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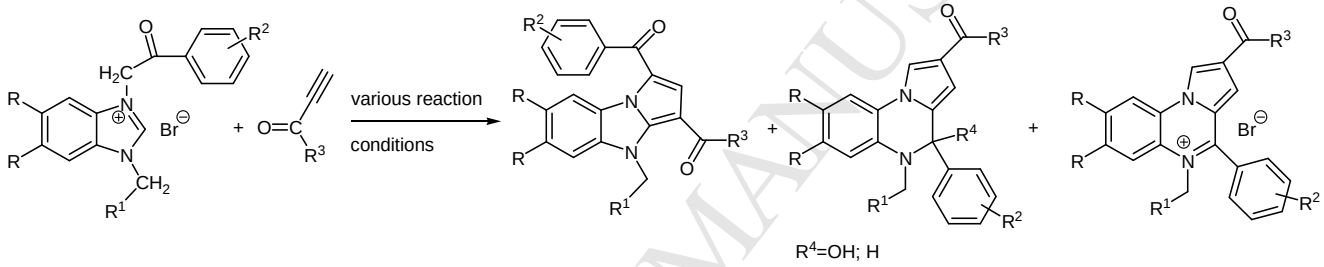

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Fine tuning the outcome of 1,3-dipolar cycloaddition reactions of benzimidazolium ylides to activated alkynes

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ABSTRACT

1,3-Dipolar cycloaddition reactions of benzimidazolium ylides, generated from 3-phenacylbenzimidazolium bromides, to non-symmetrical activated dipolarophiles in various reaction conditions led to complex mixtures of pyrrolo[1,2-*a*]benzimidazole and pyrrolo[1,2-*a*]quinoxaline derivatives. In order to explain all experimental results, the influence of reaction conditions on the reaction products was investigated. For the first time, 4-hydroxy-4,5-dihydropyrrolo[1,2-*a*]quinoxaline derivatives **6**, pyrrolo[1,2-*a*]quinoxalinium quaternary salts **8**, as well as 4-methoxy-4,5-dihydropyrrolo[1,2-*a*]quinoxalines **9**, were separated, fully characterized and their interconversions are presented, together with a proposed reaction mechanism.

1. Introduction

The interest in pyrrolo[1,2-*a*]benzimidazole and pyrrolo[1,2-*a*]quinoxaline derivatives has increased significantly over time, mainly due to their biological and pharmacological properties. Pyrrolo[1,2-*a*]quinoxalines substituted at C-4 with alkylpiperazines present both high affinity and selectivity for anti-serotonin 5-HT_3 receptors.[1] Pyrrolo[1,2-*a*]quinoxaline-carboxylic acid hydrazide derivatives showed antimycobacterial activity against *Mycobacterium tuberculosis*,[2] while 4-substituted pyrrolo[1,2-*a*]quinoxalines exhibited antiparasitic activity upon *Leishmania amazonensis* and *Leishmania infantum* strains.[3] 2-(Aminomethyl)-4-phenyl-pyrrolo[1,2-*a*]quinoxaline derivatives revealed a central dopamine antagonist activity,[4] pyrrolo[1,2-*a*]quinoxaline-5-(4*H*)-yl)sulfonyls and carbonyls were tested as estrogenic receptor modulators,[5] whereas pyrrolo[1,2-*a*]quinoxalin-4-yl-hydrazides can be used for treating cancer and disorders associated with angiogenesis function.[6] Antitumor agents based on the pyrrolo[1,2-*a*]benzimidazole ring system were designed as new DNA cross-linkers mimicking the mitomycin antitumor agents against various human cancer cells,[7] and different 2-oxo-pyrrolo[1,2-*a*]benzimidazole-3-carboxyl derivatives demonstrated therapeutic properties on central nervous system disorders.[8]

An interesting synthetic pathway to construct the pyrrolo[1,2-*a*]benzimidazole system is based on the classical 1,3-dipolar cycloaddition reaction of benzimidazolium ylides with electron-deficient alkynes or alkenes. This process usually starts with the preparation of benzimidazolium salts, *in situ* conversion into corresponding benzimidazolium ylides in the presence of an inorganic or organic base and 1,3-dipolar cycloaddition reactions of benzimidazolium ylides with dipolarophiles affording pyrrolo[1,2-*a*]benzimidazoles in low to moderate yields.[9a-h] Alternatively, the benzimidazolimum salts may also be isolated for further property studies.[9i]

Our group has developed a simple one-pot, multi-component synthetic strategy towards *N*-bridgehead heterocyclic compounds. This strategy is based on the consecutive quaternization of the *N*-heterocycle compound, *in situ* generation of the heterocyclic *N*-ylide, 1,3-dipolar cycloaddition reaction to an electron-deficient alkyne and aromatization sequence, using an epoxide as solvent and acid scavenger.[10] Trying to apply this synthetic protocol to benzimidazole derivatives we obtained in most cases mixtures of

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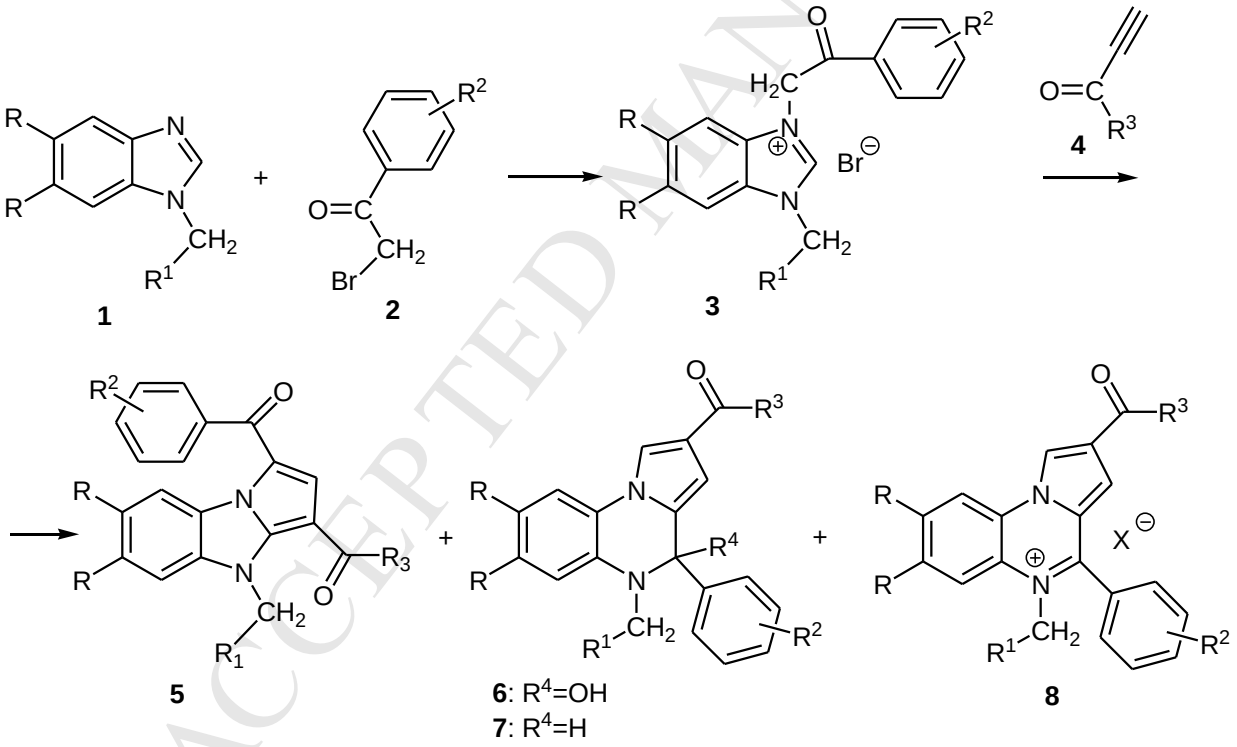
pyrrolo[1,2-*a*]benzimidazoles and pyrrolo[1,2-*a*]quinazolines.[11a-d] Thus, by 1,3-dipolar cycloaddition reactions of 1-substituted 3-(alkoxycarbonylmethyl)benzimidazolium ylides to non-symmetrical acetylenic dipolarophiles, we obtained pyrrolo[1,2-*a*]quinoxalin-4-ones as major reaction products and pyrrolo[1,2-*a*]benzimidazoles as minor reaction products.[11b] In the same reaction conditions, by the 1,3-dipolar cycloaddition reactions of 1-substituted 3-(benzoylmethyl)benzimidazolium ylides to non-symmetrical acetylenic dipolarophiles, mixtures of 4-phenyl pyrrolo[1,2-*a*]quinoxalines and pyrrolo[1,2-*a*]benzimidazoles were obtained.[11a,c] For the formation of pyrrolo[1,2-*a*]quinoxalines along with pyrrolo[1,2-*a*]benzimidazoles *via* 1,3-dipolar cycloaddition reactions of benzimidazolium ylides with non-symmetrical activated acetylenic dipolarophiles, a mechanism involving opening of the imidazole ring has been proposed.[9d,11a-c,12] The mechanism was also supported by the isolation of open chain intermediates.[11c,d]

Further research aims to clarify the reaction mechanism for the formation of 5-substituted pyrrolo[1,2-*a*]quinoxalines and pyrrolo[1,2-*a*]benzimidazoles *via* 1,3-dipolar cycloaddition reactions of benzimidazolium ylides, generated *in situ* from the benzimidazolium bromides, with activated acetylenic dipolarophiles.

Herein, we present an extensive study on the 1,3-dipolar cycloaddition reaction of benzimidazolium ylides, generated *in situ* from the 3-phenacylbenzimidazolium bromide, with non-symmetrical activated dipolarophiles in various reaction conditions in order to elucidate the formation of pyrrolo[1,2-*a*]quinoxalines along with the normal 1,3-dipolar cycloaddition compounds, pyrrolo[1,2-*a*]benzimidazoles.

2. Results and discussion

By the reactions of 1-substituted benzimidazoles **1** with phenacyl bromides **2**, 1-substituted 3-phenacylbenzimidazolium bromides **3** were easily obtained. The 1,3-dipolar cycloaddition reactions of benzimidazolium ylides, obtained *in situ* from 1-substituted 3-phenacylbenzimidazolium bromides **3**, in the presence of various acid acceptors and solvents, with two different non-symmetrical activated dipolarophiles such as ethyl propiolate **4** (R^3 = OEt) or 3-butyn-2-one **4** (R^3 = Me) led to complex mixtures of pyrrolo[1,2-*a*]benzimidazoles **5**, 4-hydroxy-4,5-dihydropyrrolo[1,2-*a*]quinoxalines **6**, 4,5-dihydropyrrolo[1,2-*a*]quinoxalines **7** and pyrrolo[1,2-*a*]quinoxaline quaternary salts **8** (Scheme 1). All crude reaction products were analyzed by HPLC. The identified reaction products were separated by crystallization based on differences in their solubility. Pyrrolo[1,2-*a*]benzimidazole derivatives **5** are very soluble in chloroform and only slightly soluble in methanol and ethyl acetate. 4,5-Dihydropyrrolo[1,2-*a*]quinoxalines **7** are the most soluble reaction products.



Scheme 1. The reaction scheme for one-pot synthesis of pyrrolo[1,2-*a*]benzimidazoles and pyrrolo[1,2-*a*]quinoxalines.

In order to explain these experimental results, we investigated the influence of reaction conditions on the reaction product yields in the above described cycloadditions. Therefore, the 1,3-dipolar cycloaddition reactions of the various benzimidazolium ylides generated *in situ* from the corresponding 3-phenacylbenzimidazolium bromide **3** with ethyl propiolate, as well as with 3-butyn-2-one, were performed in the presence of various acid acceptors and solvents, with or without tetrapyridinecobalt(II)dichromate (TPCD)[13] as oxidant to promote aromatization of the primary cycloadduct. Final reaction products have been identified by HPLC analysis of crude reaction mixtures in the same conditions, as described in the experimental section.

The 1,3-dipolar cycloaddition reactions of the corresponding benzimidazolium ylide generated *in situ* from the 1-benzyl-3-(4'-fluorophenacyl)-benzimidazolium bromide with ethyl propiolate were performed in different reaction conditions and the obtained results are presented in Table 1.

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Table 1. The influence of reaction conditions on reaction product yields in the reaction of 1-benzyl-3-(4'-fluorophenacyl)benzimidazolium bromide with ethyl propiolate.

Entry	Reaction conditions	Reaction products yields (%)*			
		5	**6**	**7**	**8**
1	1,2-epoxybutane, 70 h, rt	54	10	21	5
2	1,2-epoxybutane, 24 h, reflux	46	12	28	7
3	1,2-epoxybutane + TPCD, 24 h, reflux	66	14	5	6
4	NEt_3 in acetonitrile, 3 h, reflux	25	10	16	20
5	NEt_3 + TPCD in DMF, 2 h, 90 ^oC	77	-	6	13
6	K_2CO_3 in DMF, 2 days, rt	20	15	18	25

* Calculated from HPLC chromatograms.

Similarly, the 1,3-dipolar cycloaddition reactions of the corresponding benzimidazolium ylide generated *in situ* from the 1-benzyl-3-(4'-chlorophenacyl)-benzimidazolium bromide with 3-butyn-2-one were carried out in different reaction conditions and the results are presented in Table 2.

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Table 2. The influence of reaction conditions on reaction product yields in the reaction of 1-benzyl-3-(4'-chlorophenacyl)benzimidazolium bromide with 3-butyn-2-one.

Entry	Reaction conditions	Reaction products yields (%) *			
		5	**6**	**7**	**8**
1	1,2-epoxybutane, 150 h, 5 ºC	30	6	60	-
2	1,2-epoxybutane, 70 h, rt	24	12	48	3
3	1,2-epoxybutane, 24 h, reflux	21	19	40	7
4	1,2-epoxybutane, MW, 40 min., 125 ºC	13	25	23	33
5	NEt_3 in acetonitrile, 3 h, reflux	15	35	12	21
6	NEt_3 + TPCD in DMF, 2 h, 90 ºC	78	-	-	12
7	K_2CO_3 in DMF, 2 days, rt	20	25	8	26

* Calculated from HPLC chromatograms.

In 1,3-dipolar cycloaddition reactions of benzimidazolium ylides with ethyl propiolate, carried out in the presence of epoxides, the major reaction product is the corresponding pyrrolo[1,2-*a*]benzimidazole **5** while, in the same reaction conditions, when 3-butyn-2-one is used as dipolarophile the major reaction products are pyrrolo[1,2-*a*]quinoxaline derivatives **6-8**. The results could be explained by a better stabilization of the intermediate primary cycloadduct bearing a carbethoxy group in comparison to an acetyl group.

By increasing the reaction temperature, the amount of pyrrolo[1,2-*a*]benzimidazole **5** decreases while the amount of pyrrolo[1,2-*a*]quinoxaline derivatives **6-9** increases, independently of the employed dipolarophile.

In all 1,3-dipolar cycloaddition reactions of benzimidazolium ylides, generated *in situ* from 3-phenacylbenzimidazolium bromides **3**, with both ethyl propiolate or 3-butyn-2-one, in the presence of triethylamine and an oxidant such as TPCD in DMF at 90 ºC, normal cycloaddition products, pyrrolo[1,2-*a*]benzimidazoles **5** are the major reaction products along with small amounts of pyrrolo[1,2-*a*]quinoxalinium salts **8**. In the same reactions carried out in the presence of an epoxide and TPCD at 65 ºC, pyrrolo[1,2-*a*]benzimidazoles **5** are still the major reaction products but the amounts of pyrrolo[1,2-*a*]quinoxalines increase. Other oxidants, such as CrO_3, MnO_2 or chloranil, cannot be used together with epoxides.

These differences could be explained by a different mechanism in the generation of benzimidazolium ylides in the presence of organic or inorganic bases than in the presence of epoxides. In the presence of an inorganic or organic base, the benzimidazolium ylide is easily generated by the deprotonation of the 3-phenacylbenzimidazolium salt. In the presence of epoxides, the benzimidazolium ylide generation implies the attack of the bromide ion of 3-phenacylbenzimidazolium salt on the oxirane ring. The reactive intermediate obtained by the ring opening of the oxirane extracts a methylene proton from the 3-phenacyl-benzimidazolium salt generating slowly the corresponding benzimidazolium ylide. In both cases, the *in situ* generated benzimidazolium ylide reacts further with the acetylenic dipolarophile to give a primary cycloadduct which spontaneously dehydrogenates and rearranges to the

thermodynamically more stable aromatized pyrrolo[1,2-*a*]benzimidazole **5**. Obviously, pyrrolo[1,2-*a*]benzimidazoles **5** are major reaction products in good yields, when the 1,3-dipolar cycloaddition reactions of 3-phenacyl-benzimidazolium ylides with activated alkynes are carried out in the presence of triethylamine and an oxidant such as TPCD at 90 ºC.

The ratio of pyrrolo[1,2-*a*]quinoxalines **6-8** to pyrrolo[1,2-*a*]benzimidazole **5** increase slightly when an electron-withdrawing substituent is present on the phenyl group from 3-phenacyl-benzimidazolium bromides **3** (Table 3).

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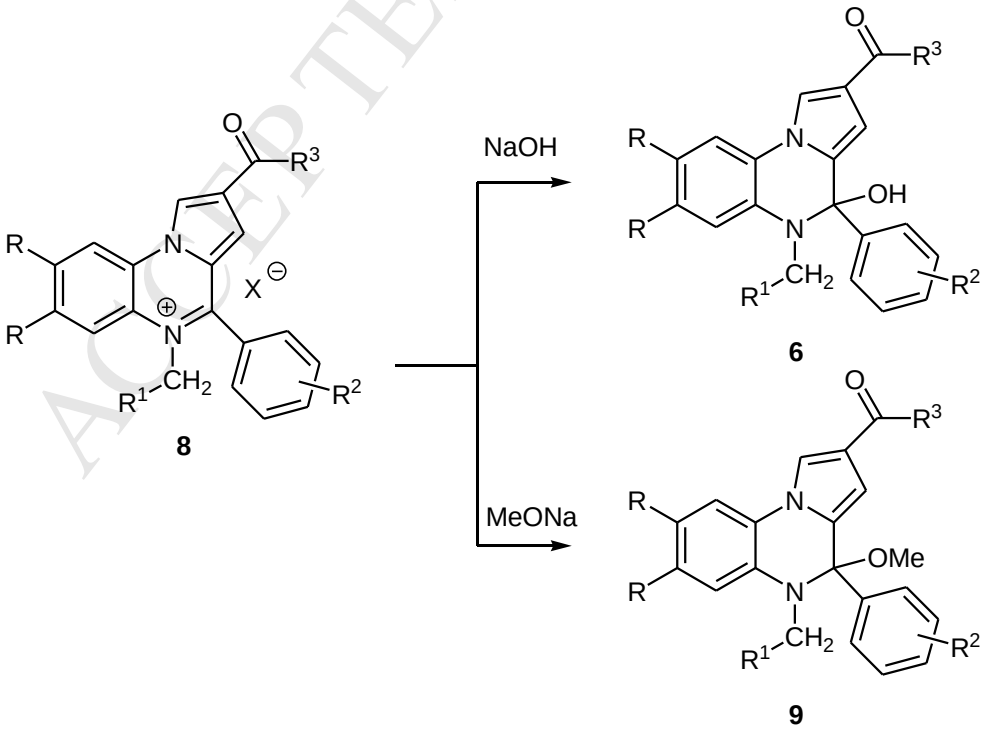
Table 3. The influence of substituents from 3-phenacyl-benzimidazolium bromides **3** on reaction product yields.

Entry	R^2	R^3	Reaction conditions	Yields ratio Σ**6-8** / **5***
1	4-F	Me	1,2-epoxybutane, 70 h, rt	2.7
			1,2-epoxybutane, 24 h, reflux	3.3
2	4-Cl	Me	1,2-epoxybutane, 70 h, rt	2.6
			1,2-epoxybutane, 24 h, reflux	3.1
3	3-NO_2	Me	1,2-epoxybutane, 70 h, rt	4.3
			1,2-epoxybutane, 24 h, reflux	4.6
4	4-NO_2	Me	1,2-epoxybutane, 70 h, rt	3.5
			1,2-epoxybutane, 24 h, reflux	3.6

* Calculated from HPLC chromatograms.

During the separation and purification procedures for the reaction products identified by HPLC, when we tried to crystallize 4-hydroxy-4,5-dihydropyrrolo[1,2-*a*]quinoxalines **6** or 4,5-dihydropyrrolo[1,2-*a*]quinoxalines **7** from $CHCl_3$ containing traces of acidity we obtained a mixture that also contained various amounts of pyrrolo[1,2-*a*]quinoxaline quaternary salts **8**. When samples of 4-hydroxy-4,5-dihydropyrrolo[1,2-*a*]quinoxalines **6** or 4,5-dihydropyrrolo[1,2-*a*]quinoxalines **7** were dissolved in a mixture of $CDCl_3$ and trifluoroacetic acid the ^1H and ^{13}C NMR spectra of pyrrolo[1,2-*a*]quinoxaline quaternary salts **8** were obtained. We observed that pyrrolo[1,2-*a*]quinoxaline quaternary salts **8** are obtained in almost quantitative yields through the reaction of dihydropyrrolo[1,2-*a*]quinoxalines **6** or **7** with acids. The treatment of pyrrolo[1,2-*a*]quinoxaline quaternary salts **8** with sodium hydroxide led back to reaction products **6**, while their treatment with sodium methoxide gave pyrrolo[1,2-*a*]quinoxalines **9** (Scheme 2), both in over 70 % yields. Moreover, 4-methoxypyrrolo[1,2-*a*]quinoxaline derivatives **9** were identified and isolated during the crystallization procedure of several pyrrolo[1,2-*a*]quinoxalines **6** from methanol.

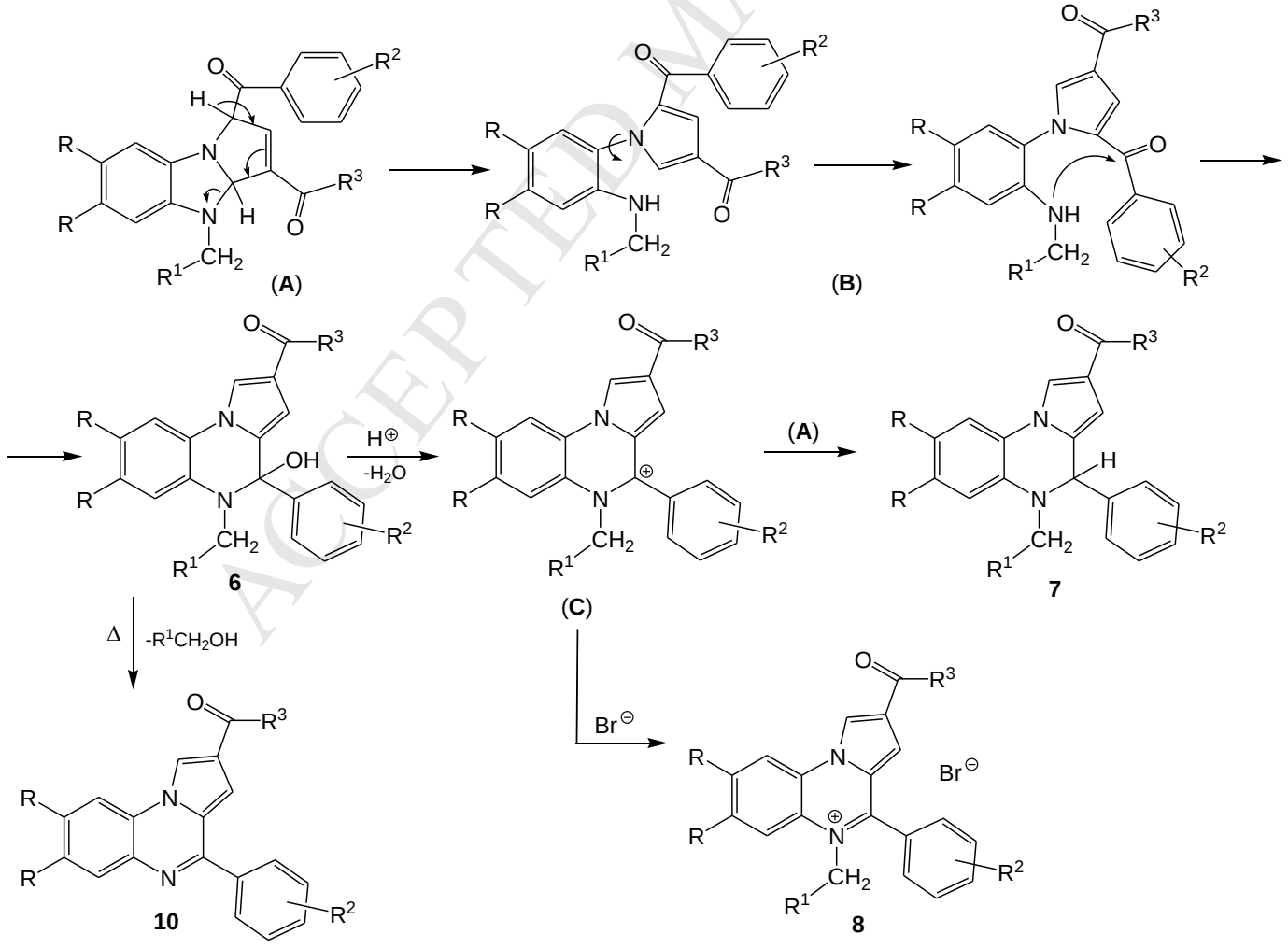


Scheme 2. The formation of 4-hydroxy-pyrrolo[1,2-*a*]quinoxalines **6** and 4-methoxy-pyrrolo[1,2-*a*]quinoxalines **9** from pyrrolo[1,2-*a*]quinoxaline quaternary salts **8**.

During the work-up of the reaction mixture resulting from the 1,3-dipolar cycloaddition reaction of 1-benzyl-3-phenacylbenzimidazolium bromide with ethyl propiolate in 1,2-epoxybutane at reflux, after major reaction products were separated, the remaining filtrate was evaporated to dryness, the residue was dissolved in acetone, the insoluble part was collected by filtration and recrystallized from methanol. Based on ^{1}H, ^{13}C and ^{15}N NMR spectra we assigned the structure of ethyl 4-phenylpyrrolo[1,2-*a*]quinoxaline-2-carboxylate (**10**) to this later compound. This product was identified in the HPLC chromatogram of crude mixture in concentration of about 6%. Similar products without a benzyl group at the N-5 position seem to be present in the majority of the crude reaction mixture HPLC chromatograms. The intensity of these peaks increase with the reaction temperature, but they still remain minor peaks, and at this stage they have not been isolated for further structure elucidation.

All experimental data confirm that the 1,3-dipolar cycloaddition reactions of the benzimidazolium ylide generated *in situ* from 3-phenacylbenzimidazolium bromides with the non-symmetrical activated dipolarophile in different reaction conditions involve the initial formation of 1,3-dipolar cycloaddition adducts (A) from which pyrrolo[1,2-*a*]benzimidazole derivatives **5** are subsequently formed (Scheme 3).[11a-d]

The reaction mechanism for the formation of 4,5-dihydropyrrolo[1,2-*a*]quinoxaline **6** (Scheme 3) involves the imidazole ring opening initiated by the deprotonation at the C-1 position of the primary cycloadduct (A), followed by the rotation of the pyrrole ring around the carbon-nitrogen single bond and the cyclization of the open intermediate (B) involving the benzoyl C=O group to give the pyrrolo[1,2-*a*]quinoxaline **6**.[11a-c] The presence of a carbethoxy group in position 3 of the primary cycloadduct (A) contributes to the better stabilization of this intermediate structure leading to increased amounts of pyrrolo[1,2-*a*]benzimidazoles in comparison with compounds bearing an acetyl group in the same position 3. The imidazole ring opening seems to be assisted by the presence of an electron-withdrawing group on the phenyl ring in the primary cycloadduct (A), as well as the cyclization of the open intermediate (B), resulting in increased amounts of pyrrolo[1,2-*a*]quinoxalines. Pyrrolo[1,2-*a*]quinoxaline derivatives **6** are relatively stable and isolable compounds in basic media, but very unstable in acid media when the OH group is easily eliminated as water with formation of pyrrolo[1,2-*a*]quinoxaline quaternary salts **8**. The elimination of the OH group from pyrrolo[1,2-*a*]quinoxaline **6** led to an intermediate carbocation (C). The transfer of a hydride ion from the primary cycloadduct (A) to the intermediate carbocation (C) led to the pyrrolo[1,2-*a*]quinoxaline **7**. From the intermediate carbocation (C), the iminium salts, pyrrolo[1,2-a]quinoxalines **8**, are also formed. The aromatized pyrrolo[1,2-*a*]quinoxalines **10** are formed from the pyrrolo[1,2-*a*]quinoxalines **6** by the formal loss of an alcohol in a dealkylative elimination process (Scheme 3).



Scheme 3. The reaction mechanism for the formation of pyrrolo[1,2-*a*]quinoxaline derivatives.

The isolation and characterization of 4-hydroxy-pyrrolo[1,2-*a*]quinoxalines **6**, intermediates in formation of pyrrolo[1,2-*a*]quinoxalines **7**, **8** and **10**, together with the previously reported separation and characterization of the open intermediates type (**B**)[11c,d] supports the above proposed reaction mechanism.

Compounds isolated and characterized from these reactions are presented in Table 4. They have been synthesized in different reaction conditions in order to characterize all reaction products.

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Table 4. The isolated reaction products.

Comp.	R	R^1	R^2	R^3	Reaction products mp (ºC)				
					5	**6**	**7**	**8**	**9**
a	H	Ph	H	Me	137-139*		155-157*	200-202	
b	H	Ph	4-Cl	Me	178-180	157-159		196-198	
c	H	Ph	4-OMe	Me	130-132			187-189	
d	H	Ph	3-NO_2	Me	209-211	168-170	99-101	223-225	
e	H	Ph	4-NO_2	Me	232-234			280-282	
f	H	Ph	H	OEt	190-192				140-142
g	H	Ph	4-F	OEt	182-183	157-159		193-195	
h	H	Ph	4-Cl	OEt	192-194*	170-172	148-150*	196-197	155-157
i	H	Ph	4-NO_2	OEt	210-212	176-178		236-238	
j	Me	Me	4-NO_2	Me	304-306	196-198		261-263	
k	Me	Me	4-Cl	OEt	173-175	154-156		240-242	
l	Me	Ph	H	Me	233-235	165-166		226-228	149-151
m	Me	Ph	H	OEt	208-209		164-166	197-198	
n	Me	Ph	4-Me	OEt	188-190		159-161		
o	Me	Ph	4-NO_2	OEt	221-223	176-178		208-210	

* reported in reference 11a.

Our studies on 1,3-dipolar cycloaddition reactions of benzimidazolium ylides with activated alkynes showed that by tuning the reaction conditions it is possible to influence the reaction course towards either pyrrolo[1,2-*a*]benzimidazole or pyrrolo[1,2-*a*]quinoxaline derivatives. Thus, pyrrolo[1,2-*a*]benzimidazoles are obtained in good yields in the presence of an oxidant, such as tetrapyridinecobalt(II)dichromate, using different tertiary amines. Pyrrolo[1,2-*a*]quinoxalin-4-ones are the major reaction products when starting from 1-alkyl-3-(alkoxycarbonylmethyl)benzimidazolium bromides and tertiary amines to generate the corresponding benzimidazolium ylides.[11b,d] 4-Phenyl-substituted pyrrolo[1,2-*a*]quinoxalines derivatives **7** are obtained as major reaction products starting from 1-alkyl-3-phenacylbenzimidazolium bromides in the presence of epoxides. The same reaction carried out in the presence of a tertiary amine led to pyrrolo[1,2-*a*]quinoxaline derivatives **6** or **8** as major reaction products.

The structures of pyrrolo[1,2-*a*]benzimidazoles **5** and pyrrolo[1,2-*a*]quinoxalines **6-10** were assigned by elemental analysis, IR and NMR spectroscopy. The ^{1}H, ^{13}C and ^{15}N NMR chemical shifts have been unambiguously assigned based on the following 2D NMR experiments: H,H-COSY, H,C-HSQC, H,C-HMBC, H,N-HMBC, H,H-NOESY.

X-ray crystallography data for the pair of compounds **6g** and **8g** (figure 1), confirm the proposed structures and support the interconversion reactions (Scheme 2).

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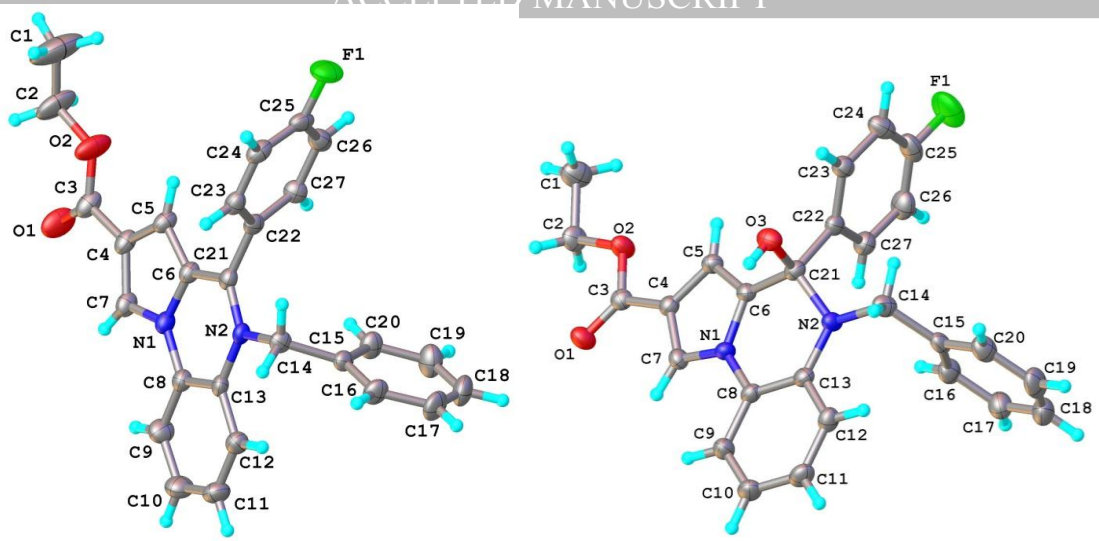

Figure 1. X-ray molecular structures for compounds **6g** (left) and **8g** (right). Thermal ellipsoids are drawn at 50% probability level.

3. Conclusion

1,3-Dipolar cycloaddition reactions of benzimidazolium ylides, generated from 3-phenacylbenzimidazolium bromides, to non-symmetrical activated dipolarophiles in various reaction conditions led to complex mixtures of pyrrolo[1,2-*a*]benzimidazole and pyrrolo[1,2-*a*]quinoxaline derivatives. In order to rationalize the results, the influence of experimental conditions on the reaction course was investigated. For the first time, 4-hydroxy-4,5-dihydropyrrolo[1,2-*a*]quinoxaline derivatives **6**, formed through the cyclization reactions of open amino intermediates type B, pyrrolo[1,2-*a*]quinoxalinium quaternary salts **8** and 4-methoxy-4,5-dihydropyrrolo[1,2-*a*]quinoxalines **9** were separated and fully characterized and their interconversion reactions were presented. A mechanism explaining the formation of all 1,3-dipolar cycloaddition reaction products was presented. The possibility of influencing the course of synthesis towards either pyrrolo[1,2-*a*]benzimidazole or pyrrolo[1,2-*a*]quinoxaline derivatives by tuning the 1,3-dipolar cycloaddition reaction conditions was described.

4. Experimental

General. Melting points were measured on a Boëtius hot plate microscope and are uncorrected. IR spectra were recorded on a Nicolet Impact 410 spectrometer, in KBr pellets. The high performance liquid chromatography (HPLC) analyses were performed with an Agilent Chromatograph 1200 Series at room temperature by isocratic elution of acetonitrile on an Agilent Zorbax SB-C18 (250x4.6) column with flow rate 1.0 mL/min. Final reaction products have been identified as follow: 2-3 drops of each crude reaction mixture resulting from the 1,3-dipolar cycloaddition reactions carried out in the presence of epoxides was transferred into a vial, the solvent was removed under vacuum, the remaining solid was dissolved in acetonitrile and analyzed by HPLC. Each crude reaction mixture resulting from the 1,3-dipolar cycloaddition reactions carried out in the presence of bases (1-2 mL) was dissolved in 15 mL of $CHCl_3$ washed with water, dried on Na_2SO_4 anh. and concentrated under vacuum. Then, 2-3 drops of each residue was transferred into a vial, the solvent was removed under vacuum, the remaining solid was dissolved in acetonitrile and analyzed by HPLC. All major reaction components were identified. The order of elution of reaction mixture components in the HPLC analysis conditions was: **6** < **7** < **8** < **5**.

The NMR spectra have been recorded on a Bruker Avance III 400 instrument operating at 400.1, 376.4, 100.6 and 40.6 MHz for ^{1}H, ^{19}F, ^{13}C, and ^{15}N nuclei respectively. Samples were transferred in 5 mm Wilmad 507 NMR tubes and recorded with either a 5 mm multinuclear inverse detection z-gradient probe (^{1}H spectra and all H-C/H-N 2D experiments) or with a 5 mm four nuclei direct detection z-gradient probe (^{13}C and ^{19}F spectra). Chemical shifts are reported in δ units (ppm) and were referenced to internal TMS for ^{1}H chemical shifts, to the internal deuterated solvent for ^{13}C chemical shifts ($CDCl_3$ referenced at 77.0 ppm), electronically referenced to $CFCl_3$ (0 ppm) for ^{19}F chemical shifts, and referenced to liquid ammonia (0.0 ppm) using nitromethane (380.2 ppm) as external standard for ^{15}N chemical shifts. Unambiguous 1D NMR signal assignments were made based on 2D NMR homo- and heterocorrelation. H,H-COSY, H,C-HSQC and H,C-HMBC experiments were recorded using standard pulse sequences in the version with z-gradients, as delivered by Bruker with TopSpin 2.1 PL6 spectrometer control and processing software. The individual chemical shifts, multiplicities and coupling constants for overlapping signals have been obtained from undecoupled H,C-HSQC experiments recorded using the pulse sequence described by S. Simova.[14] The ^{15}N chemical shifts were obtained as projections from the 2D indirectly detected H,N-HMBC spectra, employing a standard pulse sequence in the version with z-gradients as delivered by Bruker (TopSpin 2.1 PL6).

Elemental analyses for C, H and N were obtained using a COSTECH Instruments EAS32. Satisfactory microanalyses for all new compounds were obtained.

Benzimidazole, 5,6-dimethylbenzimidazole, ethyl propiolate, 3-butyn-2-one and phenacyl bromides were purchased from Aldrich and used without further purification. 1-Benzylbenzimidazole, 1-benzyl-5,6-dimethylbenzimidazole and 1-ethyl-5,6-dimethyl-benzimidazole derivatives were obtained from the corresponding benzimidazoles and benzyl chloride, or ethyl bromide respectively. 3-Phenacylbenzimidazolium bromides (**3**) were obtained from 1-substituted benzimidazole and phenacyl bromides (**2**) in acetone, according previously reported methods.[9b] Tetrapyridinecobalt(II)dichromate (TPCD) was obtained according to the previously reported method.[13] Chloroform used was stored on K_2CO_3 anhydrous.

X-Ray crystallographic measurements were carried out with an Oxford-Diffraction XCALIBUR E CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation. Single crystals were positioned at 40 mm from the detector and 832, and 211 frames were measured each for 6, and 50 s over 1° scan width for 1736, and 2037, respectively. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction.[15] The structures were solved by direct methods using Olex2[16] and refined by full-matrix least-squares on F^2 with SHELXL-97.[17] Atomic displacements for non-hydrogen, atoms were refined using an anisotropic model. All H atoms were introduced in idealized positions (dCH = 0.96 Å) using the riding model with their isotropic displacement parameters fixed at 120% of their riding atom. DMF solvate molecules were found to be disordered in two resolvable positions and their positional parameters were refined in combination with PART and SADI restraints using isotropic model for non-H atoms. The molecular plots were obtained using the Olex2 program.

Reactions of 3-phenacylbenzimidazolium bromides (3) with non-symmetrical dipolarophiles (4) in 1,2-epoxybutane at room temperature. To a suspension of a 3-phenacylbenzimidazolium bromide **3** (2 mmol) in 25 mL of 1,2-epoxybutane a non-symmetrical substituted dipolarophile **4** (2.5 mmol) was added and stirred at room temperature for 70 h. The solvent was partly evaporated *in vacuo*, 3-5 mL of MeOH added under a gentle stirring and the mixture left for 2 h in the refrigerator. The solid formed was filtered and recrystallized from $CHCl_3$/MeOH giving the pyrrolo[1,2-*a*]benzimidazole **5**. The filtrate was concentrated *in vacuo* to dryness, triturated with MeOH or EtOAc and the insoluble part containing pyrrolo[1,2-*a*]quinoxalines **6** and **8** was filtered off. The resultant solution was concentrated *in vacuo* to dryness, washed with Et_2O and triturated with EtOAc. The insoluble part containing pyrrolo[1,2-*a*]quinoxaline **7** was filtered off and recrystallized from MeOH/Et_2O.

Reactions of 3-phenacylbenzimidazolium bromides (3) with non-symmetrical dipolarophiles (4) in 1,2-epoxybutane at reflux. To a suspension of a 3-phenacylbenzimidazolium bromide **3** (2 mmol) in 25 mL of 1,2-epoxybutane a non-symmetrical substituted dipolarophile **4** (2.5 mmol) was added and the reaction mixture was heated at reflux for 24 h. The solvent was partly removed under vacuum, 5 mL of MeOH was added under a gentle stirring and the mixture was left for 2 h in the refrigerator. The solid formed was filtered off and recrystallized from $CHCl_3$/MeOH giving the pyrrolo[1,2-*a*]benzimidazole **5**. The filtrate was worked up as it was described above.

Reactions of 3-phenacylbenzimidazolium bromides (3) with non-symmetrical dipolarophiles (4) in the presence of triethylamine in acetonitrile. To a suspension of a 3-phenacylbenzimidazolium bromide **3** (2 mmol) in 20 mL of acetonitrile a non-symmetrical substituted dipolarophile **4** (2.5 mmol) was added under stirring, then a solution of 0.5 g (5 mmol) of triethylamine in 5 mL of acetonitrile was added dropwise. The reaction mixture was heated at reflux for 3 h. The solvent was partly removed *in vacuo*, the resultant suspension was dissolved in 50 mL $CHCl_3$, washed with water (2 x 50 mL), and dried on Na_2SO_4 anh. The solvent was partly removed *in vacuo*, diluted with MeOH and the solid was filtered, washed on the filter with Et_2O and the obtained pyrrolo[1,2-*a*]quinoxaline **6** recrystallized from $CHCl_3$/Et_2O. The filtrate was concentrated *in vacuo* to dryness, triturated with MeOH and the insoluble part was filtered off and recrystallized from $CHCl_3$/MeOH to obtain pyrrolo[1,2-*a*]benzimidazole **5**.

Reactions of 3-phenacylbenzimidazolium bromides (3) with non-symmetrical dipolarophiles (4) in the presence of triethylamine and TPCD in DMF. To a solution of a 3-phenacylbenzimidazolium bromide **3** (2 mmol) in 20 mL of DMF, a non-symmetrical substituted dipolarophile **4** (2.5 mmol), 0.8 g (1.3 mmol) TPCD and 0.5 g (5 mmol) triethylamine were added. The reaction mixture was heated at 90 ºC for 2 h, then cooled and poured under stirring in the 30 mL of HCl (5 % in water) and extracted with $CHCl_3$ (3 x 50mL). The combined extracts were dried on $NaSO_4$ anh. and the solvent was removed under vacuum. The solid was triturated with MeOH, the solid was recovered by filtration and recrystallized from $CHCl_3$/MeOH to obtain the pyrrolo[1,2-*a*]benzimidazole **5**. Samples for HPLC analysis were separately worked-up as it was described above.

Reactions of 3-phenacylbenzimidazolium bromides (3) with non-symmetrical dipolarophiles (4) in the presence of K_2CO_3 in DMF. To a solution of a 3-phenacylbenzimidazolium bromide **3** (2 mmol) and 0.69 g (5 mmol) of K_2CO_3 in 20 mL of DMF, a non-symmetrical substituted dipolarophile **4** (2.5 mmol), was added and the mixture was stirred for two days at room temperature. The solid was filtered off, the filtrate was concentrated *in vacuo*, diluted with 50 mL $CHCl_3$, washed with water (2 x 50 mL), and dried on Na_2SO_4 anh. The solvent was partly removed *in vacuo*, diluted with MeOH and the solid was filtered, washed on the filter with Et_2O and the obtained pyrrolo[1,2-*a*]quinoxaline **6** recrystallized from $CHCl_3$/Et_2O.

*1-(4-Chlorobenzoyl)-3-acetyl-4-benzyl-4H-pyrrolo[1,2-a]benzimidazole (**5b**).* Pale yellow crystals, mp 178-180 ºC ($CHCl_3$/MeOH). FT-IR (ν_{max}, cm^{-1}) 1651, 1613, 1548, 1495, 1446, 1392, 1296, 1265, 1203, 1157, 1086. ^{1}H NMR ($CDCl_3$) δ (ppm): 2.45 (3H, s, CH_3), 6.24 (2H, s, CH_2), 7.20-7.37 (8H, m, aromatic rings), 7.40 (1H, s, H-2), 7.52 (2H, d, *J* 8.4 Hz, H-3'), 7.85 (2H, d, *J* 8.4 Hz, H-2'), 8.89 (1H, d, *J* 7.4 Hz, H-8). The individual chemical shifts, multiplicities and coupling constants for the 7.20-7.37 ppm multiplet were obtained from undecoupled HSQC as follows: 7.20 (2H, d, *J* 6.9 Hz, H-2"), 7.23 (1H, t, *J* 7.4 Hz, H-4"), 7.26 (2H, t, *J* 7.7 Hz, H-3"), 7.33 (1H, t, *J* 7.9 Hz, H-7), 7.35 (1H, d, *J* 8.4 Hz, H-5), 7.36 (1H, t, *J* 8.1 Hz, H-6). ^{13}C NMR ($CDCl_3$) δ (ppm): 27.6 (CH_3), 49.3 (CH_2), 104.3 (C-3), 110.8 (C-5), 117.3 (C-8), 120.9 (C-1), 122.1 (C-7), 124.8 (C-6), 126.8 (C-2"), 127.2 (C-8a), 127.7 (C-4"), 128.7 (C-3'), 128.8 (C-3"), 130.38 (C-2'), 130.41 (C-2), 136.3 (C-4a), 136.8 (C-1"), 137.8 (C-4' and C-1'), 143.7 (C-3a), 181.9 (CO), 191.2 ($COCH_3$). ^{15}N NMR ($CDCl_3$) δ (ppm): 122.5 (N-4), 174.4 (N-9). Anal. Calcd. for $C_{26}H_{19}ClN_2O_2$ (426.89): C, 73.15; H, 4.49; N, 6.56%. Found: C, 73.40; H, 4.37; N, 6.60%.

*1-(4-Methoxybenzoyl)-3-acetyl-4-benzyl-4H-pyrrolo[1,2-a]benzimidazole (**5c**).* Pale yellow crystals, mp 130-132 ºC ($CHCl_3$/MeOH). FT-IR (ν_{max}, cm^{-1}) 1650, 1615, 1605, 1551, 1498, 1447, 1303, 1255, 1208, 1172, 1146, 1114. ^{1}H NMR ($CDCl_3$) δ (ppm): 2.45 (3H, s, CH_3), 3.92 (3H, s, CH_3), 6.23 (2H, s, CH_2), 7.04 (2H, d, *J* 8.0 Hz, H-3'), 7.22-7.33 (8H, m, aromatic rings), 7.43 (1H, s, H-2), 7.93 (2H, d, *J* 8.4 Hz, H-2'), 8.83 (1H, d, *J* 7.2 Hz, H-8). The individual chemical shifts, multiplicities and coupling constants for the 7.22-7.33 ppm multiplet were obtained from undecoupled HSQC as follows: 7.22 (2H, d, *J* 7.6 Hz, H-2"), 7.23 (1H, t, *J* 7.3 Hz, H-4"), 7.27 (2H, t, *J* 7.4 Hz, H-3"), 7.31 (1H, t, *J* 6.9 Hz, H-7), 7.33 (1H, d, *J* 8.2 Hz, H-5), 7.34 (1H, t, *J* 7.9 Hz, H-6). ^{13}C NMR ($CDCl_3$) δ (ppm): 27.6 (CH_3), 49.2 (CH_2), 55.5 (OCH_3), 103.7 (C-3), 110.7 (C-5), 113.7 (C-3'), 117.2 (C-8), 121.2 (C-1), 121.9 (C-7), 124.6 (C-6), 126.9 (C-2"), 127.2 (C-8a), 127.6 (C-4"), 128.7 (C-3"), 129.6 (C-2), 131.2 (C-

2'), 131.8 (C-1'), 136.3 (C-4a), 137.9 (C-1"), 143.5 (C-3a), 162.6 (C-4'), 182.5 (CO), 191.2 ($COCH_3$). ^{15}N NMR ($CDCl_3$) δ (ppm): 122.0 (N-4), 174.8 (N-9). Anal. Calcd. for $C_{27}H_{22}N_2O_3$ (422.47): C, 76.76; H, 5.25; N, 6.63%. Found: C, 76.69; H, 5.30; N, 6.56%.

*1-(3-Nitrobenzoyl)-3-acetyl-4-benzyl-4H-pyrrolo[1,2-a]benzimidazole (**5d**).* Yellow crystals, mp 209-211 ºC ($CHCl_3$/MeOH). FT-IR (ν_{max}, cm^{-1}) 1648, 1605, 1548, 1527, 1499, 1451, 1352, 1302, 1205, 1150. ^1H NMR ($CDCl_3$) δ (ppm): 2.50 (3H, s, CH_3), 6.29 (2H, bs, CH_2), 7.25-7.43 (8H, m, aromatic rings), 7.44 (1H, s, H-2), 7.79 (1H, t, *J* 8.0 Hz, H-3'), 8.26 (1H, dt, 7.7, *J* 1.3 Hz, H-2'), 8.49 (1H, ddd, *J* 8.2, 2.2, 1.0 Hz, H-4'), 8.78 (1H, t, *J* 1.8 Hz, H-6'), 8.96 (1H, d, *J* 7.4 Hz, H-8). The individual chemical shifts, multiplicities and coupling constants for the 7.25-7.43 ppm multiplet were obtained from undecoupled HSQC as follows: 7.22 (2H, d, *J* 7.4 Hz, H-2"), 7.24 (1H, t, *J* 7.3 Hz, H-4"), 7.28 (2H, t, *J* 7.5 Hz, H-3"), 7.35 (1H, t, *J* 7.8 Hz, H-7), 7.38 (1H, d, *J* 8.1 Hz, H-5), 7.39 (1H, t, *J* 8.1 Hz, H-6). ^{13}C NMR ($CDCl_3$) δ (ppm): 27.6 (CH_3), 49.4 (CH_2), 104.9 (C-3), 110.9 (C-5), 117.2 (C-8), 120.4 (C-1), 122.2 (C-7), 123.8 (C-6'), 125.0 (C-6), 125.8 (C-4'), 126.8 (C-2"), 127.1 (C-8a), 127.7 (C-4"), 128.8 (C-3"), 129.7 (C-3'), 130.7 (C-2), 134.5 (C-2'), 136.3 (C-4a), 136.6 (C-1"), 141.0 (C-1'), 143.9 (C-3a), 148.1 (C-5'), 180.1 (CO), 191.3 (CO-3). ^{15}N NMR ($CDCl_3$) δ (ppm): 118.9 (N-4), 173.9 (N-9). Anal. Calcd. for $C_{26}H_{19}N_3O_4$ (437.45): C, 71.39; H, 4.38; N, 9.61%. Found: C, 71.21; H, 4.29; N, 9.72%.

*1-(4-Nitrobenzoyl)-3-acetyl-4-benzyl-4H-pyrrolo[1,2-a]benzimidazole (**5e**).* Yellow crystals, mp 232-234 ºC ($CHCl_3$). FT-IR (ν_{max}, cm^{-1}) 1651, 1618, 1595, 1555, 1524, 1496, 1349, 1296, 1201, 1160. ^1H NMR ($CDCl_3$) δ (ppm): 2.45 (3H, s, CH_3), 6.23 (2H, s, CH_2), 7.20-7.38 (9H, m, aromatic rings), 8.02 (2H, d, *J* 8.0 Hz, H-2'), 8.38 (2H, d, *J* 8.0 Hz, H-3'), 8.94 (1H, d, *J* 7.6 Hz, H-8). The individual chemical shifts, multiplicities and coupling constants for the 7.20-7.38 ppm multiplet were obtained from undecoupled HSQC as follows: 7.20 (2H, d, *J* 7.4 Hz, H-2"), 7.23 (1H, t, *J* 7.5 Hz, H-4"), 7.26 (2H, t, *J* 7.5 Hz, H-3"), 7.35 (1H, t, *J* 7.6 Hz, H-7), 7.36 (1H, s, H-2), 7.37 (1H, d, *J* 8.0 Hz, H-5), 7.38 (1H, t, *J* 7.8 Hz, H-6). ^{13}C NMR ($CDCl_3$) δ (ppm): 27.6 (CH_3), 49.4 (CH_2), 105.0 (C-3), 111.0 (C-5), 117.3 (C-8), 120.7 (C-1), 122.3 (C-7), 123.7 (C-3'), 125.1 (C-6), 126.9 (C-2"), 127.2 (C-8a), 127.8 (C-4"), 128.8 (C-3"), 129.8 (C-2'), 131.0 (C-2), 136.3 (C-4a), 136.7 (C-1"), 143.9 (C-3a), 145.2 (C-1'), 149.4 (C-4'), 180.6 (CO), 191.1 ($COCH_3$). ^{15}N NMR ($CDCl_3$) δ (ppm): 123.2 (N-4), 173.4 (N-9), 366.7 (NO_2). Anal. Calcd. for $C_{26}H_{19}N_3O_4$ (437.45): C, 71.39; H, 4.38; N, 9.61%. Found: C, 71.45; H, 4.34; N, 9.66%.

*Ethyl 1-benzoyl-4-benzyl-4H-pyrrolo[1,2-a]benzimidazole-3-carboxylate (**5f**).* Pale yellow crystals, mp 190-192 ºC ($CHCl_3$/MeOH). FT-IR (ν_{max}, cm^{-1}) 1689, 1619, 1578, 1500, 1451, 1391, 1307, 1234, 1202, 1153, 1115, 1083. ^1H NMR ($CDCl_3$) δ (ppm): 1.33 (3H, t, *J* 7.2 Hz, CH_3-Et), 4.31 (2H, q, *J* 7.2 Hz, CH_2-Et), 6.17 (2H, s, CH_2), 7.30-7.39 (8H, m, aromatic rings), 7.57 (2H, t, *J* 7.1 Hz, H-3'), 7.59 (1H, s, H-2), 7.64 (1H, t, *J* 7.7 Hz, H-4'), 7.96 (2H, d, *J* 7.2 Hz, H-2'), 8.98 (1H, d, *J* 6.9 Hz, H-8). The individual chemical shifts, multiplicities and coupling constants for the 7.30-7.39 ppm multiplet were obtained from undecoupled HSQC as follows: 7.28 (1H, t, *J* 8.2 Hz, H-4"), 7.29 (2H, d, *J* 8.0 Hz, H-2"), 7.32 (1H, d, *J* 8.2 Hz, H-5), 7.33 (2H, t, *J* 7.8 Hz, H-3"), 7.34 (1H, t, *J* 8.1 Hz, H-7), 7.37 (1H, t, *J* 8.2 Hz, H-6). ^{13}C NMR ($CDCl_3$) δ (ppm): 14.4 (CH_3-Et), 48.6 (CH_2), 60.1 (CH_2-Et), 93.4 (C-3), 110.3 (C-5), 117.2 (C-8), 121.3 (C-1), 121.7 (C-7), 124.5 (C-6), 126.8 (C-2"), 127.4 (C-8a), 127.7 (C-4"), 128.3 (C-3'), 128.8 (C-3"), 129.1 (C-2'), 130.5 (C-2), 131.4 (C-4'), 136.3 (C-4a), 136.6 (C-1"), 139.5 (C-1'), 143.9 (C-3a), 163.4 (COO), 183.3 (CO). ^{15}N NMR ($CDCl_3$) δ (ppm): 118.6 (N-4), 173.8 (N-9), 366.7 (NO_2). Anal. Calcd. for $C_{27}H_{22}N_2O_3$ (422.47): C, 76.76; H, 5.25; N, 6.63%. Found: C, 76.81; H, 5.29; N, 6.57%.

*Ethyl 1-(4-fluorobenzoyl)-4-benzyl-4H-pyrrolo[1,2-a]benzimidazole-3-carboxylate (**5g**).* Pale yellow crystals, mp 182-183 ºC ($CHCl_3$/MeOH). FT-IR (ν_{max}, cm^{-1}) 1692, 1623, 1579, 1493, 1451, 1393, 1306, 1234, 1202, 1149, 1115, 1082. ^1H NMR ($CDCl_3$) δ (ppm): 1.29 (3H, t, *J* 7.2 Hz, CH_3-Et), 4.27 (2H, q, *J* 7.1 Hz, CH_2-Et), 6.11 (2H, bs, CH_2), 7.20 (2H, t, *J* 8.7 Hz, H-3'), 7.22-7.34 (8H, m, aromatic rings), 7.51 (1H, s, H-2), 7.93 (2H, dd, *J* 8.7, 5.5 Hz, H-2'), 8.87 (1H, d, *J* 6.8 Hz, H-8). The individual chemical shifts, multiplicities and coupling constants for the 7.22-7.34 ppm multiplet were obtained from undecoupled HSQC as follows: 7.22 (2H, d, *J* 7.3 Hz, H-2"), 7.23 (1H, t, *J* 7.4 Hz, H-4"), 7.26 (1H, d, *J* 8.1 Hz, H-5), 7.27 (2H, t, *J* 7.5 Hz, H-3"), 7.28 (1H, t, *J* 8.1 Hz, H-7), 7.31 (1H, t, *J* 8.1 Hz, H-6). ^{13}C NMR ($CDCl_3$) δ (ppm): 14.4 (CH_3-Et), 48.6 (CH_2), 60.2 (CH_2-Et), 93.5 (C-3), 110.4 (C-5), 115.4 (d, $J_{C\text{-}F}$ 22.1 Hz, C-3'), 117.1 (C-8), 121.0 (C-1), 121.7 (C-7), 124.5 (C-6), 126.7 (C-2"), 127.3 (C-8a), 127.7 (C-4"), 128.8 (C-3"), 130.3 (C-2), 131.4 (d, $J_{C\text{-}F}$ 9.1 Hz, C-2'), 135.6 (d, $J_{C\text{-}F}$ 3 Hz, C-1'), 136.3 (C-4a), 136.6 (C-1"), 143.9 (C-3a), 163.4 (COO), 164.8 (d, $J_{C\text{-}F}$ 251.5 Hz, C-4'), 181.8 (CO). ^{15}N NMR ($CDCl_3$) δ (ppm): 118.9 (N-4), 173.9 (N-9). ^{19}F NMR ($CDCl_3$) δ (ppm): -108.0. Anal. Calcd. for $C_{27}H_{21}FN_2O_3$ (440.47): C, 73.62; H, 4.81; N, 6.36%. Found: C, 73.73; H, 4.90; N, 6.25%

*Ethyl 1-(4-nitrobenzoyl)-4-benzyl-4H-pyrrolo[1,2-a]benzimidazole-3-carboxylate (**5i**).* Yellow crystals, mp 210-212 ºC ($CHCl_3$/MeOH). FT-IR (ν_{max}, cm^{-1}) 1691, 1627, 1598, 1578, 1520, 1499, 1451, 1349, 1307, 1202, 1156, 1116, 1084. ^1H NMR ($CDCl_3$) δ (ppm): 1.29 (3H, t, *J* 7.1 Hz, CH_3-Et), 4.27 (2H, q, *J* 7.0 Hz, CH_2-Et), 6.13 (2H, s, CH_2), 7.23-7.36 (8H, m, aromatic rings), 7.47 (1H, s, H-2), 8.02 (2H, d, *J* 8.4 Hz, H-2'), 8.37 (2H, d, *J* 8.4 Hz, H-3'), 8.95 (1H, d, *J* 7.08 Hz, H-8). The individual chemical shifts, multiplicities and coupling constants for the 7.23-7.36 ppm multiplet were obtained from undecoupled HSQC as follows: 7.28 (2H, d, *J* 7.40 Hz, H-2"), 7.30 (1H, t, *J* 7.60 Hz, H-4"), 7.34 (2H, t, *J* 7.60 Hz, H-3"), 7.36 (1H, d, *J* 8.1 Hz, H-5), 7.38 (1H, t, *J* 7.64 Hz, H-7), 7.40 (1H, d, *J* 8.1 Hz, H-6). ^{13}C NMR ($CDCl_3$) δ (ppm): 14.4 (CH_3-Et), 48.7 (CH_2), 60.4 (CH_2-Et), 94.6 (C-3), 110.6 (C-5), 117.1 (C-8), 120.7 (C-1), 122.0 (C-7), 123.6 (C-3'), 124.9 (C-6), 126.8 (C-2"), 127.3 (C-8a), 127.82 (C-4"), 128.85 (C-3"), 129.8 (C-2'), 131.2 (C-2), 136.2 (C-4a), 136.4 (C-1"), 144.1 (C-3a), 145.2 (C-1'), 149.3 (C-4'), 163.1 (COO), 180.5 (CO). ^{15}N NMR ($CDCl_3$) δ (ppm):120.1 (N-4), 173.7 (N-9), 367.1 (NO_2). Anal. Calcd. for $C_{27}H_{21}N_3O_5$ (467.47): C, 69.37; H, 4.53; N, 8.99%. Found: C, 69.41; H, 4.48; N, 9.03%.

*1-(4-Nitrobenzoyl)-3-acetyl-4-ethyl-6,7-dimethyl-4H-pyrrolo[1,2-a]benzimidazole (**5j**).* Yellow crystals, mp 304-306 ºC ($CHCl_3$). FT-IR (ν_{max}, cm^{-1}) 1655, 1611, 1591, 1547, 1521, 1498, 1348, 1314, 1279, 1220, 1186, 1151. ^1H NMR ($CDCl_3$+TFA) δ (ppm): 1.48 (3H, t, *J* 6.6 Hz, CH_3-Et), 2.46 (3H, s, CH_3-7), 2.47 (3H, s, CH_3-6), 2.57 (3H, s, CH_3), 4.87 (2H, q, *J* 6.8 Hz, CH_2-Et), 7.30 (1H, s, CH-5), 7.42 (1H, s, H-2), 8.00 (2H, d, *J* 8.1 Hz, H-2'), 8.43 (2H, d, *J* 8.1 Hz, H-3'), 8.56 (1H, s, H-8). ^{13}C NMR ($CDCl_3$+TFA) δ (ppm): 15.4 (CH_3-Et), 20.2 (CH_3-7), 20.6 (CH_3-6), 25.7 (CH_3), 41.7 (CH_2-Et), 106.0 (C-3), 111.0 (C-5), 117.4 (C-8), 122.0 (C-1), 124.1 (C-3'), 125.3 (C-8a), 130.0 (C-2'), 133.2 (C-7), 134.0 (C-4a), 134.8 (C-2), 135.7 (C-6), 143.3 (C-1'), 143.7 (C-3a), 149.9 (C-4'), 182.2 (CO), 194.5 (CO-CH_3). ^{15}N NMR ($CDCl_3$+TFA) δ (ppm): 130.6 (N-4), 173.3 (N-9), 366.20 (NO_2). Anal. Calcd. for $C_{23}H_{21}N_3O_4$ (403.43): C, 68.47; H, 5.25; N, 10.42%. Found: C, 68.41; H, 5.19; N, 10.47%.

*Ethyl 1-(4-chlorobenzoyl)-4-ethyl-6,7-dimethyl-4H-pyrrolo[1,2-a]benzimidazole-3-carboxylate (**5k**).* Pale yellow crystals, mp 173-175 ºC ($CHCl_3$/MeOH). FT-IR (ν_{max}, cm^{-1}) 2969, 2935, 1697, 1627, 1580, 1506, 1451, 1382, 1310, 1281, 1220, 1171, 1091. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.36 (3H, t, *J* 7.1 Hz, CH_3-3), 1.46 (3H, t, *J* 7.1 Hz, CH_3-Et), 2.43 (6H, s, CH_3-6 and CH_3-7), 4.31 (2H, q, *J* 7.1 Hz, CH_2-3), 4.81 (2H, q, *J* 7.1 Hz, CH_2-Et), 7.15 (1H, s, H-5), 7.43 (1H, s, H-2), 7.49 (2H, d, *J* 8.4 Hz, H-3'), 7.83 (2H, d, *J* 8.4 Hz, H-3'), 8.64 (1H, s, H-8). ^{13}C NMR ($CDCl_3$) δ (ppm): 14.5 (CH_3-3), 14.9 (CH_3-Et), 20.2 (CH_3-7), 20.5 (CH_3-6), 40.1 (CH_2-Et), 60.0 (CH_2-3), 93.6 (C-3), 109.9 (C-5), 117.4 (C-8), 120.7 (C-1), 125.7 (C-8a), 128.6 (C-3'), 130.3 (C-2), 130.4 (C-7), 130.4 (C-2'), 133.5 (C-6), 134.3 (C-4a), 137.4 (C-4'), 138.1 (C-1'), 143.3 (C-3a), 163.3 (COO), 181.6 (CO). ^{15}N NMR ($CDCl_3$) δ (ppm): 122.1 (N-4), 173.3 (N-9). Anal. Calcd. for $C_{24}H_{23}ClN_2O_3$ (422.90): C, 68.16; H, 5.48; N, 6.62%. Found: C, 68.22; H, 5.51; N, 6.55%.

*1-Benzoyl-3-acetyl-4-benzyl-6,7-dimethyl-4H-pyrrolo[1,2-a]benzimidazole (**5l**).* Yellow crystals, mp 233-235 ºC ($CHCl_3$/MeOH). FT-IR (ν_{max}, cm^{-1}) 1643, 1615, 1548, 1496, 1451, 1397, 1357, 1310, 1223, 1173. ^{1}H NMR ($CDCl_3$) δ (ppm): 2.35 (3H, s, CH_3-6), 2.41 (3H, s, CH_3-7), 2.42 (3H, s, CH_3), 6.18 (2H, s, CH_2), 7.09 (1H, s, CH-5), 7.19 (2H, d, *J* 6.9 Hz, H-2"), 7.24 (1H, t, *J* 6.8 Hz, H-4"), 7.27 (2H, t, *J* 6.6 Hz, H-3"), 7.39 (1H, s, H-2), 7.54 (2H, t, *J* 7.6 Hz, H-3'), 7.60 (1H, t, *J* 7.3 Hz, H-4'), 7.91 (2H, d, *J* 7.0 Hz, H-2'), 8.67 (1H, s, H-8). ^{13}C NMR ($CDCl_3$) δ (ppm): 20.2 (CH_3-7), 20.5 (CH_3-6), 27.5 (CH_3), 49.1 (CH_2), 104.2 (C-3), 111.0 (C-5), 117.5 (C-8), 121.0 (C-1), 125.6 (C-8a), 126.7 (C-2"), 127.5 (C-4"), 128.4 (C-3'), 128.7 (C-3"), 129.0 (C-2'), 130.3 (C-2), 131.0 (C-7), 131.4 (C-4'), 133.9 (C-6), 134.7 (C-4a), 137.2 (C-1"), 139.5 (C-1'), 143.4 (C-3a), 183.3 (CO), 191.1 ($COCH_3$). ^{15}N NMR ($CDCl_3$) δ (ppm): 120.4 (N-4), 173.0 (N-9). Anal. Calcd. for $C_{28}H_{24}N_2O_2$ (420.50): C, 79.98; H, 5.75; N, 6.66%. Found: C, 80.03; H, 5.71; N, 6.60%.

*Ethyl 1-benzoyl-4-benzyl-6,7-dimethyl-4H-pyrrolo[1,2-a]benzimidazole-3-carboxylate (**5m**).* Yellow crystals, mp 208-209 ºC ($CHCl_3$/MeOH). FT-IR (ν_{max}, cm^{-1}) 1690, 1613, 1561, 1496, 1449, 1223, 1314, 1153, 1113, 1082. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.31 (3H, t, *J* 7.2 Hz, CH_3-Et), 2.38 (3H, s, CH_3-6), 2.45 (3H, s, CH_3-7), 4.29 (2H, q, *J* 6.8 Hz, CH_2-Et), 6.10 (2H, s, CH_2), 7.07 (1H, s, CH-5), 7.27 (2H, d, *J* 6.9 Hz, H-2"), 7.30 (1H, t, *J* 5.4 Hz, H-4"), 7.34 (2H, t, *J* 6.6 Hz, H-3"), 7.55 (1H, s, H-2), 7.57 (2H, t, *J* 7.6 Hz, H-3'), 7.63 (1H, t, *J* 7.1 Hz, H-4'), 7.96 (2H, d, *J* 6.9 Hz, H-2'), 8.73 (1H, s, H-8). ^{13}C NMR ($CDCl_3$) δ (ppm): 14.4 (CH_3-Et), 20.2 (CH_3-7), 20.5 (CH_3-6), 48.4 (CH_2), 60.0 (CH_2-Et), 93.5 (C-3), 110.7 (C-5), 117.4 (C-8), 121.1 (C-1), 125.8 (C-8a), 126.6 (C-2"), 127.5 (C-4"), 128.3 (C-3'), 128.7 (C-3"), 129.1 (C-2'), 130.3 (C-2), 130.6 (C-7), 131.3 (C-4'), 133.5 (C-6), 134.7 (C-4a), 136.9 (C-1"), 139.5 (C-1'), 143.7 (C-3a), 163.4 (COO), 183.2 (CO). ^{15}N NMR ($CDCl_3$) δ (ppm): 117.4 (N-4), 173.4 (N-9). Anal. Calcd. for $C_{29}H_{26}N_2O_3$ (450.53): C, 77.31; H, 5.78; N, 6.22%. Found: C, 77.35; H, 5.84; N, 6.18%.

*Ethyl 1-(4-methylbenzoyl)-4-benzyl-6,7-dimethyl-4H-pyrrolo[1,2-a]benzimidazole-3-carboxylate (**5n**).* Yellow crystals, mp 188-190 ºC ($CHCl_3$/MeOH). FT-IR (ν_{max}, cm^{-1}) 1691, 1604, 1573, 1494, 1452, 1363, 1310, 1273, 1220, 1168, 1114, 1079. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.26 (3H, t, *J* 7.2 Hz, CH_3-Et), 2.32 (3H, s, CH_3-6), 2.39 (3H, s, CH_3-7), 2.47 (3H, s, CH_3), 4.24 (2H, q, *J* 7.2 Hz, CH_2-Et), 6.05 (2H, s, CH_2), 7.02 (1H, s, CH-5), 7.21-7.28 (5H, m, aromatic ring), 7.32 (2H, d, *J* 7.8 Hz, H-3'), 7.50 (1H, s, H-2), 7.82 (2H, t, *J* 7.8 Hz, H-2'), 8.65 (1H, s, H-8). The individual chemical shifts, multiplicities and coupling constants for the 7.21-7.28 ppm multiplet were obtained from undecoupled HSQC as follows: 7.24 (2H, d, *J* 7.4 Hz, H-2"), 7.26 (1H, t, *J* 7.4 Hz, H-4"), 7.30 (2H, t, *J* 7.6 Hz, H-3"). ^{13}C NMR ($CDCl_3$) δ (ppm): 14.4 (CH_3-Et), 20.2 (CH_3-7), 20.5 (CH_3-6), 21.6 (CH_3), 48.4 (CH_2), 60.0 (CH_2-Et), 93.3 (C-3), 110.7 (C-5), 117.4 (C-8), 121.1 (C-1), 125.8 (C-8a), 126.6 (C-2"), 127.5 (C-4"), 128.7 (C-3"), 129.0 (C-3'), 129.2 (C-2'), 129.9 (C-2), 130.6 (C-7), 133.4 (C-6), 134.7 (C-4a), 136.8 (C-1'), 137.0 (C-1"), 141.9 (C-4'), 143.7 (C-3a), 163.5 (COO), 183.2 (CO). ^{15}N NMR ($CDCl_3$) δ (ppm): 117.1 (N-4), 173.4 (N-9). Anal. Calcd. for $C_{30}H_{28}N_2O_3$ (464.55): C, 77.56; H, 6.07; N, 6.03%. Found: C, 77.68; H, 6.19; N, 5.97%.

*Ethyl 1-(4-nitrobenzoyl)-4-benzyl-6,7-dimethyl-4H-pyrrolo[1,2-a]benzimidazole-3-carboxylate (**5o**).* Yellow crystals, mp 221-223 ºC ($CHCl_3$). FT-IR (ν_{max}, cm^{-1}) 1686, 1620, 1568, 1520, 1493, 1452, 1349, 1311, 1222, 1171, 1145, 1118, 1080. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.27 (3H, t, *J* 6.8 Hz, CH_3-Et), 2.35 (3H, s, CH_3-6), 2.42 (3H, s, CH_3-7), 4.25 (2H, q, *J* 6.8 Hz, CH_2-Et), 6.07 (2H, bs, CH_2), 7.07 (1H, s, CH-5), 7.21 (2H, d, *J* 6.8 Hz, H-2"), 7.27 (1H, t, *J* 6.6 Hz, H-4"), 7.30 (2H, t, *J* 6.6 Hz, H-3"), 7.42 (1H, s, H-2), 8.02 (2H, d, *J* 8.6 Hz, H-2'), 8.37 (2H, d, *J* 8.6 Hz, H-3'), 8.69 (1H, s, H-8). ^{13}C NMR ($CDCl_3$) δ (ppm): 14.4 (CH_3-Et), 20.3 (CH_3-7), 20.5 (CH_3-6), 48.5 (CH_2), 60.3 (CH_2-Et), 94.8 (C-3), 110.9 (C-5), 117.4 (C-8), 120.5 (C-1), 123.6 (C-3'), 125.8 (C-8a), 126.6 (C-2"), 127.7 (C-4"), 128.8 (C-3"), 129.8 (C-2'), 131.0 (C-2), 131.1 (C-7), 134.0 (C-6), 134.7 (C-4a), 136.7 (C-1"), 143.9 (C-3a), 145.4 (C-1'), 149.3 (C-4'), 163.1 (COO), 180.4 (CO). ^{15}N NMR ($CDCl_3$) δ (ppm): 117.3 (N-4), 172.4 (N-9), 367.0 (NO2). Anal. Calcd. for $C_{29}H_{25}N_3O_5$ (495.53): C, 70.29; H, 5.08; N, 8.48%. Found: C, 70.33; H, 5.02; N, 8.53%.

*2-Acetyl-4-hydroxy-4-(4-chlorophenyl)-5-benzyl-4,5-dihydropyrrolo[1,2-a]quinoxaline (**6b**).* Pale brown crystals, mp 157-159 ºC (MeOH). FT-IR (ν_{max}, cm^{-1}) 3238, 1635, 1610, 1547, 1521, 1492, 1354, 1333, 1261, 1195, 1168, 1090. ^{1}H NMR (DMSO) δ (ppm): 2.40 (3H, s, CH_3), 4.24 (1H, d, *J* 17.2 Hz, CH_2^A), 4.49 (1H, d, *J* 17.2 Hz, CH_2^B), 5.94 (1H, d, *J* 1.6 Hz, H-3), 6.61 (1H, d, *J* 7.6 Hz, H-6), 6.92 (1H, t, *J* 6.7 Hz, H-8), 7.02 (1H, t, *J* 7.0 Hz, H-7), 7.17 (1H, t, *J* 7.2 Hz, H-4"), 7.23 (1H, s, OH), 7.25 (2H, t, *J* 7.2 Hz, H-3"), 7.31 (2H, d, *J* 7.2 Hz, H-2"), 7.39 (2H, d, *J* 8.8 Hz, H-3'), 7.58 (2H, d, *J* 8.4 Hz, H-2'), 7.92 (1H, d, *J* 8.0 Hz, H-9), 8.50 (1H, d, *J* 1.6 Hz, H-1). ^{13}C NMR (DMSO) δ (ppm): 27.0 (CH_3), 48.4 (CH_2), 84.2 (C-4), 105.8 (C-3), 115.4 (C-9), 115.6 (C-6), 118.8 (C-8), 119.4 (C-1), 123.7 (C-9a), 126.1 (C-7), 126.2 (C-2" and C-2), 126.5 (C-4"), 128.0 (C-3'), 128.3 (C-3"), 128.4 (C-2'), 132.6 (C-1'), 133.7 (C-3a), 135.0 (C-5a), 138.2 (C-1"), 142.7 (C-4'), 192.5 (CO). ^{15}N NMR (DMSO) δ (ppm): 87.9 (N-5), 170.5 (N-10). Anal. Calcd. for $C_{26}H_{21}ClN_2O_2$ (428.91): C, 72.81; H, 4.93; N, 6.53%. Found: C, 72.78; H, 4.97; N, 6.61%.

*2-Acetyl-4-hydroxy-4-(3-nitrophenyl)-5-benzyl-4,5-diydropyrrolo[1,2-a]quinoxaline (**6d**).* Orange crystals, mp 168-170 ºC ($CHCl_3$/MeOH). FT-IR (ν_{max}, cm^{-1}): 3312, 1641, 1612, 1518, 1496, 1450, 1346, 1258, 1191, 1088. ^{1}H NMR (DMSO) δ (ppm): 2.40 (3H, s, CH_3), 4.26 (1H, d, *J* 17.6 Hz, CH_2^A), 4.53 (1H, d, *J* 17.2 Hz, CH_2^B), 5.97 (1H, d, *J* 2 Hz, H-3), 6.67 (1H, dd, *J* 8.4, 0.8 Hz, H-6), 6.96 (1H, td, *J* 8.0, 1.2 Hz, H-8), 7.06 (1H, td, *J* 8.4, 1.2 Hz, H-7), 7.16 (1H, t, *J* 7.2 Hz, H-4"), 7.23 (2H, t, *J* 7.2 Hz, H-3"), 7.29 (2H, d, *J* 7.2 Hz, H-2"), 7.54 (1H, bs, OH), 7.61 (1H, t, *J* 8.0 Hz, H-5'), 7.98 (2H, d, *J* 8.0 Hz, H-6' and H-9), 8.17 (1H, ddd, *J* 8.4, 2.4, 1.2 Hz, H-4'), 8.46 (1H, t, *J* 2.0 Hz, H-2'), 8.55 (1H, d, *J* 1.6 Hz, H-1). ^{13}C NMR (DMSO) δ (ppm): 27.0 (CH_3), 48.5 (CH_2), 84.0 (C-4), 106.2 (C-3), 115.5 (C-9), 115.7 (C-6), 119.0 (C-8), 119.6 (C-1), 121.2 (C-2'), 123.1 (C-4'), 123.6 (C-9a), 126.1 (C-2"), 126.2 (C-7), 126.58 (C-4"), 126.64 (C-2), 128.3 (C-3"), 129.8 (C-5'), 133.0 (C-3a), 133.3 (C-6'), 134.8 (C-

5a), 138.0 (C-1"), 145.9 (C-1'), 147.4 (C-5'), 192.5 (CO). ^{15}N NMR (DMSO) δ (ppm): 87.6 (N-5), 169.9 (N-10) and 369.7 (NO_2). Anal. Calcd. for $C_{26}H_{21}N_3O_4$ (439.46): C, 71.06; H, 4.82; N, 9.56%. Found: C, 71.10; H, 4.77; N, 9.62%.

*Ethyl 4-hydroxy-4-(4-fluorophenyl)-5-benzyl-4,5-dihydropyrrolo[1,2-a]quinoxaline-2-carboxylate (**6g**).* Pale brown crystals, mp 157-159 ºC (MeOH). FT-IR (ν_{max}, cm^{-1}) 3332, 1704, 1670, 1605, 1524, 1450, 1388, 1273, 1206, 1154. ^{1}H NMR (DMSO) δ (ppm): 1.26 (3H, t, *J* 7.2 Hz, CH_3-Et), 4.14-4.27 (2H, m, CH_2-Et), 4.28 (1H, d, *J* 17.4 Hz, CH_2^A), 4.48 (1H, d, *J* 17.2 Hz, CH_2^B), 5.90 (1H, d, *J* 1.6 Hz, H-3), 6.61 (1H, dd, *J* 8.3, 0.9 Hz, H-6), 6.89 (1H, td, *J* 8.0, 1.1 Hz, H-8), 7.00 (1H, td, *J* 7.5, 1.4 Hz, H-7), 7.13-7.18 (3H, m, aromatic rings), 7.14 (1H, s, OH), 7.24 (2H, t, *J* 7.7 Hz, H-3"), 7.30 (2H, d, *J* 7.2 Hz, H-2"), 7.63 (2H, dd, *J* 8.9, 5.5 Hz, H-2'), 7.94 (1H, dd, *J* 8.0, 1.4 Hz, H-9), 8.30 (1H, d, *J* 1.7 Hz, H-1). The individual chemical shifts, multiplicities and coupling constants for the 7.13-7.18 ppm multiplet were obtained from undecoupled HSQC as follows: 7.16 (2H, t, *J* 8.9 Hz, H-3'), 7.17 (1H, t, *J* 7.1 Hz, H-4"). ^{13}C NMR (DMSO) δ (ppm): 14.3 (CH_3-Et), 48.3 (CH_2), 59.4 (CH_2-Et), 84.2 (C-4), 106.9 (C-3), 114.7 (d, $J_{C\text{-}F}$ 22.1 Hz, C-3'), 115.5 (C-9), 115.6 (C-6), 116.9 (C-2), 118.4 (C-1), 118.7 (C-8), 123.7 (C-9a), 126.0 (C-7), 126.1 (C-2"), 126.5 (C-4"), 128.3 (C-3"), 128.7 (d, $J_{C\text{-}F}$ 8.1 Hz, C-2'), 133.4 (C-3a), 134.9 (C-5a), 138.2 (C-1"), 139.8 (d, $J_{C\text{-}F}$ 2.4 Hz, C-1'), 161.6 (d, $J_{C\text{-}F}$ 244.5 Hz, C-4'), 163.5 (COO). ^{15}N NMR (DMSO) δ (ppm): 88.6 (N-5), 170.8 (N-10). ^{19}F NMR ($CDCl_3$) δ (ppm): -114.6. Anal. Calcd. for $C_{27}H_{23}FN_2O_3$ (442.48): C, 73.29; H, 5.24; N, 6.33%. Found: C, 73.22; H, 5.31; N, 6.37%. Single crystal X-ray: $C_{29}H_{28.5}BrFN_{2.75}O_{3.75}$, *Mr* = 574.46 g mol^{-1}, size 0.20×0.20×0.10 mm^3, triclinic, space group *P*-1, *a* 11.2429(4) Å, *b* = 11.4012(5) Å, *c* = 12.1351(5) Å, *α* = 99.621(3)°, *β* = 93.444(3)°, *γ* 107.593(4)°, *V* = 1451.73(10) Å^3, *Z* = 2, ρ_{calcd} = 1.314 g cm^{-3}, μ(Mo*Kα*) = 1.457 mm^{-1}, *F*(000) = 592, 20650 reflections in *h*(-13/13), *k*(-13/13), *l*(-14/14), measured in the range 5.8 ≤ *Θ* ≤ 50.06, T = 200 K, completeness Θ_{max} = 99.92%, 5086 independent reflections, R_{int} = 0.0373, 345 parameters, 7 restraints, R_{1obs}=0.0592, wR_{2obs} = 0.1529, R_{1all} = 0.0721, wR_{2all} = 0.1618, GoF = 1.049, largest difference peak and hole: 0.85/-0.61 e A^{-3}. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK). CCDC: 1431562.

*Ethyl 4-hydroxy-4-(4-chlorophenyl)-5-benzyl-4,5-dihydropyrrolo[1,2-a]quinoxaline-2-carboxylate (**6h**).* Off-white crystals, mp 170-172 ºC ($CHCl_3$/MeOH). FT-IR (ν_{max}, cm^{-1}) 3332, 1716, 1659, 1611, 1552, 1527, 1493, 1378, 1315, 1268, 1193, 1165, 1091. ^{1}H NMR (DMSO) δ (ppm): 1.28 (3H, t, *J* 7.2 Hz, CH_3-Et), 4.14-4.25 (2H, m, CH_2-Et), 4.26 (1H, d, *J* 17.0 Hz, CH_2^A), 4.49 (1H, d, *J* 17.2 Hz, CH_2^B), 5.91 (1H, d, *J* 0.9 Hz, H-3), 6.61 (1H, d, *J* 8.2 Hz, H-6), 6.89 (1H, t, *J* 7.6 Hz, H-8), 7.01 (1H, t, *J* 7.6 Hz, H-7), 7.17 (1H, t, *J* 7.2 Hz, H-4"), 7.20 (1H, s, OH), 7.25 (2H, t, *J* 7.2 Hz, H-3"), 7.30 (2H, d, *J* 7.2 Hz, H-2"), 7.40 (2H, d, *J* 8.4 Hz, H-3'), 7.60 (2H, d, *J* 8.4 Hz, H-2'), 7.95 (1H, d, *J* 7.6 Hz, H-9), 8.31 (1H, d, *J* 1.2 Hz, H-1). ^{13}C NMR (DMSO) δ (ppm): 14.3 (CH_3-Et), 48.3 (CH_2), 59.3 (CH_2-Et), 84.1 (C-4), 107.0 (C-3), 115.48 (C-9), 115.51 (C-6), 117.0 (C-2), 118.4 (C-1), 118.7 (C-8), 123.5 (C-9a), 126.0 (C-7), 126.1 (C-2"), 126.5 (C-4"), 127.9 (C-3'), 128.2 (C-3"), 128.4 (C-2'), 132.5 (C-4'), 133.1 (C-3a), 134.8 (C-5a), 138.1 (C-1"), 142.7 (C-1'), 163.4 (COO). ^{15}N NMR (DMSO) δ (ppm): 87.6 (N-5), 170.0 (N-10). Anal. Calcd. for $C_{27}H_{23}ClN_2O_3$ (458.94): C, 70.66; H, 5.05; N, 6.10%. Found: C, 70.57; H, 5.11; N, 6.16%.

*Ethyl 4-hydroxy-4-(4-nitrophenyl)-5-benzyl-4,5-dihydropyrrolo[1,2-a]quinoxaline-2-carboxylate (**6i**).* Pale brown crystals, mp 176-178 ºC (MeOH). FT-IR (ν_{max}, cm^{-1}) 3318, 1700, 1668, 1558, 1520, 1454, 1347, 1274, 1196. ^{1}H NMR (DMSO) δ (ppm): 1.25 (3H, t, *J* 7.2 Hz, CH_3-Et), 4.14-4.27 (2H, m, CH_2-Et), 4.21 (1H, d, *J* 16.6 Hz, CH_2^A), 4.52 (1H, d, *J* 17.3 Hz, CH_2^B), 5.96 (1H, d, *J* 1.70 Hz, H-3), 6.62 (1H, dd, *J* 8.4, 0.8 Hz, H-6), 6.91 (1H, td, *J* 8.0, 1.0 Hz, H-8), 7.03 (1H, td, *J* 8.4, 1.4 Hz, H-7), 7.14 (1H, t, *J* 7.2 Hz, H-4"), 7.25 (2H, t, *J* 7.2 Hz, H-3"), 7.31 (2H, d, *J* 7.3 Hz, H-2"), 7.52 (1H, s, OH), 7.84 (2H, d, *J* 9.0 Hz, H-2'), 7.99 (1H, dd, *J* 8.1, 1.4 Hz, H-9), 8.20 (2H, d, *J* 9.0 Hz, H-3'), 8.36 (1H, d, *J* 1.7 Hz, H-1). ^{13}C NMR (DMSO) δ (ppm): 14.3 (CH_3-Et), 48.4 (CH_2), 59.4 (CH_2-Et), 84.1 (C-4), 107.4 (C-3), 115.4 (C-6), 115.6 (C-9), 117.2 (C-2), 118.6 (C-1), 118.9 (C-8), 123.2 (C-3'), 123.3 (C-9a), 126.09 (C-7), 126.14 (C-2"), 126.5 (C-4"), 127.8 (C-2'), 128.2 (C-3"), 132.3 (C-3a), 134.5 (C-5a), 138.0 (C-1"), 147.1 (C-4'), 150.7 (C-1'), 163.3 (COO). ^{15}N NMR (DMSO) δ (ppm): 85.7 (N-5), 170.1 (N-10), 369.2 (NO_2). Anal. Calcd. for $C_{27}H_{23}N_3O_5$ (469.49): C, 69.07; H, 4.94; N, 8.95%. Found: C, 68.99; H, 4.91; N, 9.03%.

*2-Acetyl-4-hydroxy-4-(4-nitrophenyl)-5-ethyl-7,8-dimethyl-4,5-dihydropyrrolo[1,2-a]quinoxaline (**6j**).* Orange crystals, mp 196-198 ºC (MeOH). FT-IR (ν_{max}, cm^{-1}) 3111, 2986, 1680, 1594, 1522, 1501, 1452, 1366, 1348, 1280, 1196. ^{1}H NMR (DMSO) δ (ppm): 1.05 (3H, t, *J* 6.9 Hz, CH_3-Et), 2.26 (3H, s, CH_3-8), 2.27 (3H, s, CH_3-7), 2.35 (3H, s, CH_3), 3.11 (1H, dq, *J* 14.80, 7.20 Hz, CH_2^A), 3.24 (1H, dq, *J* 14.70, 7.0 Hz, CH_2^B), 5.86 (1H, d, *J* 2.0 Hz, H-3), 6.78 (1H, s, H-6), 7.11 (1H, s, OH), 7.74 (2H, d, *J* 8.8 Hz, H-2'), 7.74 (1H, s, H-9), 8.25 (2H, d, *J* 8.8 Hz, H-3'), 8.40 (1H, d, *J* 1.6 Hz, H-1). ^{13}C NMR (DMSO) δ (ppm): 13.5 (CH_3-Et), 18.4 (CH_3-8), 19.6 (CH_3-7), 26.9 (CH_3), 39.3 (CH_2), 83.9 (C-4), 105.5 (C-3), 115.0 (C-6), 116.5 (C-9), 118.8 (C-1), 120.7 (C-9a), 123.3 (C-3'), 125.9 (C-8), 126.3 (C-2), 127.8 (C-2'), 132.1 (C-5a), 132.8 (C-3a), 134.4 (C-7), 146.9 (C-4'), 151.5 (C-1'), 192.4 (CO). ^{15}N NMR (DMSO) δ (ppm): 87.2 (N-5), 170.4 (N-10) and 369.5 (NO_2). Anal. Calcd. for $C_{23}H_{23}N_3O_4$ (405.45): C, 68.13; H, 5.72; N, 10.36%. Found: C, 68.21; H, 5.80; N, 10.25%.

*Ethyl 4-hydroxy-4-(4-chlorophenyl)-5-ethyl-7,8-dimethyl-4,5-dihydropyrrolo[1,2-a]quinoxaline-2-carboxylate (**6k**).* Colourless crystals, mp 154-156 ºC ($CHCl_3$/MeOH). FT-IR (ν_{max}, cm^{-1}): 3336, 2976, 2934, 1677, 1555, 1526, 1491, 1387, 1335, 1263, 1201, 1167, 1090. ^{1}H NMR (DMSO) δ (ppm): 1.03 (3H, t, *J* 6.9 Hz, CH_3-Et-5), 1.24 (3H, t, *J* 7.2 Hz, CH_3-Et-2), 2.23 (3H, s, CH_3-8), 2.25 (3H, s, CH_3-7), 3.11 (1H, dq, *J* 14.30, 7.24 Hz, CH_2^A-Et-5), 3.22 (1H, dq, *J* 14.60, 7.24 Hz, CH_2^B-Et-5), 4.11-4.23 (2H, m, CH_2-Et-2), 5.78 (1H, d, *J* 1.7 Hz, H-3), 6.75 (1H, s, H-6), 6.81 (1H, s, OH), 7.44 (2H, d, *J* 8.7 Hz, H-3'), 7.51 (2H, d, *J* 8.6 Hz, H-2'), 7.75 (1H, s, H-9), 8.16 (1H, d, *J* 1.7 Hz, H-1). ^{13}C NMR (DMSO) δ (ppm): 13.5 (CH_3-Et-5), 14.3 (CH3-Et-2), 18.3 (CH_3-8), 19.5 (CH_3-7), 38.7 (CH_2-Et-5), 59.3 (CH_2-Et-2), 83.8 (C-4), 106.4 (C-3), 115.0 (C-6), 116.5 (C-2), 116.6 (C-9), 117.7 (C-1), 120.8 (C-9a), 125.7 (C-8), 127.9 (C-3'), 128.5 (C-2'), 132.28 (C-5a), 132.30 (C-4'), 133.1 (C-3a), 134.2 (C-7), 143.3 (C-1'), 163.6 (COO). ^{15}N NMR (DMSO) δ (ppm): 88.3 (N-5), 170.4 (N-10). Anal. Calcd. for $C_{24}H_{25}ClN_2O_3$ (424.92): C, 67.84; H, 5.93; N, 6.59%. Found: C, 67.78; H, 6.01; N, 6.55%.

*2-Acetyl-4-hydroxy-4-phenyl-5-benzyl-7,8-dimethyl-4,5-dihydropyrrolo[1,2-a]quinoxaline (**6l**).* Off-white crystals, mp 165-166 ºC (MeOH). FT-IR (ν_{max}, cm^{-1}): 3381, 2917, 1619, 1513, 1447, 1401, 1350, 1326, 1237, 1197, 1169, 1119. ^{1}H NMR (DMSO) δ (ppm): 2.01 (3H, s, CH_3-7), 2.20 (3H, s, CH_3-8), 2.39 (3H, s, CH_3-CO), 4.21 (1H, d, *J* 16.8 Hz, CH_2^A), 4.49 (1H, d, *J* 16.8 Hz, CH_2^B), 5.94 (1H, d, *J* 1.6 Hz, H-3), 6.43 (1H, s, H-6), 7.03 (1H, s, OH), 7.16 (1H, t, *J* 7.2 Hz, H-4"), 7.25 (2H, t, *J* 7.6

Hz, H-3"), 7.28 (1H, t, *J* 6.8 Hz, H-4'), 7.32 (2H, t, *J* 7.9 Hz, H-3'), 7.33 (2H, d, *J* 8.0 Hz, H-2"), 7.55 (2H, d, *J* 7.2 Hz, H-2'), 7.72 (1H, s, H-9), 8.43 (1H, d, *J* 2.0 Hz, H-1). ^{13}C NMR (DMSO) δ (ppm): 18.4 (CH_3-8), 19.6 (CH_3-7), 27.0 (CH_3-CO), 48.3 (CH_2), 84.7 (C-4), 105.4 (C-3), 116.3 (C-9), 116.8 (C-6), 119.1 (C-1), 121.6 (C-9a), 126.2 (C-2), 126.32 (C-2'), 126.36 (C-2"), 126.41 (C-8), 126.45 (C-4"), 127.8 (C-4'), 128.0 (C-3'), 128.3 (C-3"), 133.2 (C-5a), 133.6 (C-7), 134.4 (C-3a), 138.8 (C-1"), 143.8 (C-1'), 192.5 (CO). ^{15}N NMR (DMSO) δ (ppm): 85.8 (N-5), 170.1 (N-10). Anal. Calcd. for $C_{28}H_{26}N_2O_2$ (422.52): C, 79.59; H, 6.20; N, 6.63%. Found: C, 79.63; H, 6.25; N, 6.56%.

*Ethyl 4-hydroxy-4-(4-nitrophenyl)-5-benzyl-7,8-dimethyl-4,5-dihydropyrrolo[1,2-a]quinoxaline-2-carboxylate (**6o**).* Yellow crystals, mp 176-178 ºC ($CHCl_3$/MeOH). FT-IR (ν_{max}, cm^{-1}) 3345, 1698, 1669, 1623, 1554, 1518, 1451, 1378, 1346, 1263, 1196, 1101. ^{1}H NMR (DMSO) δ (ppm): 1.25 (3H, t, *J* 7.1 Hz, CH_3-Et), 2.02 (3H, s, CH_3-7), 2.20 (3H, s, CH_3-8), 4.17-4.26 (2H, m, CH_2-Et), 4.15 (1H, d, *J* 17.4 Hz, CH_2^A), 4.53 (1H, d, *J* 17.4 Hz, CH_2^B), 5.99 (1H, d, *J* 1.4 Hz, H-3), 6.44 (1H, s, H-6), 7.19 (1H, t, *J* 7.2 Hz, H-4"), 7.27 (2H, t, *J* 7.3 Hz, H-3"), 7.34 (2H, d, *J* 7.5 Hz, H-2"), 7.44 (1H, s, OH), 7.81 (2H, d, *J* 8.3 Hz, H-2'), 7.82 (1H, s, H-9), 8.20 (2H, d, *J* 8.9 Hz, H-3'), 8.29 (1H, d, *J* 1.5 Hz, H-1). ^{13}C NMR (DMSO) δ (ppm): 14.3 (CH_3-Et), 18.3 (CH_3-8), 19.5 (CH_3-7), 48.3 (CH_2), 59.4 (CH_2-Et), 84.2 (C-4), 107.2 (C-3), 116.6 (C-9), 116.8 (C-6), 121.2 (C-9a), 123.3 (C-3'), 126.3 (C-2"), 126.5 (C-4"), 126.8 (C-8), 127.6 (C-2'), 128.3 (C-3"), 132.3 (C-3a), 132.4 (C-5a), 133.8 (C-7), 138.4 (C-1"), 147.0 (C-4'), 150.9 (C-1'), 163.5 (COO). ^{15}N NMR (DMSO) δ (ppm): 84.5 (N-5), 170.4 (N-10) and 369.6 (NO_2). Anal. Calcd. for $C_{29}H_{27}N_3O_4$ (481.54): C, 72.33; H, 5.65; N, 8.73%. Found: C, 72.41; H, 5.60; N, 8.65%.

*2-Acetyl-4-(3-nitrophenyl)-5-benzyl-4,5-dihydropyrrolo[1,2-a]quinoxaline (**7d**).* Yellow crystals, mp 99-101 ºC (MeOH/Et_2O). FT-IR (ν_{max}, cm^{-1}) 1643, 1611, 1520, 1504, 1350, 1269, 1230, 1184. ^{1}H NMR (DMSO) δ (ppm): 2.41 (3H, s, CH_3), 4.48 (1H, d, *J* 16.0 Hz, CH_2^A), 4.48 (1H, d, *J* 16.4 Hz, CH_2^B), 6.11 (1H, s, H-4), 6.49 (1H, s, H-3), 6.86 (1H, d, *J* 7.6 Hz, H-6), 6.88 (1H, t, *J* 8.0 Hz, H-8), 7.08 (1H, t, *J* 7.6 Hz, H-7), 7.23 (1H, t, *J* 6.7 Hz, H-4"), 7.29 (2H, d, *J* 7.8 Hz, H-2"), 7.30 (2H, t, *J* 7.7 Hz, H-3"), 7.37 (1H, d, *J* 8.1 Hz, H-3'), 7.58 (1H, d, *J* 8.0 Hz, H-2'), 7.86 (1H, d, *J* 8.0 Hz, H-9), 8.03 (1H, bs, H-6'), 8.08-8.11 (1H, m, H-4'), 8.45 (1H, bs, H-1). ^{13}C NMR (DMSO) δ (ppm): 26.9 (CH_3), 52.5 (CH_2), 58.4 (C-4), 104.7 (C-3), 114.6 (C-6), 115.7 (C-9), 118.6 (C-8), 120.6 (C-1), 121.1 (C-6'), 122.5 (C-4'), 124.3 (C-9a), 126.5 (C-7), 127.0 (C-2" and C-2), 127.1 (C-4"), 128.5 (C-3"), 129.3 (C-3a), 130.3 (C-3'), 133.0 (C-2'), 135.3 (C-5a), 137.3 (C-1"), 143.2 (C-1'), 147.8 (C-5'), 192.3 (CO). ^{15}N NMR (DMSO) δ (ppm): 64.6 (N-5), 168.7 (N-10) and 368.8 (NO_2). Anal. Calcd. for $C_{26}H_{21}N_3O_3$ (423.46): C, 73.74; H, 5.0; N, 9.92%. Found: C, 73.83; H, 5.05; N, 9.87%.

*Ethyl 4-phenyl-5-benzyl-7,8-dimethyl-4,5-dihydropyrrolo[1,2-a]quinoxaline-2-carboxylate (**7m**).* Pale yellow crystals with mp 164-166 ºC (MeOH/Et_2O). FT-IR (ν_{max}, cm^{-1}) 1695, 1609, 1522, 1493, 1452, 1359, 1274, 1240, 1186, 1165, 1099. ^{1}H NMR (DMSO) δ (ppm): 1.27 (3H, t, *J* 6.8 Hz, CH_3-Et), 2.08 (3H, s, CH_3-7), 2.17 (3H, s, CH_3-8), 4.17-4.23 (2H, m, CH_2-Et), 4.29 (1H, d, *J* 15.6 Hz, CH_2^A), 4.63 (1H, d, *J* 15.6 Hz, CH_2^B), 5.72 (1H, s, H-4), 6.31 (1H, d, *J* 1.2 Hz, H-3), 6.64 (1H, s, H-6), 7.13 (2H, d, *J* 6.8 Hz, H-2'), 7.21-7.32 (8H, m, aromatic rings), 7.65 (1H, s, H-9), 8.12 (1H, d, *J* 1.6 Hz, H-1). The individual chemical shifts, multiplicities and coupling constants for the 7.21-7.32 ppm multiplet were obtained from undecoupled HSQC as follows: 7.216 (1H, t, *J* 7.6 Hz, H-4"), 7.26 (2H, t, *J* 7.6 Hz, H-3'), 7.29 (2H, d, *J* 7.6 Hz, H-2"), 7.309 (2H, t, *J* 7.9 Hz, H-3"), 7.310 (1H, t, *J* 8.4 Hz, H-4'). ^{13}C NMR (DMSO) δ (ppm): 14.3 (CH_3-Et), 18.3 (CH_3-8), 19.3 (CH_3-7), 52.2 (CH_2), 58.9 (C-4), 59.2 (CH_2-Et), 105.2 (C-3), 115.6 (C-6), 116.7 (C-2), 116.8 (C-9), 118.8 (C-1), 122.3 (C-5a), 126.1 (C-8), 126.5 (C-2'), 127.1 (C-2"), 127.4 (C-4"), 128.4 (C-3"), 128.5 (C-3'), 128.6 (C-4'), 129.9 (C-3a), 133.7 (C-5a), 134.0 (C-7), 137.77 (C-1"), 141.0 (C-1'), 163.6 (COO). ^{15}N NMR (DMSO) δ (ppm): 61.2 (N-5), 170.4 (N-10). Anal. Calcd. for $C_{29}H_{28}N_2O_2$ (436.54): C, 79. 97; H, 6.46; N, 6.42%. Found: C, 79.84; H, 6.51; N, 6.35%.

*Ethyl 4-(4-methylphenyl)-5-benzyl-7,8-dimethyl-4,5-dihydropyrrolo[1,2-a]quinoxaline-2-carboxylate (**7n**).* Bright pink crystals, mp 159-161 ºC (MeOH/Et_2O). FT-IR (ν_{max}, cm^{-1}) 1708, 1526, 1509, 1452, 1334, 1227, 1198, 1185, 1138, 1093. ^{1}H NMR (DMSO) δ (ppm): 1.26 (3H, t, *J* 7.1 Hz, CH_3-Et), 2.07 (3H, s, CH_3-7), 2.16 (3H, s, CH_3-8), 2.21 (3H, s, CH_3), 4.19 (2H, q, *J* 7.0 Hz, CH_2-Et), 4.25 (1H, d, *J* 15.9 Hz, CH_2^A), 4.58 (1H, d, *J* 15.8 Hz, CH_2^B), 5.63 (1H, s, H-4), 6.24 (1H, d, *J* 0.9 Hz, H-3), 6.60 (1H, s, H-6), 6.99 (2H, d, *J* 8.0 Hz, H-2'), 7.06 (2H, d, *J* 8.0 Hz, H-3'), 7.23 (1H, t, *J* 6.6 Hz, H-4"), 7.27-7.32 (4H, m, aromatic rings), 7.63 (1H, s, H-9), 8.10 (1H, d, *J* 1.4 Hz, H-1). The individual chemical shifts, multiplicities and coupling constants for the 7.27-7.32 ppm multiplet were obtained from undecoupled HSQC as follows: 7.29 (2H, d, *J* 7.8 Hz, H-2"), 7.31 (2H, t, *J* 7.5 Hz, H-3"). ^{13}C NMR (DMSO) δ (ppm): 14.4 (CH_3-Et), 18.3 (CH_3-8), 19.4 (CH_3-7), 20.5 (CH_3), 52.1 (CH_2), 58.69 (C-4), 59.22 (CH_2-Et), 105.17 (C-3), 115.64 (C-6), 116.70 (C-2), 116.72 (C-9), 118.8 (C-1), 122.4 (C-9a), 126.1 (C-8), 126.5 (C-2'), 127.0 (C-4"), 127.1 (C-2"), 128.4 (C-3"), 129.1 (C-3'), 130.2 (C-3a), 133.7 (C-5a), 134.0 (C-7), 136.7 (C-4'), 137.8 (C-1'), 138.0 (C-1"), 163.7 (COO). ^{15}N NMR (DMSO) δ (ppm): 62.8 (N-5), 169.9 (N-10). Anal. Calcd. for $C_{30}H_{30}N_2O_2$ (450.57): C, 79.97; H, 6.71; N, 6.22%. Found: C, 80.04; H, 6.66; N, 6.18%.

General procedure for the preparation of pyrrolo[1,2-*a*]quinoxalinium bromides 8. To a suspension of 0.5 mmol 4,5-dihydropyrrolo[1,2-a]quinoxaline **6** or **7** in 15 mL MeOH was added under stirring 0.15 mL solution of HBr 40% (1 mmol) and the mixture kept under stirring at room temperature for 30 min. The solvent was partly evaporated *in vacuo* and the mixture left for 20 h. The solid formed was filtered and recrystallized from MeOH.

Pyrrolo[1,2-*a*]quinoxalinium bromides **8b,d,g-l,o** were obtained starting from corresponding 4,5-dihydropyrrolo[1,2-*a*]quinoxaline **6**. Pyrrolo[1,2-*a*]quinoxalinium bromides **8a** and **8m** were obtained starting from 4,5-dihydropyrrolo[1,2-*a*]quinoxalines **7a** and **7m** respectively. Pyrrolo[1,2-*a*]quinoxalinium bromides **8c** and **8e** were separated during the work-up procedures of reaction mixtures performed in the presence of triethylamine and acetonitrile. After the separation of the corresponding pyrrolo[1,2-a]quinoxalines **6** and pyrrolo[1,2-*a*]benzimidazoles **5**, the resultant filtrate was evaporated to dryness and triturated with acetone. The insoluble part was filtered off and recrystallized from MeOH to give pyrrolo[1,2-*a*]quinoxalinium bromides **8c** and **8e** respectively.

*2-Acetyl-4-phenyl-5-benzylpyrrolo[1,2-a]quinoxalinium bromide (**8a**).* Orange crystals (0.175 g, 77%), mp 200-202 ºC (MeOH). FT-IR (ν_{max}, cm^{-1}) 3405, 3028, 2965, 1678, 1607, 1549, 1492, 1450, 1390, 1337, 1276, 1262, 1207, 1011. ^{1}H NMR ($CDCl_3$) δ (ppm): 2.63 (3H, s, CH_3), 6.11 (2H, bs, CH_2), 7.11 (2H, d, *J* 6.8 Hz, H-2"), 7.30-7.39 (6H, m, aromatic rings), 7.65 (2H, t, *J* 7.6 Hz, H-3'), 7.73 (1H, t, *J* 7.4 Hz, H-4'), 7.85 (1H, d, *J* 8.4 Hz, H-6), 8.04 (2H, d, *J* 7.2 Hz, H-2'), 9.02 (1H, d, *J* 8.4 Hz, H-9), 10.34 (1H, d, *J* 1.2 Hz, H-1). The individual chemical shifts, multiplicities and coupling constants for the 7.30-7.39 multiplet were obtained from undecoupled HSQC as follows:

7.31 (1H, t, *J* 8.1 Hz, H-4"), 7.330 (1H, t, *J* 7.9 Hz, H-8), 7.332 (1H, bs, H-3), 7.34 (2H, t, *J* 7.5 Hz, H-3"), 7.36 (1H, t, *J* 8.1 Hz, H-7). ^{13}C NMR ($CDCl_3$) δ (ppm): 29.1 (CH_3), 56.6 (CH_2), 118.8 (C-9), 121.4 (C-6), 121.6 (C-3), 125.4 (C-3a), 125.5 (C-2"), 127.1 (C-9a), 127.6 (C-5a), 128.1 (C-7), 128.5 (C-4" and C-1'), 129.0 (C-2'), 129.4 (C-3'), 129.5 (C-3"), 129.6 (C-1), 131.1 (C-8), 132.5 (C-4'), 132.9 (C-2), 133.7 (C-1"), 157.4 (C-4), 193.4 (CO). ^{15}N NMR ($CDCl_3$) δ (ppm): 169.4 (N-5), 178.2 (N-10). Anal. Calcd. for $C_{26}H_{21}BrN_2O$ (457.36): C, 68.28; H, 4.63; N, 6.12%. Found: C, 68.22; H, 4.71; N, 6.05%.

*2-Acetyl-4-(4-chlorophenyl)-5-benzylpyrrolo[1,2-a]quinoxalinium bromide (**8b**).* Yellow crystals (0.209 g, 85%), mp 196-198 ºC (MeOH). FT-IR (ν_{max}, cm^{-1}) 3401, 3018, 2974, 1680, 1601, 1548, 1489, 1451, 1390, 1378, 1335, 1272, 1206, 1091, 1012. ^{1}H NMR ($CDCl_3$) δ (ppm): 2.51 (3H, s, CH_3), 6.00 (2H, s, CH_2), 7.07 (2H, d, *J* 6.5 Hz, H-2"), 7.29-7.38 (6H, m, aromatic rings), 7.59 (2H, d, *J* 8.1 Hz, H-3'), 7.77 (1H, d, *J* 8.5 Hz, H-6), 8.04 (2H, d, *J* 7.5 Hz, H-2'), 8.89 (1H, d, *J* 8.2 Hz, H-9), 10.14 (1H, s, H-1). The individual chemical shifts, multiplicities and coupling constants for the signals from 7.29-7.38 ppm were obtained from undecoupled HSQC as follows: 7.31 (1H, t, *J* 6.9 Hz, H-8), 7.32 (1H, s, H-3), 7.34 (1H, t, *J* 7.6 Hz, H-4"), 7.36 (2H, d, *J* 7.2 Hz, H-3"), 7.38 (1H, t, *J* 8.0 Hz, H-7). ^{13}C NMR ($CDCl_3$) δ (ppm): 29.1 (CH_3), 56.9 (CH_2), 118.8 (C-9), 121.3 (C-6), 121.4 (C-3), 125.4 (C-2"), 125.5 (C-3a), 126.9 (C-1'), 127.4 (C-5a), 127.6 (C-9a), 128.3 (C-7) 128.7 (C-4"), 129.4 (C-1), 129.6 (C-3"), 129.8 (C-3'), 130.7 (C-2'), 131.2 (C-8), 133.0 (C-2), 133.6 (C-1"), 139.2 (C-4'), 156.6 (C-4), 193.1 (CO). ^{15}N NMR ($CDCl_3$) δ (ppm): 170.7 (N-5), 179.1 (N-10). Anal. Calcd. for $C_{26}H_{20}BrClN_2O$ (491.81): C, 63.49; H, 4.10; N, 5.70%. Found: C, 63.55; H, 4.14; N, 5.63%.

*2-Acetyl-4-(4-methoxyphenyl)-5-benzylpyrrolo[1,2-a]quinoxalinium bromide (**8c**).* Light yellow crystals, mp 187-189 ºC (MeOH). FT-IR (ν_{max}, cm^{-1}) 3417, 3019, 1680, 1605, 1545, 1488, 1451, 1389, 1336, 1262, 1207, 1180. ^{1}H NMR ($CDCl_3$) δ (ppm): 2.62 (3H, s, CH_3), 3.91 (3H, s, OCH_3), 6.12 (2H, s, CH_2), 7.09-7.12 (4H, m, aromatic rings), 7.32-7.36 (5H, m, aromatic rings), 7.38 (1H, s, H-3), 7.80 (1H, d, *J* 9.5 Hz, H-6), 7.93 (2H, d, *J* 7.8 Hz, H-2'), 8.96 (1H, d, *J* 9.2 Hz, H-9), 10.23 (1H, s, H-1). The individual chemical shifts, multiplicities and coupling constants for the signals from 7.09-7.12 and 7.32-7.36 ppm were obtained from undecoupled HSQC as follows: 7.107 (2H, d, *J* 8.4 Hz, H-3'), 7.108 (2H, d, *J* 7.0 Hz, H-2"), 7.31 (1H, t, *J* 7.6 Hz, H-4"), 7.32 (1H, t, *J* 7.5 Hz, H-8), 7.33 (1H, t, *J* 8.2 Hz, H-7), 7.34 (2H, t, *J* 7.7 Hz, H-3"). ^{13}C NMR ($CDCl_3$) δ (ppm): 29.2 (CH_3), 55.7 (OCH_3), 56.7 (CH_2), 114.9 (C-3'), 118.8 (C-9), 120.4 (C-1'), 121.5 (C-6), 121.8 (C-3), 125.5 (C-2"), 125.6 (C-3a), 127.3 (C-5a), 127.5 (C-9a), 128.1 (C-7) 128.5 (C-4"), 129.2 (C-1), 129.5 (C-3"), 130.9 (C-8), 131.2 (C-2'), 132.8 (C-2), 134.0 (C-1"), 157.7 (C-4), 163.0 (C-4'), 193.4 (CO). ^{15}N NMR ($CDCl_3$) δ (ppm): 169.1 (N-5), 178.5 (N-10). Anal. Calcd. for $C_{27}H_{23}BrN_2O_2$ (487.46): C, 66.53; H, 4.75; N, 5.75%. Found: C, 66.47; H, 4.71; N, 5.82%.

*2-Acetyl-4-(3-nitrophenyl)-5-benzylpyrrolo[1,2-a]quinoxalinium bromide (**8d**).* Yellow crystals (0.220 g, 88%), mp 223-225 ºC (MeOH). FT-IR (ν_{max}, cm^{-1}) 3379, 3003, 1683, 1612, 1535, 1492, 1450, 1392, 1350, 1275, 1207, 1134. ^{1}H NMR ($CDCl_3$+TFA) δ (ppm): 2.65 (3H, s, CH_3), 5.75 (1H, d, *J* 17.2 Hz, CH_2^A), 5.92 (1H, d, *J* 17.2 Hz, CH_2^B), 7.07-7.08 (2H, m, H-2"), 7.37-7.38 (3H, m, aromatic rings), 7.44 (1H, bs, H-3), 7.69 (1H, t, *J* 8.0 Hz, H-7), 7.88-7.96 (3H, m, aromatic rings), 8.25 (1H, d, *J* 7.2 Hz, H-2'), 8.42 (1H, d, *J* 8.4 Hz, H-9), 8.45 (1H, bs, H-6'), 8.56 (1H, d, *J* 8.0 Hz, H-4'), 9.28 (1H, bs, H-9). The individual chemical shifts, multiplicities and coupling constants for the 7.37-7.38 and 7.88-7.96 ppm multiplet were obtained from undecoupled HSQC as follows: 7.41 (1H, t, 8.0 Hz, H-4"), 7.42 (2H, t, *J* 7.0 Hz, H-3"), 7.94 (1H, t, *J* 7.9 Hz, H-3'), 7.95 (1H, t, *J* 8.2 Hz, H-8), 7.98 (1H, d, *J* 8.9 Hz, H-6). ^{13}C NMR ($CDCl_3$+TFA) δ (ppm): 27.9 (CH_3), 56.7 (CH_2), 117.2 (C-9), 121.8 (C-6), 122.5 (C-3), 123.4 (C-6'), 125.2 (C-2"), 125.6 (C-3a), 126.7 (C-1), 127.2 (C-1' and C-5a), 127.6 (C-4'), 129.0 (C-9a), 129.3 (C-4"), 129.8 (C-7), 129.9 (C-3"), 131.6 (C-3'), 132.3 (C-8), 132.7 (C-1"), 132.9 (C-2), 134.9 (C-2'), 148.1 (C-5'), 154.4 (C-4), 194.2 (CO). ^{15}N NMR ($CDCl_3$+TFA) δ (ppm): 169.6 (N-5), 179.4 (N-10), 363.6 (NO_2). Anal. Calcd. for $C_{26}H_{20}BrN_3O_3$ (502.36): C, 62.16; H, 4.01; N, 8.36%. Found: C, 62.22; H, 4.11; N, 8.25%.

*2-Acetyl-4-(4-nitrophenyl)-5-benzylpyrrolo[1,2-a]quinoxalinium bromide (**8e**).* Yellow crystals, mp 280-282 ºC (MeOH). FT-IR (ν_{max}, cm^{-1}) 3405, 3023, 1684, 1602, 1549, 1523, 1492, 1451, 1390, 1351, 1273, 1208, 1134. ^{1}H NMR (DMSO) δ (ppm): 2.63 (3H, s, CH_3), 5.82 (2H, s, CH_2), 7.31-7.39 (5H, m, aromatic rings), 7.62 (1H, d, *J* 1.3 Hz, H-3), 7.75 (1H, td, *J* 7.4, 1.2 Hz, H-7), 8.00 (1H, td, *J* 7.5, 0.8 Hz, H-8), 8.06 (2H, d, *J* 8.9 Hz, H-2'), 8.07 (1H, d, *J* 8.7 Hz, H-6), 8.56 (2H, d, *J* 8.9 Hz, H-3'), 8.90 (1H, dd, *J* 8.5, 1.2 Hz, H-9), 9.88 (1H, d, *J* 1.3 Hz, H-1). The individual chemical shifts, multiplicities and coupling constants for the signals from 7.31-7.39 ppm were obtained from undecoupled HSQC as follows: 7.32 (1H, t, *J* 6.8 Hz, H-4"), 7.34 (2H, t, *J* 7.5 Hz, H-3"), 7.38 (2H, d, *J* 7.6 Hz, H-2"). ^{13}C NMR (DMSO) δ (ppm): 27.9 (CH_3), 55.1 (CH_2), 117.4 (C-9), 121.6 (C-3), 121.8 (C-6), 124.5 (C-3'), 125.9 (C-3a), 126.0 (C-2"), 126.7 (C-1), 126.9 (C-9a), 127.6 (C-5a), 128.1 (C-4"), 128.7 (C-7), 128.8 (C-3"), 130.3 (C-2'), 131.3 (C-8), 132.3 (C-2), 133.8 (C-1"), 134.1 (C-1'), 149.7 (C-4'), 155.3 (C-4), 193.0 (CO). ^{15}N NMR (DMSO) δ (ppm): 170.0 (N-5), 180.0 (N-10), 367.7 (NO_2). Anal. Calcd. for $C_{26}H_{20}BrN_3O_3$ (502.36): C, 62.16; H, 4.01; N, 8.36%. Found: C, 62.11; H, 3.95; N, 8.41%.

*2-Carbethoxy-4-(4-fluorophenyl)-5-benzylpyrrolo[1,2-a]quinoxalinium bromide (**8g**).* Yellow crystals (0.215 g, 85%), mp 193-195 ºC (MeOH/Et_2O). FT-IR (ν_{max}, cm^{-1}) 3385, 3029, 1719, 1601, 1549, 1490, 1452, 1393, 1368, 1335, 1273, 1201, 1133. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.40 (3H, t, *J* 7.2 Hz, CH_3-Et), 4.38 (2H, q, *J* 7.2 Hz, CH_2-Et), 6.13 (2H, bs, CH_2), 7.12 (2H, d, *J* 8.0 Hz, H-2"), 7.28-7.36 (5H, m, aromatic rings), 7.40 (1H, d, *J* 1.2 Hz, H-3), 7.55 (1H, td, *J* 8.6, 1.2 Hz, H-7), 7.67 (1H, td, *J* 8.3. 1.0 Hz, H-8), 7.97 (1H, dd, *J* 8.8, 0.8 Hz, H-6), 8.06 (2H, dd, *J* 7.2, 4.8 Hz, H-2'), 8.46 (1H, dd, *J* 8.4, 1.2 Hz, H-9), 9.16 (1H, d, *J* 1.2 Hz, H-9). The individual chemical shifts, multiplicities and coupling constants for the 7.28-7.36 ppm multiplet were obtained from undecoupled HSQC as follows: 7.31 (2H, t, *J* 8.2 Hz, H-3'), 7.32 (1H, t, *J* 7.0 Hz, H-4"), 7.35 (2H, t, *J* 7.6 Hz, H-3"). ^{13}C NMR ($CDCl_3$) δ (ppm): 14.3 (CH_3-Et), 57.0 (CH_2), 61.5 (CH_2-Et), 116.8 (d, $J_{C\text{-}F}$ 22.1 Hz, C-3'), 117.6 (C-9), 122.1 (C-6), 122.9 (C-3), 124.4 (d, $J_{C\text{-}F}$ 3.0 Hz, C-1'), 125.4 (C-2" and C-2), 125.6 (-3a), 126.7 (C-1), 127.0 (C-9a), 127.3 (C-5a), 128.5 (C-4"), 128.7 (C-7), 129.5 (C-3"), 131.4 (C-8), 131.8 (d, $J_{C\text{-}F}$ 9.1 Hz, C-2'), 133.8 (C-1"), 156.1 (C-4), 161.7 (COO), 164.9 (d, $J_{C\text{-}F}$ 255.5 Hz, C-4'). ^{15}N NMR ($CDCl_3$) δ (ppm): 171.9 (N-5), 178.2 (N-10). ^{19}F NMR ($CDCl_3$) δ (ppm): -104.8. Anal. Calcd. for $C_{27}H_{22}BrFN_2O_2$ (505.38): C, 64.17; H, 4.39; N, 5.54%. Found: C, 64.11; H, 4.31; N, 5.62%. Single crystal X-ray: $C_{27}H_{23}FN_2O_3$, *Mr* = 442.47 g mol^{-1}, size 0.40×0.20×0.05 mm^3, tmonoclinic, space group $P2_1/c$=, *a* 17.2774(7) Å, *b* = 7.0755(3) Å, *c* = 19.4030(7) Å, β = 114.059(5)°, *V* = 2165.90(15) $Å^3$, *Z* = 4, ρ_{calcd} = 1.357 g cm^{-3}, μ(Mo*K*α) = 0.095 mm^{-1}, *F*(000) = 928, 8024 reflections in *h*(-14/20), *k*(-8/8), *l*(-22/22), measured in the range 4.26 ≤ Θ ≤ 48.8, T = 200 K, completeness Θ_{max} = 99.94%, 3541 independent reflections, R_{int} = 0.0284, 300 parameters, 0 restraints, R_{1obs} =

0.0446, wR_{2obs} = 0.0937, R_{1all} = 0.0674, wR_{2all} = 0.1037, GoF = 1.051, largest difference peak and hole: 0.15/-0.23 e A^{-3}. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK). CCDC: 1431563.

*2-Carbethoxy-4-(4-chlorophenyl)-5-benzylpyrrolo[1,2-a]quinoxalinium bromide (**8h**).* Yellow crystals (0.201 g, 77%), mp 196-197 ºC (MeOH). FT-IR (ν_{max}, cm^{-1}) 3366, 3023, 2997, 2978, 1716, 1603, 1553, 1489, 1451, 1397, 1336, 1276, 1218, 1134. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.45 (3H, t, *J* 7.2 Hz, CH_3-Et), 4.38 (2H, q, *J* 7.2 Hz, CH_2-Et), 6.18 (2H, bs, CH_2), 7.09 (2H, dd, *J* 6.0, 1.9 Hz, H-2"), 7.31-7.34 (3H, m, aromatic rings), 7.36 (1H, d, *J* 1.1 Hz, H-3), 7.51 (1H, t, *J* 7.7 Hz, H-7), 7.59 (2H, d, *J* 8.6 Hz, H-3'), 7.61 (1H, t, *J* 7.6 Hz, H-8), 7.98 (1H, d, *J* 8.5 Hz, H-6), 8.03 (2H, d, *J* 7.8 Hz, H-2'), 8.50 (1H, d, *J* 7.8 Hz, H-9), 9.22 (1H, d, *J* 1.1 Hz, H-9). The individual chemical shifts, multiplicities and coupling constants for the 7.31-7.34 ppm multiplet were obtained from undecoupled HSQC as follows: 7.31 (1H, t, *J* 7.8 Hz, H-4"), 7.33 (2H, t, *J* 7.7 Hz, H-3"). ^{13}C NMR ($CDCl_3$) δ (ppm): 14.4 (CH_3-Et), 57.2 (CH_2), 61.7 (CH_2-Et), 117.2 (C-9), 122.5 (C-6), 122.9 (C-3), 125.4 (C-2), 125.5 (C-2"), 125.8 (C-3a), 126.4 (C-1), 126.8 (C-1'), 127.1 (C-9a), 127.4 (C-5a), 128.6 (C-4"), 128.9 (C-7), 129.5 (C-3"), 129.8 (C-3'), 130.8 (C-2'), 131.3 (C-8), 134.0 (C-1"), 139.2 (C-4'), 156.2 (C-4), 161.7 (COO). ^{15}N NMR ($CDCl_3$) δ (ppm): 170.8 (N-5), 178.1 (N-10). Anal. Calcd. for $C_{27}H_{22}BrClN_2O_2$ (521.83): C, 62.14; H, 4.25; N, 5.37%. Found: C, 62.26; H, 4.29; N, 5.24%.

*2-Carbethoxy-4-(4-nitrophenyl)-5-benzylpyrrolo[1,2-a]quinoxalinium bromide (**8i**).* Yellow crystals (0.211 g, 79%), mp 236-238 ºC (MeOH). FT-IR (ν_{max}, cm^{-1}) 3426, 2997, 2877, 1707, 1608, 1555, 1525, 1493, 1457, 1349, 1279, 1205. ^{1}H NMR (DMSO) δ (ppm): 1.34 (3H, t, *J* 6.8 Hz, CH_3), 4.37 (2H, q, *J* 7.2 Hz, CH_2-Et), 5.85 (2H, s, CH_2), 7.32-7.40 (5H, m, aromatic rings), 7.45 (1H, d, *J* 1.2 Hz, H-3), 7.76 (1H, td, *J* 7.5, 1.0 Hz, H-7), 8.00 (1H, t, *J* 8.0 Hz, H-8), 8.08 (2H, d, *J* 8.8 Hz, H-2'), 8.09 (1H, d, *J* 8.7 Hz, H-6), 8.55 (2H, d, *J* 8.8 Hz, H-3'), 8.97 (1H, dd, *J* 7.6, 0.9 Hz, H-9), 9.87 (1H, d, *J* 1.2 Hz, H-1). The individual chemical shifts, multiplicities and coupling constants for the signals from 7.31-7.39 ppm were obtained from undecoupled HSQC as follows: 7.32 (1H, t, *J* 7.4 Hz, H-4"), 7.34 (2H, t, *J* 7.7 Hz, H-3"), 7.38 (2H, d, *J* 7.6 Hz, H-2"). ^{13}C NMR (DMSO) δ (ppm): 14.2 (CH_3), 55.2 (CH_2), 61.1 (CH_2-Et), 117.6 (C-9), 121.9 (C-6), 122.0 (C-3), 124.5 (C-2), 124.6 (C-3'), 125.9 (C-3a), 126.1 (C-2"), 126.8 (C-5a), 127.2 (C-1), 127.6 (C-9a), 128.1 (C-4"), 128.8 (C-7), 128.9 (C-3"), 130.3 (C-2'), 131.4 (C-8), 133.9 (C-1"), 134.1 (C-1'), 149.7 (C-4'), 155.1 (C-4), 161.8 (COO). ^{15}N NMR (DMSO) δ (ppm): 170.3 (N-5), 180.2 (N-10), 367.5 (NO_2). Anal. Calcd. for $C_{27}H_{22}BrN_3O_4$ (532.38): C, 60.91; H, 4.16; N, 7.89%. Found: C, 60.85; H, 4.11; N, 7.94%.

*2-Acetyl-4-(4-nitrophenyl)-5-ethyl-7,8-dimethylpyrrolo[1,2-a]quinoxalinium bromide (**8j**).* Yellow crystals (0.199 g, 85%), mp 261-263 ºC (MeOH). FT-IR (ν_{max}, cm^{-1}) 3400, 3111, 2985, 1679, 1595, 1521, 1502, 1367, 1348, 1282, 1198. ^{1}H NMR ($CDCl_3$+TFA) δ (ppm): 1.57 (3H, t, *J* 6.8 Hz, CH_3-Et), 2.55 (3H, s, CH_3-7), 2.58 (3H, s, CH_3-8), 2.63 (3H, s, CH_3), 4.63 (2H, q, *J* 7.2 Hz, CH_2-Et), 7.23 (1H, s, H-3), 7.86 (1H, s, CH-6), 8.06 (2H, d, *J* 8.0 Hz, H-2'), 8.13 (1H, s, H-9), 8.60 (2H, d, *J* 8.4 Hz, H-3'), 9.09 (1H, s, H-1). ^{13}C NMR ($CDCl_3$+TFA) δ (ppm): 15.0 (CH_3-Et), 20.3 (CH_3-8), 20.4 (CH_3-7), 27.9 (CH_3), 48.4 (CH_2-Et), 117.4 (C-9), 120.5 (C-6), 120.7 (C-3), 124.2 (C-5a), 124.9 (C-1), 125.1 (C-3'), 125.2 (C-3a), 125.5 (C-9a), 130.3 (C-2'), 132.4 (C-2), 133.7 (C-1'), 140.4 (C-7), 143.7 (C-8), 150.2 (C-4'), 152.2 (C-4), 194.1 (CO-CH_3). ^{15}N NMR ($CDCl_3$+TFA) δ (ppm): 174.4 (N-5), 179.9 (N-10), 365.2 (NO_2). Anal. Calcd. for $C_{23}H_{22}BrN_3O_3$ (468.34): C, 58.98; H, 4.73; N, 8.97%. Found: C, 59.06; H, 4.81; N, 8.91%.

*2-Carbethoxy-4-(4-chlorophenyl)-5-ethyl-7,8-dimethylpyrrolo[1,2-a]quinoxalinium bromide (**8k**).* Yellow crystals (0.190 g, 78%), mp 240-242 ºC (MeOH). FT-IR (ν_{max}, cm^{-1}) 3420, 2981, 1716, 1601, 1545, 1501, 1454, 1420, 1392, 1375, 1348, 1277, 1214, 1087. ^{1}H NMR ($CDCl_3$+TFA) δ (ppm): 1.39 (3H, t, *J* 6.8 Hz, CH_3-2), 1.54 (3H, t, *J* 6.8 Hz, CH_3-Et), 2.54 (3H, s, CH_3-7), 2.56 (3H, s, CH_3-8), 4.40 (2H, q, *J* 7.2 Hz, CH_2-2), 4.70 (2H, q, *J* 7.2 Hz, CH_2-Et), 7.28 (1H, s, H-3), 7.71 (4H, d, *J* 8.8 Hz, H-2' and H-3'), 7.92 (1H, s, CH-6), 8.03 (1H, s, H-9), 8.92 (1H, s, H-1). ^{13}C NMR ($CDCl_3$+TFA) δ (ppm): 14.2 (CH_3-2), 15.0 (CH_3-Et), 20.3 (CH_3-7 and CH_3-8), 48.2 (CH_2-Et), 62.1 (CH_2-2), 116.9 (C-9), 120.9 (C-6), 121.7 (C-3), 124.3 (C-5a), 124.6 (C-1), 125.3 (C-9a and C-2), 125.5 (C-3a), 126.5 (C-1'), 129.9 (C-3'), 130.3 (C-2'), 132.4 (C-2), 139.3 (C-1'), 140.0 (C-7), 143.0 (C-8), 153.4 (C-4), 162.4 (COO). ^{15}N NMR ($CDCl_3$+TFA) δ (ppm): 176.9 (N-5), 178.6 (N-10). Anal. Calcd. for $C_{24}H_{24}BrClN_2O_2$ (487.82): C, 59.09; H, 4.96; N, 5.74%. Found: C, 59.13; H, 4.89; N, 5.79%.

*2-Acetyl-4-phenyl-5-benzyl-7,8-dimethylpyrrolo[1,2-a]quinoxalinium bromide (**8l**).* Yellow crystals (0.199 g, 82%), mp 226-228 ºC (MeOH). FT-IR (ν_{max}, cm^{-1}) 3417, 3031, 2996, 1677, 1601, 1543, 1499, 1450, 1376, 1350, 1277, 1197. ^{1}H NMR ($CDCl_3$+TFA) δ (ppm): 2.35 (3H, s, CH_3-7), 2.52 (3H, s, CH_3-8), 2.73 (3H, s, CH_3), 5.82 (2H, s, CH_2), 7.06-7.08 (2H, m, H-2"), 7.36-7.38 (3H, m, aromatic rings), 7.43 (1H, d, *J* 1.0 Hz, H-3), 7.61-7.63 (4H, m, aromatic ring), 7.73-7.77 (1H, m, H-4'), 8.17 (1H, s, H-9), 9.22 (1H, d, *J* 1.0 Hz, H-1). The individual chemical shifts, multiplicities and coupling constants for the 7.36-7.38 and 7.61-7.63 ppm multiplets were obtained from undecoupled HSQC as follows: 7.37 (1H, t, *J* 7.6 Hz, H-4"), 7.38 (2H, t, *J* 7.1 Hz, H-3"), 7.62 (2H, d, *J* 7.9 Hz, H-2'), 7.63 (2H, t, *J* 7.8 Hz, H-3'). ^{13}C NMR ($CDCl_3$+TFA) δ (ppm): 20.1 (CH_3-8), 20.2 (CH_3-7), 27.7 (CH_3), 56.0 (CH_2), 117.2 (C-9), 121.7 (C-6), 122.4 (C-3), 125.11 (C-5a), 125.13 (C-9a), 125.32 (C-2"), 125.4 (C-1), 125.7 (C-3a), 127.7 (C-1'), 128.4(C-2'), 129.0 (C-4"), 129.7 (C-3"), 129.8 (C-3'), 131.7 (C-2), 133.1 (C-1"), 133.2 (C-4'), 140.2 (C-7), 143.4 (C-8), 156.2 (C-4), 197.1 (CO). ^{15}N NMR ($CDCl_3$+TFA) δ (ppm): 169.8 (N-5), 179.7 (N-10). Anal. Calcd. for $C_{28}H_{25}BrN_2O$ (485.41): C, 69.28; H, 5.19; N, 5.77%. Found: C, 69.23; H, 5.23; N, 5.64%.

*2-Carbethoxy-4-phenyl-5-benzyl-7,8-dimethylpyrrolo[1,2-a]quinoxalinium bromide (**8m**).* Yellow crystals (0.185 g, 72%), mp 197-198 ºC (MeOH). FT-IR (ν_{max}, cm^{-1}) 3392, 2979, 1714, 1602, 1545, 1496, 1451, 1374, 1350, 1284, 1203, 1111, 1022. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.40 (3H, t, *J* 7.1 Hz, CH_3-Et), 2.30 (3H, s, CH_3-7), 2.39 (3H, s, CH_3-8), 4.37 (2H, q, *J* 7.1 Hz, CH_2-Et), 6.19 (2H, s, CH_2), 7.09 (2H, d, *J* 6.2 Hz, H-2"), 7.29-7.32 (4H, m, aromatic rings), 7.59 (2H, t, *J* 7.7 Hz, H-3'), 7.67 (1H, t, *J* 7.4 Hz, H-4'), 7.84 (1H, s, H-6), 7.92 (2H, d, *J* 6.7 Hz, H-2'), 8.30 (1H, s, H-9), 9.13 (1H, s, H-1). The individual chemical shifts, multiplicities and coupling constants for the 7.29-7.32 ppm multiplet were obtained from undecoupled HSQC as follows: 7.32 (1H, t, *J* 7.6 Hz, H-4"), 7.33 (1H, s, H-3), 7.35 (2H, t, *J* 7.6 Hz, H-3"). ^{13}C NMR ($CDCl_3$) δ (ppm): 14.4 (CH_3-Et), 20.1 (CH_3-8), 20.2 (CH_3-7), 56.6 (CH_2), 61.5 (CH_2-Et), 117.0 (C-9), 122.2 (C-3), 122.5 (C-6), 125.2 (C-5a and C-3a), 125.1 (C-9a), 125.4 (C-1), 125.7 (C-2"), 128.3 (C-4"), 128.5 (C-1'), 129.1 (C-2'), 129.3 (C-3"), 129.4 (C-3'), 132.4 (C-4'), 134.2 (C-1"), 139.0 (C-7), 142.3 (C-8), 155.5 (C-4), 162.1 (COO). ^{15}N NMR ($CDCl_3$) δ (ppm): 171.5 (N-5), 178.9 (N-10). Anal. Calcd. for $C_{29}H_{27}BrN_2O_2$

(515.44): C, 67.57; H, 5.28; N, 5.43%. Found: C, 67.62; H, 5.32; N, 5.37%.

*2-Carbethoxy-4-(4-nitrophenyl)-5-benzyl-7,8-dimethylpyrrolo[1,2-a]quinoxalinium bromide (**8o**).* Yellow crystals (0.229 g, 82%), mp 208-210 ºC (MeOH). FT-IR (ν_{max}, cm^{-1}) 3323, 3024, 2977, 1712, 1668, 1596, 1525, 1499, 1452, 1349, 1284, 1208, 1135. ^{1}H NMR ($CDCl_3$+TFA) δ (ppm): 1.39 (3H, t, *J* 7.20 Hz, CH_3-Et), 2.36 (3H, s, CH_3-7), 2.53 (3H, s, CH_3-8), 4.41 (2H, q, *J* 7.20 Hz, CH_2-Et), 5.85 (2H, s, CH_2), 7.04 (2H, bs, H-2"), 7.35-7.38 (4H, m, aromatic rings), 7.71 (1H, s, H-6), 7.93 (2H, d, *J* 8.0 Hz, H-2'), 8.05 (1H, s, H-9), 8.43 (2H, d, *J* 8.0 Hz, H-3'), 9.04 (1H, s, H-1). The individual chemical shifts, multiplicities and coupling constants for the 7.35-7.38 ppm multiplet were obtained from undecoupled HSQC as follows: 7.35 (1H, t, *J* 7.9 Hz, H-4"), 7.356 (1H, s, H-3), 7.363 (2H, bs, H-3"). ^{13}C NMR ($CDCl_3$+TFA) δ (ppm): 14.1 (CH_3-Et), 20.2 (CH_3-7), 20.3 (CH_3-8), 56.3 (CH_2), 116.7 (C-9), 121.7 (C-6), 122.3 (C-3), 124.6 (C-3'), 125.0 (C-2), 125.1 (C-9a and C-5a), 125.2 (C-2"), 125.6 (C-1), 125.9 (C-3a), 129.1 (C-4"), 129.8 (C-3"), 130.4 (C-2'), 133.1 (C-1"), 133.60 (C-1'), 140.2 (C-7), 143.5 (C-8), 150.2 (C-4'), 153.0 (C-4), 162.4 (COO). ^{15}N NMR ($CDCl_3$+TFA) δ (ppm): 169.3 (N-5), 178.3 (N-10), 363.7 (NO_2). Anal. Calcd. for $C_{29}H_{26}BrN_3O_4$ (560.44): C, 62.15; H, 4.67; N, 7.50%. Found: C, 62.22; H, 4.71; N, 7.44%.

General procedure for preparation of 4-methoxy-3,4-dihydropyrrolo[1,2-*a*]quinoxalines 9. A suspension of a pyrrolo[1,2-*a*]quinoxalinium bromide **8** (0.4 mmol) in 15 mL MeOH was treated under stirring with 0.2 mL solution of CH_3ONa 25% in MeOH (0.85 mmol) and the mixture was kept under stirring at room temperature for 20 min. The solvent was partly evaporated *in vacuo*, the solid formed filtered, washed on filter with water and recrystallized from MeOH.

*Ethyl 4-methoxy-4-phenyl-5-benzyl-4,5-dihydropyrrolo[1,2-a]quinoxaline-2-carboxylate (**9f**).* Yellow crystals, mp 140-142 ºC (MeOH). FT-IR (ν_{max}, cm^{-1}) 1708, 1613, 1555, 1522, 1493, 1453, 1335, 1249, 1194, 1095. ^{1}H NMR (DMSO) δ (ppm): 1.33 (3H, t, *J* 6.80 Hz, CH_3-Et), 3.08 (3H, s, OCH_3), 4.23-4.32 (2H, m, CH_2-Et), 4.44 (1H, d, *J* 17.5 Hz, CH_2^A), 4.56 (1H, d, *J* 17.5 Hz, CH_2^B), 6.20 (1H, d, *J* 1.5 Hz, H-3), 6.68 (1H, d, *J* 8.1 Hz, H-6), 6.89 (1H, t, *J* 7.5 Hz, H-8), 7.00 (1H, t, *J* 7.2 Hz, H-7), 7.13-7.28 (8H, m, aromatic rings), 7.54 (1H, d, *J* 7.8 Hz, H-9), 7.60 (2H, d, *J* 6.6 Hz, H-2'), 7.97 (1H, d, *J* 1.5 Hz, H-1). The individual chemical shifts, multiplicities and coupling constants for the 7.13-7.28 ppm multiplet were obtained from undecoupled HSQC as follows: 7.17 (2H, d, *J* 7.8 Hz, H-2"), 7.18 (1H, t, *J* 7.7 Hz, H-4"), 7.24 (2H, t, *J* 7.5 Hz, H-3"), 7.26 (1H, t, *J* 7.6 Hz, H-4'), 7.29 (2H, t, *J* 7.7 Hz, H-3'). ^{13}C NMR (DMSO) δ (ppm): 14.4 (CH_3-Et), 48.7 (CH_2), 51.8 (OCH_3), 60.1 (CH_2-Et), 90.2 (C-4), 109.9 (C-3), 114.6 (C-9), 115.0 (C-6), 117.3 (C-1), 118.2 (C-2), 119.0 (C-8), 123.1 (C-9a), 126.1 (C-2"), 126.3 (C-7), 126.5 (C-4"), 127.2 (C-2'), 127.9 (C-3'), 128.1 (C-4'), 128.3 (C-3"), 129.4 (C-3a), 136.1 (C-5a), 137.6 (C-1"), 142.7 (C-1'), 164.5 (COO). ^{15}N NMR (DMSO) δ (ppm): 81.9 (N-5), 171.1 (N-10). Anal. Calcd. for $C_{28}H_{26}N_2O_3$ (438.52): C, 76.69; H, 5.98; N, 6.39%. Found: C, 76.74; H, 6.05; N, 6.31%.

*Ethyl 4-methoxy-4-(4-chlorophenyl)-5-benzyl-4,5-dihydropyrrolo[1,2-a]quinoxaline-2-carboxylate (**9h**).* Pale brown crystals, mp 155-157 ºC (MeOH/acetone). FT-IR (ν_{max}, cm^{-1}) 3053, 2976, 2947, 1709, 1609, 1557, 1525, 1493, 1337, 1257, 1196, 1094. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.34 (3H, t, *J* 7.2 Hz, CH_3-Et), 3.06 (3H, s, CH_3), 4.25-4.32 (2H, m, CH_2-Et), 4.44 (1H, d, *J* 17.6 Hz, CH_2^A), 4.54 (1H, d, *J* 17.6 Hz, CH_2^B), 6.17 (1H, d, *J* 1.2 Hz, H-3), 6.68 (1H, d, *J* 8.0 Hz, H-6), 6.91 (1H, t, *J* 7.6 Hz, H-8), 7.01 (1H, t, *J* 7.2 Hz, H-7), 7.17 (1H, t, *J* 7.2 Hz, H-4"), 7.25 (2H, t, 7.2 Hz, H-3"), 7.30 (2H, d, 7.2 Hz, H-2"), 7.40 (2H, d, *J* 8.4 Hz, H-3'), 7.60 (2H, d, *J* 8.4 Hz, H-2'), 7.95 (1H, d, *J* 7.6 Hz, H-9), 7.98 (1H, d, *J* 1.2 Hz, H-1). ^{13}C NMR ($CDCl_3$) δ (ppm): 14.4 (CH_3-Et), 48.6 (CH_2), 51.7 (CH_3), 60.1 (CH_2-Et), 89.7 (C-4), 110.0 (C-3), 114.6 (C-9), 115.0 (C-6), 117.4 (C-1), 118.4 (C-2), 118.9 (C-8), 123.0 (C-9a), 126.1 (C-2"), 126.4 (C-7), 126.6 (C-4"), 127.91 (C-3'), 128.24 (C-3"), 128.7 (C-2'), 128.9 (C-3a), 134.0 (C-4'), 135.9 (C-5a), 137.3 (C-1"), 141.5 (C-1'), 164.4 (COO). ^{15}N NMR ($CDCl_3$) δ (ppm): 81.4 (N-5), 170.9 (N-10). Anal. Calcd. for $C_{28}H_{25}ClN_2O_3$ (472.96): C, 71.10; H, 5.33; N, 5.92%. Found: C, 71.16; H, 5.29; N, 5.85%.

*2-Acetyl-4-methoxy-4-phenyl-5-benzyl-7,8-dimethyl-4,5-dihydropyrrolo[1,2-a]quinoxaline (**9l**).* Pale brown crystals, mp 149-151 ºC (MeOH). FT-IR (ν_{max}, cm^{-1}) 3125, 2916, 1662, 1521, 1494, 1446, 1332, 1254, 1185. ^{1}H NMR (DMSO) δ (ppm): 2.02 (3H, s, CH_3-7), 2.22 (3H, s, CH_3-8), 2.40 (3H, s, CH_3-CO), 2.98 (3H, s, CH_3-O), 4.40 (1H, d, *J* 17.6 Hz, CH_2^A), 4.48 (1H, d, *J* 17.6 Hz, CH_2^B), 5.92 (1H, d, *J* 1.6 Hz, H-3), 6.47 (1H, s, H-6), 7.14 (1H, t, *J* 5.2 Hz, H-4"), 7.16 (2H, d, *J* 6.9 Hz, H-2"), 7.21 (2H, t, *J* 7.2 Hz, H-3"), 7.27 (1H, t, *J* 7.0 Hz, H-4'), 7.30 (2H, t, *J* 6.6 Hz, H-3'), 7.55 (2H, d, *J* 6.8 Hz, H-2'), 7.81 (1H, s, H-9), 8.55 (1H, d, *J* 1.6 Hz, H-1). ^{13}C NMR (DMSO) δ (ppm): 18.3 (CH_3-8), 19.5 (CH_3-7), 27.0 (CH_3-CO), 47.8 (CH_2), 51.2 (CH_3-O), 89.7 (C-4), 107.3 (C-3), 115.7 (C-6), 116.3 (C-9), 119.0 (C-1), 120.6 (C-9a), 126.0 (C-2"), 126.3 (C-4"), 126.5 (C-2), 126.6 (C-8), 126.9 (C-2'), 127.8 (C-3'), 128.0 (C-4'), 128.1 (C-3"), 129.7 (C-3a), 133.3 (C-5a), 133.9 (C-7), 137.7 (C-1"), 142.6 (C-1'), 192.4 (CO). ^{15}N NMR (DMSO) δ (ppm): 78.4 (N-5), 172.8 (N-10). Anal. Calcd. for $C_{29}H_{28}N_2O_2$ (436.54): C, 79.79; H, 6.46; N, 6.42%. Found: C, 79.85; H, 6.40; N, 6.35%.

*Ethyl 4-phenylpyrrolo[1,2-a]quinoxaline-2-carboxylate (**10**).* Yellow crystals with mp 204-206 ºC (acetone). FT-IR (ν_{max}, cm^{-1}) 3133, 1706, 1585, 1538, 1481, 1352, 1263, 1192, 1167, 1027. ^{1}H NMR (DMSO) δ (ppm): 1.35 (3H, t, *J* 6.8 Hz, CH_3), 4.34 (2H, q, *J* 7.2 Hz, CH_2), 7.25 (1H, d, *J* 1.2 Hz, H-3), 7.58-7.68 (5H, m, aromatic rings), 7.97-8.00 (3H, m, aromatic rings), 8.53 (1H, d, *J* 8.0 Hz, H-9), 9.12 (1H, d, *J* 1.3 Hz, H-1). The individual chemical shifts, multiplicities and coupling constants for the signals from 7.58-8.00 ppm were obtained from undecoupled HSQC as follows: 7.60 (1H, t, *J* 8.3 Hz, H-7), 7.62 (2H, t, *J* 9.0 Hz, H-3'), 7.62 (1H, t, *J* 7.5 Hz, H-8), 7.65 (1H, t, *J* 8.0 Hz, H-4'), 7.97 (1H, d, *J* 8.3 Hz, H-6), 7.98 (2H, d, *J* 8.0 Hz, H-2'). ^{13}C NMR (DMSO) δ (ppm): 14.3 (CH_3), 60.2 (CH_2), 108.6 (C-3), 115.5 (C-9), 119.6 (C-2), 118.0 (C-1), 124.6 (C-3a), 126.2 (C-9a), 126.8 (C-7), 128.4 (C-2'), 128.5 (C-4'), 128.7 (C-3'), 129.7 (C-6), 130.3 (C-8), 135.8 (C-5a), 137.1 (C-1'), 153.8 (C-4), 163.4 (COO). ^{15}N NMR (DMSO) δ (ppm): 284.5 (N-5), 180.2 (N-10). Anal. Calcd. for $C_{20}H_{16}N_2O_2$ (316.35): C, 75.93; H, 5.10; N, 8.85%. Found: C, 75.86; H, 5.06; N, 8.91%.

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