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ARTICLE TYPE

An eco-friendly Pictet-Spengler approach to pyrrolo- and indolo[1,2-a]quinoxalines using *p*-dodecylbenzenesulfonic acid as an efficient Brønsted acid catalyst

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A facile and environmentally benign Pictet-Spengler strategy for the synthesis of a series of biologically important pyrrolo- and indolo[1,2-a]quinoxalines has been developed by reacting 1-(2-aminophenyl)-pyrrole or 1-(2-aminophenyl)indoles with a wide range of aromatic aldehydes, acetophenones or isatins in ethanol at ambient temperature using *p*-dodecylbenzenesulfonic acid (*p*-DBSA) as an efficient Brønsted acid surfactant combined catalyst. This methodology was found to be applicable to generate diverse quinoxaline derivatives in fairly good yields under mild reaction conditions.

Introduction

Practising the green chemistry concepts for the development of efficient, safe and sustainable synthetic procedures have been significantly recognised globally in recent years.[1] The use of hazardous solvents and reagents in chemical manufacture is one of the major factors that contribute towards environmental pollution. Therefore, a significant attention has been focused for the search of environmentally benign alternatives to these toxic solvents and consequently, designing of greener methodology for the construction of various structurally diverse molecules in one-pot operation.[2]

Quinoxaline derivatives are an important class of biologically active nitrogen heterocycles which exhibit a wide range of pharmacological profiles.[3] In particular, pyrrolo[1,2-a]quinoxalines substituted at C-4 position have shown diverse biological activities such as anti-cancer,[4] anti-malarial,[5] and anti-proliferative[6] activities. Furthermore, these molecules are reported as inhibitors of human protein kinase CK2,[7] glucagon receptor antagonist[8] and $5HT_3$ receptor agonist.[9] In addition, these compounds were also found to be applicable in the synthesis of GABA benzodiazepine receptor agonist or antagonist.[10] Similarly, indolo[1,2-a]quinoxaline analogues have demonstrated interesting anti-fungal activities.[11] Due to a wide range of applications, significant number of synthetic protocols[12] have been devised in the past for the preparation of various 4,5-dihydropyrrolo[1,2-a]quinoxalines,[13] pyrrolo[1,2-a]quinoxalines,[14] indolo[1,2-a]quinoxalines[15] and their spiro derivatives.[16] Among these, Pictet-Spengler reaction is the most extensively used approach for the construction of pyrrolo[1,2-a]quinoxaline heterocycles.[17] According to this protocol, the reaction proceeds with the initial formation of Schiff's base intermediate after the elimination of a water molecule followed by intramolecular cyclization to give dihydro derivative, which subsequently on oxidation affords pyrrolo[1,2-a]quinoxalines. Although these reported synthetic strategies are effective, still they suffer from a number of demerits such as long reaction times, harsh reaction conditions and use of hazardous organic solvents. Therefore, a search for an efficient, economical, environment friendly and versatile methodology for the synthesis of diverse pyrrolo- and indolo[1,2-a]quinoxaline scaffolds is highly desired.

Over the years, the surfactant combined catalysts have been employed as substitute for the toxic catalysts in various environmentally benign protocols.[18] Among these, *p*-dodecylbenzenesulfonic acid (*p*-DBSA) has emerged as a cheap, commercially available, non-hygroscopic, non-volatile, air-stable and efficient Brønsted acid surfactant combined catalyst for carrying out a variety of useful organic transformations.[19] This intrinsic catalytic efficiency of *p*-DBSA prompted us to investigate its further ability to catalyze Pictet-Spengler reaction for the construction of various pyrrolo[1,2-a]quinoxaline analogues.

In the course of our interest to develop eco-friendly synthetic methodologies for useful organic transformations,[20] we wish to report herein a convenient and greener practical protocol for the synthesis of a series of various 4-arylpyrrolo[1,2-a]quinoxalines, 6-arylindolo[1,2-a]quinoxalines, 4-aryl-4-methyl-4,5-dihydropyrrolo[1,2-a]quinoxalines, 5'*H*-spiro[indoline-3,4'-pyrrolo[1,2-a]quinoxalin]-2-ones and 5'*H*-spiro[indoline-3,6'-indolo[1,2-a]quinoxalin]-2-one derivatives through Pictet-Spengler condensation cyclization reaction of 1-(2-aminophenyl)pyrrole or 1-(2-aminophenyl)indoles with aromatic aldehydes, acetophenones or isatins in ethanol using *p*-DBSA as an efficient Brønsted acid surfactant combined catalyst under mild reaction conditions. The results are summarized in Tables **1**, **2**, **3** and **4**.

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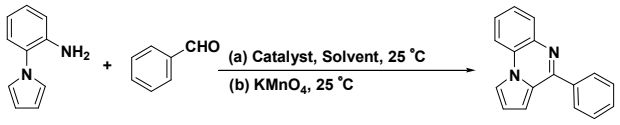
Results and discussion

For a facile and eco-friendly access of a series of pyrrolo- and indolo[1,2-a]quinoxaline scaffolds, initially a reaction was performed at room temperature by using 1-(2-aminophenyl)pyrrole and benzaldehyde as model substrates in the presence of a catalytic amount of DBSA in ethanol for 2 hours followed by the oxidation in the presence of 1 equivalent of $KMnO_4$ and the desired product **3a** was obtained as white solid in 89% yield (Table **1**, entry **1**). It is interesting to note that the yield of the product **3a** was found to be same even after decreasing the reaction time from 2 hours to 30 min (Table **1**, entry **2**). However, the yield of the reaction was significantly affected by varying the catalyst load. A significant decrease in the yield of compound **3a** was observed on decreasing the catalyst load from 10 mol % to 5 mol % (Table **1**, entry **3**) whereas, by increasing the amount of *p*-DBSA up to 20 mol % did not improve the yield of desired product significantly (Table **1**, entries **1**, **4** and **5**).

Table 1: Optimization of the reaction conditions for the synthesis of 4-phenylpyrrolo[1,2-a]quinoxaline (3a)[a]



1a 2a 3a

Entry	Catalyst (mol %)	Solvent	Time (h)[b]	Yield (%)[c] **3a**
1.	*p*-DBSA (10)	EtOH	2.0	89
2.	*p*-DBSA (10)	EtOH	0.5	89
3.	*p*-DBSA (5)	EtOH	0.5	38
4.	*p*-DBSA (15)	EtOH	0.5	90
5.	*p*-DBSA (20)	EtOH	0.5	92
6.	*p*-DBSA (0)	EtOH	0.5	Trace
7.	*p*-DBSA (10)	THF	0.5	53
8.	*p*-DBSA (10)	CH_3CN	0.5	38
9.	*p*-DBSA (10)	^{t}BuOH	0.5	38
10.	*p*-DBSA (10)	PPG	0.5	33
11.	*p*-DBSA (10)	H_2O	0.5	45
12.	*p*-DBSA (10)	EtOH:H_2O (1:1)	0.5	65
13.	*p*-DBSA (10)	-	0.5	35
14.	PTSA (10)	EtOH	0.5	68
15.	CH_3COOH (10)	EtOH	0.5	63
16.	TFA (10)	EtOH	0.5	74

[a]Reagents and conditions: (a) 1-(2-aminophenyl)pyrrole **1a** (1.0 mmol), benzaldehyde **2a** (1.2 mmol), solvent (2.0 ml), 25 °C; (b) $KMnO_4$ (1.0 mmol), 15 min. [b]Total reaction time including $KMnO_4$ treatment. [c]Isolated yields after column chromatography.

In contrast, the reaction performed in the absence of catalyst under identical conditions afforded only a trace amount of desired product **3a** (Table **1**, entry **6**), demonstrating the catalytic role of *p*-DBSA in the synthesis of 4- phenylpyrrolo[1,2-a]quinoxaline (**3a**). Therefore, the 10 mol % *p*-DBSA was selected as an optimum catalyst load for performing further reactions.

We next examined the effect of other solvents on the rate of reaction and the results are summarized in table-**1**. Best results obtained when the reaction was carried out in ethanol as solvent medium (Table **1**, entries **1**, **2**, **4** and **5**) while the reaction proceeded sluggishly in the solvents such as THF, ^{t}BuOH, CH_3CN, PPG and provided the product **3a** in poor to moderate yields (Table **1**, entries **7-10**). In addition, when the reaction was performed in water as a solvent, lower yield (45%) of the product **3a** was obtained possibly due to heterogeneous mixture of the reacting substrates (Table **1**, entry **11**). To improve the solubility of reacting substrates, a reaction was also carried out in 50% ethanol in water but the yield of desired product did not increase significantly (Table **1**, entry **12**). Furthermore, the formation of product **3a** was also found to be sluggish under solvent free conditions and only 35% isolated yield was observed (Table **1**, entry **13**). Based on these observations, ethanol was chosen as a best solvent to carry out this organic transformation.

The catalytic efficiency of *p*-DBSA was also compared with other acidic catalyst such as PTSA, acetic acid and TFA and it was observed that the *p*-DBSA is the best suited catalyst for this reaction (Table **1**, entries **14-16**). It is noteworthy to mention that the reaction in the absence of $KMnO_4$ at 25 °C has afforded only an intermediate, 4,5-dihydro-4-phenylpyrrolo[1,2-a]quinoxaline in 90% yield. Hence, the optimal conditions for a model reaction were found to be 10 mol % *p*-DBSA in ethanol followed by the oxidation in the presence of 1 equivalent of $KMnO_4$ at 25 °C temperature.

Under the optimized conditions, the scope and generality of this protocol were investigated by treating 1-(2-aminophenyl)pyrrole or 1-(2-aminophenyl)indoles with a variety of aromatic and heteroaromatic aldehydes at ambient temperature in ethanol containing 10 mol % *p*-DBSA followed by oxidation in the presence of 1 equivalent of $KMnO_4$ to afford a series of pyrrolo- and indolo[1,2-a]quinoxaline derivatives (**3a-o**) in moderate to good yields (Table **2**). In general, the reaction of aromatic aldehydes bearing both electron-withdrawing and electron-donating substituents on aromatic ring proceeded well with 1-(2-aminophenyl)pyrrole and afforded the corresponding products (**3a-f, 3k** and **3l**) in good to excellent yields (Table **2**, entries **1-6** and **11-12**). In contrast, the reaction with heterocyclic aldehydes provided relatively lower yields of the products (**3g-j**) (Table **2**, entries **7-10**). On the other hand, the reaction of 1-(2-aminophenyl)indoles and aromatic aldehydes is found to be sluggish and provided the corresponding 6-arylindolo[1,2-a]quinoxaline products (**3m-o**) in moderate yields due to the less nucleophilicity of the indole substituted anilines as compared to the 1-(2-aminophenyl)pyrrole [21](Table **2**, entries **13-15**).

After chromatographic purification, the isolated products (**3a-o**) were fully characterized on the basis of detailed spectral analysis including IR, ^{1}H NMR, ^{13}C NMR and high resolution mass. IR spectrum of compound **3a** showed a characteristic absorption peak at 1599 cm^{-1} due to the stretching of C=N bond. In ^{1}H NMR spectrum of compound **3a**, one of three pyrrolic protons was appeared as a multiplet between δ 7.79-8.06 ppm along with three phenyl protons where as other two pyrrolic

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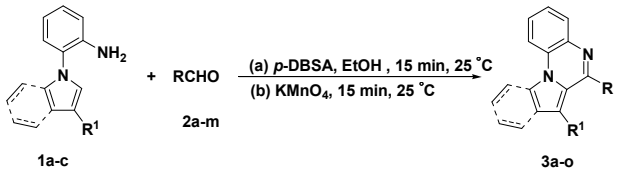
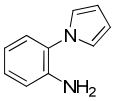
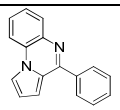
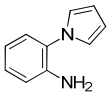
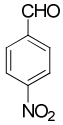
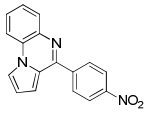
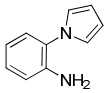
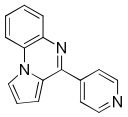
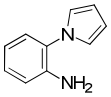
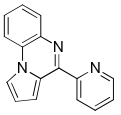
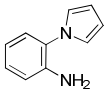
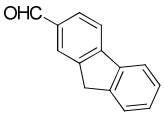
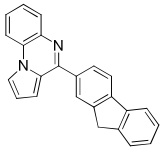
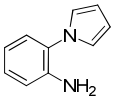
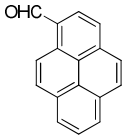
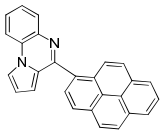
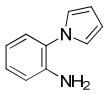
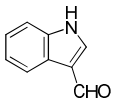
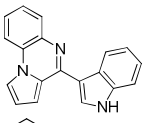
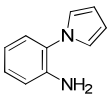
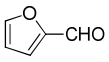
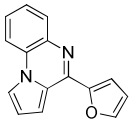
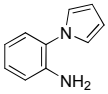
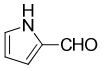
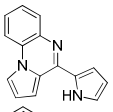
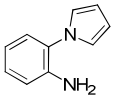
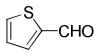
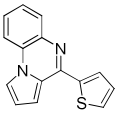
protons were found as a doublet at δ 7.00 ppm (J = 4.39 Hz) and a multiplet between δ 6.88-6.90 ppm for one proton each, respectively. Besides these, two sets of the remaining phenyl protons were also observed as a doublet for one proton at δ 7.86 ppm (J = 8.05 Hz) and a multiplet for 5 protons between δ 7.44-7.57 ppm, respectively. Additionally, the ^{13}C NMR spectrum showed the characteristic peaks at 108.7, 114.0 and 114.6 ppm due to the carbons of the pyrrolic moiety where as a peak at 154.4 ppm corresponds to the imine carbon of quinoxaline ring. The structure of the compound **3a** was further supported by the mass spectral analysis which showed a $[M+H]^+$ ion peak at m/z 245.1067 for the molecular formula $C_{17}H_{13}N_2$.

Table 2: Synthesis of 4-arylpyrrolo[1,2-a]quinoxalines (3a-l), 6-arylindolo[1,2-a]quinoxalines (3m-n), 7-methyl-6-(pyridin-4-yl)indolo[1,2-a]quinoxaline (3o).[a]



1a-c 3a-o

S. No.	Amines	Aldehydes	Products	Yields (%)[b]
1.			 3a	89
2.			 3b	90
3.			 3c	88
4.			 3d	88
5.			 3e	75
6.			 3f	75
7.			 3g	40
8.			 3h	62
9.			 3i	77
10.			 3j	80

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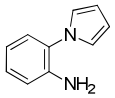
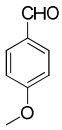
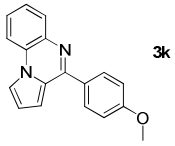
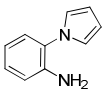
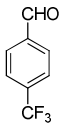
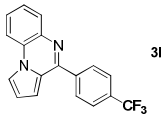
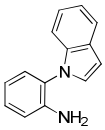
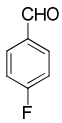
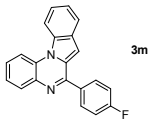
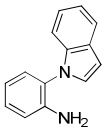
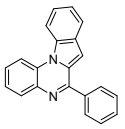
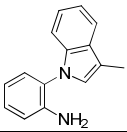
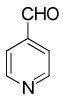
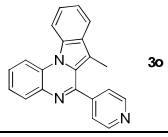
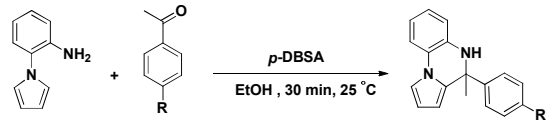
11.			 **3k**	75
12.			 **3l**	82
13.			 **3m**	52
14.			 **3n**	40
15.			 **3o**	52

[a]Reagents and conditions: (a) Amines **1a-c** (1.0 mmol), aldehydes **2a-m** (1.2 mmol), *p*-DBSA (0.10 mmol), EtOH (2.0 ml); (b) $KMnO_4$ (1.0 mmol), [b]Isolated yields after column chromatography.

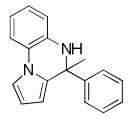
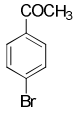
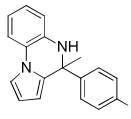
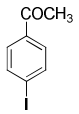
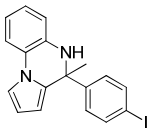
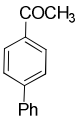
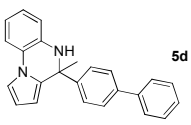
Furthermore, the optimized methodology was extended to construct various 4-methyl-4-aryl-4,5-dihydropyrrolo[1,2-a]quinoxalines in one-pot by reacting 1-(2-aminophenyl)pyrrole (**1a)** with aromatic ketones in 1:1.2 ratio in ethanol at room temperature using 10 mol % *p*-DBSA (Table **3**).

To our delight, the desired products (**5a-d**) were obtained with good yields of 82-86% within 30 minutes. As expected, the reaction proceeded with slightly slow rate in the case of less reactive aromatic ketones as compared to the aryl aldehydes and the desired products were obtained in a relatively longer reaction time. On studying the effect of substituents present in acetophenones on the rate of reaction, it has been observed that the aromatic ketones having halogen atom at para position affords the lower yields of the products with decreasing their electronegativity (Table **3**, entry **2** and **3**). The best results were obtained when the reaction of 1a was carried out with 4-phenylacetophenone possibly due to the extended conjugation of the additional phenyl ring (Table **3**, entry **4**). The structures of compounds (**5a-d**) were established on the basis of their spectral data. In the IR spectrum of compound **5a**, a characteristic absorption peak due to NH stretching was appeared at 3367 cm^{-1}. The ^1H NMR of the product **5a** showed a characteristic broad singlet at δ 4.39 ppm due to NH proton and a singlet at δ 1.90 ppm due to three methyl protons. The three pyrrolic protons appeared separately as a double doublet at δ 6.05 ppm (J_1 = 3.66 Hz and J_2 = 1.83 Hz), a triplet at δ 6.33 ppm (J = 3.05 Hz) and a multiplet between δ 7.14-7.18 ppm, respectively. In the ^{13}C NMR spectrum, peaks at δ 29.2 and 56.8 ppm were assigned to the methyl carbon and quaternary carbon of the dihydroquinoxaline ring, respectively. The high resolution ESI-mass spectral analysis further confirmed the formation of compound **5a** by showing the $[M+H]^+$ ion peak at m/z 261.1386 for the molecular formula $C_{18}H_{17}N_2$.

Table 3: Synthesis of 4-methyl-4-aryl-4,5-dihydropyrrolo[1,2-a]quinoxalines (5a-d)[a]



1a 4a-d 5a-d

S. No.	Ketones	Products	Yields (%)[b]
1.		 **5a**	82
2.		 **5b**	83
3.		 **5c**	82
4.		 **5d**	86

[a]Reagents and conditions: Amine **1a** (1.0 mmol), ketones **4a-d** (1.2 mmol), *p*-DBSA (0.10 mmol), EtOH (2.0 ml), [b]Isolated yields of products (**5a-d**) after column chromatography.

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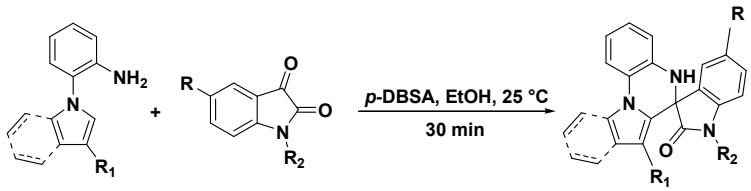
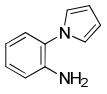
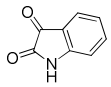
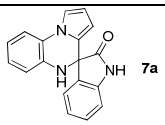
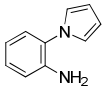
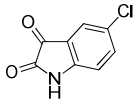
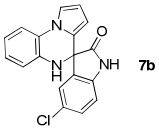
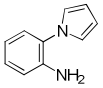
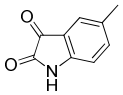
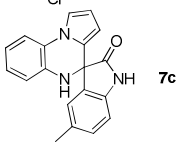
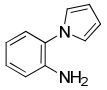
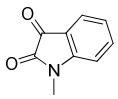
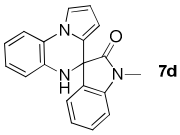
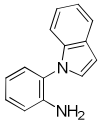
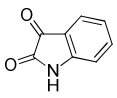
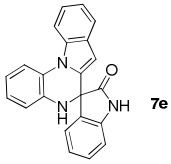
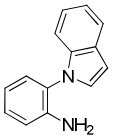
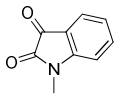
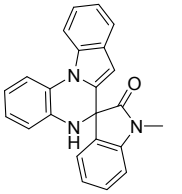
After successful synthesis of a series of pyrrolo[1,2-a]quinoxaline and dihydropyrrolo[1,2-a]quinoxaline derivatives in good yields, we turned our attention towards the synthesis of spiro[indoline-3,4'-pyrrolo[1,2-a]quinoxalin]-2-one derivatives (**7a-j**) by reacting isatin derivatives either with 1-(2-aminophenyl)pyrrole or 2-(1*H*-indol-1-yl)anilines under optimized reaction conditions. We are delighted to report that the present eco-friendly Pictet-Spengler protocol has also been successfully extended to prepare a series of spiro derivatives in good to excellent yields (Table **4**). As shown in the table **4**, this reaction proceeded satisfactorily with a variety of isatins containing both, electron donating as well as electron withdrawing substituents and provided the target products in good to excellent yields (79-87%). The isolated desired products (**7a-j**) were characterized spectroscopically. IR spectrum of compound **7a** showed characteristic absorption bands at 3313, 3239 and 1721 cm^{-1} due to stretching of NH and C=O groups, respectively. The ^{1}H NMR of compound **7a** showed two singlets at δ 8.32 and 4.30 ppm due to the presence of NH protons. Two multiplets between δ 7.21-7.50 ppm and δ 5.60-5.61 ppm appeared due to two pyrrolic protons whereas the remaining one pyrrolic proton appeared as a triplet at δ 6.24 ppm (J = 3.05 Hz). In addition, the ^{13}C NMR spectrum of **7a** showed a characteristic peak at δ 61.1 ppm which corresponds to quaternary spiro-carbon of dihydroquinoxaline ring. High resolution mass data of compound **7a** also supported the assigned structure by showing $[M+H]^+$ ion peak at m/z 288.1131. Furthermore, the structure of compound (**7d**) was finally confirmed by single crystal X-ray analysis (Fig. **1**).[22]

Table 4: Synthesis of 5'*H*-spiro[indoline-3,4'-pyrrolo[1,2-a]quinoxalin]-2-ones (7a-d), 5'*H*-spiro[indoline-3,6'-indolo[1,2-a]quinoxalin]-2-ones (7e-h) and 7'-methyl-5'*H*-spiro[indoline-3,6'-indolo[1,2-a]quinoxalin]-2-ones (7i-j).[a]



1a-c 6a-d 7a-j

S. No.	Amines	Isatins	Products	Yields (%)[b]
1.			 **7a**	83
2.			 **7b**	84
3.			 **7c**	80
4.			 **7d**	80
5.			 **7e**	82
6.			 **7f**	79

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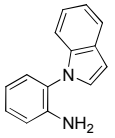
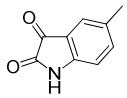
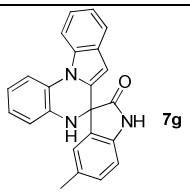
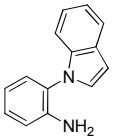
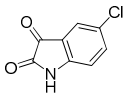
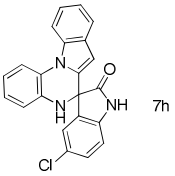
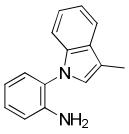
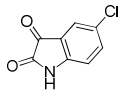
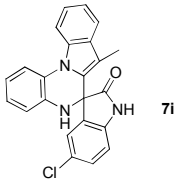
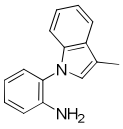
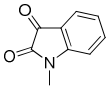
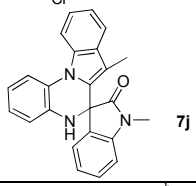
7.			 **7g**	80
8.			 7h	83
9.			 **7i**	87
10.			 **7j**	79

[a]Reagents and conditions: Amines **1a-c** (1.0 mmol), isatins **6a-d** (1.2 mmol), *p*-DBSA (0.10 mmol), EtOH (2.0 ml), [b] Isolated yields after column chromatography.

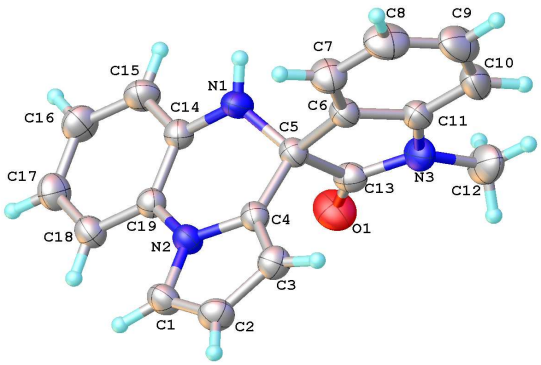


Fig **1:** X-ray crystal structure of compound **7d**.

The possible mechanistic pathway for the synthesis of pyrrolo- and indolo[1,2-a]quinoxalines is shown in Fig. **2**. Probably, the reaction proceeds *via* the protonation of the corresponding carbonyl compounds (aldehydes/ketones/diketones) in the presence of *p*-DBSA as an Brønsted acid catalyst followed by a nucleophilic attack of pyrrole or indole substituted anilines to generate an electron deficient iminium ion (**III** or **VII**) which undergoes intramolecular cyclization and deprotonation to afford desired products **5a-d** and **7a-j** in good to moderate yields where as in the case of aldehydes, the reaction initially provided a dihydro-pyrrolo-or indolo[1,2-a]quinoxaline intermediate which on oxidation in the presence of $KMnO_4$ afforded the desired products (**3a-o**) in 40-90% yields

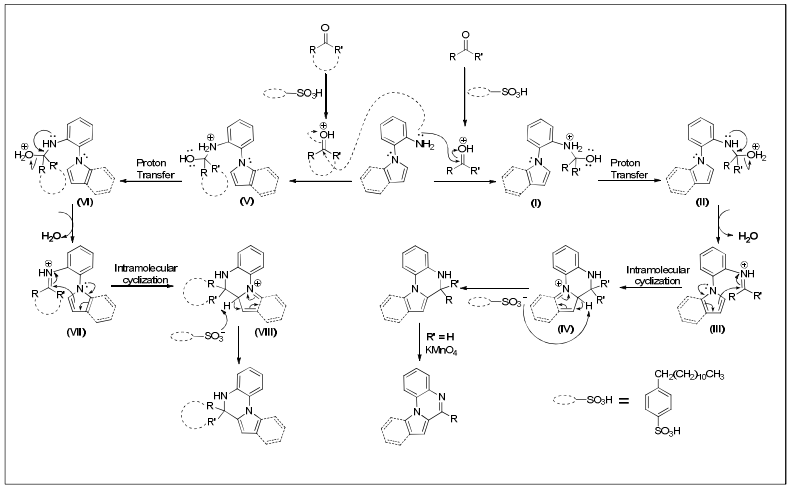


Fig. **2**: Plausible reaction mechanism for the synthesis of pyrrolo- and indolo[1,2-a]quinoxalines

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Conclusions

In summary, we have developed an energy efficient, facile, environmentally friendly practical methodology for easy access of various pyrrolo[1,2-a]quinoxaline, dihydropyrrolo[1,2-a]quinoxaline and spiro[indoline-3,4'-pyrrolo[1,2-a]quinoxalin]-2-one derivatives *via* Pictet-Spengler reaction using *p*-DBSA as an efficient Brønsted acid catalyst in ethanol at room temperature. The present synthetic protocol demonstrates many key advantages such as mild reaction conditions, short reaction times, good to excellent yields of the products and the use of non-hazardous solvent medium for the synthesis of these biologically active nitrogen heterocycles.

Experimental

General: All the chemicals were purchased from Sigma-Aldrich and used without further purification. The progress of the reaction was monitored by thin layer chromatography (TLC) using silica gel 60 F_{254} (pre coated aluminium sheets) from Merck. TLC spots were visualised by UV-light followed by iodine. NMR spectra were obtained in $CDCl_3$ or DMSO-d_6 on Jeol ECX 400 MHz NMR spectrometer by using TMS as an internal standard and chemical shifts are expressed in parts per million (ppm) and coupling constants (*J*) are reported in Hertz (Hz). Infrared spectra were recorded on Perkin Elmer IR spectrometer and absorption maxima (ν_{max}) are given in cm^{-1}. The melting points were determined in open capillary tubes on Buchi M-560 melting point apparatus and are uncorrected. Mass spectra (ESI-HRMS) were recorded on 6530 QTOF LCMS and microTOF-Q ll 10262 mass spectrometer. 2-(1*H*-indol-1-yl)aniline and 2-(3-methylindol-1-yl)phenylamine (**1b** and **1c**) were synthesized according to the literature procedure.[23]

General procedure for the synthesis of 4-arylpyrrolo[1,2-a]quinoxalines (3a-l), 6-arylindolo[1,2-a]quinoxalines (3m-n), 7-methyl-6-(pyridin-4-yl)indolo[1,2-a]quinoxaline (3o):

To a well stirred solution of *p*-DBSA (0.1 mmol) in ethanol (2 mL), aromatic aldehyde (1.2 mmol) was added followed by the addition of 1-(2-aminophenyl)pyrrole or 2-(1*H*-indol-1-yl)aniline or 2-(3-methylindol-1-yl)phenylamine (100 mg, 1.0 mmol). The reaction mixture was stirred at 25 °C for 15 minutes. After complete consumption of the starting materials as evident by TLC, the mixture was treated with $KMnO_4$ (1.0 mmol) and stirred for additional 15 min at 25 °C. The excess of solvent was then evaporated and the residue thus obtained was treated with saturated $NaHCO_3$ solution (20 mL). The product was then extracted with ethyl acetate (10 mL × 3 times). The organic layers were combined, washed with water (20 mL × 3 times) and brine solution (20 mL). Finally, the organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure to dryness. The crude product was purified by column chromatography over silica gel (60-120 mesh size) using 5-20% ethyl acetate in heptane as an eluent to furnish the desired products (**3a-o**) in good yields. The characterization data of known compounds (**3a** and **3n**) were found in good agreement with the reported data [24,25].

4-(4-Nitrophenyl)pyrrolo[1,2-a]quinoxaline(3b). Yellow solid, yield: 163 mg (90%); mp 221-223 °C; IR ($CHCl_3$) ν_{max}: 2927, 1598, 1348, 1096, 852, 751, 727 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.41 (d, *J* = 8.79 Hz, 2H, ArH), 8.20 (d, *J* = 8.79 Hz, 2H, ArH), 8.04-8.08 (m, 2H, pyrrolic H and ArH), 7.93 (d, *J* = 8.05 Hz, 1H, ArH), 7.57-7.61 (m, 1H, ArH), 7.49-7.53 (m, 1H, ArH), 6.95-6.97 (m, 2H, pyrrolic H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.8, 148.5, 144.4, 135.8, 130.4, 129.6, 128.3, 127.1, 125.6, 124.7, 123.7, 115.1, 114.4, 113.7, 108.2; HRMS (ESI, m/z) calcd for $C_{17}H_{12}N_3O_2$: 290.0924 $[M+H]^+$, found: 290.0924.

4-(Pyridin-4-yl)pyrrolo[1,2-a]quinoxaline (3c). Brown solid, yield: 136 mg (88%); mp 179-180 °C; IR ($CHCl_3$) ν_{max}: 2928, 1598, 1407, 1376, 1250, 1039, 824, 753, 729 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.82-8.83 (m, 2H, pyridyl H), 8.04-8.06 (m, 2H, pyridyl H), 7.90-7.93 (m, 3H, pyrrolic H and ArH), 7.58 (t, *J* = 7.32 Hz, 1H, ArH), 7.50 (t, *J* = 7.32 Hz, 1H, ArH), 6.93-7.00 (m, 2H, pyrrolic H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.3, 149.7, 146.0, 135.7, 130.3, 128.3, 127.1, 125.4, 124.5, 123.0, 115.0, 114.3, 113.6, 108.1; HRMS (ESI, m/z) calcd for $C_{16}H_{12}N_3$: 246.1026 $[M+H]^+$, found: 246.1033.

2-(Pyridin-2-yl)pyrrolo[1,2-a]quinoxaline (3d). Green solid, yield: 136 mg (88%); mp 106-108 °C; IR ($CHCl_3$) ν_{max}: 3061, 2925, 1583, 1531, 1475, 1441, 1367, 1096, 1037, 812, 756, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.81-8.82 (m, 1H, pyridyl H), 8.41 (d, *J* = 8.05 Hz, 1H, pyridyl H), 8.06 (d, *J* = 8.05 Hz, 1H, pyridyl H), 8.01 (s, 1H, pyridyl H), 7.90 (d, *J* = 8.05 Hz, 2H, ArH), 7.73 (d, *J* = 3.66 Hz, 1H, pyrrolic H), 7.40-7.56 (m, 3H, pyrrolic H and ArH), 6.95-6.97 (m, 1H, pyrrolic H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.3, 151.1, 148.8, 136.6, 135.6, 130.2, 127.9, 127.5, 125.0, 124.5, 124.2, 123.3, 114.39, 114.31, 113.6, 110.5; HRMS (ESI, m/z) calcd for $C_{16}H_{12}N_3$: 246.1025 $[M+H]^+$, found: 246.1026.

4-(9*H*-Fluoren-3-yl)pyrrolo[1,2-a]quinoxaline (3e). Light brown solid, yield: 157 mg (75%); mp 170-172 °C; IR ($CHCl_3$) ν_{max}: 3067, 2925, 1613, 1519, 1477, 1367, 1320, 1216, 1098, 837, 797, 753, 718 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.20 (s, 1H, ArH), 8.04-8.08 (m, 2H, ArH), 8.00-8.01 (m, 1H, pyrrolic H), 7.94 (d, *J* = 8.05 Hz, 1H, ArH), 7.86-7.90 (m, 2H, ArH), 7.60 (d, *J* = 7.32 Hz, 1H, ArH), 7.47-7.54 (m, 2H, ArH), 7.43 (t, *J* = 7.32 Hz, 1H, ArH), 7.36 (t, *J* = 7.32 Hz, 1H, ArH), 7.06-7.07 (m, 1H, pyrrolic H), 6.90-6.92 (m, 1H, pyrrolic H), 4.02 (s, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 154.4, 143.8, 143.5, 143.2, 141.0, 136.8, 136.2, 130.0, 127.4, 127.2, 127.1, 127.0, 126.7, 125.3, 125.1, 125.0, 120.2, 119.7, 114.5, 113.8, 113.5, 108.7, 36.9; HRMS (ESI, m/z) calcd for $C_{24}H_{17}N_2$: 333.1386 $[M+H]^+$, found: 333.1387.

4-(Pyren-2-yl)pyrrolo[1,2-a]quinoxaline (3f). Light brown solid, yield: 174 mg (75%); mp 218-220 °C; IR ($CHCl_3$) ν_{max}: 3041, 1596, 1474, 1418, 1374, 1093, 1036, 847, 754, 716 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.31 (s, 2H, ArH), 8.23-8.27 (m, 2H, ArH), 8.14-8.19 (m, 4H, ArH), 7.97-8.06 (m, 4H, pyrrolic H and ArH), 7.51-7.63 (m, 2H, ArH), 6.83-6.85 (m, 1H, pyrrolic H), 6.54-6.55 (m, 1H, pyrrolic H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 155.0, 136.2, 132.5, 131.9, 131.2, 130.8, 130.3, 129.3, 128.1, 127.8, 127.7, 127.3, 127.1, 126.8, 126.0, 125.4,

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125.38, 125.32, 125.0, 124.6, 124.5, 114.5, 114.1, 113.7, 109.2; HRMS (ESI, m/z) calcd for $C_{27}H_{17}N_2$: 369.1386 $[M+H]^+$, found: 369.1387.

4-(1*H*-Indol-3-yl)pyrrolo[1,2-a]quinoxaline (3g). Light brown solid, yield: 72 mg (40%); mp 118-120 °C; IR ($CHCl_3$) ν_{max}: 3412, 2923, 1644, 1447, 1337, 1239, 1025, 998, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$ + DMSO-d_6): δ(ppm) 10.80 (s, 1H, NH), 7.94-7.95 (m, 1H, pyrrolic H), 7.48-7.50 (m, 2H, ArH), 7.30-7.37 (m, 2H, ArH), 6.78-6.85 (m, 3H, ArH), 6.53-6.57 (m, 3H, pyrrolic H and ArH), 6.23 (s, 1H, pyrrolic H); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ (ppm) 149.2, 136.0, 135.4, 128.4, 126.5, 125.7, 125.67, 125.64, 124.27, 124.20, 121.6, 121.3, 119.8, 113.6, 112.9, 112.8, 111.0, 106.8 ppm; HRMS (ESI, m/z) calcd for $C_{19}H_{14}N_3$: 284.1182 $[M+H]^+$, found: 284.1189.

4-(Furan-2-yl)pyrrolo[1,2-a]quinoxaline (3h). Brown solid, yield: 92 mg (62%); mp 99-101 °C; IR ($CHCl_3$) ν_{max}: 3140, 2922, 2851, 1589, 1475, 1364, 1046, 1006, 882, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.98-8.02 (m, 2H, ArH), 7.85 (d, J = 7.32 Hz, 1H, ArH), 7.71 (s, 1H, ArH), 7.40-7.50 (m, 4H, pyrrolic H and furyl H), 6.93 (t, J = 3.36 Hz, 1H, pyrrolic H), 6.64 (br, 1H, pyrrolic H); ^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 151.9, 144.2, 143.1, 135.4, 129.6, 127.0, 126.7, 125.0, 122.8, 114.2, 113.8, 113.3, 112.6, 111.8, 108.1; HRMS (ESI, m/z) calcd for $C_{15}H_{11}N_2O$: 235.0866 $[M+H]^+$, found: 235.0872.

4-(1*H*-Pyrrol-2-yl)pyrrolo[1,2-a]quinoxaline (3i). Brown solid, yield: 114 mg (77%); mp 110-111 °C; IR ($CHCl_3$) ν_{max}: 3434, 3064, 1601, 1475, 1415, 1370, 1167, 1072, 1031, 932, 752, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.20 (brs, 1H, NH), 7.92-7.97 (m, 2H, ArH), 7.84 (d, J = 8.54 Hz, 1H, ArH), 7.39-7.47 (m, 2H, pyrrolic H), 7.31 (d, J = 3.66 Hz, 1H, pyrrolic H), 7.18 (d, J = 3.05 Hz, 1H, pyrrolic H), 7.08 (s, 1H, ArH), 6.92-6.93 (m, 1H, pyrrolic H), 6.42 (t, J = 3.05 Hz, 1H, pyrrolic H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 145.7, 144.1, 135.0, 128.4, 126.7, 126.5, 125.2, 123.1, 121.6, 114.6, 114.0, 113.5, 112.4, 110.6, 107.9; HRMS (ESI, m/z) calcd for $C_{15}H_{12}N_3$: 234.1026 $[M+H]^+$, found: 234.1035.

4-(Thiophen-2-yl)pyrrolo[1,2-a]quinoxaline (3j). Yellow solid, yield: 126 mg (80%); mp 116-117 °C; IR ($CHCl_3$) ν_{max}: 3064, 1583, 1524, 1442, 1433, 1365, 1218, 1101, 1067, 852, 754, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.96-8.01 (m, 3H, ArH), 7.85 (dd, J_1 = 8.05 Hz, J_2 = 1.46 Hz, 1H, ArH), 7.55 (dd, J_1 = 5.13 Hz, J_2 = 1.46 Hz, 1H, thienyl H), 7.42-7.52 (m, 2H, pyrrolic H), 7.28 (dd, J_1 = 4.39 Hz, J_2 = 1.46 Hz, 1H, thienyl H), 7.22 (dd, J_1 = 5.13 Hz, J_2 = 3.66 Hz, 1H, thienyl H), 6.93 (t, J = 3.29 Hz, 1H, pyrrolic H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 147.2, 142.3, 135.6, 129.8, 128.6, 128.0, 127.7, 127.3, 126.8, 125.2, 123.9, 114.6, 113.9, 113.4, 107.7; HRMS (ESI, m/z) calcd for $C_{15}H_{11}N_2S$: 251.0637 $[M+H]^+$, found: 251.0638.

4-(4-Methoxyphenyl)pyrrolo[1,2-a]quinoxaline (3k). White solid, yield: 130 mg (75%); mp 114-116 °C; IR ($CHCl_3$) ν_{max}: 2924, 2851, 1606, 1508, 1475, 1368, 1250, 1177, 1031, 834, 755, 715 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.98-8.03 (m, 4H, pyrrolic H and ArH), 7.87-7.88 (m, 1H, ArH), 7.45-7.50 (m, 2H, ArH), 7.05-7.07 (m, 2H, ArH), 7.00-7.01 (m, 1H, pyrrolic H), 6.88-6.90 (m, 1H, pyrrolic H), 3.90 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.9, 153.8, 136.2, 130.9, 130.0, 129.9, 127.1, 126.9, 125.2, 125.1, 114.4, 113.89, 113.83, 113.5, 108.5, 55.3; HRMS (ESI, m/z) calcd for $C_{18}H_{15}N_2O$: 275.1179 $[M+H]^+$, found: 275.1179.

4-(4-(Trifluoromethyl)phenyl)pyrrolo[1,2-a]quinoxaline (3l). Brown solid, yield: 161 mg (82%); mp 238-240 °C; IR ($CHCl_3$) ν_{max}: 2926, 1609, 1404, 1319, 1095, 1036, 758 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.13 (d, J = 7.79 Hz, 2H, ArH), 8.04-8.07 (m, 2H, pyrrolic H and ArH), 7.92 (dd, J_1 = 8.24 Hz, J_2 = 1.37 Hz, 1H, ArH), 7.81 (d, J = 8.24 Hz, 2H, ArH), 7.55-7.59 (m, 1H, ArH), 7.47-7.51 (m, 1H, ArH), 6.93-6.98 (m, 2H, pyrrolic H); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ (ppm) 149.7, 136.4 (d, $^2J_{C-F}$ = 6.71 Hz), 131.5, 129.9, 128.6, 128.2, 125.4 (d, $^3J_{C-F}$ = 5.75 Hz), 125.3, 124.7 (d, $^4J_{C-F}$ = 3.83 Hz), 122.7, 122.6 (d, $^1J_{C-F}$ = 280.83 Hz), 119.0, 115.8, 113.9, 112.6; HRMS (ESI, m/z) calcd for $C_{18}H_{12}F_3N_2$: 313.0947 $[M+H]^+$, found: 313.0952.

6-(4-Fluorophenyl)indolo[1,2-a]quinoxaline (3m). Yellow solid, yield: 77 mg (52%); mp 189-191 °C; IR ($CHCl_3$) ν_{max}: 2918, 2850, 1617, 1506, 1453, 1330, 1227, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.53-8.58 (m, 2H, ArH), 8.07-8.12 (m, 3H, ArH), 7.98 (d, J = 7.93 Hz, 1H, ArH), 7.67 (t, J = 7.32 Hz, 1H, ArH), 7.61 (t, J = 7.32 Hz, 1H, ArH), 7.48-7.52 (m, 2H, ArH), 7.30-7.34 (m, 3H, pyrrolic H and ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 163.8 (d, $^1J_{C-F}$ = 253.04 Hz), 155.0, 136.1, 134.3 (d, $^4J_{C-F}$ = 2.88 Hz), 133.0, 130.6, 130.5, 130.4, 130.1, 129.1, 128.9, 128.4, 124.3 (d, $^2J_{C-F}$ = 22.04 Hz), 122.7 (d, $^3J_{C-F}$ = 4.79 Hz), 115.7, 115.5, 114.6, 114.5, 102.3; HRMS (ESI, m/z) calcd for $C_{21}H_{14}FN_2$: 313.1136 $[M+H]^+$, found: 313.1141.

7-Methyl-6-(pyridin-4-yl)indolo[1,2-a]quinoxaline (3o). Orange solid, yield: 72 mg (52%); mp 235-237 °C; IR ($CHCl_3$) ν_{max}: 2922, 1597, 1451, 1399, 1211, 831, 745 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.84 (s, 2H, pyridyl H), 8.50 (t, J = 7.93 Hz, 2H, pyridyl H), 7.98-8.00 (m, 1H, ArH), 7.92 (d, J = 7.93 Hz, 1H, ArH), 7.60-7.65 (m, 4H, ArH), 7.40-7.50 (m, 2H, ArH), 2.11 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 154.7, 149.9, 147.3, 135.2, 132.0, 130.5, 130.3, 130.1, 129.0, 125.1, 124.7, 124.0, 123.4, 122.3, 120.8, 114.49, 114.40, 110.5, 11.3; HRMS (ESI, m/z) calcd for $C_{21}H_{16}N_3$: 310.1339 $[M+H]^+$, found: 310.1345.

General procedure for the synthesis of 4-methyl-4-aryl-4,5-dihydropyrrolo[1,2-a]quinoxalines (5a-d):

To a well stirred solution of *p*-DBSA (0.1 mmol) in ethanol (2 mL), aromatic ketone (1.2 mmol) and 1-(2-aminophenyl)pyrrole (1.0 mmol) were added successively at 25 °C. The reaction mixture was stirred at same temperature for 30 minutes. After completion of the reaction, the solvent was evaporated and thus the residue obtained is treated with saturated $NaHCO_3$ solution (5 mL). Then saturated brine solution (5 mL) was added. The product was extracted with ethyl acetate (10 mL × 3 times). The organic layers were combined, washed with water, dried over anhydrous sodium sulfate and evaporated under reduced pressure

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to dryness. The crude product was purified by column chromatography over silica gel (60-120 mesh size) using 5-20% ethyl acetate in heptane as an eluent to furnish the desired product in good yields. The spectral data of known compound (**5a**) are found to be in good agreement with the reported data[13a].

4-(4-Bromophenyl)-4-methyl-4,5-dihydropyrrolo[1,2-a]quinoxaline (5b). White solid, yield: 178 mg (83%); mp 165-166 °C; IR ($CHCl_3$) ν_{max}: 3349, 2980, 1613, 1517, 1482, 1334, 1187, 1077, 778, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.33-7.35 (m, 2H, ArH), 7.24-7.26 (m, 1H, ArH), 7.14-7.17 (m, 3H, pyrrolic H and ArH), 6.92-6.96 (m, 1H, ArH), 6.75-6.82 (m, 2H, ArH), 6.33 (t, J = 3.21 Hz, 1H, pyrrolic H), 6.05 (dd, J_1 = 3.21 Hz, J_2 = 1.37 Hz, 1H, pyrrolic H), 4.33 (s, 1H, NH), 1.87 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): 145.4, 134.7, 132.3, 131.2, 127.5, 125.6, 124.7, 120.8, 119.5, 115.8, 114.6, 114.4, 110.0, 104.5, 56.5, 29.0; HRMS (ESI, m/z) calcd for $C_{18}H_{16}BrN_2$: 339.0491 $[M+H]^+$, found: 339.0490.

4-(4-Iodophenyl)-4-methyl-4,5-dihydropyrrolo[1,2-a]quinoxaline (5c). White solid, yield: 200 mg (82%); mp 153-154 °C; IR ($CHCl_3$) ν_{max}: 3353, 2978, 2930, 1610, 1597, 1515, 1482, 1332, 1187, 1073, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.53-7.55 (m, 2H, ArH), 7.24-7.26 (m, 1H, ArH), 7.15-7.16 (m, 1H, pyrrolic H), 7.01-7.03 (m, 2H, ArH), 6.92-6.96 (m, 1H, ArH), 6.75-6.81 (m, 2H, ArH), 6.33 (t, J = 3.05 Hz, 1H, pyrrolic H), 6.04-6.05 (m, 1H, pyrrolic H), 4.33 (s, 1H, NH), 1.86 (s, 3H, CH_3);^{13}C NMR (100 MHz, $CDCl_3$): 146.2, 137.3, 134.8, 132.3, 127.9, 125.7, 124.8, 119.6, 115.9, 114.7, 114.5, 110.1, 104.6, 92.7, 56.7 29.1; HRMS (ESI, m/z) calcd for $C_{18}H_{16}IN_2$: 387.0353 $[M+H]^+$, found: 387.0351.

4-([1,1'-Biphenyl]-4-yl)-4-methyl-4,5-dihydropyrrolo[1,2-a]quinoxaline (5d). White solid, yield: 182 mg (86%); mp 158-159 °C; IR ($CHCl_3$) ν_{max}: 3373, 3029, 2985, 2927, 1612, 1515, 1417, 1334, 1189, 1074, 839, 746, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.47 (d, J = 7.93 Hz, 2H, ArH), 7.42 (d, J = 7.93 Hz, 2H, ArH), 7.33-7.36 (m, 4H, ArH), 7.29-7.31 (m, 1H, ArH), 7.23-7.27 (m, 1H, ArH), 7.17-7.18 (m, 1H, pyrrolic H), 6.91-6.94 (m, 1H, ArH), 6.75-6.80 (m, 2H, ArH), 6.32-6.33 (m, 1H, pyrrolic H), 6.04-6.07 (m, 1H, pyrrolic H), 4.37 (s, 1H, NH), 1.90 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): 145.3, 140.5, 139.6, 135.0, 132.8, 128.6, 127.1, 126.95, 126.90, 126.1, 125.6, 124.7, 119.2, 115.7, 114.6, 114.2, 109.9, 104.5, 56.7, 29.2; HRMS (ESI, m/z) calcd for $C_{24}H_{21}N_2$: 337.1699 $[M+H]^+$, found: 337.1708.

General procedure for the synthesis of 5'*H*-spiro[indoline-3,4'-pyrrolo[1,2-a]quinoxalin]-2-ones (7a-d) and 5'*H*-spiro[indoline-3,6'-indolo[1,2-a]quinoxalin]-2-ones (7e-j):

To a well stirred solution of *p*-DBSA (0.1 mmol) in ethanol (2 mL), isatin derivative (1.2 mmol), and 1-(2-aminophenyl)pyrrole or 2-(1*H*-indol-1-yl)aniline or 2-(3-methylindol-1-yl)phenylamine (1.0 mmol) were added at 25 °C. The reaction mixture was stirred at same temperature for the 30 minutes. After complete consumption of the starting materials as shown by TLC, the reaction mixture was then evaporated and the residue thus obtained was treated with saturated $NaHCO_3$ solution (5 mL) followed by the addition of saturated brine solution (5 mL). The product was extracted with ethyl acetate (10 mL×3 times). The organic layers were combined, washed with water, dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel (60-120 mesh size) using 5-20% ethyl acetate in heptane as an eluent to furnish the desired product in good yields. The characterization data of known compound (**7a**) are matched with the reported data [16].

5-Chloro-5'*H*-spiro[indoline-3,4'-pyrrolo[1,2-a]quinoxalin]-2-one (7b). Orange solid, yield: 170 mg (84%); mp 116-118 °C; IR ($CHCl_3$) ν_{max}: 3322, 3247, 2926, 2854, 1720, 1617, 1477, 1333, 1196, 822, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.12 (s, 1H, NH), 7.23-7.38 (m, 4H, pyrrolic H and ArH), 6.88-6.98 (m, 2H, ArH), 6.63-6.73 (m, 2H, ArH), 6.26 (t, J = 3.05 Hz, 1H, pyrrolic H), 5.61-5.62 (m, 1H, pyrrolic H), 4.32 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): 178.1, 139.7, 133.8, 131.9, 130.1, 128.4, 126.1, 124.9, 124.8, 124.3, 119.5, 116.0, 115.4, 114.2, 111.8, 110.5, 106.2, 61.4; HRMS (ESI, m/z) calcd for $C_{18}H_{13}ClN_3O$: 322.0742 $[M+H]^+$, found: 322.0738.

5-Methyl-5'*H*-spiro[indoline-3,4'-pyrrolo[1,2-a]quinoxalin]-2-one (7c). Orange solid, yield: 152 mg (80%); mp 130-132 °C; IR ($CHCl_3$) ν_{max}: 3328, 3246, 2924, 1718, 1624, 1508, 1497, 1333, 1301, 1207, 1156, 764 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.04 (s, 1H, NH), 7.36 (d, J = 7.32 Hz, 1H, ArH), 7.20-7.28 (m, 2H, ArH), 7.06 (d, J = 7.93 Hz, 1H, ArH), 6.96 (t, J = 7.32 Hz, 1H, ArH), 6.87 (t, J = 7.32 Hz, 1H, ArH), 6.66-6.69 (m, 2H, ArH and pyrrolic H), 6.25 (t, J = 3.05 Hz, 1H, pyrrolic H), 5.62 (d, J = 2.44 Hz, 1H, pyrrolic H), 4.29 (s, 1H, NH), 2.30 (s, 3H, CH_3); HRMS (ESI, m/z) calcd for $C_{19}H_{15}N_3NaO$: 324.1107 $[M+Na]^+$, found: 324.1114.

1-Methyl-5'*H*-spiro[indoline-3,4'-pyrrolo[1,2-a]quinoxalin]-2-one (7d). Pale white solid, yield: 152 mg (80%); mp 261-262 °C; IR ($CHCl_3$) ν_{max}: 3328, 2928, 1717, 1610, 1517, 1466, 1334, 1091, 737 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.37-7.45 (m, 3H, ArH), 7.28-7.29 (m, 1H, ArH), 7.13 (t, J = 7.63 Hz, 1H, ArH) 6.96-7.00 (m, 1H, ArH), 6.88-6.91 (m, 2H, ArH), 6.73-6.75 (m, 1H, pyrrolic H), 6.23 (t, J = 3.05 Hz, 1H, pyrrolic H), 5.56-5.57 (m, 1H, pyrrolic H), 4.22 (s, 1H, NH), 3.14 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): 175.3, 143.8, 134.2, 130.0, 129.6, 125.4, 125.3, 125.0, 124.5, 123.1, 119.2, 115.6, 115.1, 114.0, 110.0, 108.1, 105.5, 60.5, 25.9; HRMS (ESI, m/z) calcd for $C_{19}H_{16}N_3O$: 302.1288 $[M+H]^+$, found: 302.1275.

5'*H*-spiro[indoline-3,6'-indolo[1,2-a]quinoxalin]-2-one (7e). Orange solid, yield: 132 mg (82%); mp 130-132 °C; IR ($CHCl_3$) ν_{max}: 3332, 3193, 1716, 1616, 1508, 1452, 1321, 1198, 735 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.26 (s, 1H, NH), 8.07 (d, J = 8.54 Hz, 1H, ArH), 7.98 (dd, J_1 = 7.32 Hz, J_2 = 1.83 Hz, 1H, ArH), 7.51 (d, J = 7.93 Hz, 1H, ArH), 7.41-7.45 (m, 1H, ArH), 7.24-7.33 (m, 2H, ArH), 7.16 (t, J = 7.93 Hz, 1H, ArH), 7.05-7.09 (m, 2H, ArH), 7.00-7.04 (m, 1H, ArH), 6.83 (dd, J_1 = 7.32 Hz, J_2 = 1.83 Hz, 1H, ArH), 6.76 (d, J= 7.93 Hz, 1H, ArH), 6.00 (s, 1H, pyrrolic H), 4.35 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): 177.4, 141.1, 138.5, 134.8, 130.3, 129.6, 129.3, 127.1, 125.8, 124.1, 123.3, 123.1, 121.3, 121.0, 120.1, 116.2, 116.1,

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112.6, 112.1, 110.8, 100.7, 61.6; HRMS (ESI, m/z) calcd for $C_{22}H_{15}N_3NaO$: 360.1107 $[M+Na]^+$, found: 360.1115.

1-Methyl-5'*H*-spiro[indoline-3,6'-indolo[1,2-a]quinoxalin]-2-one (7f). Orange solid, yield: 132 mg (79%); mp 200-202 °C; IR ($CHCl_3$) ν_{max}: 3356, 2934, 1715, 1611, 1472, 1342, 1238, 1095, 762, 738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.06 (d, *J* = 8.54 Hz, 1H, ArH), 7.97-7.99 (m, 1H, ArH), 7.50 (d, *J* = 7.32 Hz, 1H, ArH), 7.38-7.46 (m, 2H, ArH), 7.25-7.32 (m, 1H, ArH), 7.13 (t, *J* = 7.93 Hz, 2H, ArH), 7.04-7.07 (m, 2H, ArH), 6.91 (d, *J* = 7.93 Hz, 1H, ArH), 6.84-6.86 (m, 1H, ArH), 5.97 (s, 1H, pyrrolic H), 4.13 (s, 1H, NH), 3.14 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): 174.6, 151.2, 143.9, 138.2, 134.9, 130.4, 129.2, 127.4, 125.7, 124.0, 123.3, 123.0, 121.1, 120.9, 120.3, 116.4, 116.0, 112.0, 109.7, 108.4, 100.2, 61.0, 26.1; HRMS (ESI, m/z) calcd for $C_{23}H_{18}N_3O$: 352.1444 $[M+H]^+$, found: 352.1439.

5-Methyl-5'*H*-spiro[indoline-3,6'-indolo[1,2-a]quinoxalin]-2-one (7g). Orange solid, yield: 134 mg (80%); mp 155-157 °C; IR ($CHCl_3$) ν_{max}: 3343, 3248, 1719, 1625, 1490, 1454, 1324, 1300, 1198, 745 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.08 (d, *J* = 8.54 Hz, 1H, ArH), 7.99 (dd, J_1 = 7.32 Hz, J_2 = 1.83 Hz, 1H, ArH), 7.88 (s, 1H, NH), 7.52 (d, *J* = 7.32 Hz, 1H, ArH), 7.28-7.32 (m, 1H, ArH), 7.14-7.17 (m, 2H, ArH), 7.02-7.09 (m, 3H, ArH), 6.82-6.84 (m, 1H, ArH), 6.69 (d, *J* = 7.93 Hz, 1H, ArH), 6.01 (s, 1H, pyrrolic H), 4.30 (s, 1H, NH), 2.29 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): 177.4, 138.7, 134.9, 134.7, 134.6, 132.8, 130.6, 129.7, 129.3, 127.1, 126.3, 124.1, 123.0, 121.2, 121.0, 120.0, 116.2, 116.0, 112.2, 110.5, 100.6, 61.7, 21.0; HRMS (ESI, m/z) calcd for $C_{23}H_{18}N_3O$: 352.1444 $[M+H]^+$, found: 352.1454.

5-Chloro-5'*H*-spiro[indoline-3,6'-indolo[1,2-a]quinoxalin]-2-one (7h). Orange solid, yield: 147 mg (83%); mp 264-266 °C; IR ($CHCl_3$) ν_{max}: 3327, 3266, 1733, 1718, 1685, 1508, 1453, 1194, 827, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.73 (s, 1H, NH), 8.03(d, *J* = 8.54 Hz, 1H, ArH), 7.93 (d, *J* = 7.32 Hz, 1H, ArH), 7.49 (d, *J* = 7.93 Hz, 1H, ArH), 7.29-7.33 (m, 1H, ArH), 7.14 -7.19 (m, 2H, ArH), 6.94-7.08 (m, 3H, ArH), 6.73 (d, *J* = 7.93 Hz, 1H, ArH), 6.42 (d, *J* = 8.54 Hz, 1H, ArH), 5.95 (s, 1H, ArH), 4.39 (s, 1H, NH); HRMS (ESI, m/z) calcd for $C_{22}H_{15}ClN_3O$: 372.0898 $[M+H]^+$, found: 372.0893.

5-Chloro-7'-methyl-5'*H*-spiro[indoline-3,6'-indolo[1,2-a]quinoxalin]-2-one (7i). Orange solid, yield: 150 mg (87%); mp 149-151 °C; IR ($CHCl_3$) ν_{max}: 3344, 3235, 2922, 1731, 1705, 1616, 1455, 1384, 1322, 1235, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.46 (s, 1H, NH), 8.24 (s, 1H, ArH), 8.04 (d, *J* = 8.54 Hz, 1H, ArH), 7.95 (d, *J* = 7.32 Hz, 1H, ArH), 7.58 (d, *J* = 7.93 Hz, 1H, ArH), 7.47-7.51 (m, 1H, ArH), 7.28-7.33 (m, 1H, ArH), 7.15-7.23 (m, 1H, ArH), 7.05-7.11 (m, 1H, ArH), 7.00-7.03 (m, 2H, ArH), 6.90 (d, *J* = 7.93 Hz, 1H, ArH), 6.80-6.85 (m, 1H, ArH), 4.30 (s, 1H, NH), 1.68 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): 177.1, 159.6, 149.4, 140.7, 138.4, 134.0, 133.6, 129.1, 127.0, 123.6, 123.3, 123.2, 120.5, 120.2, 119.1, 116.0, 115.9, 112.6, 112.2, 110.8, 109.0, 62.0, 8.2; HRMS (ESI, m/z) calcd for $C_{23}H_{18}N_3O$: 350.1289 $[M-Cl]^+$, found: 350.1288.

1,7'-Dimethyl-5'*H*-spiro[indoline-3,6'-indolo[1,2-a]quinoxalin]-2-one (7j). Orange solid, yield: 129 mg (79%); mp 88-90 °C; IR ($CHCl_3$) ν_{max}: 3315, 3053, 2922, 1717, 1610, 1492, 1455, 1363, 1093, 738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.24 (d, *J* = 8.70, 1H, ArH), 8.16 (d, *J* = 7.79 Hz, 1H, ArH), 7.69-7.78 (m, 2H, ArH), 7.59 (t, *J* = 7.73 Hz, 1H, ArH), 7.49-7.53 (m, 1H, ArH), 7.43-7.46 (m, 1H, ArH), 7.36-7.39 (m, 1H, ArH), 7.27-7.31 (m, 1H, ArH), 7.19-7.24 (m, 1H, ArH), 7.13 (d, *J* = 7.79 Hz, 1H, ArH), 7.03 (d, *J* = 7.79 Hz, 1H, ArH), 4.47 (s, 1H, NH), 3.44 (s, 3H, CH_3) 3.40 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): 174.3, 151.2, 143.3, 138.2, 134.0, 130.2, 129.4, 127.2, 125.3, 123.5, 123.3, 123.0, 120.4, 120.3, 118.9, 116.1, 116.0, 112.0, 109.8, 108.5, 108.3, 61.5, 26.2, 8.1; HRMS (ESI, m/z) calcd for $C_{24}H_{19}N_3NaO$ 388.1420 $[M+Na]^+$, found: 388.1426

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Notes and references

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† Electronic Supplementary Information (ESI) available: ^1H and ^{13}C NMR spectra of the synthesized products

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