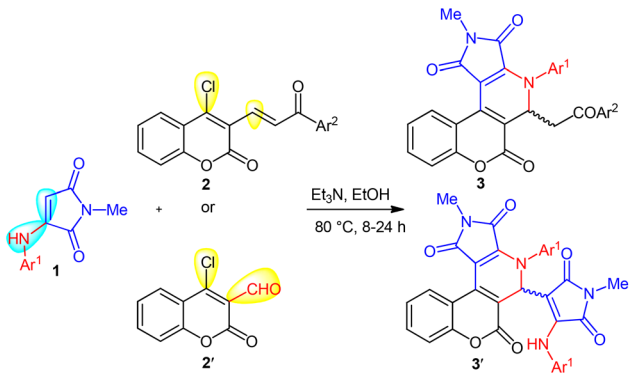
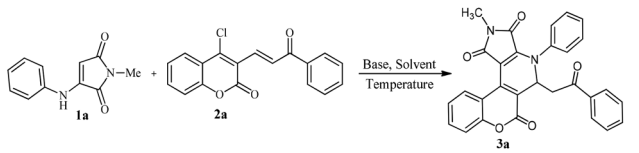


Scheme 1 One-pot synthesis of **3** and **3′**.

Table 1 Optimization of the reaction conditions for the formation of **3a** [a]

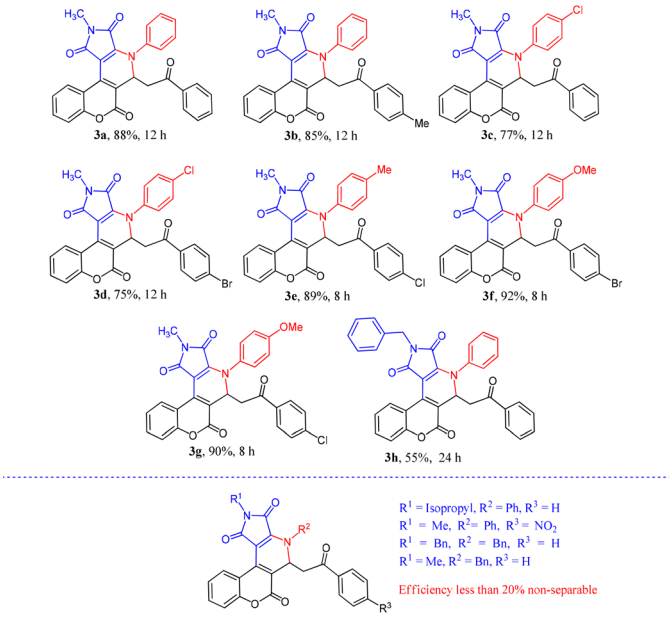


Entry	Base (mol%)	Solvent	Temp. (°C)	Time (h)	Yield[b] (%)
1	—	EtOH	80	24	>20
2	Et_3N (10%)	EtOH	80	24	25
3	Et_3N (20%)	EtOH	80	24	40
4	Et_3N (40%)	EtOH	80	12	60
5	**Et_3N (50%)**	**EtOH**	**80**	**12**	**88**
6	Et_3N (50%)	EtOH	25	24	30
7	DBU (50%)	EtOH	80	12	30
8	Piperidine (50%)	EtOH	80	12	n.r.[c]
9	Cs_2CO_3 (50%)	EtOH	80	12	50
10	K_2CO_3 (50%)	EtOH	80	12	40
11	Et_3N (50%)	MeOH	70	12	84
12	Et_3N (50%)	MeCN	80	12	65
13	Et_{3N} (50%)	DCM	25	24	50

[a] Reaction conditions: **1a** (202 mg, 1.0 mmol), **2a** (310 mg, 1.0 mmol), solvent (5 mL), and base were added to the reaction vessel under the mentioned conditions. [b] Isolated yields. [c] n.r., no reaction.

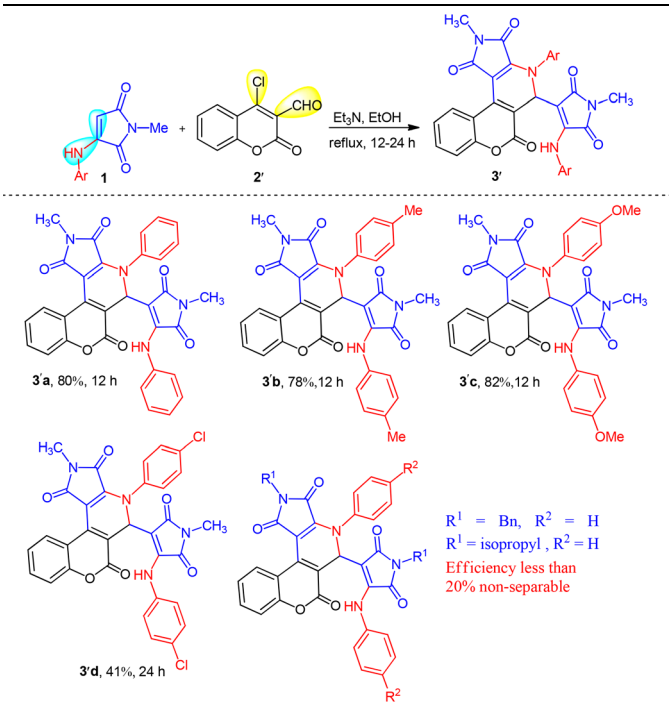
Also, when piperidine with relatively more nucleophilicity was used for this process, product **3a** was not formed, probably because of the nucleophilic replacement of piperidine with the chlorine atom of substrate **2a** (Table 1, entry 7). The yield of the reaction in the presence of K_2CO_3 and CS_2CO_3 as a base was 40 and 50%, respectively. The effect of different solvents (EtOH, MeOH, DCM, and MeCN) on the progress of the reaction was investigated. As shown in Table 1, carrying out the reaction in EtOH was found to be the best choice as it resulted in a better yield (88%). Based on this data, the optimized reaction conditions were as follows: using 50 mmol% of Et_3N in ethanol at 80 °C in an oil bath. The use of a protic solvent (EtOH and MeOH) seems essential for the reaction to proceed and may be related to the dipole moment as well as the hydrogen bonding ability of protic solvents. With the optimal reaction conditions in hand, we began to investigate the generality and substrate scope of this process. We probed the scope of the annulation with different arylamines. It is noteworthy that the electronic nature of the substituent on the aromatic rings

Table 2 Synthesis of novel tetracyclic dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine derivatives **3a–3h** [a]



[a] Reaction conditions: **1** (1.0 mmol), **2** (1.0 mmol), and Et_3N (50 mol%) in EtOH (5 mL) at 80 °C for 8–24 h.

Table 3 Synthesis of novel tetracyclic dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine derivatives **3′a–3′d** [a]



[a] Reaction conditions: **1** (2.0 mmol), **2′** (1.0 mmol), and Et_3N (50 mol%) in EtOH (5 mL) at 80 °C for 12–24 h.

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of α-aminomaleimides and 4-chloro-3-vinyl coumarins affected the time of the reaction and the yields of products **3a–3h**. It was clear that the reaction yield with α-aminomaleimides containing electron-donating groups on the aromatic rings such as Me and OMe substituents was better compared to electron-withdrawing groups such as Cl. It is noteworthy that the reaction of *N*-methyl-α-arylaminomaleimide **1a** and NO_2-substituted 4-chloro-3-vinyl coumarin **2e** did not proceed well and several overlapping spots were observed. This result may be related to the strong electron-withdrawing property of the nitro group, which reduces the electron density through induction and resonance effects. In addition, the nitro substituent can stabilize the negative charges formed at different stages of this process and prevent the reaction from progressing. Notably, attempts to synthesize the nitro-substituted *N*-methyl-α-aminomalemide were not successful. In addition, we replaced other alkylamines with *N*-methyl and aromatic amines to further expand the range of derivatives of compounds **3**. But unfortunately, acceptable results were not obtained and the efficiency of many of them was below 20%. Some of these results are shown in Table 2. Fortunately, we succeeded in synthesizing eight different derivatives of tetracyclic fused heterocycles **3a–3h**. In another experiment, the reaction of methyl-α-arylaminomaleimides **1** with 4-chloro-3-formyl coumarin **2′** under the same conditions (ethanol solvent, reflux temperature, and trimethylamine base) was investigated. The remarkable thing observed in this study is that the reaction was carried out in a pseudo-three-component manner and to complete the reaction, we had to add two equivalents of *N*-methyl-α-arylaminomaleimides **1** to the reaction mixture. As shown in Table 3, by replacing the electron-withdrawing substituent (such as chlorine) on the aryl ring of compound **1**, a significant effect on the yield and reaction time of the **3d** product was observed. Moreover, this limitation is more obvious with the substitution of alkylamines on the maleimide substrate. The structures of the synthesized compounds were characterized by FT-IR, mass spectrometry, elemental analysis, and NMR. Regarding compound **3′d**, unfortunately, we could not perform the ^{13}C NMR analysis due to its very low solubility in the solvent. In addition, the structure of **3b** was verified by single crystal X-ray crystallographic analysis (Fig. 2). Based on the experimental results and the literature, a plausible mechanism for the synthesis of **3** and **3′** was proposed, as shown in Scheme 2.

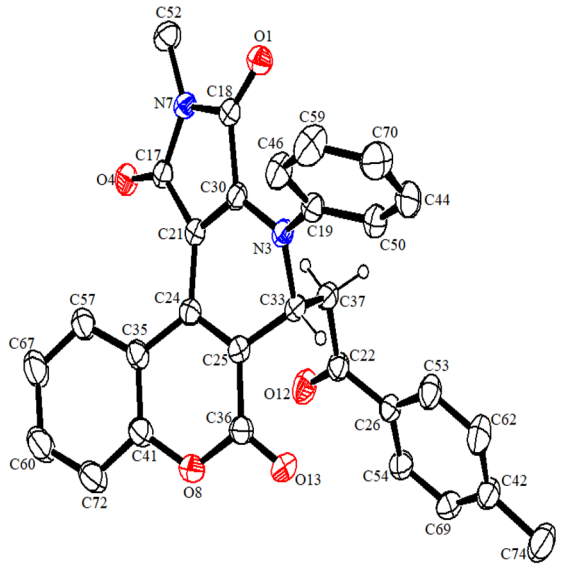
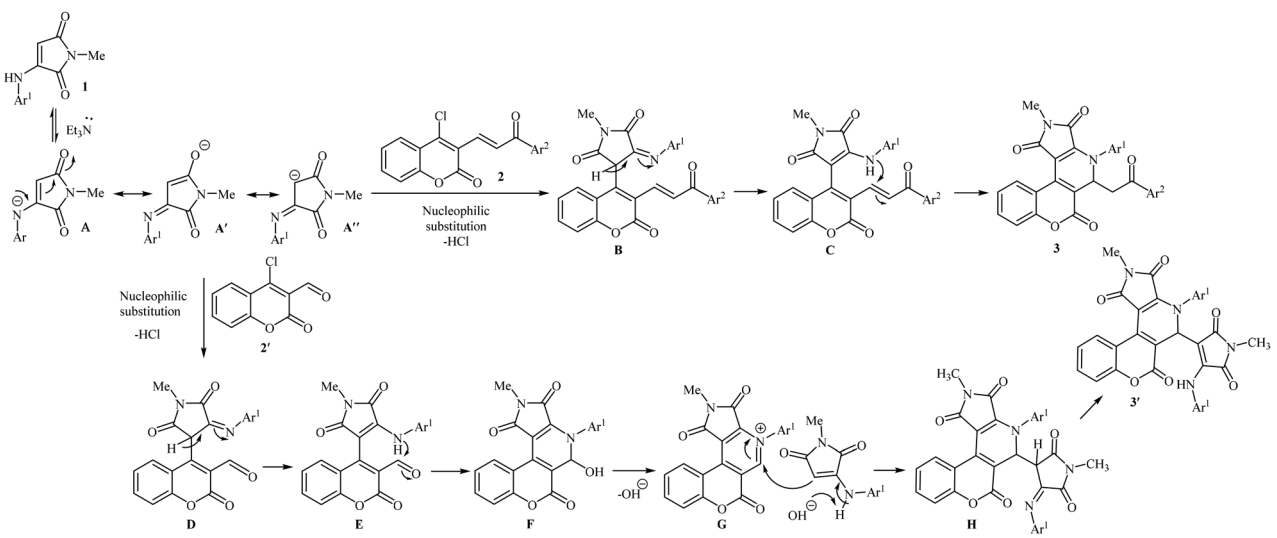


Fig. 2 ORTEP diagram of **3b**.

It can be assumed that initially compound **1** is converted into anion **A** under triethylamine. Then, the resonance structures of the conjugated enolate facilitate its nucleophilic attack on **2** to produce intermediate **B**. Finally, by the process of amine–enamine tautomerization, intermediate **B** is converted



Scheme 2 Plausible mechanism for the formation of **3** and **3′**.

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into **C**. Following this, the intramolecular aza-Michael addition of intermediate **C** results in the formation of the tetracyclic heterocycle **3**.

The mechanism of formation of compound **3′** is as follows. First, α-C of α-aminomaleimide anion **A′** which contains two other resonance structures (conjugated enolate) can easily attack C-4 of **2′** to give intermediate **D**. Then, by the process of amine–enamine tautomerization, intermediate **D** is converted into **E**. Following this, the intramolecular aza-Michael addition of intermediate **E** *via* a 1,4-nucleophilic addition process results in the formation of intermediate **F**. Then, intermediate **F** with the elimination of an OH anion is converted into the iminium ion (intermediate **G**). Finally, through the attack of the second molecule of α-aminomaleimide **1** on the iminium ion (intermediate **G**), intermediate **H** is formed and by the imine–amine tautomerization of intermediate **H**, the heterocyclic compound **3′** is produced.

Conclusions

In summary, we have presented a novel domino-type process for the synthesis of dihydrochromeno[3,4-*d*]pyrrolo[3,4-*b*]pyridines through a base-mediated nucleophilic substitution/Michael addition/*N*-cyclization and elimination reaction of 4-chloro-3-substituted coumarins with α-aminomaleimides. It is noteworthy that in this process, various products were obtained by changing the substitution at position 3 (3-formyl/3-vinyl) of 4-chloro-3-substituted coumarins (**2** and **2′**). Carbon–carbon bonds and a carbon–nitrogen bond were formed in this reaction, and highly stable four-ring aromatic products were obtained. This unprecedented strategy was carried out under relatively green conditions and the results of this effort were derivatives of maleimide-fused chromenopyridines. Until today there is no report about their synthesis. We hope that the obtained products will be of pharmacological interest.

Experimental

General information

All reactions were monitored by thin-layer chromatography (TLC) on Merck silica gel 60 F254 plates. The temperatures were monitored using a mercury laboratory thermometer. Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were recorded as KBr pellets on a Nicolet FT-IR 100 spectrophotometer. ^{1}H NMR (300 MHz) and ^{13}C{^{1}H} NMR (75 MHz) spectra were obtained using Bruker DRX-500 Avance and Bruker DRX-300 Avance spectrometers. All NMR spectra were recorded at r.t. in DMSO-d_6. Chemical shifts are reported in parts per million (δ) downfield from an internal TMS reference. Coupling constants (J values) are reported in hertz (Hz), and standard abbreviations are used to indicate spin multiplicities. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. Mass spectra were recorded on a Finnigan-MATT 8430 mass spectrometer operating at an ionization potential of 70 eV. Single crystals of compound **3b** were formed in the mixture of CH_2Cl_2 and absolute EtOH (1 : 1 v/v).

General procedure for the preparation of dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine derivatives 3a–3h.

A mixture of α-aminomaleimides (1.0 mmol), 4-chloro-3-vinyl coumarins (1.0 mmol), and triethylamine (50 mol%) in 5 mL ethanol was stirred at reflux temperature until all the starting materials were consumed (the reaction was monitored with TLC). A red solid was isolated by simple filtration. Derivatives **3a–3g** were purified by washing with hot EtOH twice and derivative **3h** was purified by column chromatography (hexane/AcOEt, 4/1, v/v).

General procedure for the preparation of dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine derivatives 3′a–3′d

A mixture of α-aminomaleimides (2.0 mmol), 4-chloro-3-formyl coumarin (1.0 mmol), and triethylamine (50 mol%) in 5 mL ethanol was stirred at reflux until all the starting materials were consumed (the reaction was monitored with TLC). A red solid was isolated by simple filtration. Derivatives **3a′—3c′** were purified by washing with hot EtOH twice and derivative **3d′** was purified by column chromatography (hexane/AcOEt, 4/1, v/v).

2-Methyl-5-(2-oxo-2-phenylethyl)-4-phenyl-4,5-dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine-1,3,6(2*H*)-trione (3a). Light red solid, m.p. = 120–122 °C (dec.), 0.42 g, yield: 88%. **IR** (KBr) (ν_{max}, cm^{-1}): 1697 (OCNCO and COO), 1672 (C═O), 1606, 1570 and 1437 (Ar), 1251 and 1101 (C–O), 1202 (C–N), 741 (C–H) cm^{-1}. **^{1}H NMR** (300.13 MHz, DMSO-d_6): 2.90 (3H, s, Me), 3.57 (1H, ABqd, $^{3}J_{HH}$ = 16.1 Hz, $^{2}J_{HH}$ = 5.1 Hz, CH of CH_2), 3.84 (1H, ABqd, $^{3}J_{HH}$ = 16.1 Hz, $^{2}J_{HH}$ = 6.2 Hz, CH of CH_2), 5.81 (1H, t, $^{3}J_{HH}$ = 5.6 Hz, CHN), 7.32–7.47 (7H, m, 5CH of Ph and 2CH of coumarin), 7.59 (1H, t, $^{3}J_{HH}$ = 7.1 Hz, CH of Ph), 7.63 (1H, d, $^{3}J_{HH}$ = 8.7 Hz, CH^{9} of coumarin), 7.72 (2H, d, $^{3}J_{HH}$ = 7.9 Hz, 2CH of Ph), 7.90 (2H, d, $^{3}J_{HH}$ = 7.9 Hz, 2CH of Ph), 9.1 (1H, dd, $^{3}J_{HH}$ = 8.8 Hz, $^{2}J_{HH}$ = 1.8 Hz, CH^{11} of coumarin). **^{13}C NMR** (75.46 MHz, DMSO-d_6): 23.90 (Me), 41.89 (CH_2), 58.54 (CHN), 107.92 (C^{5a}), 108.27 (CH^{11a}), 115.32 (CH^{11a}), 116.75 (CH^{8} of coumarin), 124.14 (CH of Ph), 124.87 (2CH of Ph), 127.64 (CH^{10} of coumarin), 128.19 (2CH of Ph), 128.69 (2CH of Ph), 128.90 (CH^{11} of coumarin), 129.08 (2CH of Ph), 131.93 (CH^{9} of coumarin), 133.43 (CH of Ph), 136.53 (C_{ipso}–CO), 136.84 (C_{ipso}–N), 141.54 (C^{3a}), 148.76 (C^{11b}), 152.35 (C^{7a}), 158.55 (COO), 161.92 (CON), 166.78 (CON), 196.9 (CO). **MS** (EI, 70 eV) m/z (%): 476 (M^{+}, 7), 371 (12), 358 (53), 357 (100), 281 (12), 104 (41), 90 (23), 77 (78), 50 (13). Anal. calcd for $C_{29}H_{20}N_2O_5$ (476.14): C, 73.10; H, 4.23; N, 5.88. Found: C, 73.15; H, 4.25; N, 5.81%.

2-Methyl-5-(2-oxo-2-(*p*-tolyl)ethyl)-4-phenyl-4,5-dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine-1,3,6(2*H*)-trione (3b). Light red solid, m.p. = 157–159 °C (dec.), 0.41 g, yield: 85%. **IR** (KBr) (ν_{max}, cm^{-1}): 1701 (OCNCO and COO), 1664 (C═O), 1598, 1566 and 1430 (Ar), 1261 and 1091 (C–O), 1197 (C–N), 764 (C–H) cm^{-1}. **^{1}H NMR** (300.13 MHz, DMSO-d_6): 2.31 (3H, s, Me), 2.89

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(3H, s, Me), 3.47 (H, ABq, $^3J_{HH}$ = 15.8 Hz, CH of CH_2), 3.82 (H, ABq, $^3J_{HH}$ = 15.8 Hz, CH of CH_2), 5.75 (1H, bs, CHN), 7.23 (2H, d, $^3J_{HH}$ = 7.7 Hz, 2CH of Ar), 7.39 (1H, d, $^3J_{HH}$ = 8.4 Hz, CH of CH^8 of coumarin), 7.40–7.46 (4H, m, CH^{10} of coumarin and 4CH of Ar), 7.58 (2H, d, $^3J_{HH}$ = 8.2 Hz, 2CH of Ar), 7.63 (1H, t, $^3J_{HH}$ = 7.5 Hz, CH^9 of coumarin), 7.78 (2H, d, $^3J_{HH}$ = 7.7 Hz, 2CH of Ar), 9.05 (1H, d, $^3J_{HH}$ = 8.1 Hz, CH^{11} of coumarin). **^{13}C NMR** (75.46 MHz, DMSO-d_6): 21.13 (Me), 23.89 (Me), 41.74 (CH_2), 58.31 (CHN), 108.31 (C^{5a}), 108.91 (CH^{11a}), 115.26 (CH^{11c}), 116.76 (CH^8 of coumarin), 124.15 (CH^{10} of coumarin), 126.69 (2CH of Ar), 128.31 (2CH of Ar), 128.86 (CH of Ar), 128.98 (2CH of Ar), 129.22 (2CH of Ar), 131.95 (CH^9 and CH^{11} of coumarin), 134.06 (C_{ipso}–N), 136.76 (C_{ipso}–CO), 140.38 (C^{3a}), 143.97 (C_{ipso}–Me), 148.57 (C^{11b}), 152.35 (C^{7a}), 158.47 (COO), 161.99 (CON), 166.77 (CON), 196.39 (CO). **MS** (EI, 70 eV) *m*/*z* (%): 490 (M^+, 3), 371 (4), 358 (26), 357 (100), 294 (11), 281 (7), 272 (6), 244 (5), 216 (4), 197 (6), 119 (46), 105 (25), 106 (6), 93 (5), 91 (43), 89 (6), 79 (9), 77 (75), 65 (25), 51 (16). Anal. calcd for $C_{30}H_{22}N_2O_5$ (490.15): C, 73.46; H, 4.52; N, 5.71. Found: C, 73.40; H, 4.55; N, 5.74%. Crystal data for **3b** $C_{30}H_{22}N_2O_5$ (CCDC 2254629†): M_W = 490.49, monoclinic, *P*121/*c*1, *a* = 11.679(2) Å, *b* = 15.814(3) Å, *c* = 13.357(3) Å, *α* = 90, *β* = 101.12 (3), *γ* = 90, *V* = 2420.6(9) Å^3, *Z* = 4, D_c = 1.346 mg m^{-3}, *F*(000) = 1024, crystal dimension 0.45 × 0.32 × 0.28 mm, radiation, Mo Kα (*λ* = 0.71073 Å), 1.777 ≤ 2*θ* ≤ 25.000, intensity data were collected at 293.15 K with a Bruker APEX area-detector diffractometer, and employing *ω*/2*θ* scanning technique, in the range of −13 ≤ *h* ≤ 13, −18 ≤ *k* ≤ 18, −15 ≤ *l* ≤ 15, the structure was solved by a direct method, all non-hydrogen atoms were positioned and anisotropic thermal parameters refined from 3675 observed reflections with *R*(into) = 0.0378 by a full-matrix least-squares technique converged to *R*1 = 0.0536, and w*R*2 = 0.1211 [*I* > 2*σ*(*I*)].

4-(4-Chlorophenyl)-2-methyl-5-(2-oxo-2-phenylethyl)-4,5-dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine-1,3,6(2*H*)-trione (3c). Light red solid, m.p. = 227–228 °C (dec.), 0.39 g, yield: 77%. **IR** (KBr) (ν_{max}, cm^{-1}): 1702 (OCNCO and COO), 1670 (C═O), 1612, 1572 and 1458 (Ar), 1250 and 1105 (C–O), 1197 (C–N), 1012 (C–Cl), 759 (C–H) cm^{-1}. **^{1}H NMR** (300.13 MHz, DMSO-d_6): 2.89 (3H, s, Me), 3.53 (1H, ABqd, $^3J_{HH}$ = 16.6 Hz, $^2J_{HH}$ = 4.8 Hz, CH of CH_2), 3.88 (1H, ABqd, $^3J_{HH}$ = 16.6 Hz, $^2J_{HH}$ = 6.0 Hz, CH of CH_2), 5.78 (1H, t, $^3J_{HH}$ = 5.6 Hz, CHN), 7.39 (2H, d, $^3J_{HH}$ = 8.3 Hz, 2CH of Ar), 7.40 (2H, d, $^3J_{HH}$ = 8.3 Hz, CH^8 of coumarin), 7.42 (1H, t, $^3J_{HH}$ = 8.4 Hz, CH^{10} of coumarin), 4.44–7.48 (3H, m, 3H of Ar), 7.59 (1H, t, $^3J_{HH}$ = 8.3 Hz, 2CH of Ar), 7.63 (1H, t, $^3J_{HH}$ = 7.5 Hz, CH^9 of coumarin), 7.89 (2H, d, $^3J_{HH}$ = 7.7 Hz, 2CH of Ar), 9.07 (1H, d, $^3J_{HH}$ = 8.1 Hz, $CH^{11}$of coumarin). **^{13}C NMR** (75.46 MHz, DMSO-d_6): 23.90 (Me), 41.85 (CH_2), 58.19 (CHN), 108.25 (C^{5a}), 108.89 (CH^{11a}), 115.26 (CH^{11c}), 116.75 (CH^8 of coumarin), 124.16 (CH^{10} of coumarin), 126.73 (2CH of Ar), 128.18 (2CH of Ar), 128.68 (2CH of Ar), 128.85 (C–Cl), 128.98 (2CH of Ar), 131.96 (CH^9 and $CH^{11}$of coumarin), 133.47 (CH of Ar), 136.42 (C_{ipso}–N), 136.77 (C_{ipso}–CO), 140.36 (C^{3a}), 148.58 (C^{11b}), 152.34 (C^{7a}), 158.48 (COO), 162.02 (CON), 166.77 (CON), 196.87 (CO). **MS** (EI, 70 eV) *m*/*z* (%): 510 (M^+, 2), 405 (4), 394 (8), 393 (35), 392 (25), 391 (100), 294 (17), 111 (5), 105 (7), 77 (9). Anal. calcd for $C_{29}H_{19}ClN_2O_5$ (510.10): C, 68.17; H, 3.75; N, 5.48. Found: C, 68.20; H, 3.77; N, 5.53%.

5-[2-(4-Bromophenyl)-2-oxoethyl]-4-(4-chlorophenyl)-2-methyl-4,5-dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine-1,3,6(2*H*)-trione (3d). Light red solid, m.p. = 238–239 °C (dec.), 0.44 g, yield: 75%. **IR** (KBr) (ν_{max}, cm^{-1}): 1701 (OCNCO and COO), 1678 (C═O), 1612, 1572 and 1445 (Ar), 1250 and 1212 (C–O), 1198 (C–N), 1086 (C–Cl), 1009 (C–Br), 761 (C–H) cm^{-1}. **^{1}H NMR** (300.13 MHz, DMSO-d_6): 2.91 (3H, s, Me), 3.52 (1H, ABqd, $^3J_{HH}$ = 16.9 Hz, $^2J_{HH}$ = 4.7 Hz, CH of CH_2), 3.87 (1H, ABqd, $^3J_{HH}$ = 16.5 Hz, $^2J_{HH}$ = 6.1 Hz, CH of CH_2), 5.76 (1H, t, $^3J_{HH}$ = 6.6 Hz, CHN), 7.39 (2H, d, $^3J_{HH}$ = 8.4 Hz, 2CH of Ar), 7.45 (1H, t, $^3J_{HH}$ = 7.0 Hz, CH^{10} of coumarin), 7.46 (2H, d, $^3J_{HH}$ = 7.6 Hz, 2CH of Ar), 7.47 (1H, d, $^3J_{HH}$ = 7.3 Hz, CH^8 of coumarin), 7.63 (1H, t, $^3J_{HH}$ = 8.2 Hz, CH^9 of coumarin), 7.65 (2H, d, $^3J_{HH}$ = 8.4 Hz, CH of Ar), 7.81 (2H, d, $^3J_{HH}$ = 7.7 Hz, 2CH of Ar), 9.07 (1H, d, $^3J_{HH}$ = 8.2 Hz, CH^{11} of coumarin). **^{13}C NMR** (75.46 MHz, DMSO-d_6): 23.92 (Me), 41.93 (CH_2), 58.12 (CHN), 108.14 (C^{5a}), 108.76 (CH^{11a}), 115.24 (CH^{11c}), 116.77 (CH^8 of coumarin), 124.19 (CH^{10} of coumarin), 126.74 (C–Br and 2CH of Ar), 127.69 (2CH of Ar), 128.87 (C–Br), 128.99 (2CH of Ar), 130.17 (2CH of Ar), 131.75 (CH^{11} of coumarin), 132.00 (CH^9 of coumarin), 135.44 (C_{ipso}–CO), 136.78 (C_{ipso}–N), 140.30 (C^{3a}), 148.56 (C^{11b}), 152.34 (C^{7a}), 158.47 (COO), 162.00 (CON), 166.76 (CON), 196.14 (CO). **MS** (EI, 70 eV) *m*/*z* (%): 590 (M^{+2}, 1), 588 (M^+, 1), 394 (8), 393 (36), 392 (25), 391 (100), 75 (5). Anal. calcd for $C_{29}H_{18}BrClN_2O_5$ (588.01): C, 59.05; H, 3.08; N, 4.75. Found: C, 59.10; H, 3.10; N, 4.68%.

5-[2-(4-Chlorophenyl)-2-oxoethyl]-2-methyl-4-(4-methylphenyl)-4,5-dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine-1,3,6(2*H*)-trione (3e). Light red solid, m.p. = 225–226 °C (dec.), 0.46 g, yield: 89%. **IR** (KBr) (ν_{max}, cm^{-1}): 1702 (OCNCO and COO), 1684 (C═O), 1612, 1572 and 1458 (Ar), 1250 and 1180 (C–O), 1197 (C–N), 1012 (C–Cl), 761 (C–H) cm^{-1}. **^{1}H NMR** (300.13 MHz, DMSO-d_6): 2.32 (3H, s, Me), 2.89 (3H, s, Me), 3.55 (1H, ABqd, $^3J_{HH}$ = 16.1 Hz, $^2J_{HH}$ = 5.2 Hz, CH of CH_2), 3.81 (1H, ABqd, $^3J_{HH}$ = 16.1 Hz, $^2J_{HH}$ = 6.1 Hz, CH of CH_2), 5.74 (1H, t, $^3J_{HH}$ = 5.6 Hz, CHN), 7.20 (2H, d, $^3J_{HH}$ = 8.0 Hz, 2CH of Ar), 7.37 (2H, d, $^3J_{HH}$ = 8.0 Hz, 2CH of Ar), 7.39 (1H, d, $^3J_{HH}$ = 8.0 Hz, CH^8 of coumarin), 7.40 (1H, t, $^3J_{HH}$ = 8.6 Hz, CH^{10} of coumarin), 7.50 (2H, d, $^3J_{HH}$ = 8.5 Hz, 2CH of Ar), 7.63 (1H, t, $^3J_{HH}$ = 8.7 Hz, CH^9 of coumarin), 7.89 (2H, d, $^3J_{HH}$ = 8.5 Hz, 2CH of Ar), 9.10 (1H, dd, $^3J_{HH}$ = 8.6 Hz, $^2J_{HH}$ = 1.7 Hz, CH^{11} of coumarin). **^{13}C NMR** (75.46 MHz, DMSO-*d*: 20.64 (Me), 23.88 (Me), 42.06 (CH_2), 58.61 (CHN), 107.17 (C^{5a}), 107.55 (CH^{11a}), 115.32 (CH^{11c}), 116.75 (CH^8 of coumarin), 124.14 (CH^{10} of coumarin), 124.78 (2CH of Ar), 128.78 (CH^{11} of coumarin), 128.98 (2CH of Ar), 129.56 (2CH of Ar), 130.07 (2CH of Ar), 131.94 (CH^9 of coumarin), 135.22 (C_{ipso}–Me), 136.87 (C_{ipso}–CO), 137.45 (C_{ipso}–N), 138.41 (C–Cl), 139.07 (C^{3a}), 148.70 (C^{11b}), 152.31 (C^{7a}), 158.56 (COO), 161.86 (CON), 166.75 (CON), 195.86 (CO). MS (EI, 70 eV) *m*/*z* (%): 524 (M^+, 1), 455 (1), 372 (25), 371 (100), 294 (7), 139 (6), 91 (15), 65 (6). Anal. calcd for $C_{30}H_{21}ClN_2O_5$ (524.11): C, 68.64; H, 4.03; N, 5.34. Found: C, 68.70; H, 4.05; N, 5.38%94 (28), 83 (57), 68 (100), 51 (14). Anal. calcd for $C_{33}H_{18}Cl_3N_5$

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(590.89): C, 67.08; H, 3.07; N, 11.85. Found: C, 67.10; H, 3.08; N, 11.86%.

5-[2-(4-Bromophenyl)-2-oxoethyl]-4-(4-methoxyphenyl)-2-methyl-4,5-dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine-1,3,6(2*H*)-trione (3f). Light red solid, m.p. = 190–191 °C (dec.), 0.54 g, yield: 92%. **IR** (KBr) (ν_{max}, cm^{-1}): 1710 (OCNCO and COO), 1681 (C═O), 1613, 1574 and 1459 (Ar), 1240, 1200 and 1099 (C–O), 1177 (C–N), 1007 (C–Br), 760 (C–H) cm^{-1}. **^{1}H NMR** (300.13 MHz, DMSO-d_6): 2.87 (3H, s, Me), 3.76 (3H, s, OMe), 3.49 (1H, ABq, $^3J_{HH}$ = 17.7 Hz, CH of CH_2), 3.81 (1H, ABq, $^3J_{HH}$ = 17.7 Hz, CH of CH_2), 5.70 (1H, bs, CHN), 6.92 (2H, d, $^3J_{HH}$ = 8.4 Hz, 2CH of Ar), 7.36 (1H, d, $^3J_{HH}$ = 8.3 Hz, CH^8 of coumarin), 7.38 (1H, d, $^3J_{HH}$ = 8.3 Hz, CH^{10} of coumarin), 7.45 (2H, d, $^3J_{HH}$ = 8.0 Hz, 2CH of Ar), 7.61 (1H, t, $^3J_{HH}$ = 7.5 Hz, CH^9 of coumarin), 7.63 (2H, d, $^3J_{HH}$ = 8.0 Hz, 2CH of Ar), 7.79 (2H, d, $^3J_{HH}$ = 8.3 Hz, 2CH of Ar), 9.12 (1H, d, $^3J_{HH}$ = 8.0 Hz, CH^{11} of coumarin). **^{13}C NMR** (75.46 MHz, DMSO-*d*: 23.86 (Me), 42.09 (CH_2), 55.50 (OMe), 58.90 (CHN), 105.85 (C^{5a}), 106.99 (CH^{11a}), 114.24 (2CH of Ar), 115.41 (CH^{11a}), 116.73 (CH^8 of coumarin), 124.11 (CH^{10} of coumarin), 126.67 (2CH of Ar), 127.60 (C–Br), 128.93 (C_{ipso}–N), 130.14 (2CH of Ar), 131.72 (2CH of Ar), 131.89 (CH^{11} of coumarin), 134.42 (CH^9 of coumarin), 135.55 (C_{ipso}–CO), 137.02 (C^{3a}), 148.77 (C^{11b}), 152.30 (C^{7a}), 158.60 (COO), 158.84 (C_{ipso}–OMe), 161.82 (CON), 166.75 (CON), 196.04 (CO). MS (EI, 70 eV) *m*/*z* (%): 586 (M^{+1}, 1), 584 (M^+, 1), 455 (7), 388 (14), 387 (59), 328 (8), 309 (6), 294 (10), 293 (18), 92 (11), 91 (100), 77 (5), 65 (7). Anal. calcd for $C_{30}H_{21}BrN_2O_6$ (584.06): C, 61.55; H, 3.62; N, 4.79. Found: C, 61.50; H, 3.60; N, 4.86%.

5-[2-(4-Chlorophenyl)-2-oxoethyl]-4-(4-methoxyphenyl)-2-methyl-4,5-dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine-1,3,6(2*H*)-trione (3g). Light red solid, m.p. = 199–200 °C (dec.), 0.48 g, yield: 90%. **IR** (KBr) (ν_{max}, cm^{-1}): 1702 (OCNCO and COO), 1684 (C═O), 1612, 1572 and 1458 (Ar), 1251, 1210 and 1104 (C–O), 1197 (C–N), 1013 (C–Cl), 761 (C–H) cm^{-1}. **^{1}H NMR** (300.13 MHz, DMSO-d_6): 2.89 (3H, s, Me), 3.78 (3H, s, OMe), 3.50 (1H, ABqd, $^3J_{HH}$ = 16.1 Hz, $^2J_{HH}$ = 5.1 Hz, CH of CH_2), 3.82 (1H, ABqd, $^3J_{HH}$ = 16.1 Hz, $^2J_{HH}$ = 6.0 Hz, CH of CH_2), 5.72 (1H, t, $^3J_{HH}$ = 6.0 Hz, CHN), 6.92 (2H, d, $^3J_{HH}$ = 8.4 Hz, 2CH of Ar), 7.37 (1H, d, $^3J_{HH}$ = 8.0 Hz, CH^8 of coumarin), 7.39 (1H, t, $^3J_{HH}$ = 8.0 Hz, CH^{10} of coumarin), 7.45 (2H, d, $^3J_{HH}$ = 8.2 Hz, 2CH of Ar), 7.50 (2H, d, $^3J_{HH}$ = 8.2 Hz, 2CH of Ar), 7.62 (1H, t, $^3J_{HH}$ = 7.6 Hz, CH^9 of coumarin), 7.88 (2H, d, $^3J_{HH}$ = 8.3 Hz, 2CH of Ar), 9.14 (1H, d, $^3J_{HH}$ = 8.1 Hz, CH^{11} of coumarin). **^{13}C NMR** (75.46 MHz, DMSO-d_6): 23.85 (Me), 42.11 (CH_2), 55.49 (OMe), 58.88 (CHN), 105.86 (C^{5a}), 107.01 (CH^{11a}), 114.24 (2CH of Ar), 115.42 (CH^{11c}), 116.73 (CH^8 of coumarin), 124.11 (CH^{10} of coumarin), 126.67 (2CH of Ar), 128.76 (2CH of Ar), 128.93 (C_{ipso}–CO), 130.06 (2CH of Ar), 131.88 (CH^{11} of coumarin), 134.42 (CH^9 of coumarin), 135.22 (C_{ipso}–CO), 137.01(C–Cl), 138.39 (C^{3a}), 148.77 (C^{11b}), 152.31 (C^{7a}), 158.60 (COO), 158.83 (C_{ipso}–OMe), 161.84 (CON), 166.76 (CON), 195.83 (CO). **MS** (EI, 70 eV) *m*/*z* (%): 540 (M^+, 1), 388 (28), 387 (100), 344 (5), 294 (13), 247 (4), 139 (8), 111 (6), 77 (4). Anal. calcd for $C_{30}H_{21}ClN_2O_6$ (540.11): C, 66.61; H, 3.91; N, 5.18. Found: C, 66.68; H, 3.89; N, 5.13%.

2-Benzyl-5-(2-oxo-2-phenylethyl)-4-phenyl-4,5 dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine-1,3,6(2*H*)-trione (3h). Light red solid, m.p. = 210–212 °C (dec.), 0.30 g, yield: 55%. **IR** (KBr) (ν_{max}, cm^{-1}): 1700 (OCNCO and COO), 1637 (C═O), 1607, 1568 and 1492 (Ar), 1248, 1200 and 1092 (C–O), 1197 (C–N), 754 (C–H) cm^{-1}. **^{1}H NMR** (300.13 MHz, $CDCl_3$): 3.28 (1H, ABqd, $^3J_{HH}$ = 14.7 Hz, $^2J_{HH}$ = 4.9 Hz, CH of CH_2), 3.60 (1H, ABqd, $^3J_{HH}$ = 14.7 Hz, $^2J_{HH}$ = 6.2 Hz, CH of CH_2), 4.67 (1H, t, $^3J_{HH}$ = 4.2 Hz, CHN), 5.91 (2H, ABq, $^2J_{HH}$ = 7.7 Hz, 2CH of CH_2). 7.24–7.43 (13H, m, 10H of Ph and 3H of coumarin), 7.56 (2H, d, $^3J_{HH}$ = 7.6 Hz, CH of Ph), 7.51 (1H, t, $^3J_{HH}$ = 7.6 Hz, CH of Ph), 7.77 (2H, d, $^3J_{HH}$ = 7.5 Hz, CH of Ph), 9.09 (1H, d, $^3J_{HH}$ = 7.8 Hz, CH^{11} of coumarin). **^{13}C NMR** (75.46 MHz, $CDCl_3$): 41.24 (CH_2), 41.83 (CH_2), 60.24 (CHN), 105.06 (C^{5a}), 108.45 (CH^{11a}), 115.29 (CH^{11c}), 116.84 (CH^8 of coumarin), 124.35 (CH^{10} of coumarin), 125.72 (2CH of Ph), 127.88 (CH of Ph), 128.17 (CH of Ar), 128.68 (2CH of Ph), 128.69 (2CH of Ph), 129.42 (CH^{11} of coumarin), 131.88 (CH^9 of coumarin), 133.41 (CH of Ph), 136.08 (C_{ipso}–CO), 136.72 (C_{ipso}–Ph), 139.11 (C^{3a}), 140.56 (C_{ipso}–Bn), 149.34 (C^{11b}), 152.77 (C^{7a}), 159.54 (COO), 166.11 (CON), 170.16 (CON), 196.80 (CO). **MS** (EI, 70 eV) *m*/*z* (%): 552 (M^+, 5), 459 (5), 433 (100), 417 (5), 370 (9), 326 (12), 107 (60), 91 (97), 77 (83), 65 (19). Anal. calcd for $C_{35}H_{24}N_2O_5$ (552.17): C, 76.08; H, 4.38; N, 5.07. Found: C, 76.04; H, 4.40; N, 5.09%.

5-(4-Anilino-1-methyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-3-yl)-2-methyl-4-phenyl-4,5-dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine-1,3,6(2*H*)-trione (3′a). Light red solid, m.p. = 284–285 °C (dec.), 0.44 g, yield: 80%. **IR** (KBr) (ν_{max}, cm^{-1}): 3237 (NH), 1703 (OCNCO and COO), 1674 (C═O), 1610, 1571 and 1449 (Ar), 1242 and 1098 (C–O), 1197 (C–N), 763 (C–H) cm^{-1}. **^{1}H NMR** (300.13 MHz, DMSO-d_6): 2.81 (3H, s, Me), 2.86 (3H, s, Me), 6.64 (2H, d, $^3J_{HH}$ = 6.6 Hz, 2CH of Ph), 7.04 (1H, t, $^3J_{HH}$ = 7.0 Hz, CH of Ph), 7.06 (2H, t, $^3J_{HH}$ = 7.0 Hz, 2CH of Ph), 7.27 (1H, d, $^3J_{HH}$ = 8.5 Hz, CH^8 of coumarin), 7.32 (2H, t, $^3J_{HH}$ = 7.0 Hz, 2CH of Ph), 7.33 (1H, t, $^3J_{HH}$ = 7.3 Hz, CH^{10} of coumarin), 7.50 (1H, t, $^3J_{HH}$ = 7.0 Hz, CH of Ph), 7.52 (2H, d, $^3J_{HH}$ = 7.0 Hz, 2CH of Ph), 7.55 (1H, t, $^3J_{HH}$ = 7.3 Hz, CH^9 of coumarin), 9.29 (1H, d, $^3J_{HH}$ = 8.2 Hz, CH^{11} of coumarin), 9.56 (1H, bs, NH). **^{13}C NMR** (75.45 MHz, DMSO-d_6): 23.60 (Me), 23.70 (Me), 55.84 (CHN), 97.81 (C^3), 98.94 (C^{5a}), 107.80 (C^{11a}), 115.55 (C^{11c}), 116.43 (CH^8 of coumarin), 123.83 (CH^{10} of coumarin), 124.26 (2CH of Ph), 125.34 (CH of Ph), 127.61 (2CH of Ph), 128.38 (2CH of Ph), 129.06 (CH of Ph), 129.35 (2CH of Ph), 129.66 (CH^{11} of coumarin), 131.77 (CH^9 of coumarin), 138.31(C_{ipso}–Ph), 138.86 (C^4), 140.22 (C_{ipso}–Ph), 141.54 (C^{3a}), 150.16 (C^{11b}), 152.12 (C^{7a}), 158.56 (COO), 161.45 (CON), 166.44 (CON), 166.88 (CON), 171.46 (CON). **MS** (EI, 70 eV) *m*/*z* (%): 559 (M^{+1}, 15), 558 (M^+, 44), 481 (9), 472 (6), 467 (29), 466 (100), 381 (13), 369 (6), 358 (23), 357 (88), 300 (7), 281 (11), 279 (8), 270 (7), 180 (27), 144 (11), 105 (7), 104 (6), 93 (60), 78 (6), 77 (70). Anal. calcd for $C_{32}H_{22}N_4O_6$ (558.15): C, 68.81; H, 3.97; N, 10.03. Found: C, 68.85; H, 4.00; N, 10.10%.

2-Methyl-5-{1-methyl-4-[(4-methylphenyl)amino]-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-3-yl}-4-(4-methylphenyl)-4,5-dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine-1,3,6(2*H*)-trione (3′b). Light red solid, m.p. = 246–247 °C (dec.), 0.45 g, yield: 78%. **IR**

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(KBr) (ν_{max}, cm^{-1}): 3310 (NH), 1695 (OCNCO and COO), 1674 (C═O), 1610, 1571 and 1439 (Ar), 1249 and 1100 (C–O), 1199 (C–N), 749 (C–H) cm^{-1}. **^{1}H NMR** (300.13 MHz, DMSO-d_6): 2.20 (3H, s, Me), 20.38 (3H, s, Me), 2.80 (3H, s, Me), 2.84 (3H, s, Me), 5.76 (1H, s, CHN), 6.67 (2H, d, $^3J_{HH}$ = 7.8 Hz, 2CH of Ar), 6.83 (2H, d, $^3J_{HH}$ = 7.8 Hz, 2CH of Ar), 7.15 (2H, d, $^3J_{HH}$ = 8.0 Hz, 2CH of Ar), 7.26 (2H, d, $^3J_{HH}$ = 8.0 Hz, 2CH of Ar), 7.27 (1H, d, $^3J_{HH}$ = 8.2 Hz, CH^8 of coumarin), 7.34 (1H, t, $^3J_{HH}$ = 7.8 Hz, CH^{10} of coumarin), 7.55 (1H, t, $^3J_{HH}$ = 7.8 Hz, CH^9 of coumarin), 9.30 (1H, d, $^3J_{HH}$ = 8.2 Hz, CH^{11} of coumarin), 9.53 (1H, bs, NH). **^{13}C NMR** (75.45 MHz, DMSO-d_6): 20.59 (Me), 20.82 (Me), 23.57 (Me), 23.67 (Me), 55.98 (CHN), 97.33 (C^3), 98.16 (C^{5a}), 107.80 (C^{11a}), 115.60 (C^{11c}), 116.43 (CH^8 of coumarin), 123.81 (CH^{10} of coumarin), 124.40 (2CH of Ph), 127.38 (2CH of Ar), 128.79 (2CH of Ar), 129.70 (2CH of Ar and CH^{11} of coumarin), 131.72 (CH^9 of coumarin), 134.74 (C$_{ipso}$–Me), 135.53 (C$_{ipso}$–Me), 137.68 (C$_{ipso}$–Ar), 138.62 (C$_{ipso}$–Ar), 139 (C^4), 141.69 (C^{3a}), 150.16 (C^{11b}), 152.14 (C^{7a}), 158.57 (COO), 161.41 (CON), 166.49 (CON), 166.85 (CON), 171.49 (CON). **MS** (EI, 70 eV) *m*/*z* (%): 586 (M$^+$, 17), 481 (12), 480 (39), 395 (8), 386 (6), 385 (5), 293 (4), 217 (13), 216 (75), 208 (6), 159 (14), 158 (83), 132 (6), 131 (40), 130 (43), 129 (8), 119 (7), 118 (6), 116 (8), 107 (74), 106 (18), 104 (9), 103 (15), 102 (6), 92 (12), 91 (100), 90 (20), 89 (21), 88 (6), 79 (9), 78 (12), 77 (25), 76 (7), 68 (7), 66 (7), 65 (74), 64 (12), 63 (20), 62 (7), 58 (18), 57 (12), 56 (10), 52 (12), 51 (19), 50 (10). Anal. calcd for $C_{34}H_{26}N_4O_6$ (586.19): C, 69.62; H, 4.47; N, 9.55. Found: C, 69.68; H, 4.45; N, 9.51%.

4-(4-Methoxyphenyl)-5-{4-[(4-methoxyphenyl)amino]-1-methyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-3-yl}-2-methyl-4,5-dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine-1,3,6(2*H*)-trione (3′c). Light red solid, m.p. = 244–245 °C (dec.), 0.51 g, yield: 82%. **IR** (KBr) (ν_{max}, cm^{-1}): 3097 (NH), 1698 (OCNCO and COO), 1639 (C═O), 1610, 1574 and 1441 (Ar), 1248, 1172 and 1028 (C–O), 1196 (C–N), 736 (C–H) cm^{-1}. **^{1}H NMR** (300.13 MHz, DMSO-d_6): 2.81 (3H, s, Me), 20.85 (3H, s, Me), 3.69 (3H, s, OMe), 3.83 (3H, s, OMe), 5.64 (1H, s, CHN), 6.58 (4H, m, 4CH of Ar), 7.01 (2H, dd, $^3J_{HH}$ = 8.8 Hz, $^2J_{HH}$ = 1.0 Hz, 2CH of Ar), 7.20 (2H, dd, $^3J_{HH}$ = 8.8 Hz, $^2J_{HH}$ = 1.0 Hz, 2CH of Ar), 7.28 (1H, d, $^3J_{HH}$ = 8.2 Hz, CH^8 of coumarin), 7.33 (1H, t, $^3J_{HH}$ = 7.8 Hz, CH^{10} of coumarin), 7.56 (1H, t, $^3J_{HH}$ = 7.8 Hz, CH^9 of coumarin), 9.32 (1H, d, $^3J_{HH}$ = 8.2 Hz, CH^{11} of coumarin), 9.49 (1H, bs, NH). **^{13}C NMR** (75.45 MHz, DMSO-d_6): 20.54 (Me), 20.64 (Me), 55.17 (OMe), 55.53 (OMe), 56.11 (CHN), 96.75 (C^3), 96.93 (C^{5a}), 107.61 (C^{11a}), 113.41 (2CH of Ar), 114.43 (2CH of Ar), 115.57 (C^{11c}), 116.38 (CH^8 of coumarin), 123.75 (CH^{10} of coumarin), 126.30 (2CH of Ar), 129.05 (2CH of Ar), 129.68 (CH^{11} of coumarin), 130.58 (C$_{ipso}$–Ar), 131.68 (CH^9 of coumarin), 132.87 (C$_{ipso}$–Ar), 139 (C^4), 142.17 (C^{3a}), 150.40 (C^{11b}), 152.11 (C^{7a}), 157.03 (C$_{ipso}$–OMe), 158.57 (COO), 159.53 (C$_{ipso}$–OMe), 161.37 (CON), 166.56 (CON), 166.81 (CON), 171.62 (CON). **MS** (EI, 70 eV) *m*/*z* (%): 496 (4), 388 (17), 387 (59), 368 (5), 294 (5), 233 (13), 232 (100), 217 (29), 160 (8), 147 (15), 146 (21), 132 (18), 123 (11), 108 (15), 97 (9), 95 (6), 92 (8), 85 (7), 83 (9), 82 (8), 77 (14), 71 (9), 69 (13), 57 (16), 55 (12). Anal. calcd for $C_{34}H_{26}N_4O_8$ (618.18): C, 66.02; H, 4.24; N, 9.06. Found: C, 65.95; H, 4.27; N, 9.10%.

4-(4-Chlorophenyl)-5-(4-((4-chlorophenyl)amino)-1-methyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-3-yl)-2-methyl-4,5-dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine-1,3,6(2*H*)-trione (3′d). Light red solid, m.p. = 245–246 °C (dec.), 0.25 g, yield: 41%. **IR** (KBr) (ν_{max}, cm^{-1}): 3126 (NH), 1700 (OCNCO and COO, 1610, 1573 and 1508 (Ar), 1246, 1173 (C–O), 1092 (C–N), 762 (C–H), 1028 (C–Cl) cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$): 2.97 (3H, s, Me), 3.05 (3H, s, Me), 5.88 (1H, s, CHN), 6.88 (2H, d, $^3J_{HH}$ = 8.6 Hz, 2CH of Ar), 7.10 (2H, d, $^3J_{HH}$ = 8.6 Hz, 2CH of Ar), 7.18 (2H, dd, $^3J_{HH}$ = 8.0 Hz), 7.29 (1H, t, $^3J_{HH}$ = 8.0 Hz, CH^9 of coumarin), 7.30 (1H, d, $^3J_{HH}$ = 8.0 Hz, CH^8 of coumarin), 7.55 (1H, dt, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.5 Hz, CH^{10} of coumarin), 7.78 (1H, bs, NH), 9.40 (1H, dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.5 Hz, CH^{11} of coumarin). MS (EI, 70 eV) *m*/*z* (%): 627 (10), 433 (52), 392 (5), 325 (5), 280 (5), 236 (52), 178 (94), 151 (52), 127 (57), 91 (73), 57 (100). Anal. calcd $C_{32}H_{20}Cl_2N_4O_6$ (626.08): C, 61.26; H, 3.21; N, 8.93. Found: C, 61.24; H, 3.20; N, 8.96%.

Conflicts of interest

There are no conflicts to declare.

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