Monatsh Chem
https://doi.org/10.1007/s00706-018-2142-x

ORIGINAL PAPER

Highly selective synthesis of mono- and bis-4,5-dihydropyrrolo[1,2-*a*]quinoxalines catalyzed by sustainable supported acidic ionic liquid in water media

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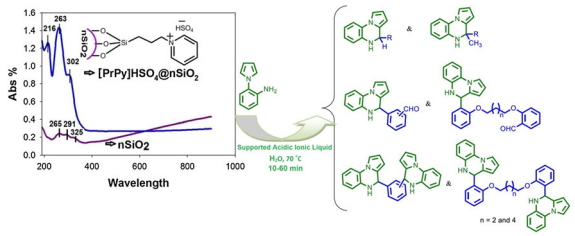
Received: 10 October 2017 / Accepted: 1 January 2018

Abstract Preparation of substituted as well as the selective synthesis of mono- and bis-4,5-dihydropyrrolo[1,2-*a*]quinoxalines using a highly efficient, sustainable, and reusable supported acidic ionic liquid is reported. The reaction method is ecofriendly and has the advantages of mild conditions, green solvent (H_2O), short reaction times, and a reusable acidic catalyst.

Graphical abstract



Keywords Heterogeneous catalysis · Heterocycles · 4,5-Dihydropyrrolo[1,2-*a*]quinoxalines · Green chemistry · Selective synthesis

Introduction

Quinoxaline is an essential category of nitrogen-containing heterocycles, which represent a broad series of pharmacological properties [1]. They were also employed as constructing blocks for the preparation of organic semiconductors, dyes, and macrocyclic receptors [2, 3]. Similarly, pyrrole is usually the core fragment of various natural and unnatural compounds with vital properties, both in materials science and pharmacology [4, 5]. The integration of quinoxaline and pyrrole into a single molecule exhibits new or improved biological properties [6, 7]. Particularly, 4,5-dihydropyrrolo[1,2-*a*]quinoxaline derivatives (Fig. 1) have been described as antifungal [8], cannabinoid type 1 receptor (CB_1R) antagonists [6, 9], estrogen receptor modifier [6, 10], and Nogo receptor modifier effects [6, 11]. Due to a wide range of applications, the development of simple methods for preparation of 4,5-dihydropyrrolo[1,2-*a*]quinoxalines is essential. A Pictet–Spengler-type reaction in the presence of acidic catalyst [12] of 1-(2-aminophenyl)pyrrole through an aldehyde is the most common method for synthesis of these heterocycles. Among the acid catalysts, Brønsted acid such as hydrochloric acid [13], acetic acid [14], sulfamic acid [15], *p*-dodecylbenzenesulfonic acid [16], *p*-toluenesulfonic acid [17], and $AlCl_3$ [18] were reported for the production of 4,5-dihydropyrrolo[1,2-*a*]quinoxalines.

Recently, acidic ionic liquid (AIL) became much significant due to useful characteristics such as high catalytic efficiency stability in water and air, and easy separation [19–21]. Despite extensive applications of AILs, the chemical companies prefer to use a heterogeneous catalyst system because of the easy recovery and reusability of them; thus, using supported acidic ionic liquids (SAILs) is extremely desirable. In this system, the acidic ionic liquid

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s00706-018-2142-x) contains supplementary material, which is available to authorized users.

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Published online: 02 February 2018

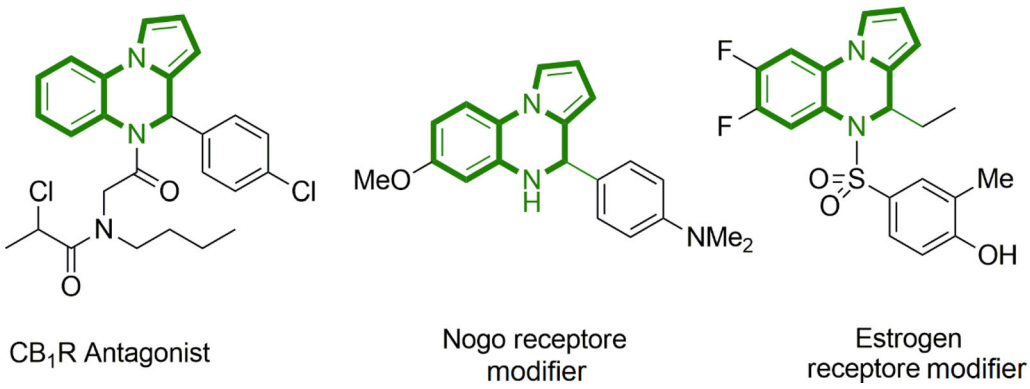


Fig. 1 Some biologically active 4,5-dihydropyrrolo[1,2-*a*]quinoxalines

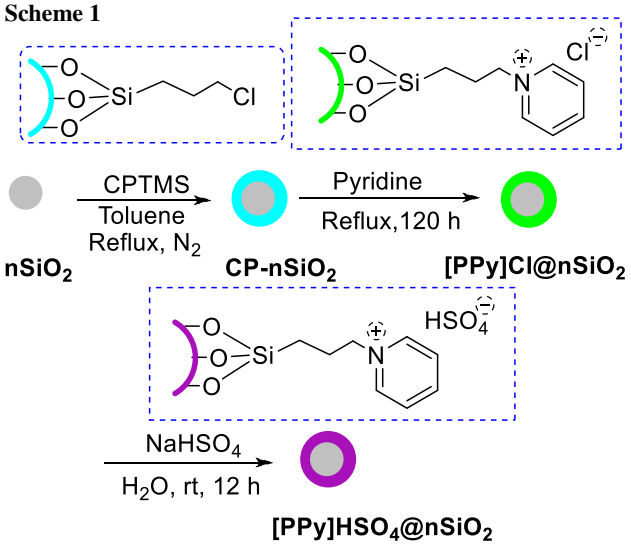
is immobilized on the surface of a high porous and area support material [22–26]. Motivated by the unique properties and many applications of nanostructures supported ILs [27–30], herein, we describe a convenient method for the selective synthesis of mono- and bis-4,5-dihydropyrrolo[1,2-*a*]quinoxalines in the presence of a highly efficient, green, and recoverable SAIL catalyst.

Results and discussion

Preparation and characterization of [PPy]HSO_4@*n*SiO_2

Scheme 1 illustrates the procedure of preparation of acidic supported ionic liquid ([PPy]HSO_4@*n*SiO_2) by covalent addition of the IL onto the silica nanoparticle surface. The process of catalyst preparation was investigated with

Scheme 1



the technical analysis such as FT-IR spectroscopy, elemental analysis, UV–Vis (DSR), SEM, and EDX. The sulfur content of [PPy]HSO_4@*n*SiO_2 catalyst was measured 0.52 by CHNS analysis. Based on this value, the amount of IL which is supported on the *n*SiO_2 is about 0.16 mmol per gram of catalyst.

The IR spectra of every preparation steps of catalyst (Scheme 1) were shown in Fig. 2a. The FT-IR spectrum of [PPy]HSO_4@*n*SiO_2 catalyst showed a characteristic band at 1637 cm^{-1} (C=N) and several other bands at 3050, 2902, and 1436 cm^{-1}, which are due to C–H stretching and vibrational of the pyridine ring and alkyl chain [31]. In addition, the characteristic band at 1267 cm^{-1} (S–O–H) was observed [32], but the characteristic S=O band (1100–1180 cm^{-1}) [32] cannot be determined due to overlapping by Si-O band.

The diffuse reflectance UV–Vis spectra of pure *n*SiO_2 and [PPy]HSO_4@*n*SiO_2 are shown in Fig. 2b. The UV–Vis spectrum of catalyst showed three significant absorption bands at 216, 263, and 302 nm. The strong and sharp absorption band at 263 and medium band at 216 nm appeared, relating to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition of C=N, respectively, resulting from the attachment of pyridine to *n*SiO_2 [33]. The band at 302 nm was related to hydrogen sulfate anion [34].

The SEM images of the *n*SiO_2 and [PPy]HSO_4@*n*SiO_2 catalyst (Fig. 3) demonstrated that the morphology of the two samples is diverse. Moreover, the energy dispersive X-ray (EDX) analysis of [PPy]HSO_4@*n*SiO_2 indicates the presence of all the expected elements C, N, S, O, and Si (Fig. 4). The results characterize that the IL has effectively been immobilized on the *n*SiO_2 surface.

Preparation of 4,5-dihydropyrrolo[1,2-*a*]quinoxaline derivatives

In an initial study on the synthesis of 4,5-dihydropyrrolo[1,2-*a*]quinoxaline, we screened the reaction

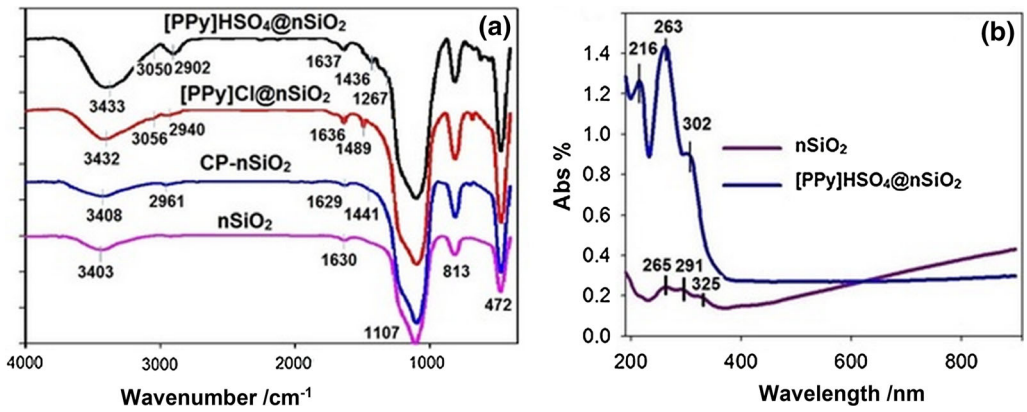


Fig. 2 Characterization of catalyst: **a** FT-IR and **b** UV–Vis

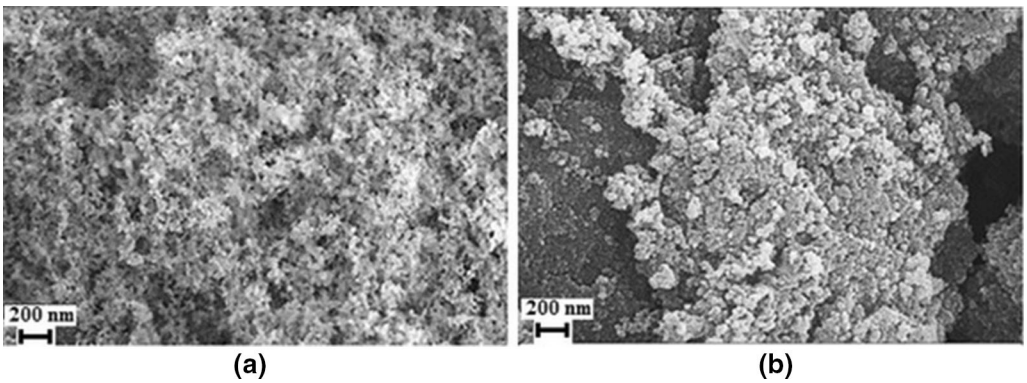


Fig. 3 SEM images of **a** the $n\text{SiO}_2$ and **b** $[\text{PPy}]\text{HSO}_4@n\text{SiO}_2$

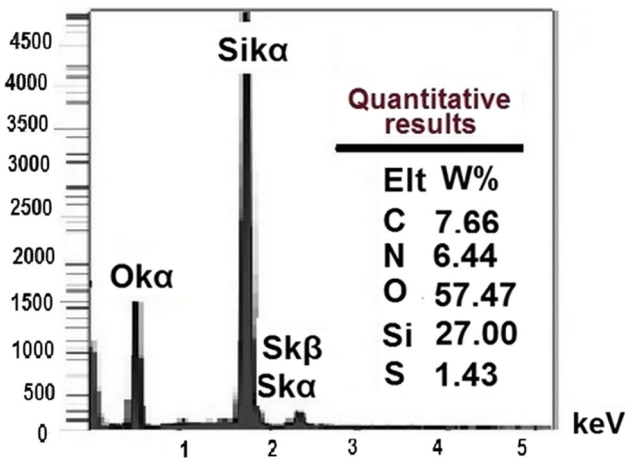
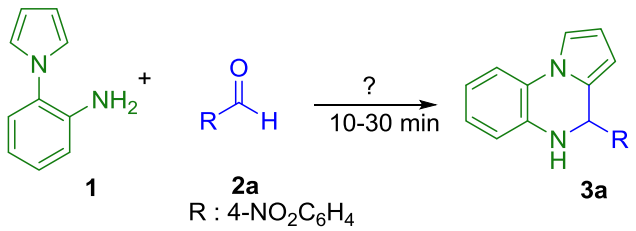


Fig. 4 EDX analysis of $[\text{PPy}]\text{HSO}_4@n\text{SiO}_2$

parameters such as solvent, the catalyst amount, and temperature in the model reaction of 1-(2-aminophenyl)pyrrole (**1**), 4-nitrobenzaldehyde (**2a**), and $[\text{PPy}]\text{HSO}_4@n\text{SiO}_2$ catalyst (Table 1, entries 1–14). The results exhibited that 50 mg of the $[\text{PPy}]\text{HSO}_4@n\text{SiO}_2$ (0.8 mol%) efficiently catalyzed the reaction at 70 °C in water media to give the desired product **3a**. It was also found that decreasing temperature lower than 70 °C reduced the yield of the product. To show the effectiveness of $[\text{PPy}]\text{HSO}_4@n\text{SiO}_2$ catalyst, we have performed this reaction in the presence of other catalysts and ILs like as $ZnCl_2$, $H_3PW_{12}O_{40}$, $[\text{PPy}]\text{Cl}@n\text{SiO}_2$, [PPy]Cl (propylpyridinium chloride), and $[\text{PPy}]\text{HSO}_4$ (propylpyridinium hydrogen sulfate). The results are listed in Table 1, which clearly indicate that $[\text{PPy}]\text{HSO}_4@n\text{SiO}_2$ is the suitable catalyst for the proposed transformation.

Verma et al. reported using $AlCl_3$ as a catalyst in the same reaction produced a mixture of 4,5-dihydropyrrolo[1,2-*a*]quinoxaline and pyrrolo[1,2-*a*]quinoxaline (oxidized form). Specially, the yield of pyrrolo[1,2-*a*]quinoxaline increased by the passage of time [18]. Accordingly, we performed the modal reaction for 24 h in the presence of our catalyst, but the oxidized product has not been produced (Table 1, entry 15).

Table 1 Optimization of the reaction conditions



1 **2a** R : 4-$NO_2C_6H_4$ **3a**

Entry	Catalyst/mol%	Solvent	Temp./°C	Yield/%[a]
1	[PPy]HSO_4@*n*SiO_2 (0.8)	Benzene	Reflux	70
2	[PPy]HSO_4@*n*SiO_2 (0.8)	THF	Reflux	60
3	[PPy]HSO_4@*n*SiO_2 (0.8)	CH_2Cl_2	Reflux	65
4	[PPy]HSO_4@*n*SiO_2 (0.8)	$CHCl_3$	Reflux	75
5	[PPy]HSO_4@*n*SiO_2 (0.8)	EtOH	Reflux	95
6	[PPy]HSO_4@*n*SiO_2 (0.8)	EtOH:H_2O	Reflux	99
7	[PPy]HSO_4@*n*SiO_2 (0.8)	H_2O	Reflux	99
8	[PPy]HSO_4@*n*SiO_2 (1.0)	H_2O	Reflux	99
9	[PPy]HSO_4@*n*SiO_2 (0.7)	H_2O	Reflux	85
10	[PPy]HSO_4@*n*SiO_2 (0.6)	H_2O	Reflux	60
11	[PPy]HSO_4@*n*SiO_2 (0.8)	H_2O	80	99
12	[PPy]HSO_4@*n*SiO_2(0.8)	H_2O	70	99
13	[PPy]HSO_4@*n*SiO_2 (0.8)	H_2O	50	45
14	[PPy]HSO_4@*n*SiO_2 (0.8)	H_2O	25	Trace
15[b]	[PPy]HSO_4@*n*SiO_2 (0.8)	H_2O	70	99
16	–	H_2O	70	Trace
17	$ZnCl_2$ (0.8)	H_2O	70	70
18	$H_3PW_{12}O_{40}$ (0.8)	H_2O	70	65
19	*n*SiO_2 (50 mg)	H_2O	70	Trace
20	[PPy]Cl@*n*SiO_2 (50 mg)	H_2O	70	20
21	[PPy]Cl (0.8)	H_2O	70	15
22	[PPy]HSO_4 (0.8)	H_2O	70	60
23	HOAc (0.8)	H_2O	70	48

Model reaction: 1-(2-aminophenyl)pyrrol (**1**, 1.0 mmol), 4-nitrobenzaldehyde (**2a**, 1.0 mmol), 5 cm^3 solvent

[a]Isolated yield

[b]The reaction was continued for 24 h on air

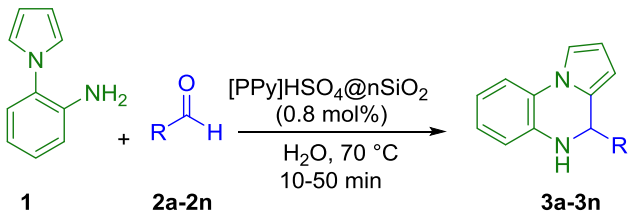
Production of 4,5-dihydropyrrolo[1,2-*a*]quinoxaline using [PPy]HSO_4@*n*SiO_2 catalyst

The efficiency of [PPy]HSO_4@*n*SiO_2 catalyst for production of various 4,5-dihydropyrrolo[1,2-*a*]quinoxaline was considered and the results are summarized in Table 2. Various aromatic aldehydes, including alkoxy, halo, nitro, or even cinnamic groups, were well reacted with 1-(2-aminophenyl)pyrrole in the presence of our catalyst. It was useful that the desired products achieved from the reaction of heterocyclic and polycyclic aldehydes (**3j**–**3m**). Aliphatic aldehyde such as 1-heptanal was used and produced the desired product (**3n**). Many of these compounds have been synthesized and reported for the first time. In addition, the selectivity of this method was also investigated in a binary mixture of 4-nitrobenzaldehyde and 1-heptanal. The aromatic aldehyde was converted to the corresponding 4,5-dihydropyrrolo[1,2-*a*]quinoxaline in 95% yield, whereas trace amount of aliphatic aldehyde has been converted to desired product (Scheme 2).

Selective synthesis of mono- and bis-4,5-dihydropyrrolo[1,2-*a*]quinoxaline

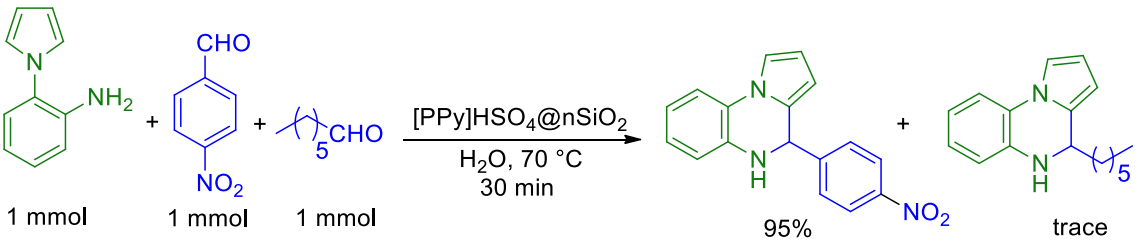
For the first time, selective synthesis of mono- and bis-4,5-dihydropyrrolo[1,2-*a*]quinoxaline from dialdehydes could

Table 2 Synthesis of substituted 4,5-dihydropyrrolo[1,2-*a*]quinoxalines **3**



Entry	R	Product	Time/min	Yield/%[a]
1	4-$NO_2C_6H_4$	**3a**	10	99
2	3-$NO_2C_6H_4$	**3b**	10	98
3	2-$NO_2C_6H_4$	**3c**	10	98
4	4-ClC_6H_4	**3d**	20	96
5	2,6-$(Cl)_2C_6H_3$	**3e**	20	97
6	4-$MeOC_6H_4$	**3f**	15	98
7	3-$MeOC_6H_4$	**3g**	15	97
8	3,4-$(MeO)_2C_6H_3$	**3h**	15	99
9	Cinnamyl	**3i**	30	90
10	Anthracen-9-yl	**3j**	45	95
11	Thiophen-3-yl	**3k**	15	98
12	1*H*-Indol-3-yl	**3l**	35	85
13	6-Chloro-4-oxo-4*H*-chromen-3-yl	**3m**	40	98
14	Hexyl	**3n**	25	85

Scheme 2



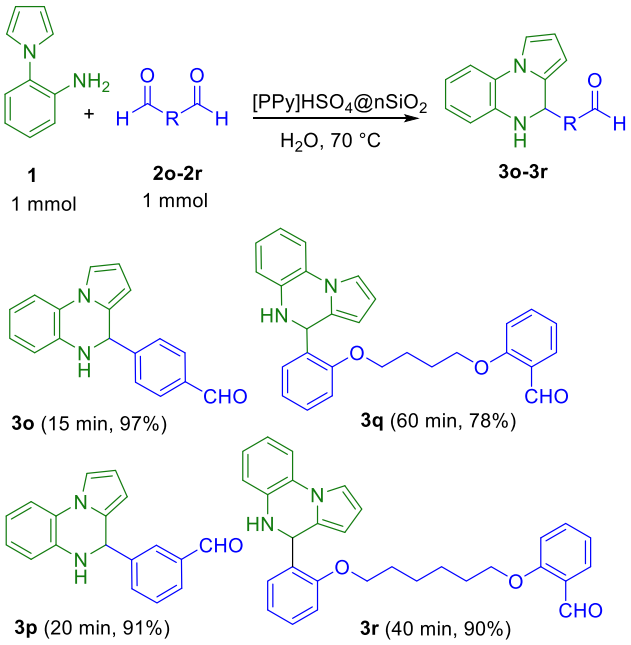
be achieved with this procedure. In this respect, using a 1:1 molar ratio of 1-(2-aminophenyl)pyrrole and dialdehydes through [PPy]HSO_4@*n*SiO_2, only one formyl group reacted selectively and the corresponding mono-4,5-dihydropyrrolo[1,2-*a*]quinoxalines **3o–3r** were obtained in good yields (Scheme 3). The remaining formyl group can be modified to some other relevant functional groups and produced various of 4,5-dihydropyrrolo[1,2-*a*]quinoxalines.

Whereas using a 2:1 molar ratio of 1-(2-aminophenyl)pyrrole and dialdehydes in the same reaction conditions proceeded efficiently and produced the corresponding bis-4,5-dihydropyrrolo[1,2-*a*]quinoxalines in high yields (Scheme 4). The use of dialdehydes with alkyl chains between two formyl groups such as **2q** and **2r** [35] produced highly flexible bis-4,5-dihydropyrrolo[1,2-*a*]quinoxalines, which can be used as ligands for complexation with metals and various ions.

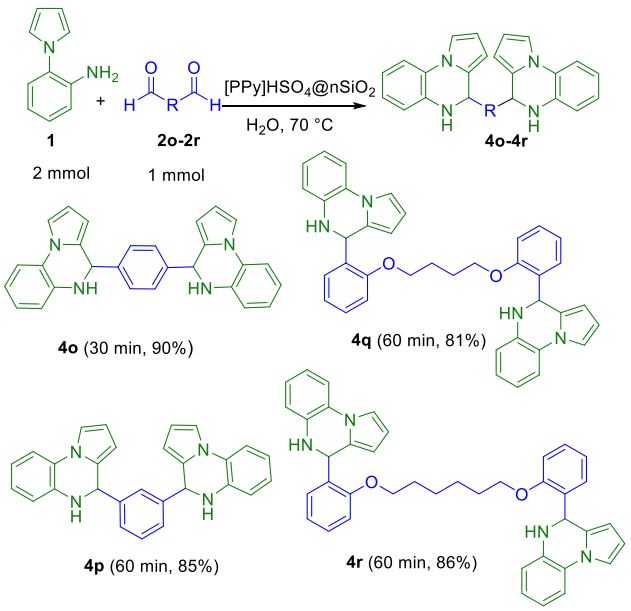
Production of 4-methyl-4,5-dihydropyrrolo[1,2-*a*]quinoxalines

Encouraged by these successes, we next turned our attention to examine the activity of this catalytic system for the production of 4-methyl-4,5-dihydropyrrolo[1,2-*a*]quinoxalines from acetophenone derivatives. As shown in Table 3, different acetophenones with alkyl, halo, nitro substituent were smoothly reacted with 1-(2-aminophenyl)pyrrole and afforded the desired products in moderate-to-high yields.

Scheme 3



Scheme 4



Recyclability of the catalyst

The reusability and resumption of catalyst, which is essential from the economic and environmental point of views, was tested in the reaction of 1-(2-aminophenyl)pyrrole and 4-nitrobenzaldehyde. In each cycle, the catalyst was recovered by simple filtration, rinsed with acetone, dried, and then reused for the next run. The catalyst could be cycled for at least six times without noticeable loss of its activity (Table 4).

A plausible mechanism for the formation of quinoxalines in the presence of $[PPy]HSO_4@nSiO_2$ catalyst is illustrated in Scheme 5. First, the carbonyl group is activated by the catalyst to afford **A**, which upon reaction with 1-(2-aminophenyl)pyrrol gives **B**. Then, elimination of water from **B** in the presence of the catalyst affords **C**. Finally, acid catalyzed cyclization of **C** followed by intramolecular hydrogen shift affords the desired product and releases the catalyst for the next cycle.

Conclusion

To sum up, $[PPy]HSO_4@nSiO_2$ is prepared and used as a catalyst for the convenient synthesis of substituted as well as mono- and bis-4,5-dihydropyrrolo[1,2-*a*]quinoxalines. In addition, 4-methyl-4,5-dihydropyrrolo[1,2-*a*]quinoxalines were produced by the reaction of 1-(2-aminophenyl)pyrrole with acetophenone derivatives. This method presents advantages such as mild conditions, green solvent (H_2O), high yields, short reaction times, and a recyclable acidic catalyst.

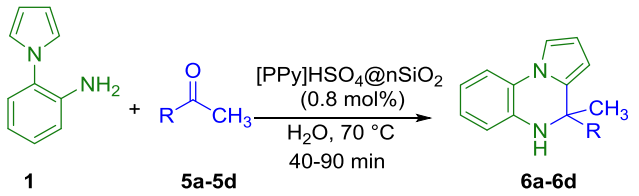
Experimental

The chemicals used in this work were purchased from Fluka and Merck chemical companies. The dialdehydes **2r** and **2q** were prepared according to the reported procedure [35]. Melting points were determined with a Stuart Scientific SMP2 apparatus. FT-IR spectra were recorded on a Nicolet-Impact 400D instrument in the range of 400–4000 cm^{-1}. ^1H and ^{13}C NMR spectra (400 and 100 MHz) were recorded on a Bruker Avance 400 MHz spectrometer using $CDCl_3$ solvent. Elemental analysis was done on LECO, CHNS-932 analyzer. Scanning electron microscopy field emission-scanning electron microscope (FE-SEM) measurements were performed on a Hitachi S-4700. The UV–Vis diffuse reflectance spectra of the samples were recorded in a JASCO V-670 spectrophotometer.

Synthesis of propylpyridinium hydrogen sulfate supported on silica nanoparticles ($[PPy]HSO_4@nSiO_2$)

A combination of 8.0 cm^3 (3-chloropropyl)trimethoxysilane (CPTMS) and 3.0 g activated $nSiO_2$ [25] in 50.0 cm^3 toluene (anhydrous) was refluxed for 24 h. The reaction

Table 3 Synthesis of 4-methyl-4,5-dihydropyrrolo[1,2-*a*]quinoxalines **6**



1 **5a-5d** **6a-6d**

Entry	R	Product	Time/min	Yield/%[a]
1	4-$NO_2C_6H_4$	**6a**	40	98
2	4-ClC_6H_4	**6b**	60	95
3	4-CyclohexylC_6H_4	**6c**	90	82
4	4-MeC_6H_4	**6d**	90	70

[a]Isolated yield

Table 4 Reusability of the [PPy]HSO_4@*n*SiO_2 catalyst in the synthesis of **3a**

Run	1	2	3	4	5	6
Yield/%[a]	99	98	95	93	93	91

Reaction conditions: 1-(2-aminophenyl)pyrrol (**1**, 1.0 mmol), 4-nitrobenzaldehyde (**2a**, 1.0 mmol) and [PPy]HSO_4@*n*SiO_2 catalyst (0.8 mol%), 70 °C

[a]Isolated yield

mixture was separated by filtration and the CP-*n*SiO_2 was washed with toluene using a Soxhlet apparatus and dried at 100 °C. In continue, a mixture of 2 g CP-*n*SiO_2 and 10.0 cm^3 pyridine was refluxed for 120 h. The solid material ([PPy]Cl@*n*SiO_2) was filtered, washed (toluene and ethanol), and then dried at 70 °C. Finally, a mixture of 2 g [PPy]Cl@*n*SiO_2 and 2.74 g sodium hydrogen sulfate (20 mmol) in 30.0 cm^3 distilled water was reacted at 25 °C for 12 h. The [PPy]HSO_4@*n*SiO_2 was separated, washed with distilled water, and dried at 70 °C.

Production of substituted 4,5-dihydropyrrolo[1,2-*a*]quinoxaline derivatives

A mixture of 1-(2-aminophenyl)pyrrole (1.0 mmol), carbonyl compound (1.0 mmol), and 50 mg [PPy]HSO_4@*n*SiO_2 (0.8 mol%) in water was stirred at 70 °C. The advancement of the reaction was checked by TLC (eluent: petroleum ether-EtOAc, 10:1). At the end 10 cm^3 EtOH were added, the catalyst was separated by filtration and washed with 10 cm^3 EtOH. The filtrate containing the crude product in a mixture of H_2O and EtOH, was evaporated. The pure product was most often obtained without any purification. If necessary, the product was recrystallized from petroleum ether-EtOAc.

4-(4-Nitrophenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline (**3a**)

Yield: 99% (288.28 mg); m.p.: 107–109 °C (106–108 °C [18]).

4-(3-Nitrophenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline (**3b**, $C_{17}H_{13}N_3O_2$)

Yield: 98% (285.38 mg); m.p.: 98–101 °C; FT-IR (KBr): $\bar{\nu}$ = 3316, 3040, 2818, 1609, 1521, 1485, 1348, 1291, 1159, 1089, 919, 744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.56 (dd, J = 2.4, 1.2 Hz, 1H, Ar-H), 5.68 (s, 1H, CH), 6.25 (t, J = 3.2 Hz, 1H, Ar-H), 6.80 (dd, J = 8.0, 1.2 Hz, 1H, Ar-H), 6.87 (td, J = 7.0, 1.2 Hz, 1H, Ar-H), 6.99 (td, J = 7.0, 1.2 Hz, 1H, Ar-H), 7.22 (t, J = 1.4 Hz, 1H, Ar-H), 7.35 (d, J = 8.0 Hz, 1H, Ar-H), 7.50–7.58 (m, 2H, Ar-H), 7.79 (d, J = 7.6 Hz, 1H, Ar-H), 8.19 (dt, J = 8.0, 1.2 Hz, 1H, Ar-H), 8.35 (s, 1H, NH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.55, 106.30, 110.43, 113.88, 114.85, 115.53, 120.00, 122.89, 123.34, 124.02, 124.93, 128.33, 129.68, 130.76, 134.10, 135.29, 143.73 ppm.

4-(2-Nitrophenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline (**3c**, $C_{17}H_{13}N_3O_2$)

Yield: 98% (285.43 mg); m.p.: 112–115 °C; FT-IR (KBr): $\bar{\nu}$ = 3424, 3135, 3067, 2864, 1722, 1609, 1525, 1477, 1351, 1146, 1097, 752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.59 (dd, J = 4.0, 1.2 Hz, 1H, CH), 6.88 (dd, J = 4.0, 1.2 Hz, 1H, Ar-H), 7.50 (td, J = 7.8, 1.4 Hz, 1H, Ar-H), 7.60 (td, J = 7.2, 1.4 Hz, 1H, Ar-H), 7.67–7.72 (m, 1H, Ar-H), 7.77–7.78 (m, 3H, Ar-H), 7.93 (dd, J = 8.2, 1.2 Hz, 1H, Ar-H), 8.00–8.04 (m, 3H, Ar-H), 8.18 (s, 1H, NH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 60.03, 107.29, 109.86, 113.88, 114.34, 115.13, 119.04, 124.81, 125.55, 128.18, 130.19, 130.26, 131.30, 133.27, 135.77, 141.18, 149.59 ppm.

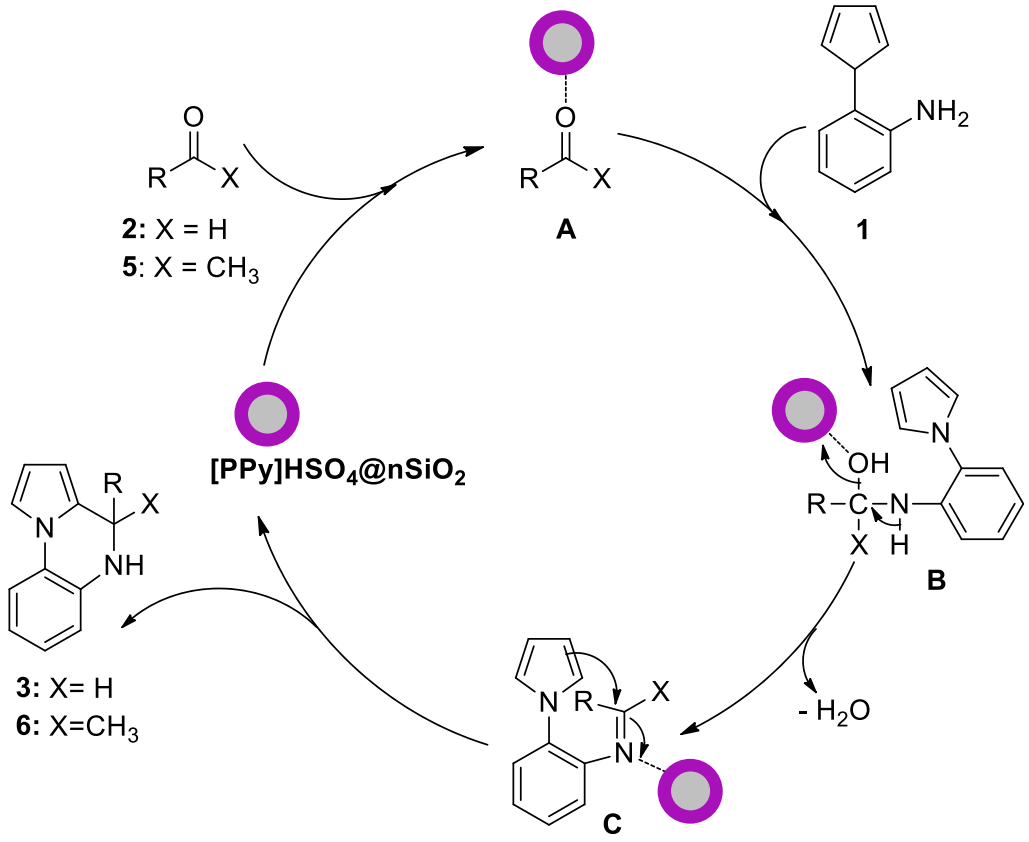
4-(4-Chlorophenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline (**3d**)

Yield: 96% (269.48 mg); m.p.: 103–107 °C (105–107 °C [15]).

4-(2,6-Dichlorophenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline (**3e**, $C_{17}H_{12}Cl_2N_2$)

Yield: 97% (305.70 mg); m.p.: 137–139 °C; FT-IR (KBr): $\bar{\nu}$ = 3312, 3134, 2829, 1720, 1609, 1588, 1513, 1463, 1332, 1291, 1154, 1045, 857, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 4.39 (s, 1H, NH), 5.84–5.85 (m, 1H, Ar-H), 6.06 (s, 1H, CH), 6.33 (t, J = 3.2 Hz, 1H, Ar-H), 6.73 (dd, J = 7.8, 1.2 Hz, 1H, Ar-H), 6.87 (td, J = 7.6, 1.6 Hz, 1H, Ar-H), 6.97 (td, J = 7.6, 1.2 Hz, 1H, Ar-H), 7.12–7.17 (m, 2H, Ar-H), 7.26 (dd, J = 3.2, 1.6 Hz, 1H, Ar-H), 7.37 (dd, J = 8.0, 1.2 Hz, 1H, Ar-H), 7.44 (d, J = 2.0 Hz, 1H, Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.48, 106.13, 110.43, 114.62, 114.73, 115.72, 119.66, 120.74, 124.90, 126.88, 127.65, 129.29, 130.19, 133.25, 134.19, 134.84, 138.24 ppm.

Scheme 5



4-(4-Methoxyphenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline (**3f**)
Yield: 98% (270.83 mg); m.p.: 112–115 °C (108–110 °C [18]).

4-(3-Methoxyphenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline (**3g**)
Yield: 97% (268.0 mg); m.p.: 127–131 °C (132–134 °C [13]).

4-(2,4-Dimethoxyphenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline (**3h**, $C_{19}H_{18}N_2O_2$)
Yield: 99% (303.28 mg); m.p.: 132–135 °C; FT-IR (KBr): $\bar{\nu}$ = 3352, 3127, 3002, 2933, 2830, 1875, 1611, 1510, 1479, 1337, 1285, 1206, 1156, 1034, 917, 832, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.77 (s, 3H, CH_3), 3.90 (s, 3H, CH_3), 4.52 (s, 1H, NH), 5.90–5.91 (m, 1H, Ar-H), 5.96 (s, 1H, CH), 6.32–6.35 (m, 2H, Ar-H), 6.49 (d, J = 2.4 Hz, 1H, Ar-H), 6.68 (dd, J = 7.6, 1.2 Hz, 1H, Ar-H), 6.78–6.83 (m, 2H, Ar-H), 6.91 (td, J = 7.6, 1.2 Hz, 1H, Ar-H), 7.24 (dd, J = 2.8, 1.2 Hz, 1H, Ar-H), 7.34 (dd, J = 8.0, 1.2 Hz, 1H, Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.87, 55.36, 55.53, 98.45, 104.03, 105.53, 110.09, 114.05, 114.54, 115.70, 118.90, 123.26, 124.62, 125.49, 128.24, 128.89, 135.80, 157.57, 160.35 ppm.

4-Styryl-4,5-dihydropyrrolo[1,2-a]quinoxaline (**3i**)
Yield: 90% (245.08 mg); m.p.: 124–127 °C (125–126 °C [14]).

4-(Anthracen-10-yl)-4,5-dihydropyrrolo[1,2-a]quinoxaline (**3j**, $C_{25}H_{18}N_2$)
Yield: 95% (329.14 mg); m.p.: 160–164 °C; FT-IR (KBr): $\bar{\nu}$ = 3386, 3045, 2916, 1616, 1515, 1473, 1329, 1291, 1156, 1037, 729 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 4.16 (s, 1H, NH), 5.30 (s, 1H, CH), 6.17 (s, 1H, Ar-H), 6.71 (d, J = 7.6 Hz, 1H, Ar-H), 6.91 (t, J = 7.4 Hz, 1H, Ar-H), 7.0 (t, J = 7.4 Hz, 1H, Ar-H), 7.16 (s, 1H, Ar-H), 7.39–7.49 (m, 6H, Ar-H), 8.00 (d, J = 8.0 Hz, 1H, Ar-H), 8.07 (d, J = 6.8 Hz, 1H, Ar-H), 8.33 (d, J = 6.8 Hz, 1H, Ar-H), 8.52 (s, 1H, Ar-H), 8.76 (d, J = 8.8 Hz, 1H, Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 50.97, 106.30, 110.46, 114.17, 115.05, 115.33, 119.38, 122.63, 124.56, 124.76, 124.87, 125.07, 126.73, 128.10, 128.79, 129.19, 129.49, 129.81, 137.06 ppm.

4-(Thiophen-3-yl)-4,5-dihydropyrrolo[1,2-a]quinoxaline (**3k**, $C_{15}H_{12}N_2S$)
Yield: 98% (247.22 mg); m.p.: 102–105 °C; FT-IR (KBr): $\bar{\nu}$ = 3426, 3357, 3138, 3066, 2927, 2785, 2696, 1761, 1605, 1513, 1497, 1330, 1278, 1148, 1037, 706 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 4.33 (s, 1H, NH), 5.85–5.86 (m, 1H, Ar-H), 5.92 (s, 1H, CH), 6.30 (t, J = 3.2 Hz, 1H, Ar-H), 6.79 (dd, J = 7.8, 1.4 Hz, 1H, Ar-H), 6.89 (td, J = 7.6, 1.4 Hz, 1H, Ar-H), 6.98–7.02 (m, 2H, Ar-H), 7.09 (dd, J = 3.4, 1.0 Hz, 1H, Ar-H), 7.21 (dd, J = 2.8, 1.6 Hz, 1H, Ar-H), 7.30 (dd, J = 5.0, 1.0 Hz, 1H, Ar-H), 7.35 (dd, J = 8.0, 1.2 Hz, 1H, Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.59, 105.87, 110.26, 113.63, 114.54, 114.79, 115.75, 119.86, 124.76, 125.49, 125.72, 126.48, 129.15, 135.32, 145.43 ppm.

4-(1H-Indol-3-yl)-4,5-dihydropyrrolo[1,2-a]quinoxaline (**3l**, $C_{19}H_{15}N_3$)
Yield: 85% (242.50 mg); m.p.: 178–182 °C; FT-IR (KBr): $\bar{\nu}$ = 3396, 3130, 3046, 2923, 2887, 1770, 1607, 1513, 1437, 1332, 1237, 1152, 1098, 911, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 4.19 (s, 1H, NH), 5.73–5.74 (m, 1H, Ar-H), 5.92 (s, 1H, CH), 6.25 (t, J = 3.2 Hz, 1H, Ar-H), 6.73 (dd, J = 7.6, 1.2 Hz, 1H, Ar-H), 6.85 (td, J = 7.6, 1.2 Hz, 1H, Ar-H), 6.96 (td, J = 7.6, 1.2 Hz, 1H, Ar-H), 7.09 (td, J = 7.6, 0.8 Hz, 1H, Ar-H), 7.19–7.25 (m, 2H, Ar-H), 7.36 (dd, J = 8.0, 1.2 Hz, 1H, Ar-H), 7.40 (d, J = 8.0 Hz, 1H, Ar-H), 7.49–7.53 (m, 2H, Ar-H), 8.15 (s, 1H, NH indole) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.82, 105.39, 110.12, 111.36, 113.71, 114.25, 114.79, 115.53, 119.35, 119.80, 121.30, 122.01, 122.41, 123.17, 124.62, 125.47, 126.94, 129.85, 136.56 ppm.

6-Chloro-3-(4,5-dihydropyrrolo[1,2-a]quinoxalin-4-yl)-4H-chromen-4-one (**3m**, $C_{20}H_{13}ClN_2O_2$)
Yield: 98% (341.86 mg); m.p.: 169–172 °C; FT-IR (KBr): $\bar{\nu}$ = 3334, 3133, 3059, 2925, 2857, 1914, 1639, 1515, 1464, 1311, 1289, 1136, 1049, 827, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.25 (s, 1H, NH), 5.92 (s, 1H, CH), 6.13 (dd, J = 3.4, 1.4 Hz, 1H, Ar-H), 6.40 (t, J = 3.2 Hz, 1H, Ar-H), 6.70 (dd, J = 7.8, 1.4 Hz, 1H, Ar-H), 6.81 (td, J = 7.6, 1.2 Hz, 1H, Ar-H), 6.92 (td, J = 7.4, 1.4 Hz, 1H, Ar-H), 7.15 (d, J = 1.2 Hz, 1H, Ar-H), 7.32–7.35 (m, 3H, Ar-H), 7.59 (dd, J = 8.8, 2.4 Hz, 1H, Ar-H), 8.20 (d, J = 2.8 Hz, 1H, Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.80, 106.15, 109.92, 110.40, 114.65, 114.96, 115.75, 116.32, 119.04, 119.38, 119.97, 123.82, 124.67, 125.10, 131.27, 134.16, 134.36, 154.43, 154.74, 176.60 ppm.

4-Hexyl-4,5-dihydropyrrolo[1,2-a]quinoxaline (**3n**, $C_{17}H_{22}N_2$)
Oil. Yield: 85% (216.20 mg); FT-IR (KBr): $\bar{\nu}$ = 3354, 3103, 3061, 2927, 2856, 2671, 1910, 1722, 1611, 1515, 1479, 1338, 1295, 1182, 1093, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, J = 4.4 Hz, 3H, CH_3), 1.2–1.3 (m, 6H, CH_2), 1.4–1.5 (m, 2H, CH_2), 1.7–1.8 (m, 2H, CH_2), 3.09 (t, J = 7.8 Hz, 1H, CH), 4.01 (s, 1H, NH), 5.99–6.00 (m, 1H, Ar-H), 6.31 (t, J = 3.2 Hz, 1H, Ar-H), 6.74 (dd, J = 7.6, 1.2 Hz, 1H, Ar-H), 6.80 (td, J = 7.6, 1.4 Hz, 1H, Ar-H), 6.95 (td, J = 7.6, 1.4 Hz, 1H, Ar-H), 7.15 (dd, J = 2.8, 1.2 Hz, 1H, Ar-H), 7.28 (dd, J = 7.6, 1.2 Hz, 1H, Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.16, 22.65, 25.60, 29.33, 31.83, 35.34, 51.08, 103.80, 109.92, 113.71, 114.11, 114.62, 115.36, 118.98, 124.59, 129.85, 135.97 ppm.

Selective synthesis of mono- and bis-4,5-dihydropyrrolo[1,2-*a*]quinoxalines A mixture of 1-(2-aminophenyl)pyrrole (1 or 2 mmol), dialdehyde (1 mmol) and $[PPy]HSO_4@nSiO_2$ (0.8 mol%) was stirred at 70 °C for the appropriate time according to Schemes 3 and 4. The workup was carried out as mentioned for preparation of 4,5-dihydropyrrolo[1,2-*a*]quinoxalines. The pure product was obtained by recrystallization from EtOAc or column chromatography (eluent: petroleum ether-EtOAc, 10:1).

4-(4,5-Dihydropyrrolo[1,2-a]quinoxalin-4-yl)benzaldehyde (**3o**, $C_{18}H_{14}N_2O$)
Yield: 97% (266.03 mg); m.p.: 115–119 °C; FT-IR (KBr): $\bar{\nu}$ = 3343, 3115, 3057, 2923, 2799, 1692, 1513, 1487, 1332, 1286, 1158, 1067, 915, 835, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 4.24 (s, 1H, NH), 5.58–5.59 (m, 1H, Ar-H), 5.65 (s, 1H, CH), 6.26 (t, J = 3.2 Hz, 1H, Ar-H), 6.78 (dd, J = 7.8, 1.4 Hz, 1H, Ar-H), 6.88 (td, J = 7.6, 1.4 Hz, 1H, Ar-H), 6.99 (td, J = 7.6, 1.2 Hz, 1H, Ar-H), 7.22 (dd, J = 2.8, 1.4, 1H, Ar-H), 7.35 (dd, J = 7.6, 1.2 Hz, 1H, Ar-H), 7.63 (d, J = 8.0 Hz, 2H, Ar-H), 7.88 (dd, J = 6.4, 1.6 Hz, 2H, Ar-H), 10.02 (s, 1H, CHO) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.89, 106.13, 110.37, 114.68, 114.85, 115.50, 119.77, 124.90, 128.47, 130.19, 135.54, 136.31, 148.29, 191.92 ppm.

3-(4,5-Dihydropyrrolo[1,2-a]quinoxalin-4-yl)benzaldehyde (**3p**, $C_{18}H_{14}N_2O$)
Yield: 91% (249.61 mg); m.p.: 110–113 °C; FT-IR (KBr): $\bar{\nu}$ = 3345, 3133, 3059, 2809, 2780, 1910, 1694, 1514, 1477, 1335, 1287, 1140, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.65 (s, 1H, NH), 6.27 (t, J = 3.2 Hz, 1H, CH), 6.79 (d, J = 8.0 Hz, 1H, Ar-H), 7.23 (d, J = 1.2 Hz, 1H, Ar-H), 7.33–7.41 (m, 3H, Ar-H), 7.46–7.60 (m, 4H, Ar-H), 7.91 (dd, J = 10.4, 7.6 Hz, 1H, Ar-H), 8.02 (s, 1H, Ar-H), 10.03 (s, 1H, CHO) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.89, 105.92, 106.08, 108.55, 110.43, 113.78, 114.95, 115.54, 119.43, 119.72, 124.91, 125.53, 128.00, 129.51, 130.55, 134.11, 134.53, 192.17 ppm.

2-[4-[2-(4,5-Dihydropyrrolo[1,2-a]quinoxalin-4-yl)phenoxy]butoxy]benzaldehyde (**3q**, $C_{28}H_{26}N_2O_3$)
Oil. Yield: 78% (342.07 mg); FT-IR (KBr): $\bar{\nu}$ = 3354, 3137, 3067, 2947, 2873, 2758, 2247, 1914, 1685, 1515, 1451, 1338, 1240, 1160, 1043, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.95 (dd, J = 6.4, 2.8 Hz, 2H, CH_2), 1.33 (dd, J = 8.0, 7.2 Hz, 2H, CH_2), 4.15 (t, J = 6.0 Hz, 4H, CH_2), 4.56 (s, 1H, NH), 5.91 (d, J = 3.2 Hz, 1H, Ar-H), 6.08 (s, 1H, CH), 6.36 (t, J = 3.0 Hz, 1H, Ar-H), 6.60–6.70 (m, 1H, Ar-H), 6.80–6.9 (m, 6H, Ar-H), 7.0–7.1 (m, 2H, Ar-H), 7.20 (d, J = 8.0 Hz, 1H, Ar-H), 7.34 (dd, J = 7.6, 4.8 Hz, 1H, Ar-H), 7.49–7.59 (m, 1H, Ar-H), 7.86–7.89 (m, 1H, Ar-H), 10.55 (s, 1H, CHO) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.46, 25.63, 48.93, 67.40, 67.50, 105.28, 109.70, 110.70, 111.97, 113.62, 114.06, 114.10, 115.08, 118.49, 120.22, 120.30, 120.39, 124.17, 127.83, 127.94, 128.03, 128.35, 128.39, 129.56, 130.21, 135.57, 155.38, 189.12 ppm.

2-[6-[2-(4,5-Dihydropyrrolo[1,2-a]quinoxalin-4-yl)phenoxy]hexyloxy]benzaldehyde (**3r**, $C_{30}H_{30}N_2O_3$)
Oil. Yield: 90% (419.90 mg); FT-IR (KBr): $\bar{\nu}$ = 3347, 3133, 3070, 2938, 2861, 2758, 2248, 1914, 1736, 1685, 1599, 1455, 1371, 1241, 1161, 1007, 910, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.61 (t, J = 3.4 Hz, 4H, CH_2), 1.90 (t, J = 4.4 Hz, 4H, CH_2), 4.05–4.14 (m, 4H, CH_2), 4.61 (s, 1H, NH), 5.91 (d, J = 1.6 Hz, 1H, Ar-H), 6.05 (s, 1H, CH), 6.34 (t, J = 3.0 Hz, 1H, Ar-H), 6.66 (dd, J = 8.0, 1.2 Hz, 1H, Ar-H), 6.77–6.82 (m, 2H, Ar-H), 6.86–6.92 (m, 2H, Ar-H), 6.94–7.04 (m, 3H, Ar-H), 7.20 (d, J = 7.6 Hz, 1H, Ar-H), 7.33 (d, J = 8.0 Hz, 1H, Ar-H), 7.49–7.57 (m, 2H, Ar-H), 7.85 (dd, J = 7.6, 1.2 Hz, 1H, Ar-H), 10.54 (s, 1H, CHO) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.36, 25.59, 28.56, 28.83, 48.98, 67.78, 67.81 105.26, 109.62, 110.64, 112.01, 112.02, 112.34, 113.24, 113.57, 114.04, 115.06, 118.41, 120.09, 124.09, 124.74, 127.67, 127.69, 127.78, 127.80, 128.26, 130.10, 135.50, 155.44, 189.33 ppm.

1,4-Bis(4,5-dihydropyrrolo[1,2-a]quinoxalin-4-yl)benzene (**4o**)
Yield: 90% (373.01 mg); m.p.: 217–220 °C (219–220 °C [14]).

1,3-Bis(4,5-dihydropyrrolo[1,2-a]quinoxalin-4-yl)benzene (**4p**, $C_{28}H_{22}N_4$)
Yield: 85% (352.37 mg); m.p.: 186–189 °C; FT-IR (KBr): $\bar{\nu}$ = 3349, 3100, 2923, 1907, 1606, 1515, 1475, 1337, 1283, 1143, 1095, 927, 806, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.65 (s, 2H, NH), 6.27 (t, J = 3.2 Hz, 2H, CH), 6.88 (dd, J = 5.6, 1.8 Hz, 2H, Ar-H), 6.99–7.03 (m, 2H, Ar-H), 7.22 (dd, J = 8.8, 1.2 Hz, 2H, Ar-H), 7.33–7.44 (m, 4H, Ar-H), 7.48–7.51 (m, 3H, Ar-H), 7.53–7.58 (m, 6H, Ar-H), 8.02 (s, 2H, Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.09, 105.90, 110.20, 113.71, 114.14, 114.43, 114.76, 115.40, 119.44, 124.70, 127.84, 128.64, 129.06, 136.14, 141.92 ppm.

1,4-Bis[2-(4,5-dihydropyrrolo[1,2-a]quinoxalin-4-yl)phenoxy]butane (**4q**, $C_{38}H_{34}N_4O_2$)
Oil. Yield: 81% (468.73 mg); FT-IR (KBr): $\bar{\nu}$ = 3349, 3136, 3061, 2947, 2872, 1916, 1684, 1515, 1484, 1336, 1238, 1047, 975, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.08 (t, J = 2.8 Hz, 4H, CH_2), 4.14–4.20 (m, 4H, CH_2), 4.49 (s, 2H, NH), 5.85–5.88 (m, 2H, CH), 6.04 (s, 2H, Ar-H), 6.33 (t, J = 3.2 Hz, 2H, Ar-H), 6.60 (dd, J = 4.0, 1.2 Hz, 2H, Ar-H), 6.61 (dd, J = 4.2, 1.4 Hz, 2H, Ar-H), 6.79–6.90 (m, 8H, Ar-H), 6.99 (dt, J = 7.6, 1.8 Hz, 2H, Ar-H), 7.23–7.24 (m, 2H, Ar-H), 7.34 (m, Hz, 2H, Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.05, 48.99, 67.33, 105.45, 109.81, 110.83, 113.71, 114.17, 115.19, 118.53, 120.45, 124.25, 124.93, 127.59, 127.93, 128.44, 130.31, 135.40, 155.45 ppm.

1,6-Bis[2-(4,5-dihydropyrrolo[1,2-a]quinoxalin-4-yl)phenoxy]hexane (**4r**, $C_{40}H_{38}N_4O_2$)
Oil. Yield: 86% (521.84 mg); FT-IR (KBr): $\bar{\nu}$ = 3384, 3137, 3061, 2927, 2856, 2242, 1717, 1613, 1515, 1489, 1337, 1234, 1101, 1047, 908, 737 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.64 (t, J = 3.4 Hz, 4H, CH_2), 1.91 (t, J = 6.2 Hz, 4H, CH_2), 4.03–4.14 (m, 4H, CH_2), 4.57 (s, 2H, NH), 5.91 (s, 2H, CH), 6.05 (d, J = 2.0 Hz, 2H, Ar-H), 6.34 (t, J = 3.0 Hz, 2H, Ar-H), 6.63 (d, J = 7.6 Hz, 2H, Ar-H), 6.80–6.90 (m, 6H, Ar-H), 6.87–6.93 (m, 6H, Ar-H), 7.19 (td, J = 8.0, 1.6 Hz, 2H, Ar-H), 7.24 (s, 2H, Ar-H), 7.33 (d, J = 7.6 Hz, 2H, Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.05, 29.22, 49.61, 68.18, 105.79, 110.15, 111.17, 112.53, 114.11, 114.56, 115.58, 118.92, 120.62, 124.64, 128.21, 128.83, 130.70, 136.03, 155.96, 161.45 ppm.

4-Methyl-4-(4-nitrophenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline (**6a**, $C_{18}H_{15}N_3O_2$)
Yield: 98% (299.20 mg); m.p.: 231–233 °C; FT-IR (KBr): $\bar{\nu}$ = 3342, 2969, 1726, 1512, 1481, 1343, 1189, 1083, 744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.95 (s, 3H, CH_3), 4.44 (s, 1H, NH), 6.16 (dd, J = 3.4, 1.4 Hz, 1H, Ar-H), 6.39 (t, J = 3.2 Hz, 1H, Ar-H), 6.82–6.88 (m, 2H, Ar-H), 6.99 (td, J = 8.0, 1.6 Hz, 1H, Ar-H), 7.21 (dd, J = 2.8, 1.6 Hz, 1H, Ar-H), 7.28 (dd, J = 8.0, 1.0 Hz, 1H, Ar-H), 7.43–7.47 (m, 2H, Ar-H), 8.07–8.11 (m, 2H, Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.99, 56.97, 104.88, 110.32, 114.85, 114.99, 116.09, 120.06, 123.57, 125.64, 125.72, 126.74, 131.50, 134.33, 146.79, 153.92 ppm.

4-(4-Chlorophenyl)-4-methyl-4,5-dihydropyrrolo[1,2-a]quinoxaline (**6b**, $C_{18}H_{15}ClN_2$)
Yield: 95% (280.01 mg); m.p.: 171–174 °C; FT-IR (KBr): $\bar{\nu}$ = 3349, 2977, 1613, 1511, 1480, 1333, 1188, 1088,

747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.90$ (s, 3H, CH_3), 4.22 (s, 1H, NH), 6.07 (dd, $J = 3.2$, 1.6 Hz, 1H, Ar-H), 6.35–6.37 (m, 2H, Ar-H), 6.79 (dd, $J = 8.0$, 1.2 Hz, 1H, Ar-H), 6.83 (dd, $J = 7.6$, 1.2 Hz, 1H, Ar-H), 6.87 (t, $J = 2.0$ Hz,1H, Ar-H), 6.97 (td, $J = 7.8$, 1.4 Hz, 1H, Ar-H), 7.19 (dd, $J = 3.0$, 1.4 Hz, 2H, Ar-H), 7.27–7.29 (m, 2H, Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 29.16$, 56.63, 104.60, 109.41, 110.09, 114.51, 114.73, 115.95, 118.41, 119.60, 121.70, 124.84, 127.28, 128.35, 134.81, 144.92 ppm.

4-(4-Cyclohexylphenyl)-4-methyl-4,5-dihydropyrrolo[1,2-a]quinoxaline (**6c**, $C_{24}H_{26}N_2$)
Yield: 82% (280.80 mg); m.p.: 168–170 °C; FT-IR (KBr): $\bar{\nu} = 3370$, 2924, 1611, 1513, 1479, 1332, 1184, 1072, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.32$–1.49 (m, 10 H, CH_2), 1.91 (s, 3H, CH_3), 2.45 (dd, $J = 8.0$, 1.2 Hz, 1H, CH), 3.67 (s, 1H, NH), 6.05 (dd, $J = 3.4$, 1.4 Hz, 1H, Ar-H), 6.35 (t, $J = 3.2$ Hz, 1H, Ar-H), 6.97 (td, $J = 7.6$, 1.2 Hz, 1H, Ar-H), 7.10 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.25 (dt, $J = 6.4$, 2.0 Hz, 2H, Ar-H), 7.33 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.93 (dt, $J = 6.4$, 2.0 Hz, 2H, Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 26.28$, 27.18, 29.67, 34.43, 44.17, 56.86, 104.65, 109.41, 109.98, 114.62, 116.09, 118.41, 119.09, 121.70, 124.70, 125.61, 126.63, 127.19, 128.55, 142.09 ppm.

4-Methyl-4-(p-tolyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline (**6d**, $C_{19}H_{18}N_2$)
Yield: 70% (192.00 mg); m.p.: 172–175 °C; FT-IR (KBr): $\bar{\nu} = 3355$, 2917, 1608, 1515, 1479, 1334, 1148, 1033, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.90$ (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 3.80 (s, 1H, NH), 6.01 (dd, $J = 3.2$, 1.6 Hz, 1H, Ar-H), 6.06 (dd, $J = 3.8$, 1.6 Hz, 1H, Ar-H), 6.17 (br s, 1H, Ar-H), 6.26 (t, $J = 3.0$ Hz, 1H, Ar-H), 6.32 (t, $J = 3.2$ Hz, 1H, Ar-H), 6.69 (dd, $J = 7.6$, 1.2 Hz, 1H, Ar-H), 7.15 (dd, $J = 3.2$, 1.6 Hz, 2H, Ar-H), 7.33 (m, 3H, Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 20.90$, 29.39, 51.19, 109.41, 109.92, 114.25, 114.68, 116.15, 118.41, 119.21, 121.70, 124.64, 125.66, 127.19, 128.61, 128.89, 142.09 ppm.

Acknowledgements The authors are grateful to the Research Council of the University of Isfahan for the financial support of this work.

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