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Lewis Acid-Catalyzed Selective Synthesis of Diversely Substituted Indolo- and Pyrrolo[1,2-*a*]quinoxalines and Quinoxalinones by Modified Pictet–Spengler Reaction

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An efficient tandem process for the selective synthesis of 1,2-annulated α-fused quinoxalines using benzotriazole methodology by a modified Pictet–Spengler reaction is described. The approach involves the reaction of arylamines **4** with aromatic aldehydes **5** to furnish 6-*endo*-*dig*-cyclized products. Dihydroquinoxalines **6** were selectively obtained by using $AlCl_3$ in tetrahydrofuran (THF) at room temperature for two hours. However, after ten hours, quinoxalines **7** were obtained exclusively in excellent yields. A series of biologically important fluoro- and piperazenyl-substituted quinoxalines were also synthesized. This developed methodology also provides access to a novel tandem synthesis of quinoxalinones **9**.

Introduction

A wide variety of biologically active natural and synthetic compounds are known to have substituted heterocycles in their core. For instance, quinoxalines are an important class of nitrogen-containing heterocycles[1] that possess a broad spectrum of physiological and biological activities and can act as anti-cancer[2] and anti-HIV[3a] agents, glucagon receptor antagonists,[3b] and angiotensin receptor antagonists.[3c] They have also been used as a template for the synthesis of GABA benzodiazepines receptor agonists or antagonists[4] and for other therapeutic applications.[5] Besides these pharmaceutical applications, this class of compounds has also been used as building blocks for the synthesis of organic semiconductors, dyes, useful rigid subunits in macrocyclic receptors, and chemically controllable switches.[1,6a] In comparison to α-fused angular polycyclic quinoxaline ring systems, compounds containing the β-fused framework have been extensively studied because of their wide range of pharmacological activities.[6b,6c] Therefore, the development of a novel route that enables their syntheses using efficient processes is an important area of research.

Among the various C–C bond-forming reactions, the Pictet–Spengler reaction[6d] has been widely used for the formation of ring systems such as tetrahydroimidazo-pyridines (THIPs), tetrahydroisoquinolines (THIQs), and tetrahydro-β-carbolines (THBCs) (Figure 1).[7] From a synthetic point of view, the opportunity to prepare complex polycyclic molecules in a limited number steps is an exciting goal for every modern organic chemist. Although a number of methods are available for the synthesis of simple substituted quinoxalines,[8,9] only a limited amount of work has been done on the synthesis of polycyclic quinoxalines, especially indoloquinoxalines.[10–11] Furthermore, to the best of our knowledge, none of the reported procedures have described the selective synthesis of dihydroquinoxalines or quinoxalines. Reported syntheses of indolo- and pyrrolo-fused quinoxalines involves the reaction of aryl amines with

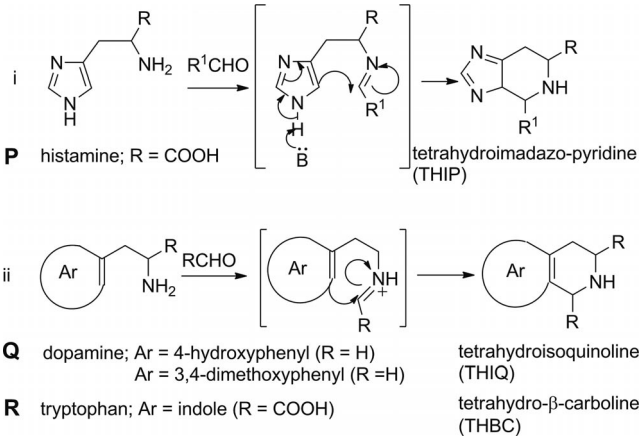

Figure 1. (i) Typical base-catalyzed Pictet–Spengler reaction. (ii) Typical acid-catalyzed Pictet–Spengler reaction.

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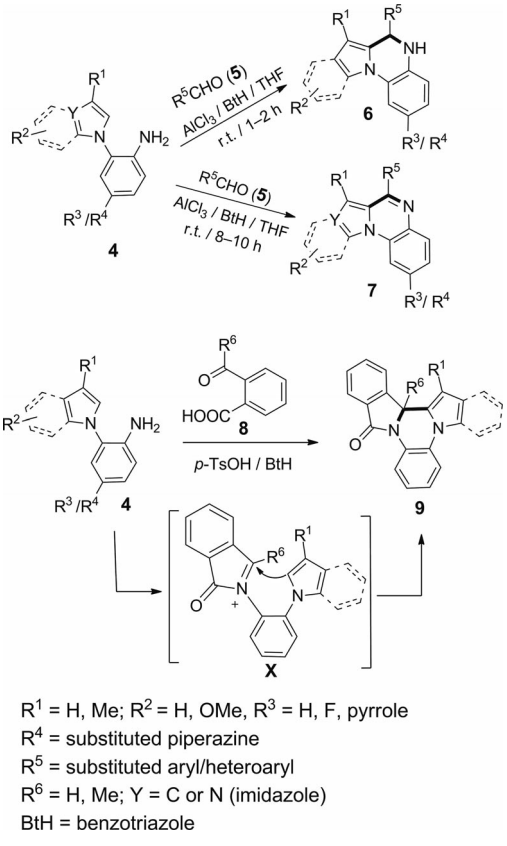
terminal alkynes in the presence of a ruthenium hydride complex for 20–24 h.[11b]

Kundu and co-workers reported the synthesis of imidazo-quinoxalines in 50–74% yields by using the Pictet–Spengler reaction on solid phase at 80 °C for 48 h.[11c] Other reported methods are multistep and required longer reaction times, and high temperature.

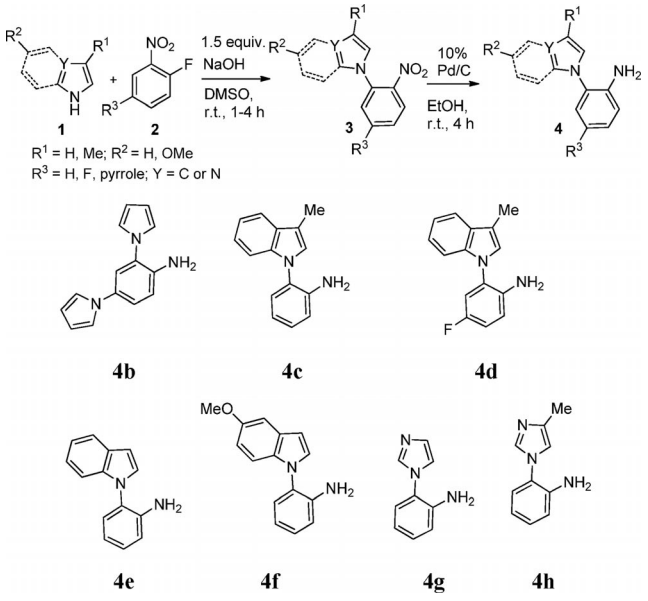
In a continuation of our interest in the synthesis of fused heterocycles by using benzotriazole[12] methodology[13] and alkyne chemistry,[14] herein we report the selective synthesis of 1,2-annulated α-fused dihydro-pyrrolo/indolo[1,2-*a*]quinoxalines **6** and pyrrolo/indolo[1,2-*a*]quinoxalines **7** in good to excellent yields by using a modified Pictet–Spengler reaction at 25 °C. The developed process is also successful for the tandem synthesis of indolo/pyrrolo[2,1-*a*]quinoxalinone **9** (Scheme 1).



Scheme 1. Synthesis of reduced and oxidized forms of quinoxalines **6**, **7**, and polycyclic quinoxalinones **9**.

Results and Discussion

In this study, we selected arylamines **4**, which linked to N-1 of indole and pyrrole **1**, as possible substrates for the synthesis of diversely-substituted indolo- and pyrrolo-quinoxalines. The arylamines **4** required for the reactions were obtained in quantitative yields by the reduction of the corresponding nitro derivatives (Scheme 2). The nitro compounds **3** were prepared by the reaction of commercially available 2-fluoronitrobenzene (**2a**) and 2,4-difluronitrobenzene (**2b**) with N-heterocycles **1** using NaOH in dimethyl sulfoxide (DMSO) at room temperature (see Table S1 in the Supporting Information).

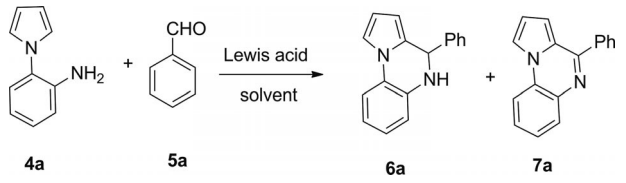


Scheme 2. Synthesis of N-heterocyclic amines.

To optimize the reaction conditions for the selective synthesis of quinoxalines, various Lewis acids and organic solvents were examined and the reaction time was varied; the results are summarized in Table 1. We first allowed **4a** (0.5 mmol) to react with 1.0 equiv. of **5a**, 10.0 mol-% of $AlCl_3$, and 1.0 equiv. of benzotriazole in 2.0 mL of CH_2Cl_2 at room temp. for 30 min, but found that 4,5-dihydropyrrolo[1,2-*a*]quinoxaline (**6a**) could be obtained in only 60% yield (Table 1, entry 1). Increasing the reaction time to 1 h and then to 2 h afforded the reduced product in 78 and 83% yields respectively (Table 1, entries 2–3). When reaction was stirred for 5 h, the desired product **6a** was obtained in 68% yield along with the oxidized form of quinoxaline **7a** in 18% yield (Table 1, entry 4). After 10 h, products **6a** and **7a** were obtained in 45 and 50% yield, respectively (Table 1, entry 5). The same results were obtained when chloroform was used (Table 1, entry 6). Using toluene as solvent, the product **6a** was obtained in 85% yield in 2 h (Table 1, entry 7). When the reaction was continued for 10 h, products **6a** and **7a** were obtained in 13 and 70% yield, respectively (Table 1, entry 8). When tetrahydrofuran (THF) was used, product **6a** was obtained in 92% yield after 2 h, however it was completely oxidized after 10 h to compound **7a**, which was selectively obtained in 90% yield (Table 1, entry 11). Lower yield of product was obtained in the absence of benzotriazole (Table 1, entry 12). When the catalyst loading was decreased from 10 to 5 mol-%, only 56% of product **6a** was obtained in 2 h (Table 1, entry 13). After 7 h, we obtained a mixture products **6a** and **7a** in 20 and 31% yield, respectively, along with 50% of starting material (Table 1, entry

14). When the reaction was stirred under the same conditions for 12 h, 50% yield of the oxidized product **7a** was obtained, along with starting material (Table 1, entry 15).

Table 1. Optimization of the reaction conditions.[a]



4a **5a** **6a** **7a**

Entry	Solvent	Catalyst / mol-%	*t* [h]	Yield [%][b]	
				6a	**7a**
1	CH_2Cl_2	$AlCl_3$ / 10	0.5	60	00
2	CH_2Cl_2	$AlCl_3$ / 10	1.0	78	00
3	CH_2Cl_2	$AlCl_3$ / 10	2.0	83	00
4	CH_2Cl_2	$AlCl_3$ / 10	5.0	68	18
5	CH_2Cl_2	$AlCl_3$ / 10	10.0	45	50
6	$CHCl_3$	$AlCl_3$ / 10	10.0	40	54
7	toluene	$AlCl_3$ / 10	2.0	85	00
8	toluene	$AlCl_3$ / 10	10.0	13	70
9	**THF**	**$AlCl_3$ / 10**	**2.0**	**92**	**00**
10	THF	$AlCl_3$ / 10	5.0	39	60
11	**THF**	**$AlCl_3$ / 10**	**10.0**	**00**	**90**
12	THF	$AlCl_3$ / 10	10.0	00	60[c]
13	THF	$AlCl_3$ / 05	2.0	50	00
14	THF	$AlCl_3$ / 05	7.0	20	31
15	THF	$AlCl_3$ / 05	12.0	00	50
16	THF	TsOH / 10	2.0	80	00
17	THF	TsOH / 10	5.0	45	30
18	THF	TsOH / 10	10.0	17	70
19	THF	$FeCl_3$ / 10	2.0	59	00
20	THF	$FeCl_3$ / 10	5.0	70	00
21	THF	$FeCl_3$ / 10	10.0	81	00
22	THF	$ZnCl_2$ / 10	2.0	45	00
23	THF	$ZnCl_2$ / 10	10.0	67	00
24	THF	–	24.0	–	10

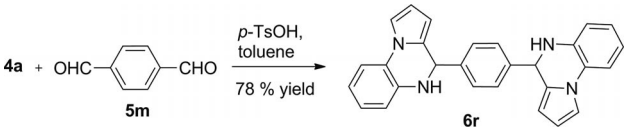
[a] Reagents and conditions: aldehyde **5a** (0.6 mmol), benzotriazole (0.5 mmol), catalyst (5.0/10 mol-%), amine **4a** (0.5 mmol), solvent (2.0 mL), 25 °C unless otherwise noted. [b] Isolated yield. [c] Reaction performed without benzotriazole.

We then examined the effect of a range of Lewis acids on the reaction. Use of TsOH in the reaction afforded the products **6a** and **7a** with slightly lower yield than with $AlCl_3$ (Table 1, entries 16–18). $FeCl_3$ afforded the reduced product in 5 h and no oxidized product **7a** was observed even after 10 h (Table 1, entries 19–21). $ZnCl_2$ afforded only the reduced product in 67% yield after 10 h (Table 1, entries 22–23). When the reaction was performed in the absence of $AlCl_3$, only 10% of the reduced form **6a** was obtained in 5 h, which was further oxidized to **7a** in 24 h. No further conversion of **4a** into the product **6a** was observed (Table 1, entry 24). Among the different solvent systems and Lewis acids examined, THF with $AlCl_3$ was found to be most effective for the selective formation of the desired products **6a** and **7a** in good to excellent yields (Table 1, entries 9 and 11).

The scope and limitations of the optimized reaction conditions were then examined by employing various substituted aldehydes and amines. First, a diverse library of dihydro-pyrrolo/indolo[1,2-*a*]quinoxalines **6a**–**r** was synthesized by reacting amines **4a**–**d** with aldehydes **5a**–**l** in the presence of $AlCl_3$ in THF at room temp. for 2 h (Table 2). The presence of an electron-withdrawing group in the aldehyde afforded the cyclized products **6d**–**k** and **6n**–**q** in good yields (Table 2, entries 4–11 and 14–17). However, aldehydes having electron-releasing groups such as methoxy or 4-ethylfuryl afforded the cyclized products **6b** and **6c** in 83 and 76% yield, respectively (Table 2, entries 2 and 3). The reaction proceeded well with π-deficient 2-bromonicotinaldehyde (**5i**), providing the desired product in 82% yield (Table 2, entry 11). However, the reaction with aliphatic aldehyde **5j**, afforded the desired product **6l** in 65% yield (Table 2, entry 12). Reaction of 2-(3-methyl-1*H*-indol-1-yl)aniline (**4c**) and 4-fluoro-2-(3-methyl-1*H*-indol-1-yl)aniline (**4d**) provided the expected products **6m**–**q** in good to excellent yields (Table 2, entries 11–15).

The formation of the desired cyclized products were confirmed by ^1H NMR and ^{13}C NMR spectroscopic analysis. Furthermore, the formation of dihydro-quinoxalines was confirmed by the disappearance of the NH proton in the NMR spectra of compound **6d** measured in D_2O (see the Supporting Information).

Reaction of terephthaldehyde (**5m**) with 2.0 equiv. of amine **4a** using $AlCl_3$ in THF afforded 1,4-bis(4,5-dihydropyrrolo[1,2-*a*]quinoxalin-4-yl)benzene (**6r**) in 78% yield (Scheme 3).

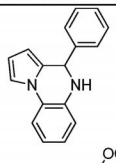
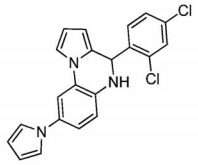
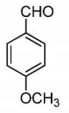
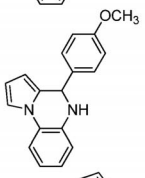
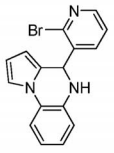
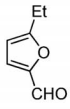
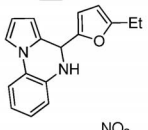
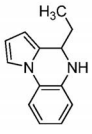
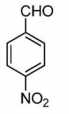
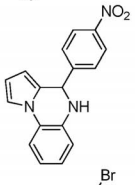
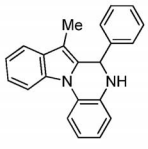
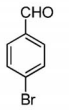
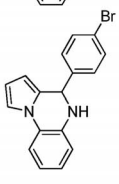
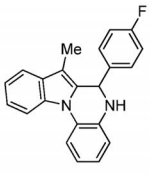
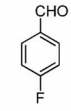
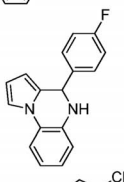
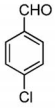
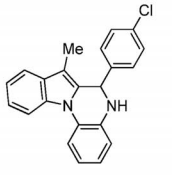
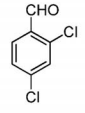
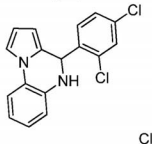
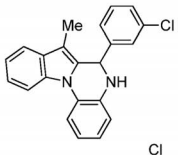
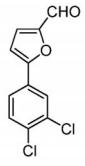
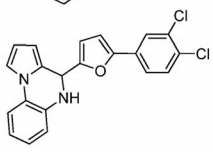
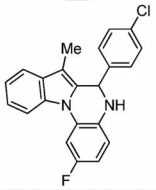
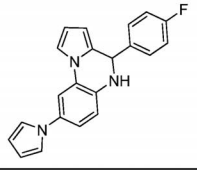


Scheme 3. Synthesis of bis-dihydroquinoxaline.

Using the optimized reaction conditions for the oxidized form of quinoxalines, a second library of quinoxalines **7a**–**r** was synthesized in good to excellent yields by reacting amines **4a**–**h** with substituted aldehydes **5a**–**p** (Table 3). It was noticed that the effect on the reaction of different substituents on the aldehyde was the same as observed in the synthesis of dihydroquinoxaline. The reaction of 2-(3-methyl-1*H*-indol-1-yl)anilines **4c**–**d**, bearing an electron-releasing methyl group at the 3-position of the indole, afforded quinoxalines **7f**–**p** in 85 to 96% yield (Table 3, entries 6–13). However, amine **4e** and **4f**, without a methyl group at the 3-position of the indole nucleus, afforded the desired products **7n**–**p** in 58–66% yields (Table 3, entries 9–11).

The scope of the reaction was further extended for the synthesis of another important class of fused imidazo[1,5-*a*]-quinoxalines (Table 3, entries 17–18). Reaction of electron-deficient 2-(1*H*-imidazol-1-yl)aniline **4g** failed to afford the desired cyclized product **7q** under the standardized conditions (Table 3, entry 17). However, reaction of 2-(4-methyl-1*H*-imidazol-1-yl)aniline **4h**, having an electron-releasing methyl group at the 4-position, afforded the cyclized product **7r** in 74% yield (Table 3, entry 18).

Table 2. Selective synthesis of 4,5-dihydropyrrolo[1,2-*a*]quinoxalines **6a**–**l** and 5,6-dihydroindolo[1,2-*a*]quinoxalines **6m**–**q**.[a]

Entry		R^5CHO		Product	Yield [%][b]	Entry		R^5CHO		Product	Yield [%][b]
1	**4a**		**5a**		**6a** 90	10	**4b**		**5g**		**6j** 82
2	**4a**		**5b**		**6b** 83	11	**4a**		**5i**		**6k** 82
3	**4a**		**5c**		**6c** 76	12	**4a**		**5j**		**6l** 65
4	**4a**		**5d**		**6d** 90	13	**4c**		**5a**		**6m** 90
5	**4a**		**5e**		**6e** 93	14	**4c**		**5f**		**6n** 88
6	**4a**		**5f**		**6f** 88	15	**4c**		**5k**		**6o** 92
7	**4a**		**5g**		**6g** 84	16	**4c**		**5l**		**6p** 85
8	**4a**		**5h**		**6h** 68	17	**4d**		**5k**		**6q** 78
9	**4b**		**5f**		**6i** 85							

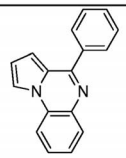
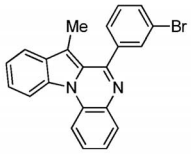
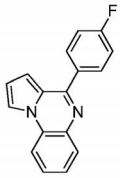
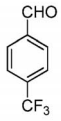
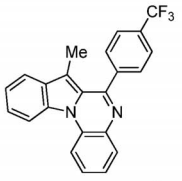
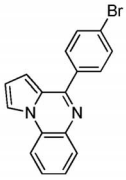
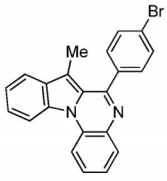
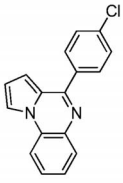
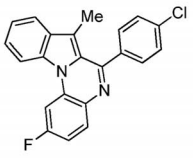
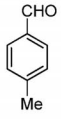
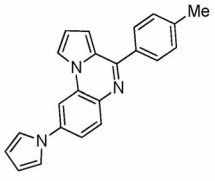
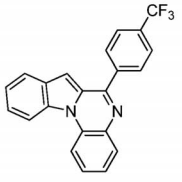
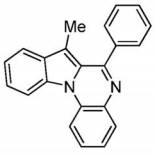
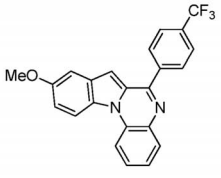
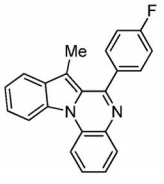
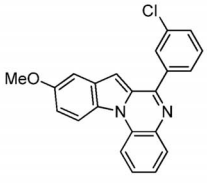
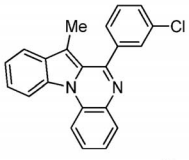
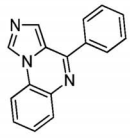
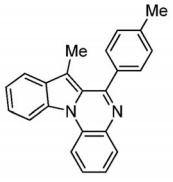
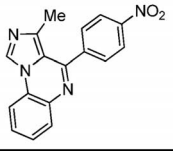
[a] Reagents and conditions: aldehyde **5** (0.6 mmol), benzotriazole (1.0 equiv.), $AlCl_3$ (10 mol-%), amine **4** (0.5 mmol), THF (2.0 mL), room temp., 1–2 h, unless otherwise noted. [b] Isolated yield.

Higher yields observed for the reaction with 3-methylindole amine were presumably due to the formation of a more stable transient tertiary carbocation, which then increases the efficiency of the cyclization (Figure 2).

The presence of an electron-releasing methyl group at the 3-position of indole-arylamine **4a**, and at the 4-position of imidazole-arylamine **4h**, increases the nucleophilicity of the ring system, which facilitates intramolecular attack of the C-2 position of indole and the C-5 position of imidazole to afford the cyclized products (Figure 2).

Piperazine scaffolds are commonly found in biologically active compounds across a number of different therapeutic areas.[15] Therefore, a novel series of piperazine fused indolo[1,2-*a*]quinoxalines were synthesized to further extend the scope of this reaction. Reaction of arylamines **4i**–**j** with aldehydes **5d**–**f**, **5k**, and *m*-nitobenzaldehyde (**5q**) af-

Table 3. Selective synthesis of pyrrolo, indolo-quinoxalines **7a**–**p** and imidazo-quinoxaline **7q**–**r**.[a]

Entry		R^5CHO		Product	Yield[%][b]	Entry		R^5CHO		Product	Yield[%][b]
1	**4a**		**5a**		**7a** 91	10	**4c**		**5o**		**7j** 96
2	**4a**		**5f**		**7b** 86	11	**4c**		**5p**		**7k** 88
3	**4a**		**5e**		**7c** 96	12	**4c**		**5e**		**7l** 90
4	**4a**		**5k**		**7d** 88	13	**4d**		**5k**		**7m** 85
5	**4b**		**5n**		**7e** 85	14	**4e**		**5p**		**7n** 66
6	**4c**		**5a**		**7f** 95	15	**4f**		**5p**		**7o** 58
7	**4c**		**5f**		**7g** 91	16	**4f**		**5l**		**7p** 64
8	**4c**		**5l**		**7h** 88	17	**4g**		**5a**		**7q** 00
9	**4c**		**5n**		**7i** 86	18	**4h**		**5d**		**7r** 74

[a] Reagents and conditions: **5** (0.6 mmol), benzotriazole (1.0 equiv.), $AlCl_3$ (10 mol-%), **4** (0.5 mmol), THF (2.0 mL), room temp., 8–10 h; unless otherwise noted. [b] Isolated yield.

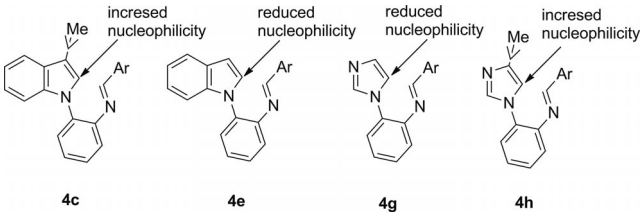
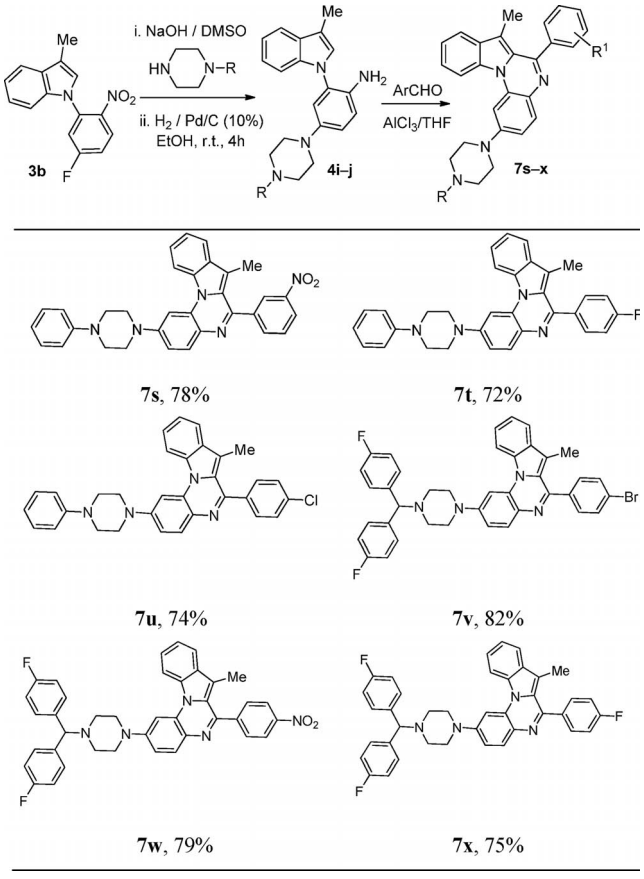


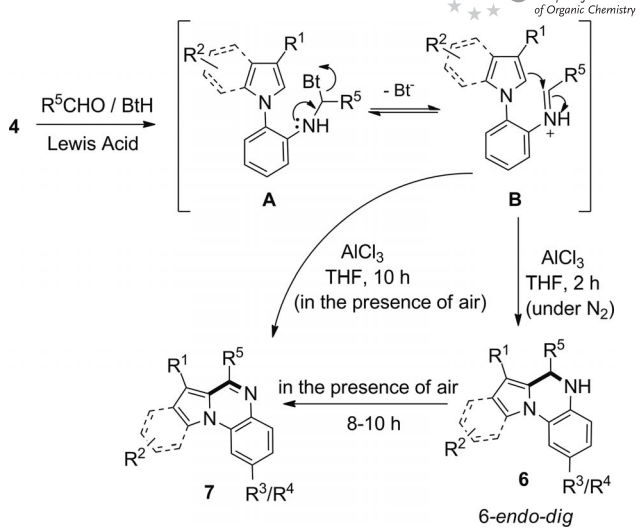
Figure 2. Effect of substituents on intramolecular cyclization.

forded the piperazine-substituted cyclized products **7s**–**x** in 72–82% yields under the standardized reaction conditions (Table 4).

Table 4. Synthesis of piperazinyl-substituted quinoxalines.



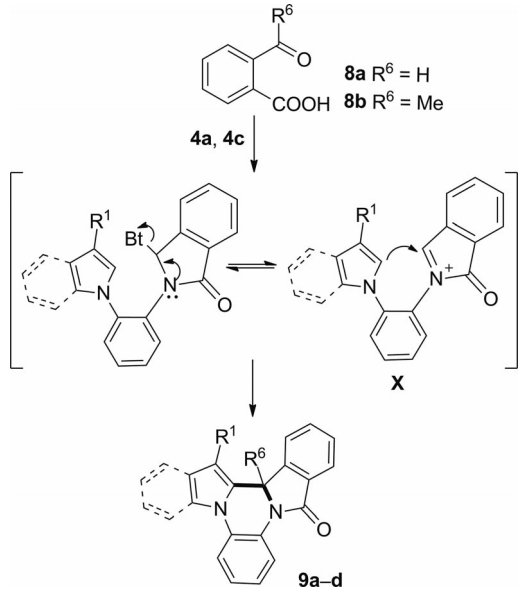
With these results, we have proposed a plausible mechanism for the selective formation of quinoxalines. The suggested reaction mechanism involves the formation of intermediate **A** in the presence of a Lewis acid and benzotriazole. This intermediate forms the true iminium ion **B** by facile removal of benzotriazole.[12] The latter intermediate **B** undergoes intramolecular C–C bond formation by 6-*endo-dig* attack at C-2 of the N-heterocycle to furnish the dihydroquinoxalines **6** (Scheme 4). These dihydroquinoxalines were oxidized in the presence of air after 8–10 h to yield the oxidized form of quinoxalines **7**.



Scheme 4. Possible mechanism for the selective synthesis of quinoxalines.

The strategy was further extended to the tandem synthesis of polycyclic quinoxalinones **9a**–**d** by the condensation of amines **4a** and **4c** with 2-formylbenzoic acid (**8a**) and 2-acetylbenzoic acid (**8b**) in the presence of benzotriazole in toluene using a Dean–Stark apparatus at 110 °C for 2–4 h (Table 5).

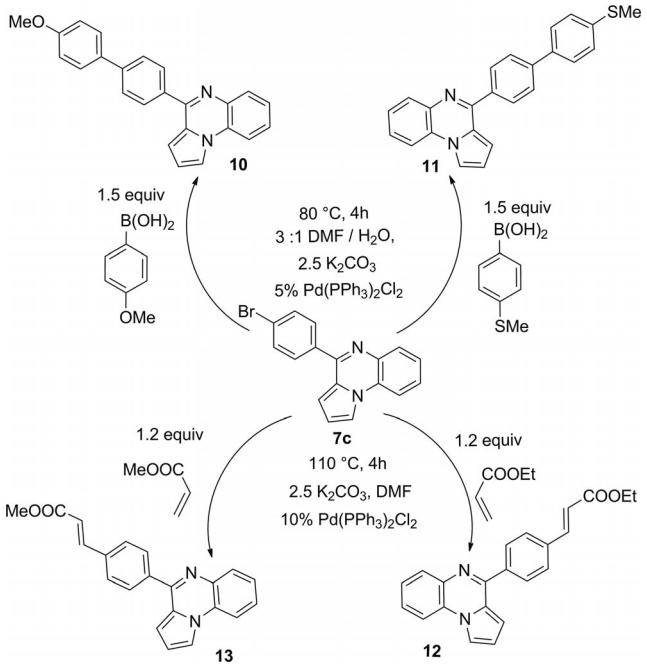
Table 5. Synthesis of quinoxalinones **9a**–**d**.[a]



Entry	Product	R^1	R^6	Yield [%][b]
1	**9a**	H	H	91
2	**9b**	H	Me	88
3	**9c**	Me	H	84
4	**9d**	Me	Me	73

[a] Reagents and conditions: carboxy-benzoic acid **8** (0.6 mmol), TsOH (5.0 mol-%), **4** (0.5 mmol), benzotriazole (0.5 mmol), toluene (2.0 mL), Dean–Stark apparatus at 110 °C for 2–4 h. [b] Isolated yield.

Quinoxaline **7c**, containing a bromo handle, could be further functionalized through palladium-catalyzed coupling reactions such as Suzuki[16] and Heck[17] reactions to afford the corresponding coupling products **10**, **11**, **12**, and **13** in 85, 81, 72, and 74% yields, respectively (Scheme 5).



Scheme 5. Palladium-catalyzed diversification.

Conclusions

We have demonstrated for the first time a simple and efficient method for the selective synthesis of oxidized and reduced forms of indolo/pyrrolo[1,2-*a*]quinoxalines, in good to excellent yields, by applying a modified Pictet–Spengler reaction under mild conditions. The reaction was facilitated by Lewis acids as a catalyst and benzotriazole as an additive. The results show that benzotriazole can be used for various types of transformation due to its unique properties. A novel series of piperazine-substituted quinoxalines were also synthesized because of their importance in medicinal chemistry. We have also extended our strategy to the tandem synthesis of indolo/pyrrolo quinoxalinones in one pot without isolating the benzotriazole intermediate. Further investigations that are focused on expanding the reaction scope are ongoing and will be reported in due course.

Experimental Section

General Procedure for the Synthesis of Piperazinyl-Substituted 3-Methyl-1-(2-nitrophenyl)-1*H*-indoles 3i and 3j: To a well-stirred solution of N-heterocycle (1.0 mmol) in DMSO (1.0 mL), NaOH (1.0 equiv.) and aryl halide (1.0 mmol) were added slowly. The reaction mixture was stirred vigorously for 1–1.5 h at room temperature until no more starting material was detectable by TLC analysis. The reaction mixture was extracted with ethyl acetate and water and dried with Na_2SO_4. The solvent was evaporated in vacuo and the solid obtained was purified by column chromatography (hexane/ethyl acetate) to afford the desired product in good yields.

3-Methyl-1-[2-nitro-5-(4-phenylpiperazin-1-yl)phenyl]-1*H*-indole (3i): The product was obtained as a yellow solid; m.p. 174–176 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 (d, J = 9.3 Hz, 1 H), 7.66–7.54 (m, 1 H), 7.31–7.28 (m, 3 H), 7.20–7.13 (m, 3 H), 6.97–6.84 (m, 5 H), 3.59–3.56 (m, 4 H), 3.36–3.33 (m, 4 H), 2.39 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.1, 150.5, 136.7, 135.8, 135.2, 129.5, 129.3, 128.5, 125.5, 122.7, 120.5, 120.0, 119.3, 116.3, 113.7, 113.2, 111.5, 109.6, 48.8, 47.00, 9.7 ppm. HRMS (ESI): calcd. for $C_{25}H_{24}N_4O_2$ $[M + H]^+$ 412.1899; found 412.1901.

1-(5-{4-[Bis(4-fluorophenyl)methyl]piperazin-1-yl}-2-nitrophenyl)-3-methyl-1*H*-indole (3j): The product was obtained as a yellow solid; m.p. 166–168 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10 (d, J = 9 Hz, 1 H), 7.60–7.57 (m, 1 H), 7.37–7.33 (m, 4 H), 7.18–7.09 (m, 3 H), 7.08–6.94 (m, 4 H), 6.89 (d, J = 9 Hz, 1 H), 6.81–6.75 (m, 2 H), 4.25 (s, 1 H), 3.38 (t, J = 5.1 Hz, 4 H), 2.50 (t, J = 4.9 Hz, 4 H), 2.35 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.5, 160.3, 154.2, 137.5, 136.5, 135.7, 134.9, 129.5, 129.1, 129.0, 128.4, 125.4, 122.6, 120.0, 119.3, 115.7, 115.5, 113.7, 113.0, 111.3, 109.6, 74.2, 51.1, 47.1, 9.6 ppm. HRMS (ESI): calcd. for $C_{32}H_{28}F_2N_4O_2$ $[M + H]^+$ 538.2180; found 538.2188.

Typical Procedure for the Synthesis of 2,4-Di(pyrrol-1-yl)phenylamine (4b): To a well-stirred solution of alkyl-substituted 1-(2-nitrophenyl)-1*H*-indole or 1-(2-nitrophenyl)-1*H*-imidazole (5.0 mmol) in absolute ethanol (25 mL), 10% Pd/C (20 mol-%) was added. The reaction mixture was stirred for 2–3 h at room temperature under a hydrogen atmosphere at 45 psi. The reaction mixture was filtered through Celite and the filtrate was evaporated in vacuo to obtain the desired amines.

2,4-Di(pyrrol-1-yl)phenylamine (4b): The product was obtained as a white solid; m.p. 96–98 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27–7.22 (m, 2 H), 7.00 (t, J = 1.8 Hz, 2 H), 6.90–6.81 (m, 3 H), 6.40–6.32 (m, 4 H), 3.77 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.9, 132.6, 127.6, 121.5, 121.1, 119.9, 119.5, 116.6, 109.8, 109.7 ppm. HRMS (ESI): calcd. for $C_{14}H_{13}N_3$ $[M + H]^+$ 223.1109; found 223.1113.

General Procedure for the Synthesis of 4,5-Dihydropyrrolo[1,2-*a*]-quinoxalines 6a–l and 6r and 5,6-Dihydroindolo[1,2-*a*]quinoxalines 6m–q: To a well-stirred solution of aldehyde **5** (0.6 mmol), benzotriazole (1.0 equiv.), and 10 mol-% $AlCl_3$ in THF, 1-(2-aminophenyl)-pyrrole or 2-(3-methylindol-1-yl)phenylamine (**4**; 0.5 mmol) was added. The reaction was stirred at room temperature for 1–2 h, then the reaction mixture was extracted with ethyl acetate and water. The organic layer was washed with NaOH, brine, and dried with Na_2SO_4. The solvent was evaporated in vacuo and the solid obtained was purified by column chromatography (hexane/ethyl acetate) to afford the desired product in good yields.

4-Phenyl-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (6a): The product was obtained as a pale-yellow solid; m.p. 98–99 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47–7.45 (m, 2 H), 7.37–7.32 (m, 4 H), 7.21–7.19 (m, 1 H), 6.96 (t, J = 7.5 Hz, 1 H), 6.84 (d, J = 7.8 Hz, 1 H), 6.72 (d, J = 7.8 Hz, 1 H), 6.24 (t, J = 3 Hz, 1 H), 5.57–5.52 (m, 2 H), 4.13 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.4, 136.1, 130.0, 128.6, 128.2, 127.9, 125.4, 119.3, 115.3, 114.7, 114.3, 110.1, 105.8, 56.2 ppm. HRMS (ESI): calcd. for $C_{17}H_{14}N_2$ $[M + H]^+$ 246.1157; found 246.1161.

4-(4-Methoxyphenyl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (6b): The product was obtained as a light-yellow solid; m.p. 108–110 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32–6.76 (m, 9 H), 6.25 (s, 1 H),

5.62 (s, 1 H), 5.52 (s, 1 H), 4.17 (br. s, 1 H), 3.79 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.5, 136.2, 133.4, 130.2, 129.1, 125.4, 124.5, 119.2, 115.2, 114.6, 114.2, 113.9, 110.0, 105.7, 55.5, 55.2 ppm. HRMS (ESI): calcd. for $C_{18}H_{16}N_2O$ [M + H]$^+$ 276.1263; found 276.1269.

4-(5-Ethylfuran-2-yl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (6c): The product was obtained as a semi-solid; m.p. 208–210 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 (d, J = 7.8 Hz, 1 H), 7.18–7.13 (m, 1 H), 7.94 (t, J = 7.5 Hz, 1 H), 6.84–6.78 (m, 1 H), 6.72 (d, J = 7.8 Hz, 1 H), 6.33–6.30 (m, 1 H), 6.00–5.96 (m, 2 H), 5.85 (d, J = 2.7 Hz, 1 H), 5.63 (s, 1 H), 4.33 (br. s, 1 H), 2.61 (q, J = 7.5 Hz, 2 H), 1.2 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.7, 152.2, 135.0, 126.2, 125.4, 124.6, 119.5, 115.7, 114.6, 116.4, 110.0, 109.3, 107.7, 105.6, 104.5, 49.3, 21.3, 12.0 ppm. HRMS (ESI): calcd. for $C_{17}H_{16}N_2O$ [M + H]$^+$ 264.1263; found 264.1267.

4-(4-Nitrophenyl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (6d): The product was obtained as a light-yellow solid; m.p. 106–108 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21–8.20 (m, 2 H), 7.63–7.60 (m, 2 H), 7.3 (d, J = 7.3 Hz, 1 H), 7.21–7.20 (m, 1 H), 7.0 (td, J = 8.0, 1.4 Hz, 1 H), 6.8 (t, J = 8 Hz, 1 H), 6.7 (m, 1 H), 6.24 (m, 1 H), 5.6 (m, 1 H), 5.6 (s, 1 H), 4.2 (br. s, 1 H) ppm. ^{13}C (100 MHz, $CDCl_3$): δ = 148.7, 147.7, 135.1, 128.6, 127.9, 125.2, 124.9, 123.9, 119.9, 115.5, 114.8, 110.3, 106.2, 55.4 ppm. HRMS (ESI): calcd. for $C_{17}H_{13}N_3O_2$ [M + H]$^+$ 291.1008; found 291.1010.

4-(4-Nitrophenyl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (6d): ^{1}H NMR (400 MHz, D_2O): δ = 8.20 (d, J = 8.8 Hz, 2 H), 7.60 (d, J = 8.8 Hz, 2 H), 7.5 (d, J = 9.4 Hz, 1 H), 7.4 (d, J = 1.4 Hz, 1 H), 6.99–6.92 (m, 2 H), 6.8 (t, J = 5.1 Hz, 1 H), 6.24 (t, J = 3.3 Hz, 1 H), 5.79 (d, J = 2.9 Hz, 1 H), 5.76 (s, 1 H) ppm.

4-(4-Bromophenyl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (6e): The product was obtained as a light-yellow solid; m.p. 116–118 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.5 (d, J = 8.1 Hz, 2 H), 7.33 (d, J = 8.4 Hz, 3 H), 7.21–7.19 (m, 1 H), 6.97 (t, J = 7.5 Hz, 1 H), 6.88 (t, J = 7.8 Hz, 1 H), 6.74 (d, J = 7.8 Hz, 1 H), 6.24–6.23 (m, 1 H), 5.55–5.48 (m, 2 H), 4.11 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.4, 135.8, 131.8, 129.6, 125.4, 124.7, 122.2, 119.6, 115.4, 114.7, 114.5, 110.2, 105.9, 55.6 ppm. HRMS (ESI): calcd. for $C_{17}H_{13}BrN_2$ [M + H]$^+$ 324.0262; found 324.0268.

4-(4-Fluorophenyl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (6f): The product was obtained as a light-yellow solid; m.p. 112–114 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.41 (m, 2 H), 7.33 (d, J = 7.8 Hz, 1 H), 7.19–7.18 (m, 1 H), 7.12–7.10 (m, 2 H), 6.97 (td, J = 1.2, 7.5 Hz, 1 H), 6.85 (td, J = 1.2, 7.8 Hz, 1 H), 6.74 (dd, J = 1.2, 7.8 Hz, 1 H), 6.27–6.23 (m, 1 H), 5.54–5.50 (m, 2 H), 4.10 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.3, 161.0, 137.2, 137.1, 136.0, 129.8, 129.7, 129.6, 125.5, 124.7, 119.5, 115.6, 115.3, 114.7, 114.4, 110.2, 105.8, 55.5 ppm. HRMS (ESI): calcd. for $C_{17}H_{13}FN_2$ [M + H]$^+$ 264.1063; found 264.1066.

4-(2,4-Dichlorophenyl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (6g): The product was obtained as a yellow solid; m.p. 240–242 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 1.5 Hz, 1 H), 7.36 (d, J = 7.8 Hz, 1 H), 7.26–7.24 (m, 1 H), 7.16–7.10 (m, 2 H), 6.96 (td, J = 1.5, 7.8 Hz, 1 H), 6.86 (td, J = 1.2, 7.8 Hz, 1 H), 6.73 (dd, J = 0.6, 2.7 Hz, 1 H), 6.32 (t, J = 3.2 Hz, 1 H), 6.05 (s, 1 H), 5.83 (d, J = 2.72 Hz, 1 H), 4.38 (br. s, 1 H) ppm. ^{13}C (75 MHz, $CDCl_3$): 138.2, 134.8, 134.1, 133.2, 130.1, 129.2, 127.6, 126.8, 125.2, 124.8, 119.6, 115.7, 114.7, 114.5, 110.4, 106.0, 51.4 ppm. HRMS (ESI): calcd. for $C_{17}H_{12}Cl_2N_2$ [M + H]$^+$ 314.0378; found 314.0380.

4-[5-(3,4-Dichlorophenyl)furan-2-yl]-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (6h): The product was obtained as a light-yellow solid; m.p. 220–222 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60 (d, J = 1.2 Hz, 1 H), 7.52–7.46 (m, 3 H), 7.22–7.20 (m, 1 H), 6.96 (td, J = 7.8, 1.4 Hz, 1 H), 6.90–6.88 (m, 1 H), 6.78–6.50 (m, 1 H), 6.50 (dd, J = 1.2, 7.8 Hz, 1 H), 6.32 (t, J = 3.3 Hz, 1 H), 6.12 (d, J = 3.3 Hz, 1 H), 6.06 (d, J = 2.7 Hz, 1 H), 5.73 (s, 1 H), 4.4 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.1, 151.2, 134.6, 132.9, 130.9, 130.6, 130.5, 127.5, 125.9, 125.5, 124.8, 123.4, 122.8, 119.8, 115.8, 114.7, 110.3, 109.2, 107.2, 105.8, 49.3 ppm. HRMS (ESI): calcd. for $C_{21}H_{14}Cl_2N_2O$ [M + H]$^+$ 380.0483; found 380.0489.

4-(4-Fluorophenyl)-8-pyrrol-1-yl-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (6i): The product was obtained as a colourless solid; m.p. 150–152 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.47 (m, 2 H), 7.34 (d, J = 2.4 Hz, 1 H), 7.17–7.19 (m, 1 H), 6.98–7.10 (m, 5 H), 6.78 (d, J = 8.4 Hz, 1 H), 6.34 (t, J = 2.1 Hz, 2 H), 6.27 (t, J = 3.1 Hz, 1 H), 5.56–5.58 (m, 1 H), 5.53 (s, 1 H), 4.17 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.8, 134.0, 133.7, 129.9, 129.7, 129.5, 125.8, 119.7, 117.6, 115.8, 115.7, 115.4, 114.5, 110.7, 109.9, 108.4, 106.4, 55.5 ppm. HRMS (ESI): calcd. for $C_{21}H_{16}FN_3$ [M + H]$^+$ 329.1328; found 329.1333.

4-(2,4-Dichlorophenyl)-8-(1*H*-pyrrol-1-yl)-4,5-dihydropyrrolo[1,2-*a*]-quinoxaline (6j): The product was obtained as a light-yellow solid; m.p. 188–189 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 (s, 1 H), 7.36 (s, 1 H), 7.26–7.24 (m, 2 H), 7.15 (q, J = 8.7 Hz, 2 H), 7.02–6.97 (m, 2 H), 6.73 (d, J = 8.2 Hz, 1 H), 6.34 (m, 3 H), 6.06 (s, 1 H), 5.86 (s, 1 H), 4.43 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.9, 134.3, 133.8, 133.2, 132.8, 130.1, 129.3, 127.7, 126.9, 125.6, 119.7, 117.7, 116.1, 114.6, 111.0, 109.9, 108.3, 106.6, 51.5 ppm. HRMS (ESI): calcd. for $C_{21}H_{15}Cl_2N_3$ [M + H]$^+$ 379.0643; found 379.0645.

4-(2-Bromopyridin-3-yl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (6k): The product was obtained as a light-yellow solid; m.p. 145–148 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (t, J = 2.9 Hz, 1 H), 7.36–7.35 (m, 2 H), 7.26–7.25 (m, 1 H), 7.16–7.15 (m, 1 H), 6.99–6.98 (m, 1 H), 6.88–6.81 (m, 1 H), 6.73–6.72 (m, 1 H), 6.33 (t, J = 3.3 Hz, 1 H), 6.1 (s, 1 H), 5.89–5.88 (m, 1 H), 4.57 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.3, 142.3, 138.6, 137.8, 134.3, 126.2, 125.2, 124.9, 123.3, 119.7, 115.8, 114.6, 110.5, 106.3, 53.6 ppm. HRMS (ESI): calcd. for $C_{16}H_{12}BrN_3$ [M + H]$^+$ 326.1906; found 326.1909.

4-Ethyl-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (6l): The product was obtained as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20–7.17 (m, 1 H), 7.06–7.05 (m, 1 H), 6.85 (td, J = 7.8, 1.4 Hz, 1 H), 6.71 (td, J = 8.0, 1.4 Hz, 2 H), 6.65 (dd, J = 7.8, 0.9 Hz, 1 H), 6.22–6.20 (m, 1 H), 5.91–5.90 (m, 1 H), 4.29 (q, J = 1.8 Hz, 2 H), 3.2 (br. s, 1 H), 0.95 (t, J = 7.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.2, 129.7, 125.6, 124.7, 119.1, 115.7, 114.8, 114.2, 110.1, 104.0, 52.2, 27.1, 9.8 ppm. HRMS (ESI): calcd. for $C_{13}H_{14}N_2$ [M + H]$^+$ 198.2637; found 198.2639.

7-Methyl-6-phenyl-5,6-dihydroindolo[1,2-*a*]quinoxaline (6m): The product was obtained as a light-yellow solid; m.p. 148–150 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, J = 8.2 Hz, 1 H), 7.90 (t, J = 4.3 Hz, 1 H), 7.56 (d, J = 7.7 Hz, 1 H), 7.31–7.17 (m, 7 H), 6.95 (t, J = 4.3 Hz, 2 H), 6.75 (t, J = 4.5 Hz, 1 H), 5.60 (s, 1 H), 4.22 (br. s, 1 H), 2.03 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.7, 135.6, 133.3, 132.5, 130.6, 128.7, 127.8, 127.1, 123.6, 122.4, 120.3, 119.7, 118.8, 116.3, 116.1, 114.3, 111.7, 107.3, 55.0, 8.3 ppm. HRMS (ESI): calcd. for $C_{22}H_{18}N_2$ [M + H]$^+$ 310.1470; found 310.1479.

6-(4-Fluorophenyl)-7-methyl-5,6-dihydroindolo[1,2-*a*]quinoxaline (6n): The product was obtained as a light-yellow solid; m.p. 218–220 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (d, J = 7.9 Hz, 1 H), 7.91 (d, J = 3.8 Hz, 1 H), 7.57 (d, J = 6.8 Hz, 1 H), 7.30–7.22

(m, 4 H), 6.97 (d, J = 4.6 Hz, 4 H), 6.78 (s, 1 H), 5.68 (s, 1 H), 4.20 (br. s, 1 H), 2.03 (d, J = 2.7 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.3, 135.8, 134.3, 130.5, 128.9, 128.2, 126.8, 124.1, 121.8, 121.3, 120.5, 119.6, 118.5, 116.7, 114.8, 111.5, 108.4, 54.8, 7.9 ppm. HRMS (ESI): calcd. for $C_{22}H_{17}FN_2$ $[M + H]^+$ 328.1376; found 328.1380.

6-(4-Chlorophenyl)-7-methyl-5,6-dihydroindolo[1,2-*a*]quinoxaline (6o): The product was obtained as a light-yellow solid; m.p. 190–192 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, J = 8.2 Hz, 1 H), 7.91–7.89 (m, 1 H), 7.59 (d, J = 7.8 Hz, 1 H), 7.32 (td, J = 6.8, 1.3 Hz, 1 H), 7.24–7.21 (m, 3 H), 7.15 (d, J = 8.2 Hz, 2 H), 6.98–6.95 (m, 2 H), 6.77–6.74 (m, 1 H), 5.60 (s, 1 H), 2.06 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.4, 135.4, 133.9, 133.6, 132.3, 130.7, 129.1, 128.7, 127.5, 124.0, 122.9, 120.7, 120.7, 120.2, 119.1, 116.6, 116.5, 112.0, 107.4, 54.2, 8.3 ppm. HRMS (ESI): calcd. for $C_{22}H_{17}ClN_2$ $[M + H]^+$ 344.1080; found 344.1087.

6-(3-Chlorophenyl)-7-methyl-5,6-dihydroindolo[1,2-*a*]quinoxaline (6p): The product was obtained as a light-yellow solid; m.p. 168–170 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (d, J = 8.1 Hz, 1 H), 7.91–7.88 (m, 1 H), 7.59 (d, J = 7.5 Hz, 1 H), 7.33–7.15 (m, 5 H), 7.08 (d, J = 6.9 Hz, 1 H), 6.98–6.94 (m, 2 H), 6.77 (t, J = 4.5 Hz, 1 H), 5.66 (s, 1 H), 4.31 (br. s, 1 H), 2.07 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.7, 135.1, 134.6, 133.5, 131.8, 130.6, 130.1, 128.1, 127.3, 125.3, 123.8, 122.7, 120.5, 120.1, 119.0, 116.5, 116.3, 111.8, 107.6, 54.4, 8.4 ppm. HRMS (ESI): calcd. for $C_{22}H_{17}ClN_2$ $[M + H]^+$ 344.0924; found 344.0928.

6-(4-Chlorophenyl)-2-fluoro-7-methyl-5,6-dihydroindolo[1,2-*a*]-quinoxaline (6q): The product was obtained as a yellow solid; m.p. 190–192 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, J = 8.4 Hz, 1 H), 7.64–7.57 (m, 2 H), 7.33 (td, J = 1.2, 7.2 Hz, 1 H), 7.25–7.21 (m, 3 H), 7.15–7.12 (m, 2 H), 6.67 (dd, J = 1.2, 6.6 Hz, 2 H), 5.63 (s, 1 H), 4.19 (br. s, 1 H), 2.04 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.4, 139.8, 133.8, 131.9, 130.7, 129.0, 128.5, 127.9, 123.1, 120.9, 119.2, 116.7, 111.5, 109.9, 109.6, 108.1, 104.4, 104.0, 54.3, 8.3 ppm. HRMS (ESI): calcd. for $C_{22}H_{16}ClFN_2$ $[M + H]^+$ 362.0986; found 362.0996.

1,4-Bis(4,5-dihydropyrrolo[1,2-*a*]quinoxalin-4-yl)benzene (6r): The product was obtained as a yellow solid; m.p. 190–192 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.6 (d, J = 8.3 Hz, 1 H), 7.48–7.46 (m, 3 H), 7.33–7.31 (m, 2 H), 7.21–7.18 (m, 2 H), 6.95 (td, J = 8.7, 1.3 Hz, 2 H), 6.8 (td, J = 7.8, 0.9 Hz, 2 H), 6.73–6.71 (m, 2 H), 6.3–6.2 (m, 2 H), 5.56–5.53 (m, 2 H), 5.5 (s,2 H), 4.13 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.5, 136.0, 129.6, 128.1, 125.4, 124.6, 119.3, 115.3, 114.7, 114.3, 110.1, 105.8, 55.7 ppm. HRMS (ESI): calcd. for $C_{28}H_{22}N_4$ $[M + H]^+$ 414.1844; found 414.1848.

General Procedure for the Synthesis of Pyrrolo/Indolo-quinoxalines 7a–e, 7f–p and 7s–x and Imidazoquinoxalines 7q–r: To a well-stirred solution of aldehyde **5** (0.6 mmol), benzotriazole (1.0 equiv.) and 10 mol-% $AlCl_3$ in THF, 1-(2-aminophenyl)pyrrole or 2-(3-methylindol-1-yl)phenylamine (**4**; 0.5 mmol) was added. The reaction was stirred at room temperature for 8–10 h. The reaction mixture was extracted with ethyl acetate and water and the organic layer was washed with NaOH, brine, and dried with Na_2SO_4. The solvent was evaporated in vacuo and the solid obtained was purified by column chromatography (hexane/ethyl acetate) to afford the desired product in good yields.

4-Phenylpyrrolo[1,2-*a*]quinoxaline (7a): The product was obtained as a light-yellow solid; m.p. 118–120 °C. ^{1}H (400 MHz, $CDCl_3$): δ = 8.13 (d, J = 8 Hz, 1 H), 7.99–7.97 (m, 3 H), 7.80 (d, J = 7.3 Hz, 1 H), 7.50–7.40 (m, 5 H), 6.90 (t, J = 3 Hz, 1 H), 6.80 (t, J = 2.9 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4, 138.4, 136.2, 130.2, 129.8, 128.5, 127.4, 127.1, 125.3, 125.2, 114.5, 113.9, 113.6, 108.8 ppm. HRMS (ESI): calcd. for $C_{17}H_{12}N_2$ $[M + H]^+$ 244.1000; found 244.1002.

4-(4-Fluorophenyl)pyrrolo[1,2-*a*]quinoxaline (7b): The product was obtained as a light-yellow solid; m.p. 108–110 °C. ^{1}H NMR (300 MHz, $CHCl_3$): δ = 8.01 (d, J = 13.9 Hz, 4 H), 7.90 (d, J = 7.2 Hz, 1 H), 7.53–7.44 (m, 2 H), 7.25–7.20 (m, 2 H), 6.95–6.90 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.9, 153.2, 136.2, 134.6, 130.6, 130.2, 127.5, 127.1, 125.3, 115.5, 115.3, 114.7, 113.6, 108.5 ppm. HRMS (ESI): calcd. for $C_{17}H_{11}FN_2$ $[M + H]^+$ 262.0906; found 262.0912.

4-(4-Bromophenyl)pyrrolo[1,2-*a*]quinoxaline (7c): The product was obtained as a white solid; m.p. 104–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00–7.90 (m, 2 H), 7.90–7.80 (m, 3 H), 7.70–7.60 (m, 2 H), 7.50 (td, J = 8.7, 1.5 Hz, 1 H), 7.50 (td, J = 8.0, 1.4 Hz, 1 H), 6.94 (t, J = 3 Hz, 1 H), 6.93 (t, J = 2.9 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.0, 137.2, 136.0, 131.7, 130.2, 127.7, 127.0, 125.3, 124.9, 124.1, 114.8, 114.1, 113.6, 108.5 ppm. HRMS (ESI): calcd. for $C_{17}H_{11}BrN_2$ $[M + H]^+$ 322.0106; found 322.0108.

4-(4-Chlorophenyl)pyrrolo[1,2-*a*]quinoxaline (7d): The product was obtained as a pale-yellow solid; m.p. 110–112 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, J = 7.2 Hz, 2 H), 7.96 (d, J = 8.4 Hz, 2 H), 7.89 (d, J = 8.1 Hz, 1 H), 7.56–7.44 (m, 4 H), 6.97–6.90 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.1, 136.8, 136.1, 135.8, 130.2, 129.9, 128.8, 127.7, 125.4, 125.0, 114.8, 114.1, 113.6, 108.4 ppm. HRMS (ESI): calcd. for $C_{17}H_{11}ClN_2$ $[M + H]^+$ 278.0611; found 278.0616.

8-(1*H*-Pyrrol-1-yl)-4-*p*-tolylpyrrolo[1,2-*a*]quinoxaline (7e): The product was obtained as a light-yellow crystals; m.p. 174–176 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.13 (s, 1 H), 7.96 (s, 1 H), 7.86 (d, J = 7.5 Hz, 2 H), 7.77–7.75 (m, 1 H), 7.44 (d, J = 8.4 Hz, 1 H), 7.30 (d, J = 7.8 Hz, 1 H), 7.17 (d, J = 6.6 Hz, 3 H), 7.03 (s, 1 H), 6.91 (s, 1 H), 6.37 (m, 2 H), 2.4 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.8, 140.0, 139.5, 135.5, 134.2, 131.4, 129.3, 128.5, 127.7, 125.5, 119.6, 117.8, 114.5, 114.4, 111.2, 109.0, 105.1, 21.5 ppm. HRMS (ESI): calcd. for $C_{22}H_{17}N_3$ $[M + H]^+$ 323.1422; found 323.1426.

7-Methyl-6-phenylindolo[1,2-*a*]quinoxaline (7f): The product was obtained as a yellow solid; m.p. 94–96 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.48 (d, J = 8.2 Hz, 2 H), 8.01 (d, J = 7.8 Hz, 1 H), 7.90 (d, J = 8.1 Hz, 1 H), 7.25–7.63 (m, 9 H), 2.05 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.6, 139.8, 136.2, 135.9, 133.1, 132.5, 131.2, 130.1, 130.0, 129.6, 128.8, 128.3, 128.1, 125.3, 124.5, 123.6, 122.0, 121.7, 120.5, 114.2, 110.7, 11.2 ppm. HRMS (ESI): calcd. for $C_{22}H_{16}N_2$ $[M + H]^+$ 308.1313; found 308.1323.

6-(4-Fluorophenyl)-7-methylindolo[1,2-*a*]quinoxaline (7g): The product was obtained as a greenish-yellow solid; m.p. 112–114 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.49 (d, J = 7.7 Hz, 2 H), 7.99 (d, J = 7.6 Hz, 1 H), 7.91 (d, J = 7.9 Hz, 1 H), 7.21–7.66 (m, 8 H), 2.09 (t, J = 19.8 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.5, 135.6, 131.6, 130.5, 130.1, 128.4, 127.7, 126.5, 125.8, 124.8, 123.8, 123.6, 122.1, 121.1, 120.4, 115.6, 115.4, 114.4, 110.5, 11.3 ppm. HRMS (ESI): calcd. for $C_{22}H_{15}FN_2$ $[M + H]^+$ 326.1219; found 326.1226.

6-(3-Chlorophenyl)-7-methylindolo[1,2-*a*]quinoxaline (7h): The product was obtained as a pale-yellow solid; m.p. 114–116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43–8.41 (m, 2 H), 7.99 (dd, J = 7.7, 1.3 Hz, 1 H), 7.88 (dd, J = 8.2, 0.9 Hz, 1 H), 7.64 (t, J = 1.4 Hz, 1 H), 7.57–7.56 (m, 3 H), 7.52–7.50 (m, 2 H), 7.48–7.44 (m, 1 H),

7.39 (td, J = 5.9, 0.9 Hz, 1 H), 2.08 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.9, 141.1, 135.4, 134.4, 131.9, 130.4, 130.1, 129.7, 129.3, 128.8, 128.5, 126.8, 125.2, 124.8, 123.8, 122.1, 120.7, 114.34, 114.32, 110.6, 11.2 ppm. HRMS (ESI): calcd. for $C_{22}H_{15}ClN_2$ $[M + H]^+$ 342.0924; found 342.0928.

7-Methyl-6-*p*-tolylindolo[1,2-*a*]quinoxaline (7i): The product was obtained as a pale-yellow solid; m.p. 118–120 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.48 (d, J = 8.4 Hz, 2 H), 8.00 (dd, J = 7.8, 1.5 Hz, 1 H), 7.90 (d, J = 8.1 Hz, 1 H), 7.60–7.51 (m, 4 H), 7.47–7.41 (m, 2 H), 7.39–7.32 (m, 2 H), 2.47 (s, 3 H), 2.1 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.8, 139.2, 136.8, 135.8, 132.0, 130.5, 130.3, 130.1, 129.1, 128.5, 128.1, 125.9, 124.6, 123.1, 122.0,120.7, 114.4, 114.3, 110.8, 21.5, 11.3 ppm. HRMS (ESI): calcd. for $C_{23}H_{18}N_2$ $[M + H]^+$ 322.1470; found 322.1470.

6-(3-Bromophenyl)-7-methylindolo[1,2-*a*]quinoxaline (7j): The product was obtained as a pale-yellow solid; m.p. 102–104 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.49 (dd, J = 3.4, 8.4 Hz, 2 H), 7.99 (d, J = 7.5 Hz, 1 H), 7.92 (d, J = 8.1 Hz, 1 H), 7.81 (s, 1 H), 7.69–7.58 (m, 4 H), 7.49–7.39 (m, 3 H), 2.11 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.0, 141.4, 135.5, 132.0, 131.7, 130.6, 130.2, 130.0, 128.6, 12.7.3, 125.5, 125.0, 123.9, 122.5, 122.2, 120.8, 114.4, 110.7, 11.3 ppm. HRMS (ESI): calcd. for $C_{22}H_{15}BrN_2$ $[M + H]^+$ 386.0419; found 386.0427.

7-Methyl-6-[4-(trifluoromethyl)phenyl]indolo[1,2-*a*]quinoxaline (7k): The product was obtained as a white solid; m.p. 220–224 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, J = 6 Hz, 2 H), 7.90 (d, J = 8.1 Hz, 1 H), 7.80 (d, J = 8.1 Hz, 1 H), 7.70 (d, J = 8hz, 4 H), 7.54–7.52 (m, 2 H), 7.40 (t, J = 7.4 Hz, 1 H), 7.36 (t, J = 7.4 Hz, 1 H), 2.00 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.9, 142.9, 135.4, 134.7, 132.1, 130.5, 130.2, 130.2, 129.1, 128.7, 125.5, 125.4, 125.0, 123.9, 122.3, 120.8, 114.4, 114.4, 110.6, 11.3 ppm. HRMS (ESI): calcd. for $C_{23}H_{15}F_3N_2$ $[M + H]^+$ 376.1187; found 376.1187.

6-(4-Bromophenyl)-7-methylindolo[1,2-*a*]quinoxaline (7l): The product was obtained as a yellow solid; m.p. 200–202 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.48 (dd, J = 3.4, 7.7 Hz, 2 H), 7.99 (dd, J = 1.1, 7.8 Hz, 1 H), 7.91 (d, J = 8 Hz, 1 H), 7.69 (d, J = 8.3 Hz, 2 H), 7.60 (t, J = 7.4 Hz, 2 H), 7.54 (d, J = 8.2 Hz, 2 H), 7.49 (t, J = 7.6 Hz, 1 H), 7.41 (t, J = 7.8 Hz, 1 H), 2.12 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.6, 138.7, 135.8, 132.3, 131.8, 130.7, 130.5, 130.4, 130.3, 128.7, 125.6, 125.1, 124.1, 123.8, 122.4, 121.0, 114.6, 110.3, 11.7 ppm. HRMS (ESI): calcd. for $C_{22}H_{15}BrN_2$ $[M + H]^+$ 386.0419; found 386.0425.

6-(4-Chlorophenyl)-2-fluoro-7-methylindolo[1,2-*a*]quinoxaline (7m): The product was obtained as a pale-yellow solid; m.p. 220–222 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.37 (d, J = 8.7 Hz, 1 H), 8.16 (dd, J = 2.4, 8.1 Hz, 1 H), 7.96–7.89 (m, 2 H), 7.64–7.46 (m, 6 H), 7.10 (td, J = 2.7, 5.7 Hz, 1 H), 2.09 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.3, 137.6, 135.3, 132.0, 131.8, 131.5, 131.3, 130.2, 125.0, 124.8, 122.4, 120.7, 113.9, 111.6, 110.9, 110.7, 101.7, 101.4, 11.2 ppm. HRMS (ESI): calcd. for $C_{22}H_{14}ClFN_2$ $[M + H]^+$ 360.0830; found 360.0839.

6-[4-(Trifluoromethyl)phenyl]indolo[1,2-*a*]quinoxaline (7n): The product was obtained as a pale-yellow solid; m.p. 140–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (d, J = 8 Hz, 2 H), 8.10 (d, J = 8.1 Hz, 2 H), 8.03 (d, J = 8.1 Hz, 1 H), 7.80 (d, J = 8.1 Hz, 1 H), 7.78 (d, J = 8 Hz, 2 H), 7.60 (td, J = 8.7 Hz, 1 H), 7.50 (td, J = 8.1 Hz, 1 H), 7.40 (td, J = 3.7 Hz, 2 H), 7.20 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.6, 139.8, 135.9, 134.6, 133.0, 130.5, 130.1, 130.0, 129.9, 129.5, 129.0, 128.7, 128.6, 126.7, 124.5, 124.2, 122.7, 122.7, 114.6, 114.5, 102.2 ppm. HRMS (ESI): calcd. for $C_{22}H_{13}F_3N_2$ $[M + H]^+$ 362.1031; found 362.1036.

9-Methoxy-6-[4-(trifluoromethyl)phenyl]indolo[1,2-*a*]quinoxaline (7o): The product was obtained as a pale-yellow solid; m.p. 200–205 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, J = 8 Hz, 1 H), 8.30 (d, J = 9.4 Hz, 1 H), 8.10 (d, J = 8.1 Hz, 2 H), 8.01 (d, J = 7.4 Hz, 1 H), 7.70 (d, J = 8.1 Hz, 2 H), 7.60 (td, J = 7.4, 1.4 Hz, 1 H), 7.40 (t, J = 7.1 Hz, 1 H), 7.20 (d, J = 2 Hz, 1 H), 7.20 (d, J = 14.7 Hz, 1 H), 7.05 (s, 1 H), 3.8 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.8, 154.1, 141.9, 136.0, 131.6, 131.1, 130.7, 130.2, 129.9, 129.2, 129.0, 128.8, 125.6, 125.6, 124.2, 116.1, 115.6, 114.3, 102.2, 101.5, 55.5 ppm. HRMS (ESI): calcd. for $C_{23}H_{15}F_3N_2O$ $[M + H]^+$ 392.1136; found 392.1140.

6-(3-Chlorophenyl)-9-methoxyindolo[1,2-*a*]quinoxaline (7p): The product was obtained as a yellow solid; m.p. 190–192 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, J = 7.4 Hz, 1 H), 8.36 (d, J = 8.7 Hz, 1 H), 8.04 (d, J = 8 Hz, 1 H), 7.9 (d, J = 1.3 Hz, 1 H), 7.8 (dt, J = 7.4, 2 Hz, 1 H), 7.6 (td, J = 7.1, 1.3 Hz, 1 H), 7.51–7.48 (m, 2 H), 7.44–7.40 (m, 1 H), 7.2 (d, J = 2.7 Hz, 1 H), 7.2 (d, J = 8.7 Hz, 1 H), 7.12 (s, 1 H), 3.9 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.7, 154.5, 140.0, 135.6, 134.2, 130.6, 130.4, 130.2, 130.0, 129.9, 129.8,129.3, 128.7, 128.4, 126.7, 124.1, 115.9, 115.5, 114.3, 102.2, 101.6, 55.6 ppm. HRMS (ESI): calcd. for $C_{22}H_{15}ClN_2O$ $[M + H]^+$ 358.0873; found 358.0876.

3-Methyl-4-(4-nitrophenyl)imidazo[1,5-*a*]quinoxaline (7r): The product was obtained as a pale-yellow solid; m.p. 126–128 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.60 (s, 1 H), 8.31 (d, J = 8.3 Hz, 2 H), 8.00 (d, J = 8.7 Hz, 2 H), 7.67–7.65 (m, 1 H), 7.45–7.39 (m, 1 H), 7.27–7.22 (m, 1 H), 6.96 (s, 1 H), 2.29 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.6, 149.5, 144.0, 140.9, 138.2, 137.5, 131.8, 129.7, 128.4, 127.9, 125.0, 124.1, 119.2, 116.8, 13.6 ppm. HRMS (ESI): calcd. for $C_{17}H_{12}N_4O_2$ $[M + H]^+$ 304.0960; found 304.0960.

7-Methyl-6-(3-nitrophenyl)-2-(4-phenylpiperazin-1-yl)indolo[1,2-*a*]-quinoxaline (7s): The product was obtained as a orange solid; m.p. 248–250 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.55 (t, J = 2 Hz, 1 H), 8.45–8.37 (m, 2 H), 8.03–7.98 (m, 2 H), 7.93–7.88 (m, 2 H), 7.75–7.50 (m, 1 H), 7.64–7.62 (m, 1 H), 7.52–7.47 (m, 1 H), 7.35–7.34 (m, 2 H), 7.09–7.03 (m, 3 H), 6.97–6.94 (m, 1 H), 3.64 (t, J = 5 Hz, 4 H), 3.49–3.46 (m, 4 H), 2.10 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.7, 150.9, 148.1, 141.4, 134.9, 131.8, 131.6, 130.9, 130.5, 129.4, 129.3, 128.9, 125.4, 124.5, 124.2, 123.8, 122.3, 120.7, 120.3, 116.4, 114.2, 112.8, 112.2, 109.2, 100.3, 49.3, 48.9, 11.6 ppm. HRMS (ESI): calcd. for $C_{32}H_{27}N_5O_2$ $[M + H]^+$ 513.2165; found 513.2168.

6-(4-Fluorophenyl)-7-methyl-2-(4-phenylpiperazin-1-yl)indolo-[1,2-*a*]quinoxaline (7t): The product was obtained as a yellowish orange crystals; m.p. 254–256 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.44 (d, J = 8.7 Hz, 1 H), 8.00 (d, J = 2.4 Hz, 1 H), 7.94–7.90 (m, 2 H), 7.66–7.59 (m, 2 H), 7.49 (t, J = 7.2 Hz, 1 H), 7.39–7.33 (m, 2 H), 7.28–7.21 (m, 3 H), 7.10–7.05 (m, 3 H), 6.96 (t, J = 7.2 Hz, 1 H), 3.63 (t, J = 2.7 Hz, 4 H), 3.48 (t, J = 4.5 Hz, 4 H), 2.10 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.0, 151.4, 151.1, 138.2, 135.1, 131.7, 131.5, 130.7, 130.6, 129.3, 129.2, 126.0, 124.3, 122.05, 120.6, 120.3, 116.4, 115.6, 115.3, 114.2, 112.2, 109.7, 100.6, 49.4, 49.1, 11.3 ppm. HRMS (ESI): calcd. for $C_{32}H_{27}FN_4$ $[M + H]^+$ 486.2220; found 486.2226.

6-(4-Chlorophenyl)-7-methyl-2-(4-phenylpiperazin-1-yl) indolo[1,2-*a*]quinoxaline (7u): The product was obtained as a yellow solid; m.p. 272–275 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.43 (d, J = 8.7 Hz, 1 H), 7.99 (d, J = 1.2 Hz, 1 H), 7.94–7.89 (m, 2 H), 7.64–7.58 (m, 3 H), 7.54–7.47 (m, 3 H), 7.35 (t, J = 7.8 Hz, 2 H), 7.09–7.05 (m, 3 H), 6.95 (t, J = 7.2 Hz, 1 H), 3.63 (t, J = 4.6 Hz, 4 H), 3.48 (t, J = 5.1 Hz, 4 H), 2.11 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ

= 152.8, 151.4, 151.1, 138.3, 135.0, 131.7, 131.5, 130.8, 130.6, 130.2, 129.3, 129.1, 128.6, 125.8, 124.3, 122.1, 120.6, 120.3, 116.4, 114.2, 112.2, 109.6, 100.6, 49.4, 49.1, 11.4 ppm. HRMS (ESI): calcd. for $C_{32}H_{27}ClN_4$ [M + H]$^+$ 502.1924; found 502.1928.

2-{4-[Bis(4-fluorophenyl)methyl]piperazin-1-yl}-6-(4-bromophenyl)-7-methylindolo[1,2-*a*]quinoxaline (7v): The product was obtained as a yellow solid; m.p. 264–266 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.33 (d, J = 8.4 Hz, 1 H), 7.89–7.83 (m, 3 H), 7.65 (d, J = 8.4 Hz, 2 H), 7.55–7.40 (m, 8 H), 7.05–6.99 (m, 5 H), 4.31 (s, 1 H), 3.46 (s, 4 H), 2.65 (s, 4 H), 2.10 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.3, 131.7, 131.6, 130.7, 130.5, 129.3, 129.2, 129.1, 128.7, 128.1, 127.8, 125.9, 125.8, 124.0, 123.4, 122.1, 115.7, 115.5, 114.9, 114.1, 111.8, 109.5, 100.0, 51.7, 48.9, 29.7, 11.4 ppm. HRMS (ESI): calcd. for $C_{39}H_{31}BrF_2N_4$ [M + H]$^+$ 672.1700; found 672.1708.

2-{4-[Bis(4-fluorophenyl)methyl]piperazin-1-yl}-7-methyl-6-(4-nitrophenyl)indolo[1,2-*a*]quinoxaline (7w): The product was obtained as a pale-yellow solid; m.p. 269–271 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.33 (d, J = 8.4 Hz, 1 H), 7.88–7.83 (m, 3 H), 7.58–7.41 (m, 10 H), 7.05–6.96 (m, 5 H), 4.31 (s, 1 H), 3.46 (s, 4 H), 2.65 (s, 4 H), 2.08 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.0, 161.0, 152.6, 151.4, 137.9, 135.0, 131.7, 130.7, 130.2, 129.3, 128.8, 128.6, 125.8, 124.2, 122.0, 120.6, 115.7, 115.4, 114.1, 111.8, 109.5, 99.9, 78.0, 51.7, 48.9, 29.7, 11.4 ppm. HRMS (ESI): calcd. for $C_{39}H_{31}F_2N_5O_2$ [M + H]$^+$ 639.2417; found 639.2420.

2-{4-[Bis(4-fluorophenyl)methyl]piperazin-1-yl}-6-(4-fluorophenyl)-7-methylindolo[1,2-*a*]quinoxaline (7x): The product was obtained as a yellow solid; m.p. 258–260 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.34 (d, J = 8.4 Hz, 1 H), 7.87 (t, J = 9.3 Hz, 3 H), 7.60 (d, J = 8.4 Hz, 2 H), 7.5 (t, J = 7.5 Hz, 1 H), 7.47–7.41 (m, 4 H), 7.21 (t, J = 8.7 Hz, 3 H), 7.05–6.96 (m, 5 H), 4.32 (s, 1 H), 3.47 (t, J = 4.5 Hz, 4 H), 2.66 (t, J = 4.5 Hz, 4 H), 2.09 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.2, 159.7, 148.7, 146.3, 145.1, 138.3, 137.6, 135.4, 131.7, 130.7, 129.3, 124.8, 120.5, 115.7, 115.4, 115.2, 114.8, 112.7, 111.8, 109.5, 105.1, 100.4, 80.2, 51.7, 48.9, 29.7, 11.6 ppm. HRMS (ESI): calcd. for $C_{39}H_{31}F_3N_4$ [M + H]$^+$ 612.2501; found 612.2507.

General Procedure for the Synthesis of Indolo- and Pyrrolo[1,2-*a*]quinoxalinones (9a–d): To a well-stirred solution of 1-(2-aminophenyl) pyrrole or 2-(3-methylindol-1-yl)phenylamine (1.0 mmol) in toluene (2.0 mL), benzotriazole (1.0 equiv.) and 2-carboxybenzaldehyde (1.0 equiv.) were added followed by addition of a catalytic amount of TsOH (10 mol-%). The reaction was heated to reflux in a Dean–Stark apparatus for 2–4 h until no more starting material was detectable by TLC analysis. The reaction mixture was extracted with ethyl acetate and water and the organic layer was washed with brine and dried with Na_2SO_4. The solvent was removed in vacuo and the crude material was purified by column chromatography (hexane/ethyl acetate) using silica mesh (100–200). The desired product was recrystallied from diethyl ether.

Isoindolo[1,2-*c*]pyrrolo[1,2-*a*]quinoxalin-10(14b*H*)-one (9a): The product was obtained as a pale-yellow solid; m.p. 220–224 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.20–8.17 (m, 1 H), 7.98 (d, J = 7.5 Hz, 1 H), 7.86 (d, J = 7.8 Hz, 1 H), 7.72 (t, J = 7.5 Hz, 1 H), 7.59 (t, J = 7.5 Hz, 1 H), 7.53–7.50 (m, 1 H), 7.30–7.25 (m, 3 H), 6.35–6.30 (m, 2 H), 5.81 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.7, 145.0, 136.1, 134.3, 130.8, 128.6, 128.4, 128.3, 127.1, 125.5, 123.5, 101.0, 71.5 ppm. HRMS (ESI): calcd. for $C_{18}H_{12}N_2O$ [M + H]$^+$ 272.0950; found 272.0954.

14*b*-Methylisoindolo[1,2-*c*]pyrrolo[1,2-*a*]quinoxalin-10(14b*H*)-one (9b): The product was obtained as a yellow solid; m.p. 228–230 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04–8.01 (m, 1 H), 7.86 (d, J = 7.8 Hz, 1 H), 7.76 (d, J = 7.8 Hz, 1 H), 7.63 (t, J = 7.2 Hz, 1 H), 7.49–7.41 (m, 2 H), 7.24–7.16 (m, 2 H), 7.10–7.09 (m, 1 H), 6.19 (t, J = 3.3 Hz, 1 H), 6.11–6.10 (m, 1 H), 1.51 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.6, 147.1, 132.8, 130.6, 130.0, 128.9, 128.8, 125.9, 124.8, 124.7, 124.5, 124.1, 122.2, 116.0, 115.0, 110.6, 104.0, 61.6, 28.0 ppm. HRMS (ESI): calcd. for $C_{19}H_{14}N_2O$ [M + H]$^+$ 286.1106; found 286.1109.

16-Methylindolo[1,2-*a*]isoindolo[1,2-*c*]quinoxalin-11(15b*H*)-one (9c): The product was obtained as a pale-yellow solid; m.p. 140–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (dd, J = 1.3, 7.8 Hz, 1 H), 8.06–7.97 (m, 4 H), 7.72 (td, J = 1.4, 6.4 Hz, 1 H), 7.64–7.57 (m, 2 H), 7.38 (td, J = 1.3, 7.8 Hz, 1 H), 7.31–7.28 (m, 2 H), 7.27–7.22 (m, 1 H), 5.9 (s, 1 H), 2.39 (s, 3 H) ppm. ^{13}C NMR (100 MHz): δ = 164.7, 138.6, 133.7, 133.1, 131.3, 130.7, 130.2, 129.3, 127.9, 127.2, 126.3, 125.6, 124.7, 123.9, 123.6, 122.5, 120.9, 119.3, 117.5, 111.1, 108.5, 58.2, 9.8 ppm. HRMS (ESI): calcd. for $C_{23}H_{16}N_2O$ [M + H]$^+$ 336.1263; found 336.1267.

15b,16-Dimethylindolo[1,2-*a*]isoindolo[1,2-*c*]quinoxalin-11(15b*H*)-one (9d): The product was obtained as a yellow solid; m.p. 192–194 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04–7.95 (m, 5 H), 7.72 (t, J = 7.8 Hz, 1 H), 7.58 (t, J = 7.3 Hz, 1 H), 7.54 (d, J = 5.6 Hz, 1 H), 7.40 (t, J = 6.8 Hz, 1 H), 7.30–7.26 (m, 2 H), 7.18 (t, J = 7 Hz, 1 H), 2.35 (s, 3 H), 1.65 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.6, 144.5, 133.3, 132.6, 131.8, 131.5, 130.6, 130.5, 129.1, 126.0, 125.6, 125.0, 124.7, 124.4, 123.9, 123.5, 120.9, 119.1, 117.1, 111.1, 107.2, 63.6, 25.7, 10.1 ppm. HRMS (ESI): calcd. for $C_{24}H_{18}N_2O$ [M + H]$^+$ 350.4125; found 350.1479.

General Procedure for the Synthesis of Compounds 10–11: To a vial was added 4-(4-bromophenyl)pyrrolo[1,2-*a*]quinoxaline (1.0 mmol), boronic acid (1.2 equiv.), $[Pd(PPh_3)_2Cl_2]$ (10 mol-%), K_2CO_3 (2.5 equiv.), and DMF/H_2O (4:1, 2.0 mL). The solution was flushed with argon and then heated to 80 °C for 1 h until TLC revealed complete conversion of the starting material. The solution was allowed to cool and diluted with H_2O and then extracted with EtOAc. The combined organic layers were dried with Na_2SO_4, concentrated, and purified by column chromatography to afford the corresponding product.

4-(4′-Methoxybiphenyl-4-yl)pyrrolo[1,2-*a*]quinoxaline (10): The product was obtained as a white solid; m.p. 187–190 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.06 (d, J = 7.5 Hz, 4 H), 7.90 (d, J = 8.1 Hz, 1 H), 7.73 (d, J = 7.8 Hz, 2 H), 7.60 (d, J = 8.4 Hz, 2 H), 7.50–7.40 (m, 2 H), 7.07–7.01 (m, 3 H), 6.90 (s, 1 H), 3.90 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.3, 154.0, 142.2, 136.7, 136.2, 133.0, 130.1, 129.0, 128.2, 127.0, 126.8, 125.3, 125.2, 114.6, 114.3, 114.0, 113.6, 108.6, 55.3 ppm. HRMS (ESI): calcd. for $C_{24}H_{18}N_2O$ [M + H]$^+$ 350.1419; found 350.1421.

4-[4′-(Methylthio)biphenyl-4-yl]pyrrolo[1,2-*a*]quinoxaline (11): The product was obtained as a off-white solid; m.p. 173–175 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10–8.00 (m, 3 H), 7.99–7.98 (m, 1 H), 7.88–7.86 (m, 1 H), 7.73 (d, J = 8 Hz, 2 H), 7.60 (d, J = 8 Hz, 2 H), 7.51–7.45 (m, 2 H), 7.34 (d, J = 8.8 Hz, 2 H), 7.04 (m, 1 H), 6.90 (t, J = 3.3 Hz, 1 H), 2.53 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.8, 141.8, 138.1, 137.2, 136.2, 130.2, 129.1, 127.4, 127.1, 127.0, 126.9, 126.8, 125.2, 114.6, 113.9, 113.6, 108.5, 15.7 ppm. HRMS (ESI): calcd. for $C_{24}H_{18}N_2S$ [M + H]$^+$ 366.1191; found 366.1193.

General Procedure for the Synthesis of Compounds 12 and 13: To a vial was added 4-(4-bromophenyl)pyrrolo[1,2-*a*]quinoxalin (1.0 mmol), acrylate (1.2 equiv.), $[Pd(PPh_3)_2Cl_2]$ (10 mol-%), K_3PO_4 (2.5 equiv.), and DMF (2.0 mL). The solution was flushed with argon, and then heated to 120 °C for 4 h until TLC revealed

complete conversion of the starting material. The solution was allowed to cool and diluted with H_2O and then extracted with EtOAc. The combined organic layers were dried with Na_2SO_4, concentrated, and purified by column chromatography to afford the corresponding product.

Ethyl (*E*)-3-[4-(Pyrrolo[1,2-*a*]quinoxalin-4-yl)phenyl]acrylate (12): The product was obtained as a white solid; m.p. 89–91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05–8.01 (m, 4 H), 7.90 (d, J = 8 Hz, 1 H), 7.80 (d, J = 16.1 Hz, 1 H), 7.70 (d, J = 8 Hz, 2 H), 7.50 (td, J = 8 Hz, 1 H), 7.49 (td, J = 9.5 Hz, 1 H), 7.01–6.99 (m, 1 H), 6.90 (t, J = 3 Hz, 1 H), 6.53 (d, J = 16.1 Hz, 1 H), 4.29 (q, J = 8 Hz, 2 H), 1.35 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 153.3, 143.8, 140.0, 136.1, 135.7, 130.2, 129.1, 128.2, 127.7, 127.1, 125.3, 125.1, 119.1, 114.7, 114.1, 113.6, 108.4, 60.6, 14.3 ppm. HRMS (ESI): calcd. for $C_{22}H_{18}N_2O_2$ $[M + H]^+$ 342.1368; found 342.1371.

Methyl (*E*)-3-[4-(Pyrrolo[1,2-*a*]quinoxalin-4-yl)phenyl]acrylate (13): The product was obtained as a pale-yellow solid; m.p. 102–104 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, J = 7.8 Hz, 4 H), 7.90 (d, J = 7.8 Hz, 1 H), 7.80–7.70 (m, 3 H), 7.50–7.40 (m, 2 H), 7.03 (d, J = 18.3 Hz, 2 H), 6.50 (d, J = 15.9 Hz, 1 H), 3.80 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.3, 153.3, 144.2, 140.2, 136.1, 135.7, 130.3, 129.2, 128.3, 127.8, 127.2, 125.4, 125.1, 119.7, 114.8, 114.1, 113.7, 108.5, 51.8 ppm. HRMS (ESI): calcd. for $C_{21}H_{16}N_2O_2$ $[M + H]^+$ 328.1212; found 328.1212.

Supporting Information (see footnote on the first page of this article): Copies of ^{1}H and ^{13}C NMR spectra of all new compounds.

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[1] S. Antoniotti, E. Dunach, *Tetrahedron Lett.* **2002**, *43*, 3971–3973.

[2] S. Alleca, P. Corona, M. Lorigo, G. Paglietti, R. Loddo, V. Mascia, B. Busonera, P. La Colla, *Farmaco* **2003**, *58*, 639–650, and references cited therein.

[3] a) M. Patel, R. J. Mc Hugh, B. C. Cordova, R. M. Klabe, S. Erickson-Vitanen, G. L. Trainor, J. D. Rodger, *Bioorg. Med. Chem. Lett.* **2000**, *10*, 1729–31; b) J. Guillon, P. Dallemagne, B. Pfeiffer, P. Renard, D. Manechez, A. Kervran, S. Rault, *Eur. J. Med. Chem.* **1998**, *33*, 293–308; c) K. S. Kim, L. Qian, J. E. Bird, K. E. J. Dickinson, S. Moreland, T. R. Schaeffer, T. L. Waldron, C. L. Delaney, H. N. Weller, A. V. Miller, *J. Med. Chem. Soc.* **1951**, *73*, 5687–5699.

[4] a) E. J. Jacobsen, L. S. Stelzer, K. L. Belonga, D. B. Carter, W. B. Im, V. H. Sethy, A. H. Tang, P. F. VonVoigtlander, J. D. Petke, *J. Med. Chem.* **1996**, *39*, 3820–3836; b) D. D. Davey, P. W. Erhardt, E. H. Cantor, S. S. Greenberg, W. R. Ingebretsen, J. Wiggins, *J. Med. Chem.* **1991**, *34*, 2671–2677; c) V. Colotta, L. Cecchi, D. Catarzi, G. Filacchioini, C. Martini, P. Tacchi, A. Lucacchini, *Eur. J. Med. Chem.* **1995**, *30*, 133–139.

[5] a) G. Sakata, K. Makino, Y. Kurasawa, *Heterocycles* **1998**, *27*, 2481–2515; b) L. E. Seitz, W. J. Suling, R. C. Reynolds, *J. Med. Chem.* **2002**, *45*, 5604–5606; c) A. Gzit, H. App, G. Mcmohan, J. Chen, A. Levtzki, F. D. Bohmer, *J. Med. Chem.* **1996**, *39*, 2170–2177; d) M. M. Ali, M. M. F. Ismail, M. S. A. El-Gaby, M. A. Zahran, Y. A. Ammar, *Molecules* **2000**, *5*, 864–873; e) G. Campiani, V. Nacci, F. Corelli, M. Anzini, *Synth. Commun.* **1991**, *21*, 1567–1576.

[6] a) J. C. Crossley, L. A. Johnston, *Chem. Commun.* **2002**, 1122–1123; b) C. Escude, C. H. Nguyen, S. Kukreti, Y. Janin, J. S. Sun, E. Bisagni, T. Garestier, C. Helene, *Proc. Natl. Acad. Sci. USA* **1998**, *95*, 3591–3596; c) L. W. Deady, A. J. Kaye, G. J. Finlay, B. C. Baguley, W. A. Denny, *J. Med. Chem.* **1997**, *40*, 2040–2046; d) A. Pictet, T. Spengler, *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 2030–2036.

[7] a) B. Kundu, D. Sawant, P. Partani, A. P. Kesarwani, *J. Org. Chem.* **2005**, *70*, 4889–4892; b) N. Srinivasan, A. Ganesan, *Chem. Commun.* **2003**, 916–917; c) K. Manabe, D. Nobutou, S. Kobayashi, *Bioorg. Med. Chem.* **2005**, *13*, 5154–5158; d) S. W. Youn, *J. Org. Chem.* **2006**, *71*, 2521–2523; e) S. Tussetschläger, A. Baro, S. Lashat, W. Frey, *Eur. J. Org. Chem.* **2007**, 5590–5602.

[8] a) C. Venkatesh, B. Singh, P. K. Mahata, H. Ila, H. Junjappa, *Org. Lett.* **2005**, *7*, 2169–2172; b) F. Juncai, L. Yang, M. Qinghua, L. Bin, *Synth. Commun.* **1998**, *28*, 193–196; c) S. A. Raw, C. D. Wilfred, R. J. K. Taylor, *Chem. Commun.* **2003**, 2286–2287; d) G. Kaupp, M. R. Naimi-Jamal, *Eur. J. Org. Chem.* **2002**, *8*, 1368–1373; e) P. Chen, J. C. Barrish, E. Iwanowicz, J. Lin, M. S. Bednarz, B. C. Chen, *Tetrahedron Lett.* **2001**, *42*, 4293–4311; f) B. C. G. Soderberg, J. M. Wallace, J. Tamariz, *Org. Lett.* **2002**, *4*, 1339–1342; g) M. Suginome, S. Collet, Y. Ito, *Org. Lett.* **2002**, *4*, 351–354; h) R. Mukhopadhyay, N. G. Kundu, *Tetrahedron Lett.* **2000**, *41*, 9927–9930; i) R. A. Bunce, D. M. Herron, M. L. Ackerman, *J. Org. Chem.* **2000**, *65*, 2847–2850; j) B. K. Banik, I. Banik, L. Hackfeld, F. F. Becker, *Heterocycles* **2002**, *56*, 467–470; k) S. Goswami, A. K. Adak, *Chem. Lett.* **2003**, *32*, 678–679.

[9] a) O. A. Attanasi, L. De Crescentini, P. Filippone, F. Mantellini, S. Santeusanio, *Synlett* **2003**, 1183–1185; b) K. Tanaka, H. Takahashi, K. Takimoto, M. Sugita, K. Mitsuhashi, *J. Heterocycl. Chem.* **1992**, *29*, 771–786; c) K. H. Popat, K. S. Nimavat, K. M. Thaker, H. S. Joshi, *J. Indian Chem. Soc.* **2003**, *80*, 709–710; d) K. V. S. Rao, M. Subrahmanyam, *Chem. Lett.* **2002**, 234–235; e) J. T. Reeves, D. R. Fandrick, Z. Tan, J. J. Song, H. Lee, N. K. Yee, C. H. Senanayake, *J. Org. Chem.* **2010**, *75*, 992–994.

[10] a) S. Raines, S. Y. Chai, F. P. Palopoli, *J. Heterocycl. Chem.* **1976**, *13*, 711–716; b) X. C. Zhang, W. Y. Huang, *Tetrahedron Lett.* **1997**, *38*, 4827–4830 and refrences thereinc) S. Veeraraghavan, F. D. Popp, *J. Heterocycl. Chem.* **1981**, *18*, 775–777; d) H. S. Kim, Y. Kurasawa, C. Yoshii, M. Masuyama, A. Takada, Y. Okamoto, *J. Heterocycl. Chem.* **1990**, *27*, 1115–1117; e) G. W. H. Cheeseman, M. Rafiq, *J. Chem. Soc. C* **1971**, 2732–2734.

[11] a) A. Atfah, M. Y. Abu-Shuheil, J. Hill, *Tetrahedron* **1990**, *46*, 6483–6500; b) C. S. Yi, S. Y. Yun, *J. Am. Chem. Soc.* **2005**, *127*, 17000–17006; c) B. Kundu, D. Sawant, R. Chhabra, *J. Comb. Chem.* **2005**, *7*, 317–321.

[12] A. R. Katritzky, X. F. Lan, J. Z. Yang, O. V. Denisko, *Chem. Rev.* **1998**, *98*, 409–548.

[13] a) A. R. Katritzky, A. K. Verma, H. He, R. Chandra, *J. Org. Chem.* **2003**, *68*, 4938–4940; b) R. K. Tiwari, D. Singh, J. Singh, V. Yadav, A. K. Phatak, R. Dabur, A. Chhillar, R. Singh, G. L. Sharma, R. Chandra, A. K. Verma, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 413–416; c) R. K. Tiwari, D. Singh, J. Singh, A. Chhillar, R. Chandra, A. K. Verma, *Eur. J. Med. Chem.* **2006**, *41*, 40–49; d) R. K. Tiwari, J. Singh, D. Singh, A. K. Verma, R. Chandra, *Tetrahedron* **2005**, *61*, 9513–9518; e) P. Chaudhary, R. Kumar, A. K. Verma, D. Singh, J. Yadav, A. Chillar, G. L. Sharma, R. Chandra, *Bioorg. Med. Chem.* **2006**, *14*, 1819–1826; f) A. K. Verma, J. Singh, V. K. Sankar, R. Chaudhary, R. Chandra, *Tetrahedron Lett.* **2007**, *48*, 4207–4210; g) A. K. Verma, J. Singh, R. Chaudhary, *Tetrahedron Lett.* **2007**, *48*, 7199–7202.

[14] a) A. K. Verma, T. Keshwarwani, J. Singh, V. Tandon, R. C. Larock, *Angew. Chem.* **2009**, *121*, 1158; *Angew. Chem. Int. Ed.*

2009, *48*, 1138–1143; b) A. K. Verma, T. Aggarwal, V. Rustagi, R. C. Larock, *Chem. Commun.* **2010**, *46*, 4064–4066; c) A. K. Verma, V. Rustagi, T. Aggarwal, A. P. Singh, *J. Org. Chem.* **2010**, *75*, 7691–7703; d) A. K. Verma, M. Joshi, V. P. Singh, *Org. Lett.* **2011**, *13*, 1630–1633; e) V. Rustagi, T. Aggarwal, A. K. Verma, *Green Chem.* **2011**, *13*, 1640–1643; f) A. K. Verma, S. P. Shukla, J. Singh, V. Rustagi, *J. Org. Chem.* **2011**, *76*, 5670–5684.

[15] a) S. Butini, R. Budriesi, M. Hamon, E. Morelli, S. Gemma, M. Brindisi, G. Borrelli, E. Novellino, I. Fiorini, P. Ioan, A. Chiarini, A. Cagnotto, T. Mennini, C. Fracasso, S. Caccia, G. Campiani, *J. Med. Chem.* **2009**, *52*, 6946–6950; b) R. A. Smits, M. Adami, E. P. Istyastono, O. P. Zuiderveld, C. M. E. V. Dam, F. J. J. de Kanter, A. Jongejan, G. Coruzzi, R. Leurs, I. J. P. de Esch, *J. Med. Chem.* **2010**, *53*, 2390–2400.

[16] a) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483; b) A. Suzuki, *J. Organomet. Chem.* **1999**, *576*, 147–168.

[17] R. F. Heck, *Org. React.* **1982**, *27*, 345–390.

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