

A convenient approach to the synthesis of bio-promising 4-amino-substituted pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acids

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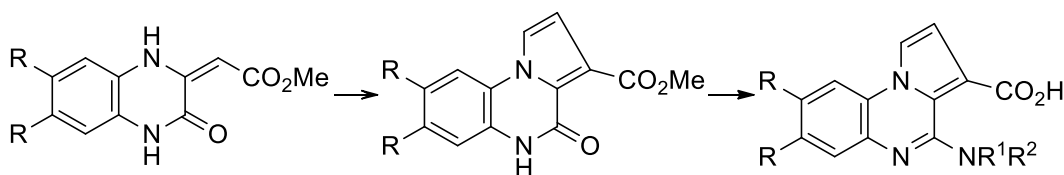
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Abstract

The subject of the presented synthetic study relates to 4-amino-pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acids, among which potent inhibitors of human CK2 protein kinase were found. At the same time, the described method of their preparation is characterized by a multi-stage process and the use of aggressive reagents. We present a new convenient variant of their synthesis, in which the cyclocondensation of 2-[3,4-dihydro-3-oxoquinoxaline-2(1*H*)-ylidene]carboxylates with bromoacetaldehyde diethyl acetal became the basis for obtaining key intermediates, 4-oxopyrrolo[1,2-*a*]quinoxaline-3-carboxylic acids. The subsequent preparatively simple stages of their esterification, triflation, and aminolysis were successfully used to create a focused library of target compounds.



Keywords: Quinoxalines, bromoacetaldehyde, pyrrolo[1,2-*a*]quinoxalines, triflic anhydride, amines, carboxylic acids

Introduction

Pyrrolo[1,2-*a*]quinoxalines are representatives of nitrogen-containing tricyclic angular systems with powerful synthetic and biomedical potential. Methods for constructing their various derivatives developed over the past decades and summarized in literature reviews,¹⁻⁵ have become a reliable basis for the rational search for compounds with a broad pharmacological profile, in particular 5-HT₃ receptor agonists, anti-HIV, anticancer, anti-ulcer and anti-malarial agents, as well as PARP-1 inhibitors.

A detailed analysis of pyrrolo[1,2-*a*]quinoxaline structures showed that their pharmacological action largely depends on the functionalization of both the quinoxaline and the pyrrole nuclei. It was found that 4-piperazinyl-substituted pyrrolo[1,2-*a*]quinoxalines (I, Fig. 1) are effective 5-HT₃ receptor agonists.⁶⁻¹¹ Their *N*-carboxamide derivatives are fatty acid amide hydrolase inhibitors and may be useful for the treatment of neuropathic pain.¹² In turn, 4-arylamino pyrrolo[1,2-*a*]quinoxalines are pronounced antiproliferative agents,¹³ 4-(*N*-methylaminopropyl)dimethylamino derivatives are non-peptide glucagon receptor antagonists,¹⁴ 4-(2-amino-1-hydroxy)analogs show antimalarial activity,¹⁵ and 4-hydrazide-substituted pyrrolo[1,2-*a*]quinoxalines were identified as agents with a wide range of anticancer activity.¹⁶

Also important for their biological properties was the presence of alkoxy carbonyl or carboxyl substituents in the pyrrole fragment of the pyrroloquinoxaline platform. For instance, esters of 4-aryl-substituted pyrrolo[1,2-*a*]quinoxalines (II, Fig. 1) are characterized by an antiproliferative effect,¹⁷ and their 4-piperazinyl-substituted analogs exhibit antimicrobial action.¹⁸ It is also worth noting that a number of 4-aminopyrrolo[1,2-*a*]quinoxalin-2- and 3-carboxylic acids (III, Fig. 1), among which agents with CNS action¹⁹ and potent inhibitors of the human protein kinase CK2²⁰ were identified. Among the latter, 4-[3-chlorophenyl]amino]pyrrolo[1,2-*a*]quinoxalin-3-carboxylic acid **9i** with IC₅₀ = 49 nM deserves special attention as a powerful scaffold for the development and optimization of new CK2 inhibitors.

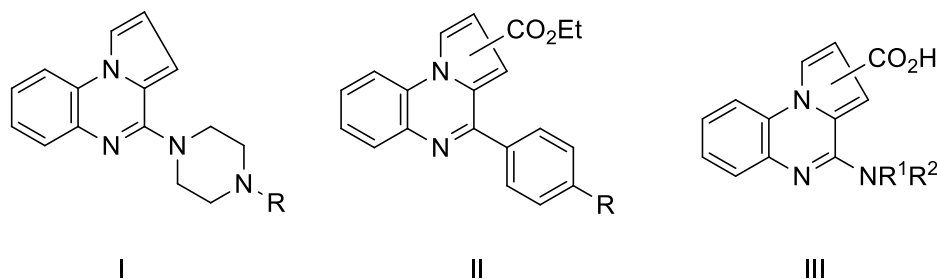
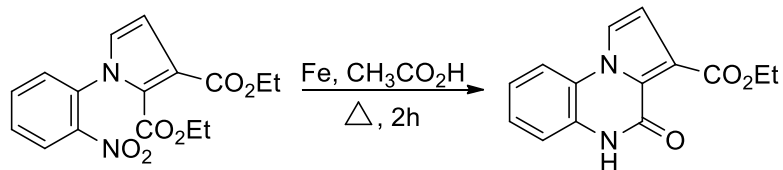


Figure 1. Examples of functionalized bioactive pyrrolo[1,2-*a*]quinoxalines

Analysis of the synthetic pathways for this type of compounds showed that their basic intermediates, ethyl 4-oxo-5*H*-pyrrolo[1,2-*a*]quinoxaline-3-carboxylates, are obtained by annelating the quinoxaline ring¹⁷ to difficult-to-obtain (6 synthetic stages) 1-(2-nitrophenyl)diethyl pyrrole-2,3-dicarboxylates.²¹



Scheme 1. Previously described synthesis of 4-oxopyrrolo[1,2-*a*]quinoxaline-3-carboxylates²¹

That is why the development of an effective method for the synthesis of pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acids, additionally functionalized at position 4 with various amino groups, is an important tool for the search for new substances with a pronounced biological activity. It can be expected that the results obtained from this kind of a study will also be in high demand among specialists in the field of synthetic and medicinal chemistry of nitrogen-containing heterocyclic compounds.

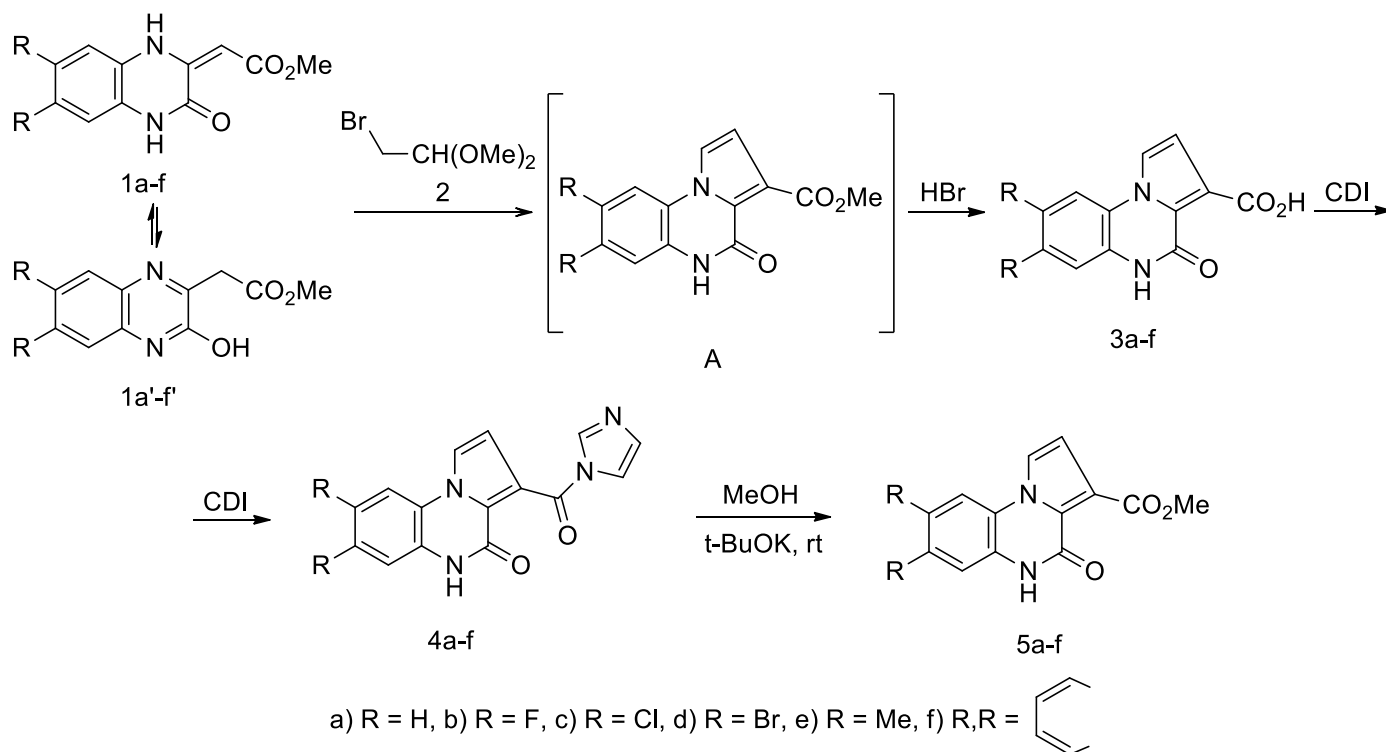
Results and Discussion

We propose a two-step synthesis methodology. Its first stage involves the annelation of the carboxy-substituted pyrrole nucleus to key ylidene-functionalized quinoxaline substrates, 2-[3,4-dihydro-3-oxoquinoxaline-2(1*H*)-ylidene]carboxylates **1a-f**. Compounds of this type are heterocyclic models of deactivated enamines and are easily prepared by cyclocondensation of 1,2-diaminoarenes with dialkyl acetylene dicarboxylates²²⁻²⁵, 2,4-dioxobutanoates²⁶ or sodium diethyl oxaloacetate.²⁷ They were used as intermediates in the multicomponent synthesis of functionalized pyrrolo[1,2-*a*]quinoxaline derivatives,²⁸⁻³⁰ as well as substrates for the preparation of imidazo[1,2-*a*]quinoxalines,³¹ pyrido[1,2-*a*]quinoxalines^{22, 32, 33} and pyrimido[1,6-*a*]quinoxalines.³⁴ The peculiarity of 2-[3,4-dihydro-3-oxoquinoxalin-2(1*H*)-ylidene]carboxylates **1a-f** is the tendency to tautomerize to (3-hydroxyquinoxalin-2-yl)carboxylates **1a'-f'**, which was recorded by time-resolved ¹H NMR spectra (see Supplementary Table S1). Bromoacetaldehyde diethyl acetal **2** was used as a 1,2-bi-electrophilic reagent for the formation of the pyrrole nucleus which proved to be quite effective for the recently synthesized 1-oxo-1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrazine-8-carboxylic acids³⁵ and 1-oxo-3,4-dihydropyrrolo[2,1-*c*][1,4]oxazine-8-carboxylic acids.³⁶

It was shown that 8 hours of heating of ylidenequinoxalines **1a-f** with acetal **2** in AcOH at 80 °C leads to the formation of the corresponding 4-oxopyrrolo[1,2-*a*]quinoxaline-3-carboxylic acids **3a-f** in 85-97% yields. This experimental result is most likely explained by the susceptibility of the primary pyrroloannulation products – esters **A** – to acid hydrolysis under the action of HBr as a byproduct of the reaction, which had already been observed earlier in the case of the carboxylic acids mentioned above.^{35, 36} It is worth noting that esters of 4-oxopyrrolo[1,2-*a*]quinoxaline-1,3-dicarboxylic acids formed by the three-component reaction of 1,2-diaminobenzene, DEAD, and ethyl bromopyruvate in boiling MeCN do not undergo such a transformation.²⁸

The structure of acids **3a-f**, as the key products of the discovered cyclization, is consistent with their spectral data. In particular, their ¹H NMR spectra show characteristic doublets of the pyrrole core protons in the range of 7.17–7.24 ppm and 8.26–8.55 ppm, as well as singlets of the N–H protons (12.40–12.74 ppm) and the O–H protons of the carboxyl group (15.15–15.42 ppm). In the ¹³C NMR spectra, the carbon atoms of the C=O group of the quinoxalinone core appear in the range of 157.2–158.0 ppm, while those of the exocyclic carboxylate fragment are observed in the range of 161.8–162.6 ppm.

Subsequently, acids **3a-f** were transformed by treatment with carbonyl diimidazole (CDI) into 3-imidazolylcarbonyl derivatives **4a-f** which appear to be quite promising intermediates for further amidation and esterification processes of the pyrroloquinoxaline scaffold. In particular, the study showed that compounds **4a-f** at room temperature in the presence of catalytic amounts of *t*-BuOK readily undergo methanolysis to form methyl 4-oxopyrrolo[1,2-*a*]quinoxaline-3-carboxylates **5a-f** in high yields (Scheme 2). When imidazolides **4a-f** were exposed to DMSO-*d*₆ solution, their partial hydrolysis was observed, which did not allow us to obtain correct ¹³C NMR spectra.

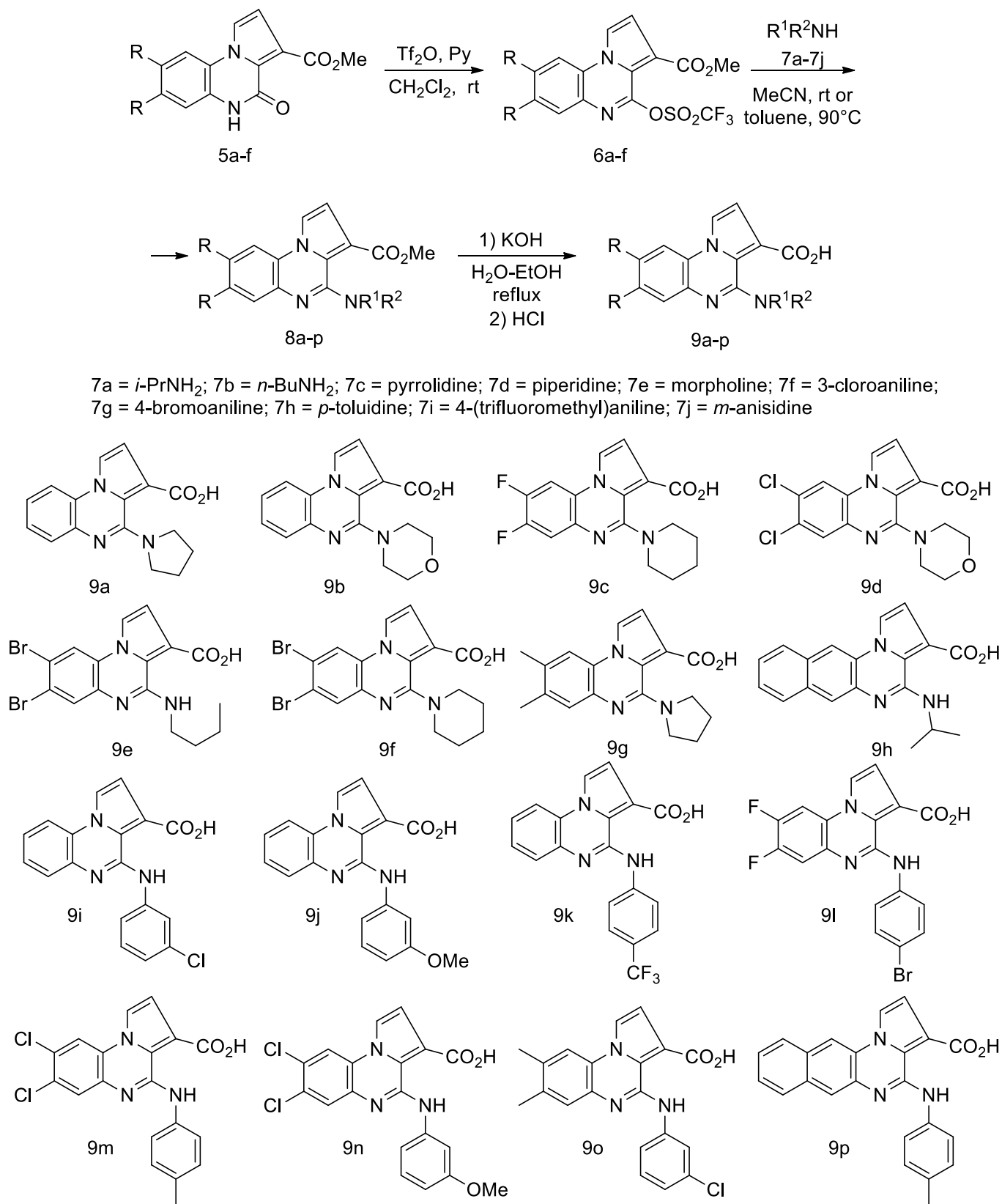


Scheme 2. Synthesis of 4-oxopyrolo[1,2-*a*]quinoxaline-3-carboxylates **5a-f**

The transformation of imidazolides **4a-f** into esters **5a-f** is reflected in their IR spectra by a shift in the absorption frequencies of the exocyclic carboxyl groups. For example, compound **4b** shows absorption bands of the C=O groups at 1691 and 1663 cm^{-1} , whereas compound **5c** exhibits them at 1716 and 1665 cm^{-1} .

The amino functionalization of 4-oxopyrolo[1,2-*a*]quinoxalincarboxylates¹⁸⁻²⁰ was accomplished by their initial conversion into 4-chloro derivatives using POCl_3 , after which nucleophilic substitution with various amines was carried out. To avoid the use of POCl_3 as an aggressive and highly toxic reagent, we developed a safer and synthetically more attractive procedure. To this end, triflic anhydride, was used to activate the cyclic amide group compounds **5a-f** instead of POCl_3 .³⁷ The result of its interaction, which proceeds smoothly in dichloromethane solution in the presence of pyridine, is the formation of triflates **6a-f**. Their interaction with aliphatic amines **7a-e** at room temperature or anilines **7f-j** when heated to 90 °C in toluene leads to 4-amino derivatives **8a-p**, the alkaline hydrolysis of **8a-p** yielded the desired library of amino acids **9a-p** (Scheme 3).

The selective transformation of 4-oxo-3-carboxylates **5a-f** into 4-triflate derivatives **6a-f** is confirmed by NMR spectral data. In particular, the ^1H NMR spectra of compounds **6a-f** show no signals corresponding to N-H protons, while the ^{13}C NMR spectra lack signals of the C=O group of the quinoxalinone ring.



Scheme 3. Synthesis of 4-aminopyrrolo[1,2-*a*]quinoxaline-3-carboxylic acids **9a-p**

The structure of the 4-amino-substituted 3-carboxylates **8a-p** and the corresponding target acids **9a-p** has been reliably confirmed not only by spectral data but also by an X-ray study of compound **8j** (see Experimental Section).

Conclusions

Using the cyclocondensation of 2-[3,4-dihydro-3-oxoquinoxalin-2(1*H*)-ylidene]carboxylates with bromoacetaldehyde diethyl acetal, we synthesized 4-oxopyrrolo[1,2-*a*]quinoxalin-3-carboxylic acids which were modified into the corresponding esters. The activation of their quinoxalin-4-one nucleus by triflic anhydride followed by nucleophilic substitution with aliphatic and aromatic amines proved to be an effective approach for the preparation of attractive 4-aminopyrrolo[1,2-*a*]quinoxalin-3-carboxylic acids.

Experimental Section

General. ¹H NMR, ¹³C NMR and ¹⁹F NMR were recorded on a Varian Mercury 200 (¹⁹F: 188 MHz), Varian Mercury Plus 300 (¹H: 300 MHz, ¹³C: 75 MHz), Varian UNITY INOVA 400 (¹H: 400 MHz), Bruker AVANCE III 400 (¹³C: 100 MHz, ¹⁹F: 376 MHz), Varian VNMRS 500 (¹³C: 125 MHz), Bruker AVANCE DRX 500 (¹³C: 125 MHz) and Agilent ProPulse 600 (¹³C: 150 MHz), using solvent peak as internal reference or apparatus SR. The chemical shifts (δ) and coupling constants (J) are expressed in ppm and hertz respectively. IR spectra were recorded on a Bruker Vertex 70 instrument in KBr pellets and are reported in cm⁻¹. Melting points were determined on a Kofler bench and are uncorrected. Mass spectrometry was performed using a Agilent LC/MSD SL instrument, at atmospheric pressure, electrospray ionization. X-ray diffraction study of methyl 4-[(3-methoxyphenyl)amino]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**8j**) was solved by direct method using SHELXTL package. Other reagents and starting materials were directly used as obtained commercially.

General procedure for the synthesis of methyl 2-(3-oxo-3,4-dihydroquinoxalin-2(1*H*)-ylidene)acetates **1a-f**.

To a suspension of corresponding *benzene-1,2-diamine* (20 mmol) in methanol (40 mL) was added by drops a solution of dimethyl acetylenedicarboxylate (2.58 mL, 21 mmol) in methanol (10 mL) at 0 °C. After stirring overnight at room temperature, the precipitate filtered, washed with methanol and dried at 90-100 °C.

Methyl 2-(3-oxo-3,4-dihydroquinoxalin-2(1*H*)-ylidene)acetate (1a).^{23, 38, 39} Yellow solid (4.059 g, 93%). mp 229-230 (decomp.) °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ_H 3.68 (3H, s, CH₃), 5.52 (1H, s, CH=CNH), 6.99 – 7.08 (3H, m, 3CH aromatic), 7.38 – 7.41 (1H, m, CH aromatic), 11.03 (1H, s, NH), 11.73 (1H, s, NH). ESI-MS: m/z 219.0 [M+H]⁺. Anal. calcd for C₁₁H₁₀N₂O₃ (218.21): C, 60.55; H, 4.62; N, 12.84. Found: C, 60.37; H, 4.65; N, 12.77.

Methyl 2-(6,7-difluoro-3-oxo-3,4-dihydroquinoxalin-2(1*H*)-ylidene)acetate (1b) + methyl (6,7-difluoro-3-hydroxyquinoxalin-2-yl)acetate (1b'). Gray solid (4.423 g, 87%). mp 239-240 (decomp.) °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ_H 3.63 (3H, s, CH₃O, **1b'**), 3.68 (3H, s, CH₃O, **1b**), 3.82 (2H, s, CH₂, **1b'**), 5.53 (1H, s, CH-CO, **1b**), 6.98 (1H, dd, ³J_{HF} 10.7, ⁴J_{HF} 7.9 Hz, CH aromatic, **1b**), 7.23 (1H, dd, ³J_{HF} 11.7, ⁴J_{HF} 7.8 Hz, CH aromatic, **1b'**), 7.72 (1H, dd, ³J_{HF} 11.8, ⁴J_{HF} 7.7 Hz, CH aromatic, **1b**), 7.87 (1H, dd, ³J_{HF} 11.1, ⁴J_{HF} 7.4 Hz, CH aromatic, **1b**), 10.98 (1H, s, NH, **1b**), 11.74 (1H, s, NH-CO, **1b**), 12.61 (1H, s, OH, **1b'**). ¹³C NMR (DMSO-*d*₆, 101 MHz): δ_C 50.7 (CH₃O, **1b**), 51.9 (CH₃O, **1b'**), 84.6 (CH-CO, **1b**), 103.3 (d, ²J_{CF} 21.1 Hz, CH aromatic, **1b'**), 103.6 (d, ²J_{CF} 22.3 Hz, CH aromatic, **1b**), 104.6 (d, ²J_{CF} 23.4 Hz, CH aromatic, **1b**), 116.2 (d, ²J_{CF} 18.0 Hz, CH aromatic, **1b'**), 121.6, 121.7, 143.0, 144.6 (dd, ¹J_{CF} 240.0, ²J_{CF} 13.7 Hz, CF aromatic, **2d**), 145.2 (dd, ¹J_{CF} 239.3, ²J_{CF} 13.5 Hz, CF aromatic, **2d**), 154.0, 155.3

(C=O, **1b**), 156.6, 169.0 (COOCH₃, **1b**), 169.3 (COOCH₃, **1b'**). ¹⁹F NMR (376 MHz, DMSO-*d*₆): δ_H -145.78 (ddd, ³J_{FF} 23.8, ³J_{HF} 11.1, ⁴J_{HF} 7.6 Hz, **1b**), -144.39 (ddd, ³J_{FF} 23.7, ³J_{HF} 12.1, ⁴J_{HF} 7.6 Hz, **1b**), -143.64 (ddd, ³J_{FF} 23.3, ³J_{HF} 11.2, ⁴J_{HF} 8.0 Hz, **1b'**), -133.47 (ddd, ³J_{FF} 22.9, ³J_{HF} 11.0, ⁴J_{HF} 8.3 Hz, **1b'**). ESI-MS: m/z 255.0 [M+H]⁺. Anal. calcd for C₁₁H₈F₂N₂O₃ (254.19): C, 51.98; H, 3.17; N, 11.02. Found: C, 52.10; H, 3.14; N, 10.89.

Methyl 2-(6,7-dichloro-3-oxo-3,4-dihydroquinoxalin-2(1H)-ylidene)acetate (1c) + methyl (6,7-dichloro-3-hydroxyquinoxalin-2-yl)acetate (1c'). Beige solid (5.397 mg, 94%). mp 252-253 (decomp.) °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ_H 3.63 (3H, s, CH₃O **1c'**), 3.69 (3H, s, CH₃O **1c**), 3.83 (2H, s, CH₂ **1c'**), 5.56 (1H, s, CH=CNH **1c**), 7.14 (1H, s, CH aromatic **1c**), 7.46 (1H, s, CH aromatic **1c'**), 7.85 (1H, s, CH aromatic **1c**), 8.01 (1H, s, CH aromatic **1c'**), 10.95 (1H, s, NH **1c**), 11.80 (1H, s, NH **1c**), 12.63 (1H, s, OH **1c'**). ¹³C NMR (DMSO-*d*₆, 151 MHz): δ_C 39.4 (CH₂ **1c'**), 50.8 (CH₃O **1c**), 51.9 (CH₃O **1c'**), 85.6 (CH-CO **1c**), 115.8, 116.5, 116.8, 123.5, 124.8, 125.2, 125.2, 125.4, 129.3, 130.7, 131.9, 132.3, 142.7, 153.9, 155.4, 157.8, 168.8 (COOCH₃ **1c**), 169.2 (COOCH₃ **1c'**). ESI-MS: m/z 287.0 [M+H]⁺. Anal. calcd for C₁₁H₈Cl₂N₂O₃ (287.10): C, 46.02; H, 2.81; N, 9.76. Found: C, 45.83; H, 2.79; N, 9.84.

Methyl 2-(6,7-dibromo-3-oxo-3,4-dihydroquinoxalin-2(1H)-ylidene)acetate (1d) + methyl (6,7-dibromo-3-hydroxyquinoxalin-2-yl)acetate (1d'). Light yellow solid (6.317 mg, 84%). mp 253-254 (decomp.) °C. IR (solid, KBr, ν_{max}, cm⁻¹): 3204, 1693, 1643, 1348, 1235, 771, 596, 532. ¹H NMR (400 MHz, DMSO-*d*₆): δ_H 3.64 (3H, s, -CH₃O **1d'**), 3.70 (3H, s, CH₃O **1d**), 3.83 (2H, s, CH₂ **1d'**), 5.59 (1H, s, CH=CNH **1d**), 7.31 (1H, s, CH aromatic **1d**), 7.64 (1H, s, CH aromatic **1d'**), 7.92 (1H, s, CH aromatic **1d**), 8.08 (1H, s, CH aromatic **1d'**), 10.90 (1H, s, NH **1d**), 11.64 (1H, s, NH **1d**), 12.47 (1H, s, OH **1d'**). ¹³C NMR (DMSO-*d*₆, 151 MHz): δ_C 51.3 (CH₃O), 86.1 (CH-CO), 115.7, 117.2, 119.2, 120.2, 126.3, 126.5, 143.1, 155.8, 169.2 (COOCH₃). ESI-MS: m/z 378.8 [M+H]⁺. Anal. calcd for C₁₁H₈Br₂N₂O₃ (376.00): C, 35.14; H, 2.14; N, 7.45. Found: C, 35.30; H, 2.10; N, 7.39.

Methyl 2-(6,7-dimethyl-3-oxo-3,4-dihydroquinoxalin-2(1H)-ylidene)acetate (1e) + methyl (3-hydroxy-6,7-dimethylquinoxalin-2-yl)acetate (1e'). Yellow solid (4.039 g, 82%). mp 224-225 (decomp.) °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ_H 2.16 + 2.17 (3H+3H, s + s, 2 CH₃ **1e**), 2.28 + 2.30 (1H+1H, s + s, 2CH₃ **1e'**), 3.63 (3H, s, CH₃O **1e'**), 3.67 (3H, s, CH₃O **1e**), 3.79 (2H, s, CH₂ **1e'**), 5.47 (1H, s, CH=CNH **1e**), 6.82 (1H, s, CH aromatic **1e**), 7.06 (1H, s, CH aromatic **1e'**), 7.13 (1H, s, CH aromatic **1e**), 7.49 (1H, s, CH aromatic **1e'**), 10.95 (1H, s, NH **1e**), 11.56 (1H, s, NH **1e**), 12.27 (1H, s, OH **1e'**). ¹³C NMR (DMSO-*d*₆, 126 MHz): δ_C 18.9 + 18.9 + 19.0 + 19.7 (4CH₃ **1e** and **1e'**), 39.4 (CH₂ **1e'**), 50.6 + 51.8 (2CH₃O **1e** and **1e'**), 82.5 (CH-CO **1e**), 115.4, 115.8, 116.0, 122.5, 122.9, 128.1, 130.0, 130.1, 130.7, 131.6, 132.0, 139.7, 144.2, 154.4 + 155.4 (2CO-NH **1e** and **1e'**), 169.6 + 169.7 (2COOCH₃ **1e** and **1e'**). ESI-MS: m/z 247.2 [M+H]⁺. Anal. calcd for C₁₃H₁₄N₂O₃ (246.26): C, 63.40; H, 5.73; N, 11.38. Found: C, 63.19; H, 5.77; N, 11.42.

Methyl 2-(3-oxo-3,4-dihydrobenzo[*g*]quinoxalin-2(1H)-ylidene)acetate (1f). Yellow solid (4.292 g, 80%). mp 253-254 (decomp.) °C. IR (solid, KBr, ν_{max}, cm⁻¹): 3229, 1697, 1650, 1227, 772, 742. ¹H NMR (400 MHz, DMSO-*d*₆): δ_H 3.72 (3H, s, CH₃), 5.61 (1H, s, CH-CO), 7.33 – 7.39 (2H, m, CH aromatic), 7.46 (1H, s, CH aromatic), 7.74 – 7.79 (2H, m, CH aromatic), 7.84 (7H, s, CH aromatic), 11.09 (1H, s, NH), 11.96 (1H, s, NH-CO). ¹³C NMR (DMSO-*d*₆, 151 MHz): δ_C 51.3 (CH₃O), 85.6 (CH-CO), 111.2, 111.4, 125.2, 125.5, 125.5, 126.3, 127.0, 127.11, 129.5, 130.3, 143.7, 156.2 (CO-NH), 169.8 (COOCH₃). ESI-MS: m/z 267.0 [M+H]⁺. Anal. calcd for C₁₅H₁₂N₂O₃ (268.27): C, 67.16; H, 4.51; N, 10.44. Found: C, 67.30; H, 4.53; N, 10.30.

General procedure for the synthesis of 4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acids 3a-f.

To a suspension of corresponding methyl 2-(3-oxo-3,4-dihydroquinoxalin-2(1H)-ylidene)acetate **1a-f** (15 mmol) in acetic acid (50 mL) was added bromoacetaldehyde diethyl acetal (2.26 mL, 15 mmol) and 3 drops of conc. hydrobromic acid. After stirring at 80 °C for 24 hours, the precipitate was filtered, washed with acetic acid, hexane and dried at 110-120 °C.

4-Oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (3a). Light yellow solid (3.252 g, 95%). mp >290 (decomp.) °C. IR (solid, KBr, ν_{\max} , cm^{-1}): 3143, 2999, 1703, 1619, 1508, 1384, 748, 539. ^1H NMR (400 MHz, DMSO- d_6): δ_{H} 7.22 (1H, d, $^3J_{\text{HH}}$ 2.8 Hz, CH pyrrole), 7.38 – 7.49 (3H, m, 3CH aromatic), 8.26 (1H, d, $^3J_{\text{HH}}$ 8.2 Hz, CH aromatic), 8.44 (1H, d, $^3J_{\text{HH}}$ 2.9 Hz, CH pyrrole), 12.64 (1H, s, NH), 15.42 (1H, s, OH). ^{13}C NMR (DMSO- d_6 , 126 MHz): δ_{C} 115.8, 116.9, 117.4, 118.9, 120.0, 120.2, 122.4, 124.4, 127.0, 127.2, 157.4 (CO-NH), 162.2 (COOH). ESI-MS: m/z 228.9 [M+H] $^+$. Anal. calcd for $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_3$ (228.20): C, 63.16; H, 3.53; N, 12.28. Found: C, 62.94; H, 3.56; N, 12.40.

7,8-Difluoro-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (3b). Gray solid (3.844 g, 97%). mp >290 (decomp.) °C. ^1H NMR (400 MHz, DMSO- d_6): δ_{H} 7.17 (1H, d, $^3J_{\text{HH}}$ 3.0 Hz, CH pyrrole), 7.35 (1H, dd, $^3J_{\text{HF}}$ 10.9, $^3J_{\text{HH}}$ 7.5 Hz, CH aromatic), 8.29 (1H, d, $^3J_{\text{HH}}$ 3.1 Hz, CH pyrrole), 8.47 (1H, dd, $^3J_{\text{HF}}$ 11.5, $^3J_{\text{HH}}$ 7.4 Hz, CH aromatic), 12.59 (1H, s, NH), 15.15 (1H, s, OH). ^{13}C NMR (DMSO- d_6 , 101 MHz): δ_{C} 106.3 (d, $^2J_{\text{CF}}$ 23.8 Hz, CH aromatic), 106.1 (d, $^2J_{\text{CF}}$ 22.4 Hz, CH aromatic), 117.5, 119.2 (d, $^3J_{\text{CF}}$ 9.6 Hz, C aromatic), 119.8, 120.1, 120.7, 124.5 (d, $^3J_{\text{CF}}$ 9.1 Hz, C aromatic), 146.4 (dd, $^1J_{\text{CF}}$ 243.1, $^2J_{\text{CF}}$ 13.9 Hz, CF aromatic), 148.0 (dd, $^1J_{\text{CF}}$ 246.1, $^2J_{\text{CF}}$ 13.6 Hz, CF aromatic), 157.5 (CO-NH), 162.3 (COOH). ^{19}F NMR (DMSO- d_6 , 188 MHz): δ_{F} -141.12 (ddd, $^3J_{\text{FF}}$ 23.8, $^3J_{\text{HF}}$ 11.5, $^4J_{\text{HF}}$ 7.6 Hz), -138.42 (ddd, $^3J_{\text{FF}}$ 23.7, $^3J_{\text{HF}}$ 10.8, $^4J_{\text{HF}}$ 7.6 Hz). ESI-MS: m/z 265.0 [M+H] $^+$. Anal. calcd for $\text{C}_{12}\text{H}_6\text{F}_2\text{N}_2\text{O}_3$ (264.18): C, 54.56; H, 2.29; N, 10.60. Found: C, 54.71; H, 2.26; N, 10.44.

7,8-Dichloro-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (3c). Gray solid (4.048 g, 94%). mp >290 (decomp.) °C. IR (solid, KBr, ν_{\max} , cm^{-1}): 3116, 3051, 1667, 1629, 1497, 1379, 750, 545, 481. ^1H NMR (400 MHz, DMSO- d_6): δ_{H} 7.21 (1H, d, $^3J_{\text{HH}}$ 3.1 Hz, CH pyrrole), 7.54 (1H, s, CH aromatic), 8.44 (1H, d, $^3J_{\text{HH}}$ 3.1 Hz, CH pyrrole), 8.64 (1H, s, CH aromatic), 12.73 (1H, s, NH), 15.11 (1H, s, OH). ^{13}C NMR (DMSO- d_6 , 126 MHz): δ_{C} 117.2, 117.6, 118.0, 119.7, 119.9, 120.6, 122.1, 126.4, 127.2, 128.8, 157.2 (CO-NH), 161.8 (COOH). ESI-MS: m/z 297.0 [M+H] $^+$. Anal. calcd for $\text{C}_{12}\text{H}_6\text{Cl}_2\text{N}_2\text{O}_3$ (297.09): C, 48.51; H, 2.04; N, 9.43. Found: C, 48.69; H, 2.07; N, 9.56.

7,8-Dibromo-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (3d). Gray solid (4.921 g, 85%). mp >290 (decomp.) °C. ^1H NMR (400 MHz, DMSO- d_6): δ_{H} 7.20 (1H, d, $^3J_{\text{HH}}$ 2.9 Hz, CH pyrrole), 7.68 (1H, s, CH aromatic), 8.48 (1H, d, $^3J_{\text{HH}}$ 3.0 Hz, CH pyrrole) 8.72 (1H, s, CH aromatic), 12.69 (1H, s, NH), 15.11 (1H, s, OH). ^{13}C NMR (DMSO- d_6 , 101 MHz): δ_{C} 117.2, 118.4, 119.7, 120.1, 120.5, 120.6, 121.1, 121.2, 122.9, 127.9, 157.3 (CO-NH), 161.8 (COOH). ESI-MS: m/z 388.8 [M+H] $^+$. Anal. calcd for $\text{C}_{12}\text{H}_6\text{Br}_2\text{N}_2\text{O}_3$ (386.00): C, 37.34; H, 1.57; N, 7.26. Found: C, 37.20; H, 1.60; N, 7.35.

7,8-Dimethyl-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (3e). Gray solid (3.421 g, 89%). mp 282-283 (decomp.) °C. ^1H NMR (400 MHz, DMSO- d_6): δ_{H} 2.25 (3H, s, CH_3), 2.29 (3H, s, CH_3), 7.12 – 7.16 (2H, m, CH pyrrole + CH aromatic), 7.93 (1H, s, CH aromatic), 8.26 (1H, s, CH pyrrole), 12.40 (1H, s, NH), 15.42 (1H, s, OH). ^{13}C NMR (DMSO- d_6 , 126 MHz): δ_{C} 19.1 + 19.1 (2 CH_3), 115.6, 116.7, 117.3, 118.2, 119.6, 119.8, 120.0, 124.7, 133.2, 135.6, 157.0 (CO-NH), 162.3 (COOH). ESI-MS: m/z 257.2 [M+H] $^+$. Anal. calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_3$ (256.26): C, 65.62; H, 4.72; N, 10.93. Found: C, 65.73; H, 4.75; N, 11.00.

4-Oxo-4,5-dihydrobenzo[*g*]pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (3f). Gray solid (3.756 g, 90%). mp >290 (decomp.) °C. ^1H NMR (400 MHz, DMSO- d_6): δ_{H} 7.24 (1H, d, $^3J_{\text{HH}}$ 3.0 Hz, CH pyrrole), 7.53 – 7.57 (2H, m, 2CH aromatic), 7.86 (1H, s, CH aromatic), 7.95 – 7.99 (2H, m, 2CH aromatic), 8.53 (1H, d, $^3J_{\text{HH}}$ 3.1 Hz, CH pyrrole), 8.81 (1H, s, CH aromatic), 12.74 (1H, s, NH), 15.37 (1H, s, OH). ^{13}C NMR (DMSO- d_6 , 101 MHz): δ_{C} 113.7, 114.0, 117.3, 120.0, 120.4, 121.3, 122.7, 126.4, 126.9, 127.2, 127.4, 127.8, 129.9, 131.4, 158.0 (CO-NH), 162.6 (COOH). ESI-MS: m/z 279.0 [M+H] $^+$. Anal. calcd for $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_3$ (278.26): C, 69.06; H, 3.62; N, 10.07. Found: C, 69.17; H, 3.58; N, 10.15.

General procedure for the synthesis of 3-(1*H*-imidazol-1-ylcarbonyl)pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-ones 4a-f. To a suspension of corresponding **4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid 3a-f** (10 mmol) in DMF (30 mL) was added carbonyldiimidazole (2.27 g, 14 mmol). After stirring at 90 °C for 3 hours, the reaction mixture was cooled to room temperature, the precipitate was filtered, washed with acetonitrile, MTBE and dried at 60-70 °C at a reduced pressure.

3-(1*H*-Imidazole-1-carbonyl)pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (4a). Beige solid (2.504 g, 90%). mp 275-276 °C. ¹H NMR (302 MHz, DMSO-*d*₆): δ_H 7.06 (1H, dd, ³J_{HH} 1.7, ⁴J_{HH} 0.8 Hz, CH imidazole), 7.08 (1H, d, ³J_{HH} 2.9 Hz, CH pyrrole), 7.26 – 7.41 (3H, m, 3CH aromatic), 7.68 (1H, t, ³J_{HH} 1.5 Hz, CH imidazole), 8.14 (1H, t, ⁴J_{HH} 1.1 Hz, CH imidazole), 8.19 (1H, d, ³J_{HH} 7.6 Hz, CH aromatic), 8.38 (1H, d, ³J_{HH} 3.0 Hz, CH pyrrole), 11.58 (1H, s, NH). Anal. calcd for C₁₅H₁₀N₄O₂ (278.26): C, 64.74; H, 3.62; N, 20.13. Found: C, 64.61; H, 3.58; N, 20.02.

7,8-Difluoro-3-(1*H*-imidazole-1-carbonyl)pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (4b). Gray solid (2.577 g, 82%). mp 281-282 °C. IR (solid, KBr, ν_{max}, cm⁻¹): 3114, 1691, 1663, 1529, 1304, 1219, 873, 751. ¹H NMR (302 MHz, DMSO-*d*₆): δ_H 7.06 (1H, s, CH imidazole), 7.10 (1H, d, ³J_{HH} 2.9 Hz, CH pyrrole), 7.29 (1H, dd, ³J_{HF} 11.2, ⁴J_{HF} 7.5 Hz, CH aromatic), 7.68 (1H, s, CH imidazole), 8.13 (1H, s, CH imidazole), 8.32 (1H, d, ³J_{HH} 3.0 Hz, CH pyrrole), 8.50 (1H, dd, ³J_{HF} 11.6, ⁴J_{HF} 7.5 Hz, CH aromatic), 11.65 (1H, s, NH). ¹⁹F NMR (DMSO-*d*₆, 188 MHz): δ_F -143.70 (ddd, ³J_{FF} 23.7, ³J_{HF} 11.6, ⁴J_{HF} 7.6 Hz), -139.61 (ddd, ³J_{FF} 23.7, ³J_{HF} 11.3, ⁴J_{HF} 8.3 Hz). Anal. calcd for C₁₅H₈F₂N₄O₂ (314.25): C, 57.33; H, 2.57; N, 17.83. Found: C, 57.24; H, 2.54; N, 17.75.

7,8-Dichloro-3-(1*H*-imidazole-1-carbonyl)pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (4c). Gray solid (2.742 g, 79%). mp 269-270 (decomp.) °C. ¹H NMR (302 MHz, DMSO-*d*₆): δ_H 7.07 (1H, s, CH imidazole), 7.09 (1H, d, ³J_{HH} 3.0 Hz, CH pyrrole), 7.47 (1H, s, CH aromatic), 7.68 (1H, s, CH imidazole), , 8.13 (1H, s, CH imidazole), 8.41 (1H, d, ³J_{HH} 2.8 Hz, CH pyrrole), 8.60 (1H, s, CH aromatic), 11.71 (1H, s, NH). Anal. calcd for C₁₅H₈Cl₂N₄O₂ (347.16): C, 51.90; H, 2.32; N, 16.14. Found: C, 51.74; H, 2.35; N, 16.06.

7,8-Dibromo-3-(1*H*-imidazole-1-carbonyl)pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (4d). Gray solid (3.183 g, 73%). mp >290 °C. ¹H NMR (302 MHz, DMSO-*d*₆): δ_H 7.06-7.10 (2H, m, CH pyrrole + CH imidazole), 7.10 (1H, s, CH aromatic), 7.62 + 7.68 (2H, s + s, CH imidazole + CH aromatic), 8.13 (1H, s, CH imidazole), 8.44 (1H, d, ³J_{HH} 3.1 Hz, CH pyrrole), 8.69 (1H, s, CH aromatic), 11.69 (1H, s, NH). Anal. calcd for C₁₅H₈Br₂N₄O₂ (436.06): C, 41.32; H, 1.85; N, 12.85. Found: C, 41.12; H, 1.89; N, 12.92.

3-(1*H*-Imidazole-1-carbonyl)-7,8-dimethylpyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (4e). Beige solid (2.726 g, 89%). mp 270-271 °C. IR (solid, KBr, ν_{max}, cm⁻¹): 3147, 2856, 1738, 1659, 1374, 1216, 867, 751. ¹H NMR (302 MHz, DMSO-*d*₆): δ_H 2.27 (3H, s, CH₃), 2.32 (3H, s, CH₃), 7.04-7.06 (2H, m, CH pyrrole + CH imidazole), 7.10 (1H, s, CH aromatic), 7.66 (1H, t, ³J_{HH} 1.5 Hz, CH imidazole), 8.01 (1H, s, CH aromatic), 8.11 (1H, t, ⁴J_{HH} 0.9 Hz, CH imidazole), 8.29 (1H, d, ³J_{HH} 3.0 Hz, CH pyrrole), 11.46 (1H, s, NH). Anal. calcd for C₁₇H₁₄N₄O₂ (306.32): C, 66.66; H, 4.61; N, 18.29. Found: C, 66.82; H, 4.59; N, 18.42.

3-(1*H*-imidazole-1-carbonyl)benzo[*g*]pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (4f). Gray solid (2.462 g, 75%). mp >290 °C. ¹H NMR (302 MHz, DMSO-*d*₆): δ_H 7.08 (1H, s, CH imidazole), 7.11 (1H, d, ³J_{HH} 2.9 Hz, CH pyrrole), 7.48 – 7.55 (2H, m, 2CH aromatic), 7.71 (1H, t, ³J_{HH} 1.5 Hz, CH imidazole), 7.73 (1H, s, CH aromatic), 7.90 – 7.99 (2H, m, 2CH aromatic), 8.19 (1H, s, CH imidazole), 8.50 (1H, d, ³J_{HH} 3.0 Hz, CH pyrrole), 8.77 (1H, s, CH aromatic), 11.74 (1H, s, NH). Anal. calcd for C₁₉H₁₂N₄O₂ (328.32): C, 69.51; H, 3.68; N, 17.06. Found: C, 69.23; H, 3.70; N, 16.94.

General procedure for the synthesis of methyl 4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylates 5a-f.

To a suspension of corresponding **3-(1*H*-imidazol-1-ylcarbonyl)pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one 4a-f** (10 mmol) in methanol (40 mL) was added potassium *tert*-butoxide (112 mg, 1 mmol). After stirring overnight at

room temperature, the reaction mixture was neutralized with acetic acid. The precipitate was filtered, washed with water, methanol and dried at 90-100 °C.

Methyl 4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylate (5a). Light yellow solid (2.228 g, 92%). mp 246-247 (decomp.) °C. IR (solid, KBr, ν_{max} , cm^{-1}): 3136, 3027, 2896, 1724, 1655, 1359, 1288, 1050, 757, 451. ^1H NMR (400 MHz, DMSO- d_6): δ_{H} 3.79 (3H, s, CH_3O), 6.97 (1H, d, $^3J_{\text{HH}}$ 2.5 Hz, CH pyrrole), 7.20 – 7.36 (3H, m, 3CH aromatic), 8.12 (1H, d, $^3J_{\text{HH}}$ 8.2 Hz, CH aromatic), 8.23 (1H, d, $^3J_{\text{HH}}$ 2.9 Hz, CH pyrrole), 11.48 (1H, s, NH). ^{13}C NMR (DMSO- d_6 , 126 MHz): δ_{C} 51.7 (CH_3O), 114.6, 115.5, 116.4, 117.4, 118.3, 121.8, 121.8, 122.6, 126.5, 128.8, 153.4 (CO-NH), 164.1 ($\underline{\text{C}}\text{OOCH}_3$). ESI-MS: m/z 243.2 [$\text{M}+\text{H}$] $^+$. Anal. calcd for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_3$ (242.23): C, 64.46; H, 4.16; N, 11.56. Found: C, 64.63; H, 4.20; N, 11.61.

7,8-Difluoro-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylate (5b). Colorless solid (2.699 g, 97%). mp 280-281 (decomp.) °C. ^1H NMR (400 MHz, DMSO- d_6): δ_{H} 3.80 (3H, s, CH_3O), 6.95 (1H, d, $^3J_{\text{HH}}$ 3.0 Hz, CH pyrrole), 7.27 (1H, dd, $^3J_{\text{HF}}$ 11.2, $^3J_{\text{HH}}$ 7.5 Hz, CH aromatic), 8.12 (1H, d, $^3J_{\text{HH}}$ 3.0 Hz, CH pyrrole), 8.31 (1H, dd, $^3J_{\text{HF}}$ 11.5, $^3J_{\text{HH}}$ 7.6 Hz, CH aromatic), 11.28 (1H, s, NH). ^{13}C NMR (TFA- d_1 , 151 MHz): δ_{C} 56.7 (OCH_3) 107.4 (d, $^2J_{\text{CF}}$ 24.1 Hz, CH aromatic), 110.8 (d, $^2J_{\text{CF}}$ 23.7 Hz, CH aromatic), 119.5, 122.1 (d, $^3J_{\text{CF}}$ 8.3 Hz, C aromatic), 122.7, 123.0 (d, $^3J_{\text{CF}}$ 9.1 Hz, C aromatic), 124.7, 152.7 (dd, $^1J_{\text{CF}}$ 256.5, $^2J_{\text{CF}}$ 13.1 Hz, CF aromatic), 152.9 (dd, $^1J_{\text{CF}}$ 256.4, $^2J_{\text{CF}}$ 13.5 Hz, CF aromatic), 158.6 (CO-NH), 171.6 (COOH). ^{19}F NMR (DMSO- d_6 , 188 MHz): δ_{F} -144.06 (ddd, $^3J_{\text{FF}}$ 23.4, $^3J_{\text{HF}}$ 11.7, $^4J_{\text{HF}}$ 8.0 Hz), -139.73 (ddd, $^3J_{\text{FF}}$ 24.3, $^3J_{\text{HF}}$ 11.2, $^4J_{\text{HF}}$ 8.2 Hz). ESI-MS: m/z 279.0 [$\text{M}+\text{H}$] $^+$. Anal. calcd for $\text{C}_{13}\text{H}_8\text{F}_2\text{N}_2\text{O}_3$ (278.21): C, 56.12; H, 2.90; N, 10.07. Found: C, 55.91; H, 2.93; N, 9.91.

Methyl 7,8-dichloro-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylate (5c). Gray solid (3.049 g, 98%). mp 285-286 °C. IR (solid, KBr, ν_{max} , cm^{-1}): 3254, 1716, 1665, 1346, 1295, 1052, 754, 483. ^1H NMR (400 MHz, DMSO- d_6): δ_{H} 3.78 (1H, s, CH_3O), 6.97 (1H, d, $^3J_{\text{HH}}$ 3.0 Hz, CH pyrrole), 7.43 (1H, s, CH aromatic), 8.27 (1H, d, $^3J_{\text{HH}}$ 3.1 Hz, CH pyrrole), 8.51 (1H, s, CH aromatic), 11.60 (1H, broad s, NH). ^{13}C NMR (TFA- d_1 , 151 MHz): δ_{C} 56.8 (CH_3O), 119.5, 119.7, 121.3, 123.0, 123.0, 124.5, 124.8, 125.4, 136.5, 136.8, 158.8 (CO-NH), 171.7 ($\underline{\text{C}}\text{OOCH}_3$). ESI-MS: m/z 311.0 [$\text{M}+\text{H}$] $^+$. Anal. calcd for $\text{C}_{13}\text{H}_8\text{Cl}_2\text{N}_2\text{O}_3$ (311.12): C, 50.19; H, 2.59; N, 9.00. Found: C, 49.89; H, 2.62; N, 8.86.

Methyl 7,8-dibromo-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylate (5d). Gray solid (3.840 g, 96%). mp 278-279 °C. ^1H NMR (400 MHz, DMSO- d_6): δ_{H} 3.79 (3H, s, CH_3O), 6.97 (1H, d, $^3J_{\text{HH}}$ 2.9 Hz, CH pyrrole), 7.58 (1H, s, CH aromatic), 8.31 (1H, d, $^3J_{\text{HH}}$ 3.1 Hz, CH pyrrole) 8.60 (1H, s, CH aromatic), 11.58 (1H, s, NH). ^{13}C NMR (DMSO- d_6 , 126 MHz): δ_{C} 51.8 (CH_3O), 114.8, 116.2, 118.4, 119.1, 120.0, 120.3, 120.5, 121.4, 122.5, 129.5, 153.1 (CO-NH), 163.9 ($\underline{\text{C}}\text{OOCH}_3$). ESI-MS: m/z 402.8 [$\text{M}+\text{H}$] $^+$. Anal. calcd for $\text{C}_{13}\text{H}_8\text{Br}_2\text{N}_2\text{O}_3$ (400.02): C, 39.03; H, 2.02; N, 7.00. Found: C, 39.24; H, 2.05; N, 6.87.

Methyl 7,8-dimethyl-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylate (5e). Light yellow solid (2.649 g, 98%). mp 284-285 (decomp.) °C. ^1H NMR (400 MHz, DMSO- d_6): δ_{H} 2.24 (3H, s, CH_3), 2.28 (3H, s, CH_3), 3.78 (3H, s, CH_3O), 6.92 (1H, d, $J=3.0$ Hz, CH pyrrole), 7.06 (1H, s, CH aromatic), 7.88 (1H, s, CH aromatic), 8.12 (1H, d, $J=3.0$ Hz, CH pyrrole), 11.23 (1H, s, NH). ^{13}C NMR (DMSO- d_6 , 126 MHz): δ_{C} 19.0 + 19.2 (2 CH_3), 51.6 (- CH_3O), 114.4, 115.9, 116.6, 116.9, 117.9, 119.7, 121.7, 126.5, 131.1, 135.0, 153.4 (CO-NH), 164.2 ($\underline{\text{C}}\text{OOCH}_3$). ESI-MS: m/z 271.2 [$\text{M}+\text{H}$] $^+$. Anal. calcd for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_3$ (270.28): C, 66.66; H, 5.22; N, 10.36. Found: C, 66.79; H, 5.17; N, 10.22.

Methyl 4-oxo-4,5-dihydrobenzo[*g*]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (5f). Light yellow solid (2.835 g, 97%). mp 283-284 °C. ^1H NMR (400 MHz, DMSO- d_6): δ_{H} 3.81 (3H, s, CH_3O), 7.01 (1H, s, CH pyrrole), 7.45 – 7.52 (2H, m, 2CH aromatic), 7.69 (1H, s, CH aromatic), 7.87 – 7.93 (2H, m, 2CH aromatic), 8.37 (1H, s, CH pyrrole), 8.69 (1H, s, CH aromatic), 11.63 (1H, s, NH). ^{13}C NMR (DMSO- d_6 , 126 MHz): δ_{C} 51.8 (CH_3O), 111.7, 112.9, 114.6, 118.2, 119.3, 121.6, 122.4, 125.2, 126.4, 126.7, 127.4, 128.3, 128.8, 131.2, 153.5 (CO-NH), 164.2 ($\underline{\text{C}}\text{OOCH}_3$).

ESI-MS: m/z 293.0 $[M+H]^+$. Anal. calcd for $C_{17}H_{12}N_2O_3$ (292.29): C, 69.86; H, 4.14; N, 9.58. Found: C, 69.68; H, 4.06; N, 9.71.

General procedure for the synthesis of methyl 4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylates 6a-f.

To the mixture of corresponding **methyl 4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-3-carboxylate 5a-f** (5 mmol) and pyridine (0.41 mL, 7 mmol) in dichloromethane (60 mL) was added by drops a solution of trifluoromethanesulfonic anhydride (1.01 mL, 6 mmol) in dichloromethane (10 mL) at 0 °C. After stirring overnight at room temperature, the organic layer was washed with water, then brine, dried over anhydrous sodium sulfate and filtered through a thin layer of silica gel. Evaporation of the solvents gave a yellow solid which was purified by crystallization from methanol and dried at 50-60 °C.

Methyl 4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (6a). Light yellow solid (1.628 g, 87%). mp 163-164 °C. 1H NMR (400 MHz, $CDCl_3$): δ_H 3.98 (3H, s, CH_3O), 7.44 (1H, d, $^3J_{HH}$ 2.9 Hz, CH pyrrole), 7.57 (1H, t, $^3J_{HH}$ 7.6 Hz, CH aromatic), 7.67 (1H, t, $^3J_{HH}$ 7.8 Hz, CH aromatic), 7.93 (2H, d, $^3J_{HH}$ 9.1 Hz, CH aromatic), 8.04 (1H, d, $^3J_{HH}$ 3.0 Hz, CH pyrrole). ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 52.2 (CH_3O), 113.8, 114.1, 116.6, 116.8, 118.5, 118.7 (q, $^1J_{CF}$ 321.1 Hz, CF_3), 126.5, 127.1, 129.7, 129.8, 132.5, 146.1, 163.0 ($COOCH_3$). ^{19}F NMR ($DMSO-d_6$, 188 MHz): δ_F -74.16. EI-MS: m/z 374 $[M]^+$. Anal. calcd for $C_{14}H_9F_3N_2O_5S$ (374.29): C, 44.92; H, 2.42; N, 7.48; S, 8.57. Found: C, 45.11; H, 2.39; N, 7.55; S, 8.68.

Methyl 7,8-difluoro-4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (6b). Light yellow solid (1.785 g, 87%). mp 230-231 °C. IR (solid, KBr, ν_{max} , cm^{-1}): 1741, 1402, 1215, 1125, 813, 739, 597, 579. 1H NMR (400 MHz, $CDCl_3$): δ_H 3.97 (3H, s, CH_3O), 7.47 (1H, d, $^3J_{HH}$ 2.9 Hz, CH pyrrole), 7.72 – 7.79 (2H, m, 2CH aromatic), 7.90 (1H, d, $^3J_{HH}$ 2.9 Hz, CH pyrrole). ^{13}C NMR ($CDCl_3$, 76 MHz): δ_C 52.5 (OCH_3) 103.3 (d, $^2J_{CF}$ 22.9 Hz, CH aromatic), 114.8, 116.6, 117.1, 117.6 (d, $^2J_{CF}$ 18.8 Hz, CH aromatic), 118.8 (q, $^1J_{CF}$ 321.7 Hz, CF_3), 119.3, 123.4 (d, $^3J_{CF}$ 8.2 Hz, C aromatic), 129.4 (d, $^3J_{CF}$ 9.7 Hz, C aromatic), 146.8 (C=N), 149.4 (dd, $^1J_{CF}$ 251.4, $^2J_{CF}$ 13.7 Hz, CF aromatic), 151.2 (dd, $^1J_{CF}$ 255.5, $^2J_{CF}$ 14.9 Hz, CF aromatic), 162.9 ($COOCH_3$). ^{19}F NMR ($DMSO-d_6$, 188 MHz): δ_F -139.15 (ddd, $^3J_{FF}$ 22.3, $^3J_{HF}$ 10.6, $^4J_{HF}$ 7.4 Hz), -133.31 (ddd, $^3J_{FF}$ 22.2, $^3J_{HF}$ 11.2, $^4J_{HF}$ 8.2 Hz), -74.26. EI-MS: m/z 410 $[M]^+$. Anal. calcd for $C_{14}H_7F_5N_2O_5S$ (410.27): C, 40.98; H, 1.72; N, 6.83; S, 7.82. Found: C, 41.11; H, 1.69; N, 6.75; S, 7.98.

Methyl 7,8-dichloro-4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (6c). Light yellow solid (1.861 g, 84%). mp 242-243 °C. 1H NMR (400 MHz, $CDCl_3$): δ_H 3.97 (3H, s, CH_3O), 7.46 (1H, d, $^3J_{HH}$ 3.0 Hz, CH pyrrole), 7.96 (1H, d, $^3J_{HH}$ 3.1 Hz, CH pyrrole), 8.03 (1H, s, CH aromatic), 8.03 (1H, s, CH aromatic). ^{13}C NMR ($CDCl_3$, 76 MHz): δ_C 52.6 (CH_3O), 115.3, 116.0, 116.7, 117.3, 118.8 (q, $^1J_{CF}$ 321.1 Hz, CF_3), 119.3, 125.8, 130.8, 131.6, 132.0, 134.1, 147.3 (C=N), 162.8 (C=O). ^{19}F NMR ($DMSO-d_6$, 188 MHz): δ_F -74.32. ESI-MS: m/z 443.0 $[M+H]^+$. Anal. calcd for $C_{14}H_7Cl_2F_3N_2O_5S$ (443.18): C, 37.94; H, 1.59; N, 6.32; S, 7.24. Found: C, 38.07; H, 1.62; N, 6.17; S, 7.40.

Methyl 7,8-dibromo-4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (6d). Light yellow solid (2.394 mg, 90%). mp 236-237 °C. IR (solid, KBr, ν_{max} , cm^{-1}): 1730, 1527, 1407, 1209, 1087, 826, 749, 618. 1H NMR (400 MHz, $CDCl_3$): δ_H 3.97 (3H, s, CH_3O), 7.45 (1H, d, $^3J_{HH}$ 3.0 Hz, CH pyrrole), 7.97 (1H, d, $^3J_{HH}$ 2.9 Hz, CH pyrrole), 8.18 (1H, s, CH aromatic), 8.19 (1H, s, CH aromatic). ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 52.6 (CH_3O), 115.4, 116.7, 117.3, 118.8 (q, $^1J_{CF}$ 321.2 Hz, CF_3), 119.1, 119.3, 123.1, 125.9, 126.3, 132.6, 133.9, 147.3 (C=N), 162.8 ($COOCH_3$). ^{19}F NMR ($DMSO-d_6$, 188 MHz): δ_F -74.34. ESI-MS: m/z 534.8 $[M+H]^+$. Anal. calcd for $C_{14}H_7Br_2F_3N_2O_5S$ (532.08): C, 31.60; H, 1.33; N, 5.26; S, 6.03. Found: C, 31.45; H, 1.35; N, 5.17; S, 6.17.

Methyl 7,8-dimethyl-4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (6e). Light yellow solid (1.790 g, 89%). mp 215-216 °C. 1H NMR (400 MHz, $CDCl_3$): δ_H 2.38 (3H, s, CH_3), 2.46 (3H, s, CH_3),

3.96 (3H, s, CH₃O), 7.36 (1H, d, ³J_{HH} 2.9 Hz, CH pyrrole), 7.61 (2H, s, 2CH aromatic), 7.90 (1H, d, ³J_{HH} 3.1 Hz, CH pyrrole). ¹³C NMR (151 MHz, CDCl₃): δ_c 19.6 (CH₃), 20.6 (CH₃), 52.3 (CH₃O), 113.3, 114.5, 116.2, 117.0, 118.4, 118.8 (q, ¹J_{CF} 320.4 Hz, CF₃), 124.7, 129.7, 130.8, 136.8, 140.0, 145.6, 163.3 (COOCH₃). ¹⁹F NMR (DMSO-*d*₆, 188 MHz): δ_F -74.21. EI-MS: *m/z* 402 [M]⁺. Anal. calcd for C₁₆H₁₃F₃N₂O₅S (402.34): C, 47.76; H, 3.26; N, 6.96; S, 7.97. Found: C, 47.90; H, 3.24; N, 7.03; S, 7.88.

Methyl 4-(((trifluoromethyl)sulfonyl)oxy)benzo[*g*]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (6f). Light yellow solid (1.931 g, 91%). mp 231-232 °C. ¹H NMR (400 MHz, CDCl₃): δ_H 3.97 (3H, s, CH₃O), 7.32 (1H, d, ³J_{HH} 3.0 Hz, CH pyrrole), 7.53 (1H, t, ³J_{HH} 7.3 Hz, CH aromatic), 7.60 (1H, t, ³J_{HH} 7.5 Hz, CH aromatic), 7.93 (2H, t, ³J_{HH} 7.9 Hz, 2CH aromatic), 8.05 (1H, d, ³J_{HH} 3.0 Hz, CH pyrrole), 8.16 (1H, s, CH aromatic), 8.30 (1H, s, CH aromatic). ¹³C NMR (CDCl₃, 76 MHz): δ_c 52.4 (CH₃O), 111.4, 115.5, 116.3, 117.9, 118.0, 118.8 (q, ¹J_{CF} 321.2 Hz, CF₃), 124.9, 126.7, 127.5, 128.2, 128.4, 128.7, 131.0, 131.7, 132.9, 146.2, 163.1 (COOCH₃). ¹⁹F NMR (DMSO-*d*₆, 188 MHz): δ_F -74.28. ESI-MS: *m/z* 425.0 [M+H]⁺. Anal. calcd for C₁₈H₁₁F₃N₂O₅S (424.35): C, 50.95; H, 2.61; N, 6.60; S, 7.56. Found: C, 51.07; H, 2.58; N, 6.53; S, 7.49.

General procedure for the synthesis of methyl 4-(alkyl)pyrrolo[1,2-*a*]quinoxaline-3-carboxylates 8a-h.

To a suspension of corresponding methyl 4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate 6a-f (3 mmol) in acetonitrile (30 mL) was added an corresponding aliphatic amine (6.3 mmol). After stirring overnight at room temperature, the volatile substances were evaporated and the residue was dispersed in water. The precipitate was filtered, washed with water, ice-cold methanol (5 mL) and dried at 90-100 °C.

Methyl 4-pyrrolidin-1-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylate (8a). Beige solid (762 mg, 86%). mp 128-129 °C. ¹H NMR (300 MHz, CDCl₃): δ_H 1.88-1.92 (4H, m, 2CH₂ pyrrolidine), 3.70-3.74 (4H, m, 2CH₂ pyrrolidine), 3.89 (3H, s, OCH₃), 7.09 (1H, d, ³J_{HH} 3.1 Hz, CH pyrrole), 7.18-7.23 (1H, m, CH aromatic), 7.31-7.37 (1H, m, CH aromatic), 7.64-7.70 (2H, m, 2 CH aromatic), 7.74 (1H, d, ³J_{HH} 3.1 Hz, CH pyrrole). ¹³C NMR (CDCl₃, 151 MHz): δ_c 25.6 (2CH₂ pyrrolidine), 49.5 (2CH₂ pyrrolidine), 52.0 (OCH₃), 113.3, 113.6, 114.0, 115.4, 120.0, 123.0, 124.9, 126.3, 126.9, 137.2, 151.4 (N=C), 165.5 (C=O). ESI-MS: *m/z* 296.2 [M+H]⁺. Anal. calcd for C₁₇H₁₇N₃O₂ (295.34): C, 69.14; H, 5.80; N, 14.23. Found: C, 68.93; H, 5.78; N, 14.34.

Methyl 4-morpholin-4-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylate (8b). White solid (869 mg, 93%). mp 139-140 °C. ¹H NMR (302 MHz, DMSO-*d*₆): δ_H 3.31-3.43 (4H, m, 2CH₂ morpholine), 3.74 (4H, t, ³J_{HH} 4.6 Hz, 2CH₂ morpholine), 3.83 (3H, s, CH₃O), 7.20 (1H, d, ³J_{HH} 3.0 Hz, CH pyrrole), 7.40-7.48 (2H, m, 2CH aromatic), 7.60-7.73 (1H, m, CH aromatic), 8.23-8.26 (1H, m, CH aromatic), 8.45 (1H, d, ³J_{HH} 3.1 Hz, CH pyrrole). ¹³C NMR (CDCl₃, 151 MHz): δ_c 50.2 (2CH₂ morpholine), 52.1 (CH₃O), 66.6 (2CH₂ morpholine), 112.4, 113.7, 114.5, 116.5, 120.0, 125.2, 125.3, 126.3, 128.1, 136.0, 153.0 (N=C), 164.4 (C=O). ESI-MS: *m/z* 312.0 [M+H]⁺. Anal. calcd for C₁₇H₁₇N₃O₃ (311.34): C, 65.58; H, 5.50; N, 13.50. Found: C, 65.77; H, 5.48; N, 13.36.

Methyl 7,8-difluoro-4-piperidin-1-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylate (8c). Beige solid (901 mg, 87%). mp 164-165 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ_H 1.57-1.63 (6H, m, 3CH₂ piperidine), 3.37-3.42 (4H, m, 2CH₂ piperidine), 3.83 (3H, s, OCH₃), 7.15 (1H, d, ³J_{HH} 3.0 Hz, CH pyrrole), 7.59 (1H, dd, ³J_{HF} 11.7, ³J_{HH} 8.1 Hz, CH aromatic), 8.34 (1H, d, ³J_{HH} 3.1 Hz, CH pyrrole), 8.43 (1H, dd, ³J_{HF} 11.8, ³J_{HH} 7.8 Hz, CH aromatic). ¹³C NMR (CDCl₃, 76 MHz): δ_c 24.9 (CH₂ piperidine), 25.6 (2CH₂ piperidine), 50.6 (2CH₂ piperidine), 52.2 (CH₃O), 102.3 (d, ²J_{CF} 23.6 Hz, CH aromatic), 113.2, 114.5, 114.9 (d, ²J_{CF} 16.5 Hz, CH aromatic) 116.3, 119.5, 121.0, 133.4, 147.5 (dd, ¹J_{CF} 249.0, ²J_{CF} 16.9 Hz, CF aromatic), 148.8 (dd, ¹J_{CF} 248.8, ²J_{CF} 15.9 Hz, CF aromatic), 153.3 (C=N), 164.3 (C=O). ¹⁹F NMR (DMSO-*d*₆, 376 MHz): δ_F -140.06-(-139.77) (m, 2CF aromatic). ESI-MS: *m/z* 346.2 [M+H]⁺. Anal. calcd for C₁₈H₁₇F₂N₃O₂ (345.34): C, 62.60; H, 4.96; N, 12.17. Found: C, 62.38; H, 4.99; N, 12.24.

Methyl 7,8-dichloro-4-morpholin-4-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylate (8d). Yellow solid (1.072 g, 94%). mp 203-204 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ_H 3.42 (4H, t, ³J_{HH} 4.7 Hz, 2CH₂ morpholine), 3.72 (4H, t, ³J_{HH} 4.7 Hz, 2CH₂ morpholine), 3.83 (3H, s, OCH₃), 7.20 (1H, d, ³J_{HH} 3.1 Hz, CH pyrrole), 7.80 (1H, s, CH aromatic), 8.49 (1H, d, ³J_{HH} 3.2 Hz, CH pyrrole), 8.63 (1H, s, CH aromatic). ¹³C NMR (CDCl₃, 76 MHz): δ_C 50.1 (2CH₂ morpholine), 52.3 (OCH₃), 66.6 (2CH₂ morpholine), 113.7, 115.2, 115.3, 117.0, 119.3, 124.2, 128.2, 128.5, 130.1, 135.4, 153.2 (C=N), 164.1 (C=O). ESI-MS: *m/z* 380.2 [M+H]⁺. Anal. calcd for C₁₇H₁₅Cl₂N₃O₃ (380.23): C, 53.70; H, 3.98; N, 11.05. Found: C, 53.86; H, 4.01; N, 10.97.

Methyl 7,8-dibromo-4-(butylamino)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (8e). Beige solid (1.215 g, 89%). mp 162-163 °C. ¹H NMR (400 MHz, CDCl₃): δ_H 1.00 (3H, t, ³J_{HH} 7.4 Hz, CH₃), 1.47-1.56 (2H, m, CH₂), 1.71-1.78 (2H, m, CH₂), 3.60-3.68 (2H, m, CH₂), 3.93 (3H, s, OCH₃), 7.20 (1H, d, ³J_{HH} 3.0 Hz, CH pyrrole), 7.60 (1H, d, ³J_{HH} 3.2 Hz, CH pyrrole), 7.89-7.95 (2H, m, 2CH aromatic), 9.77 (1H, s, NH). ¹³C NMR (CDCl₃, 126 MHz): δ_C 14.0 (CH₃), 20.6 (CH₂), 31.3 (CH₂), 40.9 (CH₂), 52.4 (OCH₃), 111.1, 114.0, 116.2, 116.5, 118.2, 121.5, 121.8, 123.7, 130.4, 138.5, 149.7 (N=C), 166.6 (C=O). ESI-MS: *m/z* 456.0 [M+H]⁺. Anal. calcd for C₁₇H₁₇Br₂N₃O₂ (455.14): C, 44.86; H, 3.76; N, 9.23. Found: C, 45.02; H, 3.77; N, 9.14.

Methyl 7,8-dibromo-4-piperidin-1-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylate (8f). Yellow solid (1.275 g, 91%). mp 177-178 °C. IR (solid, KBr, ν_{max}, cm⁻¹): 2945, 1725, 1518, 1483, 1229, 1187, 1046, 870, 717. ¹H NMR (400 MHz, DMSO-*d*₆): δ_H 1.57-1.63 (6H, m, 3CH₂ piperidine), 3.41-3.49 (4H, m, 2CH₂ piperidine), 3.84 (3H, s, OCH₃), 7.13 (1H, d, ³J_{HH} 3.0 Hz, CH pyrrole), 7.86 (1H, s, CH aromatic), 8.44 (1H, d, ³J_{HH} 3.1 Hz, CH pyrrole), 8.64 (1H, s, CH aromatic). ¹³C NMR (CDCl₃, 126 MHz): δ_C 25.0 (CH₂ piperidine), 25.7 (2CH₂ piperidine), 50.5 (2CH₂ piperidine), 52.2 (OCH₃), 113.8, 114.7, 116.3, 118.2, 118.4, 119.4, 121.4, 124.8, 131.4, 136.8, 153.4 (N=C aromatic), 164.2 (C=O). ESI-MS: *m/z* 468.0 [M+H]⁺. Anal. calcd for C₁₈H₁₇Br₂N₃O₂ (467.16): C, 46.28; H, 3.67; N, 8.99. Found: C, 46.51; H, 3.71; N, 8.86.

Methyl 7,8-dimethyl-4-(pyrrolidin-1-yl)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (8g). Beige solid (941 mg, 97%). mp 207-208 °C. ¹H NMR (400 MHz, CDCl₃): δ_H 1.90 (4H, s, 2CH₂), 2.33 (3H, s, CH₃), 2.37 (3H, s, CH₃), 3.70 (4H, s, 2N-CH₂), 3.88 (3H, s, CH₃O), 7.07 (1H, s, CH pyrrole), 7.45 (2H, s, 2CH aromatic), 7.70 (1H, s, CH pyrrole). ¹³C NMR (CDCl₃, 126 MHz): δ_C 19.6 (CH₃), 20.0 (CH₃), 25.5 (2CH₂), 49.5 (N(CH₂)₂), 51.9 (OCH₃), 112.9, 113.6, 114.1, 115.4, 120.2, 122.9, 127.3, 132.4, 135.1, 151.2 (C=N), 165.6 (C=O). ESI-MS: *m/z* 324.2 [M+H]⁺. Anal. calcd for C₁₉H₂₁N₃O₂ (323.39): C, 70.57; H, 6.55; N, 12.99. Found: C, 70.71; H, 6.47; N, 13.06.

Methyl 4-(isopropylamino)benzo[*g*]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (8h). Light yellow solid (870 mg, 87%). mp 214-215 °C. ¹H NMR (400 MHz, CDCl₃): δ_H 1.43 (6H, d, ³J_{HH} 6.5 Hz, (CH₃)₂CH), 3.94 (3H, s, CH₃O), 4.49 – 4.79 (1H, m, (CH₃)₂CH), 7.21 (1H, d, *J* = 3.1 Hz, CH pyrrole), 7.37 – 7.44 (2H, m, CH aromatic), 7.84 – 7.88 (3H, m, 2CH aromatic + CH pyrrole), 8.07 (2H, s, 2CH aromatic), 9.65 (1H, s, NH). ¹³C NMR (CDCl₃, 126 MHz): δ_C 22.8 ((CH₃)₂CH), 42.2 (CH₃)₂CH, 52.3 (CH₃O), 110.7, 111.3, 114.7, 115.9, 122.2, 122.4, 124.4, 124.7, 125.5, 127.3, 127.3, 129.4, 132.7, 136.9, 148.0 (C=N), 166.8 (C=O). ESI-MS: *m/z* 334.2 [M+H]⁺. Anal. calcd for C₂₀H₁₉N₃O₂ (333.38): C, 72.05; H, 5.74; N, 12.60. Found: C, 72.26; H, 5.71; N, 12.44.

General procedure for the synthesis of methyl 4-(aryl)pyrrolo[1,2-*a*]quinoxaline-3-carboxylates 8i-p. To a suspension of corresponding methyl 4-(((trifluoromethyl)sulfonyl)oxy)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate 6a-f (3 mmol) in toluene (40 mL) was added an corresponding aromatic amine (3.3 mmol). After stirring at 90 °C for 24 h, the precipitate was filtered and worked up with 5% solution of K₂CO₃ in water. The insoluble precipitate was filtered off, washed with water, hot methanol and dried at 90-100 °C.

Methyl 4-((3-chlorophenyl)amino)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (8i). Beige solid (992 mg, 94%). mp 250-251 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ_H 3.98 (3H, s, CH₃O), 7.11 (1H, d, ³J_{HH} 8.0 Hz, CH aromatic), 7.33 (1H, d, ³J_{HH} 3.2 Hz, CH pyrrole), 7.42 (2H, t, ³J_{HH} 7.9 Hz, CH aromatic), 7.49 (1H, t, ³J_{HH} 7.6 Hz, CH aromatic), 7.70

(1H, d, $^3J_{HH}$ 8.1 Hz, CH aromatic), 7.78 (1H, d, $^3J_{HH}$ 8.4 Hz, CH aromatic), 8.24 (1H, d, $^3J_{HH}$ 8.3 Hz, CH aromatic), 8.32 (1H, s, CH aromatic), 8.45 (1H, d, J 3.2 Hz, CH pyrrole), 12.06 (1H, s, NH). ^{13}C NMR (TFA- d_1 , 76 MHz): δ_{C} 55.2 (CH₃O), 117.3, 118.7, 120.6, 121.5, 122.1, 122.4, 125.0, 126.1, 126.3, 128.3, 130.1, 130.8, 132.6, 134.0, 135.0, 139.2, 148.1 (C=N), 169.6 (COOCH₃). ESI-MS: m/z 352.2 [M+H]⁺. Anal. calcd for C₁₉H₁₄ClN₃O₂ (351.79): C, 64.87; H, 4.01; N, 11.94. Found: C, 64.70; H, 3.98; N, 11.99.

Methyl 4-[(3-methoxyphenyl)amino]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (8j). Beige solid (792 mg, 76%). mp 165-166 °C. IR (solid, KBr, ν_{max} , cm⁻¹): 3050, 1683, 1651, 1534, 1483, 1280, 1198, 1045, 748. ^1H NMR (400 MHz, DMSO- d_6): δ_{H} 3.81 (3H, s, OCH₃), 3.93 (3H, s, OCH₃), 6.62-6.65 (1H, m, CH aromatic), 7.24-7.30 (3H, m, 3CH aromatic), 7.35 (1H, t, $^3J_{HH}$ 7.8 Hz, CH aromatic), 7.44 (1H, t, $^3J_{HH}$ 7.6 Hz, CH aromatic), 7.63 (1H, d, $^3J_{HH}$ 7.9 Hz, CH aromatic), 7.99 (1H, d, $^3J_{HH}$ 2.1 Hz, CH pyrrole), 8.18 (1H, d, $^3J_{HH}$ 8.2 Hz, CH aromatic), 8.38 (1H, d, $^3J_{HH}$ 3.5 Hz, CH pyrrole), 11.92 (1H, s, NH). ^{13}C NMR (CDCl₃, 76 MHz): δ_{C} 52.6 (CH₃O), 55.4 (CH₃O), 106.0, 108.3, 109.9, 112.6, 113.8, 114.1, 116.4, 121.9, 124.0, 124.1, 126.6, 127.4, 129.4, 136.8, 141.8, 146.3 (N=C aromatic), 160.2 (O-C aromatic), 167.2 (C=O). ESI-MS: m/z 348.2 [M+H]⁺. Anal. calcd for C₂₀H₁₇N₃O₃ (347.37): C, 69.15; H, 4.93; N, 12.10. Found: C, 69.34; H, 4.92; N, 12.16.

X-ray of methyl 4-[(3-methoxyphenyl)amino]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (8j). The colourless crystals of compound **8j** (C₂₀H₁₇N₃O₃) are triclinic. At 173 K $a = 7.5231(3)$, $b = 9.8646(3)$, $c = 11.4752(3)$ Å, $\alpha = 99.718(2)^\circ$, $\beta = 94.883(2)^\circ$, $\gamma = 97.226(2)^\circ$, $V = 827.77(5)$ Å³, $M_r = 347.36$, $Z = 2$, space group $P\bar{1}$, $d_{\text{calc}} = 1.394$ g/cm³, $\mu(\text{MoK}\alpha) = 0.096$ mm⁻¹, $F(000) = 364$. Intensities of 12074 reflections (2904 independent, $R_{\text{int}} = 0.0312$) were measured on the Bruker APEX II diffractometer (graphite monochromated MoK α radiation, CCD detector, ϕ - and ω -scanning, $2\theta_{\text{max}} = 50^\circ$). The structure was solved by direct method using OLEX2^[40] package with SHELXT^[41] and SHELXL modules.^[42] Positions of the hydrogen atoms were located from electron density difference maps and refined using "riding" model with $U_{\text{iso}} = nU_{\text{eq}}$ of the carrier atom ($n = 1.5$ for methyl groups and $n = 1.2$ for other hydrogen atoms). Full-matrix least-squares refinement against F^2 in anisotropic approximation for non-hydrogen atoms using 2904 reflections was converged to $wR_2 = 0.1113$ ($R_1 = 0.0413$ for 2289 reflections with $F > 4\sigma(F)$, $S = 1.018$). The final atomic coordinates, and crystallographic data for molecule **8j** have been deposited to with the Cambridge Crystallographic Data Centre, 12 Union Road, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) and are available on request quoting the deposition numbers CCDC 2453292).

Methyl 4-[(4-(trifluoromethyl)phenyl)amino]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (8k). White solid (902 mg, 78%). mp 214-215 °C. ^1H NMR (400 MHz, DMSO- d_6): δ_{H} 3.96 (3H, s, OCH₃), 7.31 (1H, d, $^3J_{HH}$ 2.8 Hz, CH pyrrole), 7.42 (1H, t, $^3J_{HH}$ 7.7 Hz, CH aromatic), 7.49 (1H, t, $^3J_{HH}$ 7.6 Hz, CH aromatic), 7.72 (3H, d, $^3J_{HH}$ 8.4 Hz, 3CH aromatic), 8.19-8.24 (3H, m, 3CH aromatic), 8.44 (1H, d, $^3J_{HH}$ 3.1 Hz, CH pyrrole), 12.21 (1H, s, NH). ^{13}C NMR (CDCl₃, 76 MHz): δ_{C} 52.7 (OCH₃), 110.0, 113.9, 114.4, 116.7, 119.5, 121.7, 123.8 (q, $^2J_{\text{CF}}$ 32.7 Hz, C aromatic), 124.3, 124.7, 124.7 (q, $^1J_{\text{CF}}$ 270.8 Hz, CF₃), 126.1 (q, $^3J_{\text{CF}}$ 3.6 Hz, 2CH aromatic), 126.9, 127.7, 136.6, 143.7, 146.1, 167.4. ^{19}F NMR (CDCl₃, 376 MHz): δ_{F} -62.16. ESI-MS: m/z 386.2 [M+H]⁺. Anal. calcd for C₂₀H₁₄F₃N₃O₂ (385.34): C, 62.34; H, 3.66; N, 10.90. Found: C, 62.49; H, 3.64; N, 10.79.

Methyl 4-[(4-bromophenyl)amino]-7,8-difluoropyrrolo[1,2-*a*]quinoxaline-3-carboxylate (8l). Beige solid (1.089 g, 84%). mp 282-283 °C. ^1H NMR (400 MHz, DMSO- d_6): δ_{H} 3.96 (3H, s, CH₃O), 7.30 (1H, d, $^3J_{HH}$ 3.1 Hz, CH pyrrole), 7.54 (2H, d, $^3J_{HH}$ 7.6 Hz, 2CH aromatic), 7.63 (1H, dd, $^3J_{\text{HF}}$ 11.6, $^3J_{HH}$ 8.0 Hz, CH aromatic), 7.92 (2H, d, $^3J_{HH}$ 9.0 Hz, 2CH aromatic), 8.35 (1H, d, $^3J_{HH}$ 3.3 Hz, CH pyrrole), 8.42 (1H, dd, $^3J_{\text{HF}}$ 11.4, $^3J_{HH}$ 7.9 Hz, CH aromatic), 11.98 (1H, s, NH). ^{13}C NMR (TFA- d_1 , 101 MHz): δ_{C} 55.4 (OCH₃) 107.2 (d, $^2J_{\text{CF}}$ 24.2 Hz, CH aromatic), 109.8 (d, $^2J_{\text{CF}}$ 23.9 Hz, CH aromatic), 118.7, 121.6 (d, $^3J_{\text{CF}}$ 7.9 Hz, C aromatic), 121.8, 122.7, 122.8, 123.2 (d, $^3J_{\text{CF}}$ 9.0 Hz, C aromatic), 126.9, 129.6, 132.5, 136.5, 148.4 (C=N), 151.7 (dd, $^1J_{\text{CF}}$ 253.6, $^2J_{\text{CF}}$ 13.6 Hz, CF aromatic), 152.3 (dd, $^1J_{\text{CF}}$ 253.3, $^2J_{\text{CF}}$ 12.9 Hz, CF aromatic), 169.4 (COOCH₃). ^{19}F NMR (DMSO- d_6 , 188 MHz): δ_{F} -140.68

(ddd, $^3J_{FF}$ 23.6, $^3J_{HF}$ 11.7, $^4J_{HF}$ 8.1 Hz), -139.62 (ddd, $^3J_{FF}$ 23.6, $^3J_{HF}$ 11.3, $^4J_{HF}$ 7.6 Hz). ESI-MS: m/z 434.0, 432.0 [M+H]⁺. Anal. calcd for C₁₉H₁₂BrF₂N₃O₂ (432.22): C, 52.80; H, 2.80; N, 9.72. Found: C, 53.03; H, 2.82; N, 9.60.

Methyl 7,8-dichloro-4-(*p*-tolylamino)pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (8m). Light yellow solid (1.057 g, 88%). mp 283-284 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ_H 2.31 (3H, s, CH₃), 3.92 (3H, s, CH₃O), 7.11-7.17 (3H, m, 2CH aromatic + CH pyrrole), 7.60 (1H, s, CH aromatic), 7.76 (2H, d, $^3J_{HH}$ 7.9 Hz, 2CH aromatic), 8.29 (1H, s, CH aromatic), 8.36 (1H, d, $^3J_{HH}$ 3.6 Hz, CH pyrrole), 11.76 (1H, s, NH). ¹³C NMR (TFA-*d*₁, 151 MHz): δ_C 21.6 (CH₃), 55.2 (CH₃O), 118.8, 119.1, 121.6, 121.8, 122.5, 122.8, 124.0, 125.8, 127.6, 130.5, 133.7, 134.2, 135.4, 144.1, 148.4 (C=N), 169.2 (COOCH₃). ESI-MS: m/z 400.0 [M+H]⁺. Anal. calcd for C₂₀H₁₅Cl₂N₃O₂ (400.26): C, 60.01; H, 3.78; N, 10.50. Found: C, 59.85; H, 3.80; N, 10.43.

Methyl 7,8-dichloro-4-[(3-methoxyphenyl)amino]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (8n). Beige solid (1.136 mg, 91%). mp 204-205 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ_H 3.81 (3H, s, OCH₃), 3.93 (3H, s, OCH₃), 6.65 (1H, s, CH aromatic), 7.20 (1H, s, CH pyrrole), 7.24-7.26 (2H, m, 2CH aromatic), 7.64 (1H, s, CH aromatic), 7.79 (1H, s, CH aromatic), 8.36 (1H, s, CH aromatic), 8.45 (1H, s, CH pyrrole), 11.92 (1H, s, NH). ¹³C NMR (CDCl₃, 76 MHz): δ_C 52.8 (CH₃O), 55.5 (CH₃O), 106.5, 108.7, 111.1, 113.0, 114.6, 115.4, 117.0, 121.6, 123.3, 127.0, 128.0, 129.6, 130.4, 136.5, 141.1, 146.8 (C=N aromatic), 160.2 (CH₃O-C aromatic), 167.1 (C=O). ESI-MS: m/z 416.0 [M+H]⁺. Anal. calcd for C₂₀H₁₅Cl₂N₃O₃ (416.26): C, 57.71; H, 3.63; N, 10.09. Found: C, 57.86; H, 3.65; N, 10.01.

Methyl 4-[(3-chlorophenyl)amino]-7,8-dimethylpyrrolo[1,2-*a*]quinoxaline-3-carboxylate (8o). Beige solid (1.014 g, 89%). mp 251-252 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ_H 2.31 (3H, s, CH₃), 2.35 (3H, s, CH₃), 3.94 (3H, s, CH₃O), 7.06 (1H, d, $^3J_{HH}$ 8.0 Hz, CH aromatic), 7.21 (1H, s, CH pyrrole), 7.35-7.39 (2H, m, 2CH aromatic), 7.72 (1H, d, $^3J_{HH}$ 8.2 Hz, CH aromatic), 7.90 (1H, s, CH aromatic), 8.22-8.25 (2H, m, CH aromatic + CH pyrrole), 11.87 (1H, s, NH). ¹³C NMR (TFA-*d*₁, 151 MHz): δ_C 20.1 (CH₃), 20.4 (CH₃), 55.1 (OCH₃), 118.6, 120.6, 121.4, 121.4, 121.9, 123.0, 124.1, 126.0, 128.2, 132.3, 134.0, 135.2, 139.1, 140.8, 141.6, 147.6 (C=N), 169.7 (COOCH₃). ESI-MS: m/z 380.2 [M+H]⁺. Anal. calcd for C₂₁H₁₈ClN₃O₂ (379.84): C, 66.40; H, 4.78; N, 11.06. Found: C, 66.17; H, 4.74; N, 10.98.

Methyl 4-(*p*-tolylamino)benzo[*g*]pyrrolo[1,2-*a*]quinoxaline-3-carboxylate (8p). Yellow solid (938 mg, 82%). mp 233-234 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ_H 2.33 (3H, s, CH₃), 3.97 (3H, s, OCH₃), 7.24 (2H, d, $^3J_{HH}$ 8.0 Hz, 2CH aromatic), 7.31 (1H, s, CH pyrrole), 7.47-7.52 (2H, m, 2CH aromatic), 7.95-8.02 (4H, m, 4CH aromatic), 8.15 (1H, s, CH aromatic), 8.53 (1H, s, CH aromatic), 8.72 (1H, s, CH pyrrole), 11.90 (1H, s, NH). ¹³C NMR (CDCl₃, 76 MHz): δ_C 21.1 (CH₃), 52.6 (OCH₃), 110.8, 111.2, 115.2, 116.1, 120.4, 122.0, 123.6, 124.2, 125.2, 125.6, 127.4, 127.5, 129.4, 130.0, 132.3, 132.4, 135.5, 137.8, 145.8 (C=N aromatic), 167.1 (C=O). ESI-MS: m/z 382.2 [M+H]⁺. Anal. calcd for C₂₄H₁₉N₃O₂ (381.43): C, 75.57; H, 5.02; N, 11.02. Found: C, 75.36; H, 4.99; N, 11.10.

General procedure for the synthesis of pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid 9a-p. A mixture of corresponding methyl pyrrolo[1,2-*a*]quinoxaline-3-carboxylate 8a-p (1 mmol) and KOH (280 mg, 5 mmol) in water (30 mL) and ethanol (30 mL) was refluxed for 24 h. Then the hot reaction mixture was filtered, the residue was washed with hot water (10 mL). Ethanol from the filtrate was evaporated and the water solution was neutralized by 5% HCl. The precipitate was filtered off, washed with water, ice-cold methanol (3 mL) and dried at 90-100 °C.

4-Pyrrolidin-1-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (9a). White solid (222 mg, 79%). mp 234-235 °C. ¹H NMR (300 MHz, DMSO-*d*₆): δ_H 1.95-2.03 (4H, m, 2CH₂ pyrrolidine), 3.84-3.92 (4H, m, 2CH₂ pyrrolidine), 7.23 (1H, s, CH pyrrole), 7.42-7.52 (2H, m, 2CH aromatic), 8.06-8.13 (1H, m, CH aromatic), 8.28 (1H, d, $^3J_{HH}$ 7.9 Hz, CH aromatic), 8.58 (1H, s, CH pyrrole) 12.21 (1H, broad s, OH). ¹³C NMR (TFA-*d*₁, 126 MHz): δ_C 27.0 (2CH₂ pyrrolidine), 55.1 (2CH₂ pyrrolidine), 117.0, 118.2, 120.6, 120.8, 122.4, 123.1, 125.5, 127.7, 129.4, 130.8, 149.0

(C=N), 171.1 (C=O). ESI-MS: m/z 282.2 [M+H]⁺. Anal. calcd for C₁₆H₁₅N₃O₂ (281.31): C, 68.31; H, 5.37; N, 14.94. Found: C, 68.52; H, 5.39; N, 14.88.

4-Morpholin-4-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (9b). Beige solid (247 mg, 83%). mp 256-257 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ_H 3.44-3.47 (4H, m, 2CH₂ morpholine), 3.79-3.81 (4H, m, 2CH₂ morpholine), 7.22 (1H, d, ³J_{HH} 3.0 Hz, CH pyrrole), 7.46-7.49 (2H, m, 2CH aromatic), 7.76-7.78 (1H, m, CH aromatic), 8.24-8.26 (1H, m, CH aromatic), 8.45 (1H, d, ³J_{HH} 3.0 Hz, CH pyrrole). ¹³C NMR (DMSO-*d*₆, 126 MHz): δ_C 50.2 (2CH₂ morpholine), 65.5 (2CH₂ morpholine), 114.9, 116.5, 117.1, 117.8, 124.8, 125.8, 126.0, 126.3, 131.4, 133.3, 151.8 (C=N), 164.4 (C=O). ESI-MS: m/z 298.2 [M+H]⁺. Anal. calcd for C₁₆H₁₅N₃O₃ (297.31): C, 64.64; H, 5.09; N, 14.13. Found: C, 64.81; H, 5.06; N, 14.04.

7,8-Difluoro-4-piperidin-1-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (9c). Yellow solid (252 mg, 76%). mp 226-227 °C. ¹H NMR (400 MHz, CDCl₃): δ_H 1.56-1.85 (2H, m, CH₂ piperidine), 1.91-1.99 (4H, m, 2CH₂ piperidine), 3.27-3.34 (4H, m, 2CH₂ piperidine), 7.60 (1H, d, ³J_{HH} 3.0 Hz, CH pyrrole), 7.71 (1H, dd, ³J_{HF} 10.2, ³J_{HH} 7.1 Hz, CH aromatic), 7.78 (1H, dd, ³J_{HF} 10.4, ³J_{HH} 8.0 Hz, CH aromatic), 7.84 (1H, d, ³J_{HH} 3.0 Hz, CH pyrrole). ¹³C NMR (CDCl₃, 76 MHz): δ_C 23.2 (CH₂ piperidine), 24.4 (2CH₂ piperidine), 53.2 (2CH₂ piperidine), 103.1 (d, ²J_{CF} 22.6 Hz, CH aromatic), 115.4, 116.2, 117.1 (d, ²J_{CF} 18.2 Hz, CH aromatic), 119.8, 120.0, 123.2 (d, ³J_{CF} 7.5 Hz, C aromatic), 131.8 (d, ³J_{CF} 9.4 Hz, C aromatic), 148.9 (dd, ¹J_{CF} 249.9, ²J_{CF} 14.0 Hz, CF aromatic), 150.5 (dd, ¹J_{CF} 254.0, ²J_{CF} 14.8 Hz, CF aromatic), 154.6 (C=N aromatic), 164.1 (C=O). ¹⁹F NMR (DMSO-*d*₆, 188 MHz): δ_F -139.88 (ddd, ³J_{FF} 23.0, ³J_{HF} 11.4, ⁴J_{HF} 7.9 Hz), -138.48 (ddd, ³J_{FF} 23.3, ³J_{HF} 12.0, ⁴J_{HF} 7.8 Hz). ESI-MS: m/z 332.2 [M+H]⁺. Anal. calcd for C₁₇H₁₅F₂N₃O₂ (331.32): C, 61.63; H, 4.56; N, 12.68. Found: C, 61.39; H, 4.59; N, 12.78.

7,8-Dichloro-4-morpholin-4-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (9d). Colorless solid (344 mg, 94%). mp 260-261 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ_H 3.42-3.49 (4H, m, CH₂ morpholine), 3.71-3.78 (4H, m, CH₂ morpholine), 7.17 (1H, s, CH pyrrole), 7.79 (1H, s, CH aromatic), 8.44 (1H, s, CH pyrrole), 8.56 (1H, s, CH aromatic), 12.75 (1H, s, OH). ¹³C NMR (DMSO-*d*₆, 76 MHz): δ_C 49.5 (2CH₂ morpholine), 65.6 (2CH₂ morpholine), 114.9, 116.4, 116.6, 117.3, 117.7, 124.5, 126.4, 127.4, 128.1, 135.2, 153.2 (C=N), 164.7 (C=O). ESI-MS: m/z 366.2 [M+H]⁺. Anal. calcd for C₁₆H₁₃Cl₂N₃O₃ (366.20): C, 52.48; H, 3.58; N, 11.47. Found: C, 52.65; H, 3.59; N, 11.34.

7,8-Dibromo-4-(butylamino)pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (9e). Colorless solid (349 mg, 85%). mp 265-266 °C. IR (solid, KBr, ν_{max}, cm⁻¹): 3347, 2869, 1664, 1461, 1375, 1241, 893, 742. ¹H NMR (400 MHz, DMSO-*d*₆): δ_H 0.96 (3H, t, ³J_{HH} 7.4 Hz, CH₃), 1.44-1.54 (2H, m, CH₂), 1.67-1.74 (2H, m, CH₂), 3.71-3.75 (2H, CH₂N), 7.27 (1H, d, ³J_{HH} 3.1 Hz, CH pyrrole), 8.35 (1H, s, CH aromatic), 8.51 (1H, d, ³J_{HH} 3.2 Hz, CH pyrrole), 8.67 (1H, s, CH aromatic), 11.43 (1H, s, NH). ¹³C NMR (DMSO-*d*₆, 76 MHz): δ_C 13.6 (CH₃), 19.5 (CH₂), 29.9 (CH₂), 42.6 (CH₂N), 116.9, 117.7, 118.4, 118.8, 119.3, 120.1, 121.5, 123.0, 124.4, 129.8, 146.8 (C=N), 167.6 (C=O). ESI-MS: m/z 442.0 [M+H]⁺. Anal. calcd for C₁₆H₁₅Br₂N₃O₂ (441.12): C, 43.56; H, 3.43; N, 9.53. Found: C, 43.39; H, 3.47; N, 9.47.

7,8-Dibromo-4-piperidin-1-ylpyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (9f). Yellow solid (390 mg, 86%). mp 237-238 °C. ¹H NMR (302 MHz, CDCl₃): δ_H 1.59-1.83 (2H, m, CH₂ piperidine), 1.89-1.99 (4H, m, 2CH₂ piperidine), 3.24-3.33 (4H, m, 2CH₂ piperidine), 7.59 (1H, s, CH pyrrole), 7.91 (1H, s, CH pyrrole), 8.18 (1H, s, CH aromatic), 8.22 (1H, s, CH aromatic). ¹³C NMR (CDCl₃, 75.5 MHz): δ_C 23.3 (CH₂ piperidine), 24.4 (2CH₂ piperidine), 53.2 (2CH₂ piperidine), 116.0, 116.3, 119.1, 120.0, 120.2, 122.2, 124.6, 126.4, 133.8, 135.2, 155.5 (C=N), 163.9 (C=O). ESI-MS: m/z 454.0 [M+H]⁺. Anal. calcd for C₁₇H₁₅Br₂N₃O₂ (453.13): C, 45.06; H, 3.36; N, 9.27. Found: C, 45.21; H, 3.33; N, 9.19.

7,8-Dimethyl-4-(pyrrolidin-1-yl)pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (9g). Beige solid (294 mg, 95%). mp 299-300 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ_H 1.93 – 1.99 (4H, m, 2CH₂), 2.30 (3H, s, CH₃), 2.34 (3H, s, CH₃), 3.80 – 3.87 (4H, m, 2CH₂), 7.14 (1H, d, *J* = 2.9 Hz, CH pyrrole), 7.81 (1H, s, CH aromatic), 8.00 (1H, s, CH

aromatic), 8.39 (1H, d, $J = 2.9$ Hz, CH pyrrole). ^{13}C NMR (TFA- d_1 , 76 MHz): δ_{C} 20.2 (CH₃), 20.4 (CH₃), 27.0 (2CH₂), 54.9 (N(CH₂)₂), 117.3, 118.2, 120.6, 120.9, 121.8, 122.3, 123.5, 125.6, 140.1, 141.4, 148.7 (C=N), 171.4 (C=O). ESI-MS: m/z 310.2 [M+H]⁺. Anal. calcd for C₁₈H₁₉N₃O₂ (309.36): C, 69.88; H, 6.19; N, 13.58. Found: C, 70.06; H, 6.17; N, 13.40.

4-(isopropylamino)benzo[*g*]pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (9h). Beige solid (281 mg, 88%). mp > 300 °C. ^1H NMR (400 MHz, DMSO- d_6): δ_{H} 1.29 (6H, d, $J = 6.5$ Hz, 2CH₃), 4.33-4.42 (1H, m, CH-NH), 7.16 (1H, d, $J = 3.1$ Hz, CH pyrrole), 7.37-7.43 (2H, m, 2CH aromatic), 7.89 (2H, d, $J = 7.6$ Hz, 2CH aromatic), 7.95 (1H, s, CH aromatic), 8.40 (1H, d, $J = 3.1$ Hz, CH pyrrole), 8.63 (1H, s, CH aromatic), 10.01 (1H, s, NH). ^{13}C NMR (TFA- d_1 , 126 MHz): δ_{C} 22.4 ((CH₃)₂CH), 47.8 ((CH₃)₂CH), 115.6, 117.8, 119.6, 120.5, 121.7, 122.2, 123.1, 125.0, 129.1, 129.6, 129.9, 130.3, 133.3, 134.2, 147.0 (C=N), 172.0 (C=O). ESI-MS: m/z 320.2 [M+H]⁺. Anal. calcd for C₁₉H₁₇N₃O₂ (319.36): C, 71.46; H, 5.37; N, 13.16. Found: C, 71.29; H, 5.34; N, 12.98.

4-((3-Chlorophenyl)amino)pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (9i).^[20] Beige solid (243 mg, 72%). mp > 300 °C. ^1H NMR (400 MHz, DMSO- d_6): δ_{H} 7.10 (1H, d, $^3J_{\text{HH}}$ 8.0 Hz, CH aromatic), 7.31 (1H, d, $^3J_{\text{HH}}$ 3.1 Hz, CH pyrrole), 7.41 (2H, t, $^3J_{\text{HH}}$ 8.2 Hz, CH aromatic), 7.48 (1H, t, $^3J_{\text{HH}}$ 7.5 Hz, CH aromatic), 7.69 (1H, d, $^3J_{\text{HH}}$ 7.7 Hz, CH aromatic), 7.73 (1H, d, $^3J_{\text{HH}}$ 8.0 Hz, CH aromatic), 8.26 (1H, d, $^3J_{\text{HH}}$ 8.2 Hz, CH aromatic), 8.37 (1H, s, CH aromatic), 8.46 (1H, d, J 3.1 Hz, CH pyrrole), 12.62 (1H, s, NH), 13.62 (1H, s, OH). ^{13}C NMR (DMSO- d_6 , 101 MHz): δ_{C} 111.2, 115.5, 116.7, 117.2, 117.9, 119.0, 120.9, 122.1, 124.5, 125.1, 127.0, 127.2, 130.9, 133.7, 136.1, 142.2, 146.0 (C=N), 169.0 (C=O). ESI-MS: m/z 338.0 [M+H]⁺. Anal. calcd for C₁₈H₁₂ClN₃O₂ (337.76): C, 64.01; H, 3.58; N, 12.44. Found: C, 63.92; H, 3.56; N, 12.56.

4-((3-Methoxyphenyl)amino)pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (9j). Beige solid (280 mg, 84%). mp 290-291 °C. ^1H NMR (400 MHz, DMSO- d_6): δ_{H} 3.82 (3H, s, OCH₃), 6.69-6.72 (1H, m, CH aromatic), 7.30-7.36 (3H, m, 3CH aromatic), 7.41 (1H, t, $^3J_{\text{HH}}$ 7.6 Hz, CH aromatic), 7.48 (1H, t, $^3J_{\text{HH}}$ 7.6 Hz, CH aromatic), 7.70 (1H, d, $^3J_{\text{HH}}$ 8.0 Hz, CH aromatic), 7.85 (1H, s), 8.26 (1H, d, $^3J_{\text{HH}}$ 8.1 Hz, CH aromatic), 8.48 (1H, d, $^3J_{\text{HH}}$ 3.2 Hz, CH pyrrole), 12.69 (1H, s, NH). ^{13}C NMR (CDCl₃, 126 MHz): δ_{C} 55.1 (OCH₃), 106.8, 110.0, 113.3, 115.3, 117.3, 117.5, 119.9, 123.7, 124.1, 124.2, 124.9, 127.0, 130.0, 132.6, 139.4, 145.7 (N=C aromatic), 160.0 (O-C aromatic), 168.4 (C=O). ESI-MS: m/z 334.0 [M+H]⁺. Anal. calcd for C₁₉H₁₅N₃O₃ (333.34): C, 68.46; H, 4.54; N, 12.61. Found: C, 68.25; H, 4.55; N, 12.53.

4-[[4-(Trifluoromethyl)phenyl]amino]pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (9k). White solid (327 mg, 88%). mp 261-262 °C. ^1H NMR (302 MHz, DMSO- d_6): δ_{H} 7.33 (1H, d, $^3J_{\text{HH}}$ 3.1 Hz, CH pyrrole), 7.43 (1H, d, $^3J_{\text{HH}}$ 7.6 Hz, CH aromatic), 7.50 (1H, d, $^3J_{\text{HH}}$ 7.5 Hz, CH aromatic), 7.72-7.78 (3H, m, 3CH aromatic), 8.19-8.31 (3H, m, 3CH aromatic), 8.49 (1H, d, $^3J_{\text{HH}}$ 3.2 Hz, CH pyrrole), 12.81 (1H, s, NH), 13.66 (1H, s, OH). ^{13}C NMR (DMSO- d_6 , 76 MHz): δ_{C} 110.8, 115.1, 116.4, 116.8, 118.8, 118.9, 120.4, 121.8 (q, $^2J_{\text{CF}}$ 31.8 Hz, C aromatic), 124.2, 124.6 (q, $^1J_{\text{CF}}$ 270.8 Hz, CF₃), 124.9, 126.1 (q, $^3J_{\text{CF}}$ 3.8 Hz, 2CH aromatic), 126.7, 135.5, 143.8, 145.5 (C=N), 168.5 (C=O). ^{19}F NMR (DMSO- d_6 , 188 MHz): δ_{F} -59.90. ESI-MS: m/z 372.0 [M+H]⁺. Anal. calcd for C₁₉H₁₂F₃N₃O₂ (371.31): C, 61.46; H, 3.26; N, 11.32. Found: C, 61.22; H, 3.21; N, 11.43.

4-((4-Bromophenyl)amino)-7,8-difluoropyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (9l). Light yellow solid (347 mg, 83%). mp > 300 °C. ^1H NMR (400 MHz, DMSO- d_6): δ_{H} 7.22 (1H, d, $^3J_{\text{HH}}$ 2.7 Hz, CH pyrrole), 7.46-7.58 (3H, m, 3CH aromatic), 7.86 (2H, d, $^3J_{\text{HH}}$ 8.5 Hz, 2CH aromatic), 8.27 (1H, d, $^3J_{\text{HH}}$ 2.8 Hz, CH pyrrole), 8.35 (1H, dd, $^3J_{\text{HF}}$ 11.7, $^3J_{\text{HH}}$ 7.9 Hz, CH aromatic), 12.48 (1H, s, NH) 13.60 (1H, s, OH). ^{13}C NMR (TFA- d_1 , 151 MHz): δ_{C} 107.3 (d, $^2J_{\text{CF}}$ 24.0 Hz, CH aromatic), 109.9 (d, $^2J_{\text{CF}}$ 24.0 Hz, CH aromatic), 119.2, 121.3, 121.5 (d, $^3J_{\text{CF}}$ 8.0 Hz, C aromatic), 122.8, 123.0, 123.2 (d, $^3J_{\text{CF}}$ 8.7 Hz, C aromatic), 127.1, 129.6, 132.2, 136.6, 148.3 (C=N), 151.8 (dd, $^1J_{\text{CF}}$ 254.7, $^2J_{\text{CF}}$ 14.0 Hz, CF aromatic), 152.5 (dd, $^1J_{\text{CF}}$ 254.4, $^2J_{\text{CF}}$ 13.7 Hz, CF aromatic), 171.7 (C=O). ^{19}F NMR (DMSO- d_6 , 188 MHz): δ_{F} -140.79 (ddd, $^3J_{\text{FF}}$ 23.7, $^3J_{\text{HF}}$ 11.5, $^4J_{\text{HF}}$ 8.5 Hz), -139.77 (ddd, $^3J_{\text{FF}}$ 23.9, $^3J_{\text{HF}}$ 11.5, $^4J_{\text{HF}}$ 8.3

H_z). ESI-MS: *m/z* 417.8, 419.8 [M+H]⁺. Anal. calcd for C₁₈H₁₀BrF₂N₃O₂ (418.19): C, 51.70; H, 2.41; N, 10.05. Found: C, 51.83; H, 2.39; N, 9.98.

7,8-Dichloro-4-(*p*-tolylamino)pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (9m). Light yellow solid (274 mg, 71%). mp > 300 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ_H 2.30 (3H, s, CH₃), 7.17 (2H, d, ³*J*_{HH} 8.2 Hz, 2CH aromatic), 7.24 (1H, d, ³*J*_{HH} 3.2 Hz, CH pyrrole), 7.73 (1H, s, CH aromatic), 7.83 (2H, d, ³*J*_{HH} 8.0 Hz, 2CH aromatic), 8.40 (1H, d, ³*J*_{HH} 3.2 Hz, CH pyrrole), 8.50 (1H, s, CH aromatic), 12.42 (1H, s, NH), 13.61 (1H, s, OH). ¹³C NMR (TFA-*d*₁, 151 MHz): δ_C 21.6 (CH₃), 115.7, 117.5, 119.2, 121.4, 121.9, 122.6, 122.8, 124.0, 125.8, 127.6, 130.2, 133.7, 134.5, 135.7, 144.3, 148.3 (C=N), 171.6 (C=O). ESI-MS: *m/z* 386.0 [M+H]⁺. Anal. calcd for C₁₉H₁₃Cl₂N₃O₂ (386.23): C, 59.08; H, 3.39; N, 10.88. Found: C, 58.91; H, 3.41; N, 10.70.

7,8-Dichloro-4-[(3-methoxyphenyl)amino]pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (9n). Light brown solid (370 mg, 92%). mp 280-281 °C. ¹H NMR (300 MHz, DMSO-*d*₆): δ_H 3.80 (3H, s, OCH₃), 6.65 (1H, d, ³*J*_{HH} 7.3 Hz, CH aromatic), 7.24-7.29 (2H, m, CH pyrrole + CH aromatic), 7.36 (1H, d, ³*J*_{HH} 8.0 Hz, CH aromatic), 7.73 (1H, s, CH aromatic), 7.77 (1H, s, CH aromatic), 8.41 (1H, d, ³*J*_{HH} 3.2 Hz, CH pyrrole), 8.53 (1H, s, CH aromatic), 12.52 (1H, s, NH), 13.70 (1H, s, OH). ¹³C NMR (DMSO-*d*₆, 76 MHz): δ_C 54.9 (CH₃O), 105.1, 108.3, 111.5, 111.8, 116.7, 116.9, 120.3, 123.5, 125.6, 126.8, 128.6, 129.5, 136.0, 141.0, 146.4 (C=N), 159.6 (C-OCH₃), 168.3 (C=O). ESI-MS: *m/z* 402.0 [M+H]⁺. Anal. calcd for C₁₉H₁₃Cl₂N₃O₃ (402.23): C, 56.73; H, 3.26; N, 10.45. Found: C, 56.57; H, 3.24; N, 10.55.

4-((3-Chlorophenyl)amino)-7,8-dimethylpyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (9o). Beige solid (274 mg, 75%). mp > 300 °C. ¹H NMR (302 MHz, DMSO-*d*₆): δ_H 2.33 (3H, s, CH₃), 2.36 (3H, s, CH₃), 7.08 (1H, d, ³*J*_{HH} 7.9 Hz, CH aromatic), 7.26 (1H, d, ³*J*_{HH} 3.1 Hz, CH pyrrole), 7.39 (1H, t, ³*J*_{HH} 8.1 Hz, CH aromatic), 7.44 (1H, s, CH aromatic), 7.70 (1H, d, ³*J*_{HH} 8.2 Hz, CH aromatic), 8.01 (1H, s, CH aromatic), 8.29-8.38 (2H, m, CH aromatic + CH pyrrole), 12.53 (1H, s, NH), 13.50 (1H, s, OH). ¹³C NMR (TFA-*d*₁, 151 MHz): δ_C 20.1 (CH₃), 20.4 (CH₃), 117.6, 119.1, 119.9, 120.7, 122.2, 122.6, 123.0, 124.2, 126.1, 128.3, 132.6, 134.1, 134.9, 139.2, 141.2, 142.1, 147.6 (C=N), 172.2 (C=O). ESI-MS: *m/z* 366.0 [M+H]⁺. Anal. calcd for C₂₀H₁₆ClN₃O₂ (365.81): C, 65.67; H, 4.41; N, 11.49. Found: C, 65.81; H, 4.39; N, 11.60.

4-(*p*-Tolylamino)benzo[*g*]pyrrolo[1,2-*a*]quinoxaline-3-carboxylic acid (9p). Light brown solid (331 mg, 90%). mp 269-270 °C. IR (solid, KBr, ν_{max}, cm⁻¹): 3422, 2754, 1655, 1512, 1466, 816, 746, 546. ¹H NMR (400 MHz, DMSO-*d*₆): δ_H 2.35 (3H, s, CH₃), 7.29 (2H, d, ³*J*_{HH} 7.9 Hz, 2CH aromatic), 7.34 (1H, d, ³*J*_{HH} 2.8 Hz, CH pyrrole), 7.50-7.52 (2H, m, 2CH aromatic), 7.81 (2H, d, ³*J*_{HH} 7.8 Hz, 2CH aromatic), 7.96-7.98 (2H, m, 2CH aromatic), 8.16 (1H, s, CH aromatic), 8.59 (1H, d, ³*J*_{HH} 3.0 Hz, CH pyrrole), 8.78 (1H, s, CH aromatic), 12.87 (1H, s, NH). ¹³C NMR (TFA-*d*₁, 76 MHz): δ_C 21.7 (CH₃), 115.7, 118.3, 119.2, 121.2, 123.1, 123.3, 124.5, 127.6, 129.2, 129.6, 130.1, 130.4, 130.5, 133.5, 133.9, 134.2, 144.2, 148.0 (N=C), 172.1 (C=O). ESI-MS: *m/z* 368.2 [M+H]⁺. Anal. calcd for C₂₃H₁₇N₃O₂ (367.40): C, 75.19; H, 4.66; N, 11.44. Found: C, 75.38; H, 4.65; N, 11.33.

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Supplementary Material

For details, please see Supplementary Material available.

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