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Metal-Free Synthesis of Pyrrolo[1,2-*a*]quinoxalines Mediated by TEMPO Oxoammonium Salts

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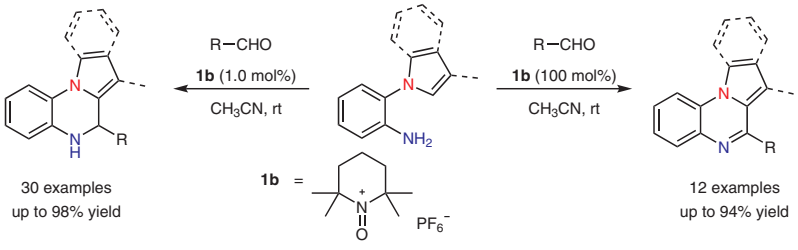

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Abstract We herein describe a novel TEMPO oxoammonium salt initiated Pictet–Spengler reaction of imines, generated in situ from carbonyl compounds and pyrrole- or indole-containing substrates, to afford 4,5-dihydropyrrolo[1,2-*a*]quinoxalines or 5,6-dihydroindolo[1,2-*a*]quinoxalines in good to excellent yields. Moreover, a one-pot synthesis of a biologically important quinoxaline is achieved via a cyclization–dehydrogenation process using one equivalent of the oxoammonium salt.

Key words TEMPO oxoammonium salts, Pictet–Spengler reaction, imines, dihydroquinoxalines, quinoxalines

Among nitrogen-containing heterocyclic natural products, dihydropyrrolo-/indolo[1,2-*a*]quinoxalines and their derivatives are very important scaffolds due to their presence in a wide range of natural products and pharmaceutically active compounds.[1] As shown in Figure 1, cannabinoid receptor antagonist **A** is a CB1R antagonist,[2] playing a special role in energy homeostasis and in reducing human body weight. The 5-HT3 receptor antagonist **B** shows important activity in the treatment of postoperative nausea and vomiting.[3] Compound **C** is reported to have anti-HIV activity,[4] whilst compound **D** demonstrates antiproliferative activity.[5]

Thus, numerous efforts have been devoted to construct these fused ring systems. Dihydroquinoxalines and quinoxalines are usually synthesized via the Pictet–Spengler reaction[6] of 2-(1*H*-pyrrol-1-yl)aniline or 2-(1*H*-indol-1-yl)anilines with carbonyl compounds under aerobic heating,[7] or under the catalysis of Lewis acids,[8] Brønsted acids[9] or I_2.[9g,10] Considering their important pharmacological activity, herein, we report a novel TEMPO oxoammonium salt initiated intramolecular cyclization of imines possessing pyrrolyl/indolyl rings, which provides a metal-free and environmentally friendly construction of 4,5-dihydroquinoxalines and 5,6-dihydroquinoxalines.

At the outset, we investigated the model cyclocondensation reaction between 2-(1*H*-pyrrol-1-yl)aniline (**2a**) and benzaldehyde (**3a**) at room temperature in the presence of different oxoammonium salt initiators and solvents (Table 1). When 3.0 mol% of initiator **1a** was used, the reaction was complete within 12 hours and gave product dihydroquinazolinone **4aa** in 87% yield (Table 1, entry 1). On reducing the amount of **1a** to 1.0 mol%, the reaction proceeded readily to give a slightly higher yield of **4aa**, whereas a further reduction to 0.5 mol% of **1a** led to a detectable decline in the reaction rate (Table 1, entries 2 and 3). To our delight,

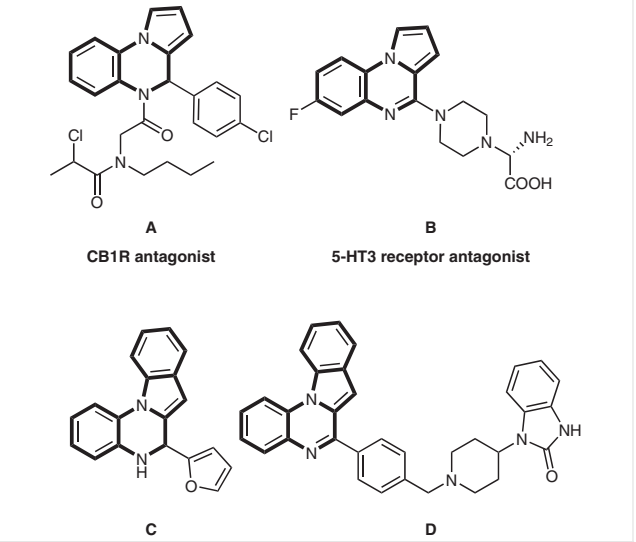

Figure 1 Examples of biologically active dihydroquinoxalines and quinoxalines

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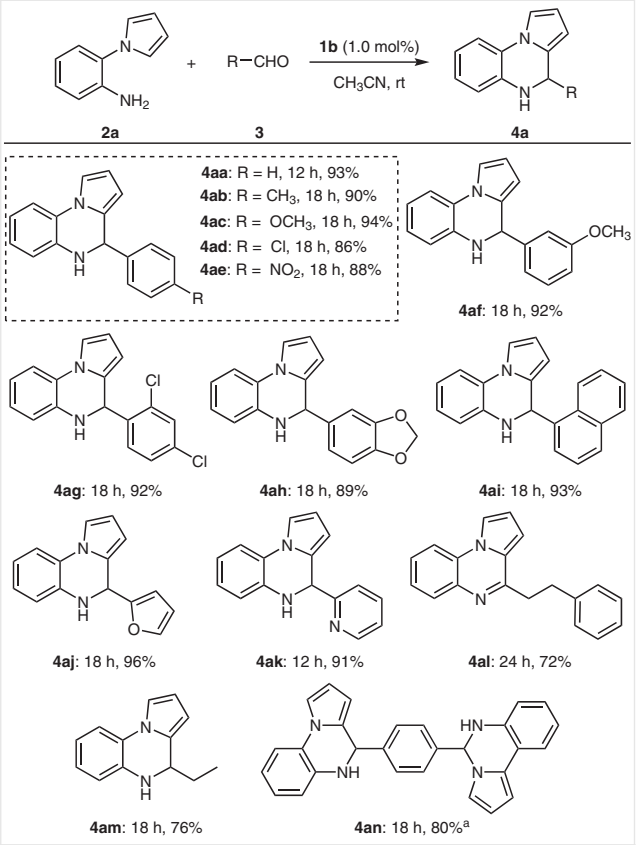
other oxoammonium salts such as **1b–d** were effective in this reaction and delivered the desired product **4aa** in excellent yields; among these salts, **1b** proved to be the best (Table 1, entries 4–6). Next, the effect of the reaction time was assessed in the presence of 1.0 mol% of **1b** (Table 1, entries 7 and 8). Shortening the time to 6 hours reduced the conversion significantly, while extending the reaction time to 18 hours resulted in complete consumption of the substrate, but the yield was slightly reduced. Next, the effect of other solvents such as dichloromethane (CH_2Cl_2), dichloroethane (DCE), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO) and ethanol on the reaction was examined (Table 1, entries 9–13), with the results indicating that acetonitrile was still the most appropriate solvent in terms of the product yield. No reaction occurred when oxoammonium salt **1** was not present (Table 1, entry 14). In addition, we found that **4a** could be further oxidized by oxoammonium salt **1** or air to produce a small amount of **5a**.

Using the above optimized conditions, we next turned our efforts to determining the substrate scope of this methodology. The reactions of **2a** with different aromatic aldehydes all proceeded smoothly to give the corresponding products **4ab–ai** in high yields (Scheme 1). Heteroaromatic aldehydes were also tolerated under the reaction conditions, and products **4aj** and **4ak** were obtained in 96% and 91% yields, respectively. For cinnamaldehyde, the cyclocondensation was sluggish, providing **4al** in a slightly lower yield (72%), probably due to the chemical instability of cinnamaldehyde under the reaction conditions. Notably, the aliphatic aldehyde *n*-propyl aldehyde was also suitable for this cyclization, giving **4am** in 76% yield. When 1,4-phthalaldehyde was employed as the substrate, the double Pictet–Spengler reaction readily took place to give **4an** in 80% yield.



Scheme 1 Substrate scope of the methodology. *Reagents and conditions*: **2a** (0.5 mmol), **3** (0.6 mmol), **1b** (1.0 mol%), CH_3CN (2.5 mL), rt. [a] *Reagents and conditions*: **2a** (1.2 mmol), **3n** (0.5 mmol), **1b** (1.0 mol%), CH_3CN (2.5 mL), rt, 18 h.

Further investigation of the Pictet–Spengler reactions of aldehydes with 2-(1*H*-indol-1-yl)anilines **2b** and **2c** was conducted. As can be seen in Scheme 2, the reactions of aromatic aldehydes with 2-(1*H*-indol-1-yl)anilines **2b** or **2c** all proceeded well to provide the desired products **4ba–cn** in good to excellent yields. For heteroaromatic aldehydes such as furaldehyde and picolinaldehyde, the reactions proceeded smoothly to furnish products **4cj** and **4ck** in 98% and 92% yields, respectively. Treatment of chromone-3-carboxaldehyde and isopropyl aldehyde under the standard reaction conditions led to the desired products **4cl** and **4cm** in isolated yields of 86% and 80%, respectively. Interestingly, when 1,4-phthalaldehyde was employed as the substrate the expected product **4cn** was obtained in 93% yield. Furthermore, treatment of 2-(1-methyl-1*H*-indol-3-yl)aniline (**2d**) with benzaldehyde (**3a**) provided the corresponding product **4da** in 85% yield (Scheme 3).

Since the cyclized products could be further oxidized into the corresponding biologically active quinoxalines, we performed the cyclization using oxoammonium salt **1b** (1.0 equiv). As shown in Scheme 4, four representative substrates **2a–d** were chosen to investigate this tandem cyclization–dehydrogenation process. The corresponding products **5aa–ae**, **5ba**, **5ca–5ce** and **5da** were obtained in good to excellent yields.

Based on the above observations, we next synthesized biologically active compound **4ea**, which possesses anticancer activity,[11] by treating **2e** with acetone in the presence of 1.0 mol% of **1b**. Gratifyingly, the desired product **4ea** was successfully isolated in 86% yield (Scheme 5). The operational simplicity, metal-free and mild conditions of this method make this protocol practical for the synthesis of such drug candidates.

Although the actual mechanism for the above transformations remains to be elucidated, the two reaction pathways outlined in Scheme 6 are postulated to explain the role of the TEMPO oxoammonium salt. In order to verify whether the interaction between the imine (formed from amine **2** and aldehyde **3**) and the TEMPO oxoammonium salt promoted the reaction, we determined the chemical shifts of the protons of the imine and the mixture of imine/TEMPO oxoammonium salt, respectively. However, no detectable change was observed in the chemical shift of

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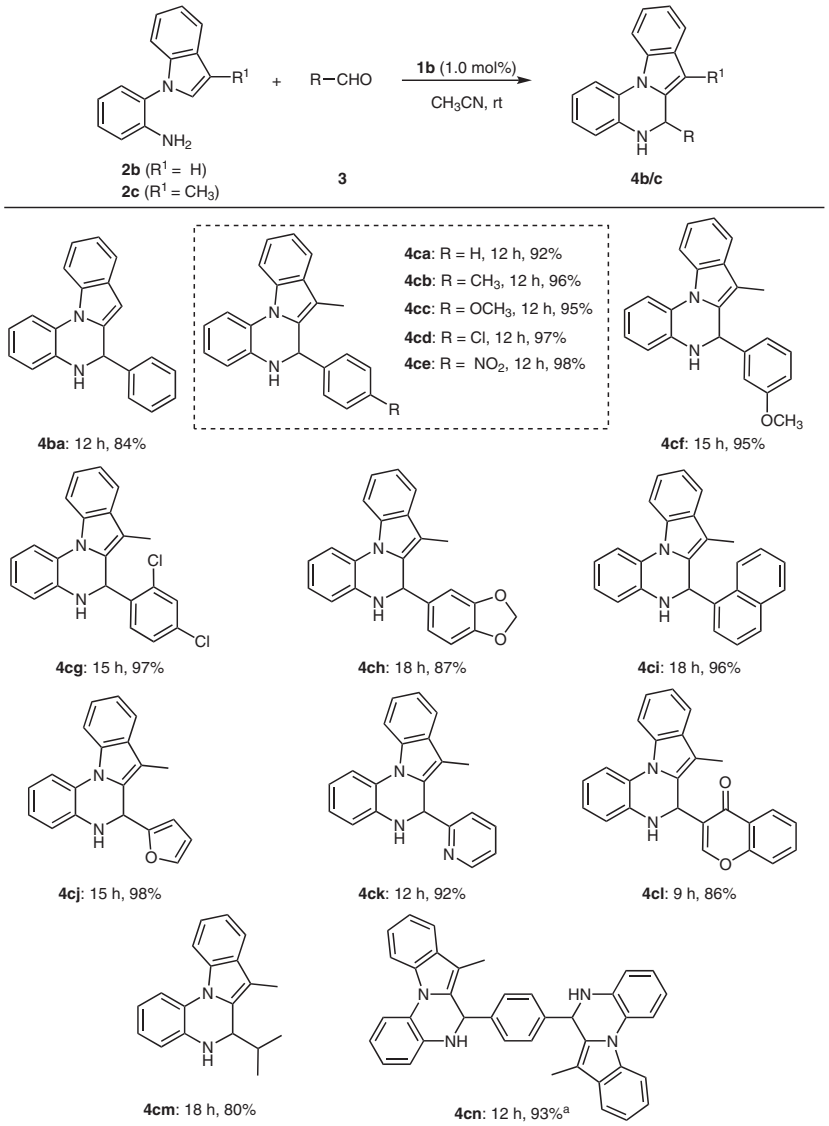
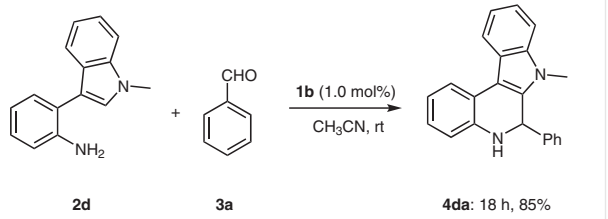


Scheme 2 Further investigations of the substrate scope. *Reagents and conditions*: **2b** or **2c** (0.5 mmol), **3** (0.6 mmol), **1b** (1.0 mol%), CH_3CN (2.5 mL), rt. [a] *Reagents and conditions*: **2c** (1.2 mmol), **3n** (0.5 mmol), **1b** (1.0 mol%), CH_3CN (2.5 mL), rt, 12 h.

the proton of the CH=N group. This observation provided negative evidence for the direct activation of an imine by the TEMPO oxoammonium salt through the formation of complex **8** (path a). On the other hand, we found that the TEMPO oxoammonium salts can be readily reduced by aromatic amines such as **2a**, and the reaction mixture was subjected to flash chromatography to afford a little amount of TEMPO. Hence, the proton could be simultaneously released during oxidation of the aromatic amine. Thus, we postulate that the above cyclization process might be catalyzed by the proton generated in situ.

In conclusion, we have described TEMPO oxoammonium salts as environmentally friendly and efficient reagents for initiating the intramolecular Pictet–Spengler reactions of imines possessing pyrrolyl/indolyl rings. The easy to handle and metal-free conditions for this process are beneficial



Scheme 3 *Reagents and conditions*: **2d** (0.5 mmol), **3a** (0.6 mmol), **1b** (1.0 mol%), CH_3CN (2.5 mL), rt, 18 h.

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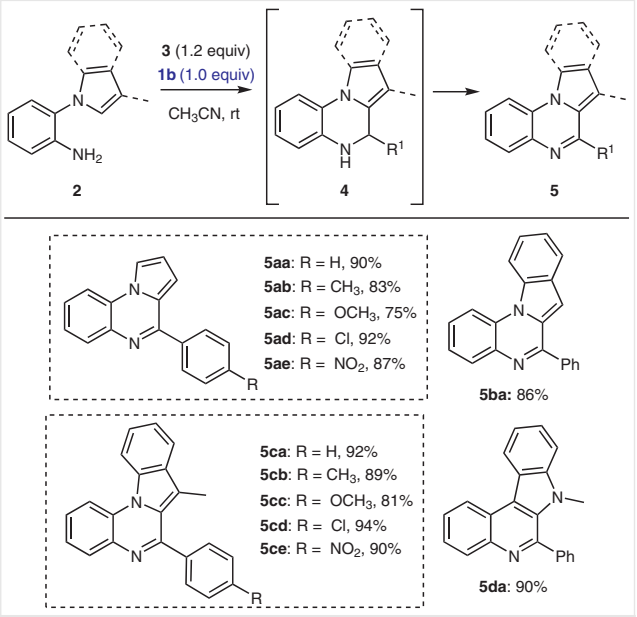
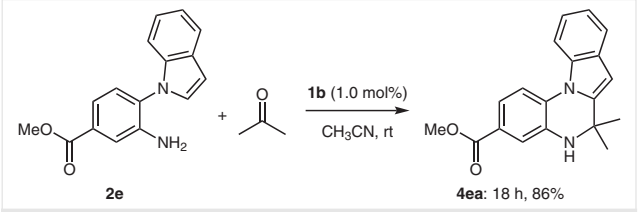


Scheme 4 One-pot synthesis of quinoxalines. *Reagents and conditions*: **2** (0.5 mmol), **3** (0.6 mmol), **1b** (1.0 mol%), CH_3CN (2.5 mL), 12–18 h, then **1b** (0.5 mmol) was added and the mixture stirred for an additional 6 h at rt.

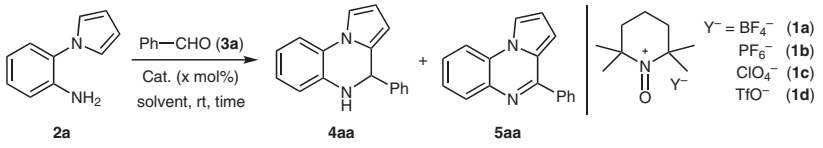
for the practical production of biologically important 4,5-dihydropyrrolo[1,2-*a*]quinoxalines and 5,6-dihydroindolo[1,2-*a*]quinoxalines.

All reagents and solvents were purchased from Reagent Co. and were used without further purification. Reactions were monitored by TLC analysis using Yantai Jiangyou Silicone Development Co., Ltd. silica gel 60 Å F-254 thin-layer plates. Flash column chromatography was performed on Qingdao Haiyang Chemical Co., Ltd. silica gel 60 Å, 10–40 µm. Melting points were determined with an Electrothermal melting point apparatus and are uncorrected. IR spectra were recorded as thin films between KBr plates using a Bruker FT-IR spectrophotometer. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AV 400 spectrometer. Chemical shifts are reported in ppm relative to tetramethylsilane with the solvent resonance as the internal



Scheme 5 Synthesis of biologically active compound **4ea**

Table 1 Optimization of the Reaction Conditions[a]



Entry	Cat. (x)	Solvent	Time (h)	Yield of **4aa** (%)[b]	Yield of **5aa** (%)[b]
1	**1a** (3.0)	CH_3CN	12	87	8
2	**1a** (1.0)	CH_3CN	12	90	<5
3	**1a** (0.5)	CH_3CN	12	68	<5
4	**1b (1.0)**	**CH_3CN**	**12**	**93**	**<5**
5	**1c** (1.0)	CH_3CN	12	89	<5
6	**1d** (1.0)	CH_3CN	12	85	<5
7	**1b** (1.0)	CH_3CN	6	62	<5
8	**1b** (1.0)	CH_3CN	18	85	11
9	**1b** (1.0)	CH_2Cl_2	12	88	<5
10	**1b** (1.0)	DCE	12	89	<5
11	**1b** (1.0)	THF	12	35	<5
12	**1b** (1.0)	DMSO	12	46	<5
13	**1b** (1.0)	EtOH	12	74	<5
14	–	CH_3CN	12	ND[c]	ND[c]

[a] Unless otherwise specified, all reactions were carried out using **2a** (0.5 mmol), **3a** (0.6 mmol), **1** (x mol%) in the indicated solvent (2.5 mL) at rt for the given time.
[b] Yield of isolated product.
[c] ND = not detected.

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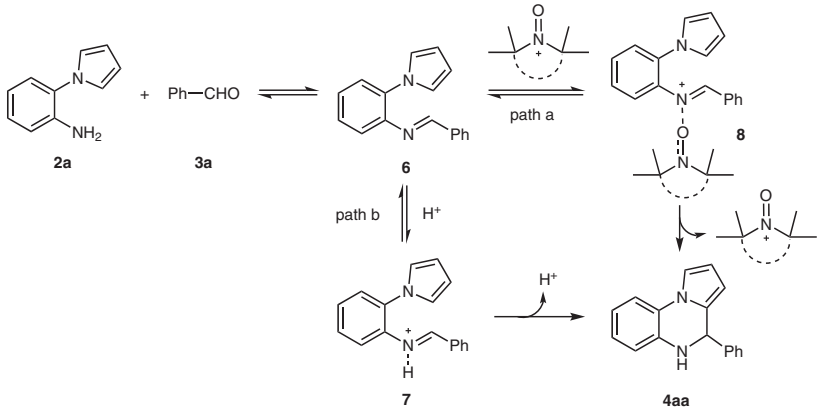
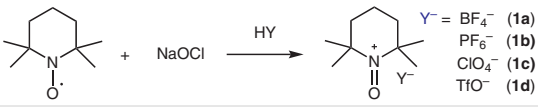


Scheme 6 A proposed mechanism for the catalytic process

standard. Data are reported as follows: chemical shift, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, and br s: broad singlet), coupling constant(s) (Hz), integration. ^{13}C NMR spectra were recorded with complete proton decoupling. Chemical shifts are reported in ppm relative to tetramethylsilane with the solvent resonance as internal standard. High-resolution mass spectrometry was performed using a TOF-Q mass spectrometer equipped with an ESI source.

TEMPO$^+BF_4^-$ (1a); Typical Procedure (Scheme 7)



Scheme 7

Synthesis of TEMPO$^+BF_4^-$ (**1a**). Tetrafluoroboric acid (HBF_4) (50% in H_2O, 7.8 mL, 61.4 mmol, 1.2 equiv) was added dropwise to a solution of TEMPO (8.0 g, 51.2 mmol, 1 equiv) in Et_2O (40 mL) over 0.5 h at 0 °C. After the solution had become amber in color, NaOCl (18.0 mL, 25.6 mmol) was added over 1 h at 0 °C and the mixture was stirred for an additional 1 h at 0 °C. The formed yellow precipitate was filtered and washed with ice-cold 5% $NaHCO_3$ (15 mL), H_2O (30 mL) and Et_2O (100 mL). The solid was dried in vacuo at 50 °C over 24 h to yield TEMPO$^+BF_4^-$ (**1a**) (9.0 g, 36.9 mmol, 72%) as a bright yellow solid; mp 155–156 °C (Lit.[12] 162–163 °C).

HRMS (ESI): m/z [M_2 – BF_4]$^+$ calcd for $C_{18}H_{36}N_2O_2BF_4$: 399.2800; found: 399.2790.

TEMPO$^+PF_6^-$ (1b)

The same procedure with 60% HPF_6 instead of 50% HBF_4 provided TEMPO$^+PF_6^-$ (**1b**) (11.4 g, 37.9 mmol, 74%) as a yellow solid; mp 144–145 °C.

HRMS (ESI): m/z [M_2 – PF_6]$^+$ calcd for $C_{18}H_{36}N_2O_2PF_6$: 457.2413; found: 457.2385.

TEMPO$^+ClO_4^-$ (1c)

The same procedure with 70% $HClO_4$ instead of 50% HBF_4 provided TEMPO$^+ClO_4^-$ (**1c**) (8.9 g, 34.8 mmol, 68%) as a yellow solid; mp 125–126 °C.

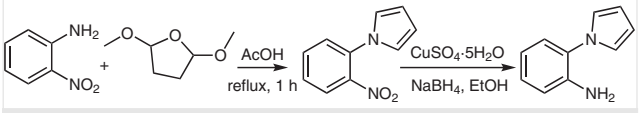
HRMS (ESI): m/z [M_2 – ClO_4]$^+$ calcd for $C_{18}H_{36}N_2O_6Cl$: 411.2256; found: 411.2248.

TEMPO$^+OTf^-$ (1d)

The same procedure with TfOH instead of 50% HBF_4 provided TEMPO$^+OTf^-$ (**1d**) (9.1 g, 29.7 mmol, 58%) as a yellow solid; mp 147–148 °C.

HRMS (ESI): m/z [M_2 – OTf]$^+$ calcd for $C_{18}H_{36}N_2O_3Tf$: 461.2292; found: 461.2270.

2-(1*H*-Pyrrol-1-yl)aniline (2a)[13] (Scheme 8)



Scheme 8

A mixture of *o*-nitroaniline (3.45 g, 25.00 mmol) and 2,5-dimethoxytetrahydrofuran (3.2 mL, 25.00 mmol) in AcOH was refluxed for 1 h with vigorous stirring. The reaction mixture was cooled to ambient temperature and then poured into H_2O. The precipitate was filtered, washed with H_2O, dissolved in EtOAc, dried over Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was filtered through a short pad of silica gel (hexane/EtOAc, 20:1), to afford 1-(2-nitrophenyl)-1*H*-pyrrole, which was used directly in the next step without any further purification.

Yield: 4.42 g (94%); brown oil.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.85 (dd, J = 8.4, 1.2 Hz, 1 H), 7.67–7.63 (m, 1 H), 7.49 (dd, J = 1.2, 1.2 Hz, 1 H), 7.47–7.44 (m, 1 H), 6.79 (dd, J = 2.0, 2.0 Hz, 2 H), 6.37–6.36 (dd, J = 2.0, 2.0 Hz, 2 H).

2-(1*H*-Pyrrol-1-yl)aniline (2a)

To a solution of 1-(2-nitrophenyl)-1*H*-pyrrole (3.76 g, 20 mmol) in EtOH (80 mL) was added $CuSO_4·5H_2O$ (6.24 g, 25 mmol). $NaBH_4$ (1.51 g, 40 mmol) was then added portionwise at 0 °C and the reaction mixture was stirred at room temperature for 1 h. The mixture was filtered through a short pad of silica gel using EtOAc (3 × 40 mL) as eluent. The solvent was evaporated in vacuo and the residue was subjected to flash chromatography (petroleum ether/EtOAc, 20:1) to afford 2-(1*H*-pyrrol-1-yl)aniline (**2a**).

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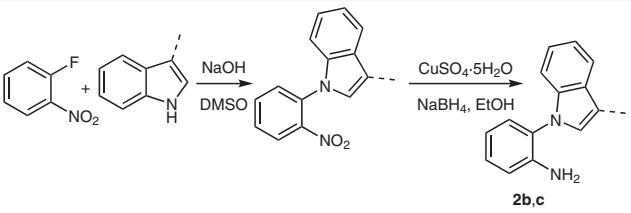
Yield: 2.69 g (85%); white crystalline solid; mp 94–95 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.17–7.13 (m, 2 H), 6.83–6.78 (m, 4 H), 6.34 (d, J = 2.0 Hz, 2 H), 3.53 (br s, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 137.3, 123.8, 122.8, 122.4, 117.0, 113.7, 111.4, 104.7.

2-(1*H*-Indol-1-yl)aniline (2b) and 2-(3-Methyl-1*H*-indol-1-yl)aniline (2c)[9d] (Scheme 9)



Scheme 9

To a well-stirred solution of 1*H*-indole (2.34 g, 20 mmol) or 3-methyl-1*H*-indole (2.62 g, 20 mmol) in DMSO (40 mL) were added slowly NaOH (0.80 g, 20 mmol) and 1-fluoro-2-nitrobenzene (2.1 mL, 20 mmol). 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 EtOAc and the combined organics washed with H_2O and dried over Na_2SO_4. The solvent was evaporated in vacuo and the obtained solid was purified by column chromatography on silica gel (petroleum ether/EtOAc, 20:1) to afford 1-(2-nitrophenyl)-1*H*-indole or 3-methyl-1-(2-nitrophenyl)-1*H*-indole.

1-(2-Nitrophenyl)-1*H*-indole

Yield: 3.81 g (80%); yellow crystalline solid; mp 84–85 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (dd, J = 8.4, 1.6 Hz, 1 H), 7.67–7.63 (m, 2 H), 7.50 (m, 2 H), 7.19–7.14 (m, 2 H), 7.13–7.10 (m, 2 H), 6.70 (d, J = 3.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.3, 136.7, 133.8, 132.9, 129.8, 129.0, 128.4, 128.1, 125.5, 123.0, 121.4, 121.0, 109.6, 105.1.

3-Methyl-1-(2-nitrophenyl)-1*H*-indole

Yield: 4.14 g (82%); brown crystalline solid; mp 56–57 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (dd, J = 8.0, 1.2 Hz, 1 H), 7.64 (ddd, J = 8.0, 8.0, 1.6 Hz, 1 H), 7.62–7.57 (m, 1 H), 7.51 (dd, J = 8.0, 1.2 Hz, 1 H), 7.48–7.43 (m, 1 H), 7.20–7.14 (m, 2 H), 7.13–7.08 (m, 1 H), 6.90 (d, J = 0.8 Hz, 1 H), 2.35 (d, J = 1.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.0, 136.8, 133.6, 133.1, 129.7, 129.5, 127.8, 125.5, 125.3, 123.0, 120.5, 119.5, 114.5, 109.4, 9.7.

$CuSO_4$·5H_2O (4.49 g, 18 mmol) and $NaBH_4$ (0.85 g, 22.5 mmol) were added portionwise at 0 °C to a solution of 1-(2-nitrophenyl)-1*H*-indole (3.57 g, 15 mmol) or 3-methyl-1-(2-nitrophenyl)-1*H*-indole (3.78 g, 15 mmol) in EtOH (50 mL). The reaction mixture was then stirred at room temperature for 1 h. The mixture was filtered through a short pad of silica gel using EtOAc (3 × 30 mL) as the eluent. The solvent was evaporated in vacuo and the residue was subjected to flash chromatography (petroleum ether/EtOAc, 15:1) to afford the expected indole.

2-(1*H*-Indol-1-yl)aniline (2b)

Yield: 3.17 g (95%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (dd, J = 7.2, 1.2 Hz, 1 H), 7.18 (m, 6 H), 6.82 (dd, J = 7.6, 7.6 Hz, 2 H), 6.68 (d, J = 3.2 Hz, 1 H), 3.41 (br s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.1, 136.4, 129.1, 128.60, 128.57, 124.9, 122.2, 120.9, 120.1, 118.5, 116.2, 110.7, 103.2.

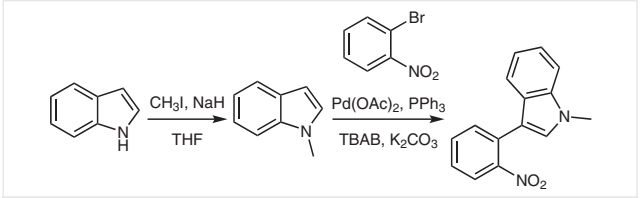
2-(3-Methyl-1*H*-indol-1-yl)aniline (2c)

Yield: 3.46 g (95%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (dd, J = 6.8, 2.4 Hz, 1 H), 7.23–7.15 (m, 4 H), 7.14–7.09 (m, 1 H), 6.98 (d, J = 0.8 Hz, 1 H), 6.85–6.79 (m, 2 H), 3.41 (br s, 2 H), 2.38 (d, J = 1.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.1, 136.7, 129.0, 128.9, 128.6, 126.1, 125.2, 122.2, 119.5, 119.1, 118.6, 116.3, 112.4, 110.6, 9.7.

2-(1-Methyl-1*H*-indol-3-yl)aniline (2d)[14] (Scheme 10)



Scheme 10

To a solution of 1*H*-indole (1.41 g, 12 mmol) in THF (30 mL) at 0 °C was added NaH (60% in mineral oil, 720 mg, 18 mmol). The reaction was warmed to room temperature and allowed to stir for 30 min as a dark blue color developed. After 30 min, the reaction flask was cooled to 0 °C and iodomethane (0.93 mL, 15 mmol) was added dropwise. The mixture was warmed to room temperature and allowed to stir until all the starting material had been consumed. The mixture was cooled to 0 °C and quenched with saturated NH_4Cl. The product was extracted with Et_2O (3 × 30 mL) and washed with H_2O (60 mL) and sat. NaCl (60 mL). The organic phase was concentrated in vacuo to give a yellow liquid, which was purified via flash chromatography on silica gel (petroleum ether/EtOAc, 60:1) to give 1-methyl-1*H*-indole.

1-Methyl-1*H*-indole

Yield: 1.54 g (98%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (dd, J = 8.0, 2.4 Hz, 1 H), 7.29 (d, J = 8.4 Hz, 1 H), 7.23–7.18 (m, 1 H), 7.11–7.07 (m, 1 H), 7.00 (dd, J = 2.8, 1.6 Hz, 1 H), 6.47 (dd, J = 2.4, 2.4 Hz, 1 H), 3.72 (d, J = 0.8 Hz, 3 H).

1-Methyl-1*H*-indole (1.31 g, 10 mmol), $Pd(OAc)_2$ (225 mg, 1.0 mmol), PPh_3 (197 mg, 0.75 mmol), K_2CO_3 (4.15 g, 30 mmol) and TBAB (739 mg, 2 mmol) were added to an oven-dried 100 mL round-bottom flask. The flask was closed with a septum, evacuated and backfilled with argon. Next, a solution of 2-bromo-1-nitrobenzene (2.02 g, 10 mmol) in dry DMF (50 mL) was added under an inert atmosphere at room temperature. The resulting mixture was heated at 115 °C under an argon atmosphere. After completion of the reaction, the mixture was washed with H_2O (2 × 30 mL) and extracted with EtOAc. The combined organic layers were dried and evaporated. The residue was purified by column chromatography (hexanes/EtOAc, 60:1) to afford pure 1-methyl-3-(2-nitrophenyl)-1*H*-indole.

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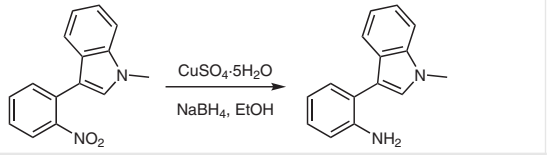
1-Methyl-3-(2-nitrophenyl)-1*H*-indole

Yield: 0.78 g (31%); brown solid; mp 128–130 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 7.6 Hz, 1 H), 7.71 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1 H), 7.63 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1 H), 7.58 (d, *J* = 7.6 Hz, 1 H), 7.46 (dd, *J* = 7.6, 1.2 Hz, 1 H), 7.33 (d, *J* = 8.0 Hz, 1 H), 7.29–7.25 (m, 2 H), 7.15 (dd, *J* = 7.6, 7.6 Hz, 1 H), 3.51 (s, 3 H).

2-(1-Methyl-1*H*-indol-3-yl)aniline (2d) (Scheme 11)



Scheme 11

To a solution of 1-methyl-3-(2-nitrophenyl)-1*H*-indole (757 mg, 3 mmol) in EtOH (12 mL) was added $CuSO_4{\cdot}5H_2O$ (899 mg, 3.6 mmol). $NaBH_4$ (170 mg, 4.5 mmol) was then added portionwise at 0 °C and the mixture was stirred at room temperature for 1 h. The reaction mixture was filtered through a short pad of silica gel using EtOAc (3 × 15 mL) as the eluent. The solvent was evaporated in vacuo and the residue was subjected to flash chromatography (petroleum ether/EtOAc, 20:1) to afford 2-(1-methyl-1*H*-indol-3-yl)aniline (**2d**).

Yield: 433 mg (65%); yellow crystalline solid; mp 127–128 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.0 Hz, 1 H), 7.36 (d, *J* = 8.0 Hz, 1 H), 7.30–7.24 (m, 2 H), 7.16–7.12 (m, 3 H), 6.81 (dd, *J* = 13.2, 7.2 Hz, 2 H), 3.81 (s, 3 H), 3.69 (br s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.8, 137.1, 131.3, 127.8, 127.7, 127.0, 122.1, 120.7, 120.5, 119.7, 118.4, 115.5, 113.3, 109.6, 32.9.

Methyl 3-Amino-4-(1*H*-indol-1-yl)benzoate (2e)[15] (Scheme 12)

To a stirred solution of indoline (941 µL, 8.4 mmol) in dry CH_2Cl_2 (20 mL) was added methyl 4-fluoro-3-nitrobenzoate (1.84 g, 9.2 mmol) and K_2CO_3 (2.32 g, 16.8 mmol) under an argon atmosphere, and the resulting mixture was refluxed for 4 h. Upon completion of the reaction, the solvent was removed, and the crude product was partitioned between H_2O and EtOAc. The aqueous layer was extracted with EtOAc (3 × 30 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated in vacuo to furnish methyl 4-(indolin-1-yl)-3-nitrobenzoate as a red solid (2.38 g, 95%). The crude product was used for further transformation without further purification.

A mixture of methyl 4-(indolin-1-yl)-3-nitrobenzoate (2.10 g, 7.0 mmol), ammonium formate (2.2 g, 35.2 mmol) and Zn powder (4.6 g, 70.4 mmol) in dry MeOH (50 mL) was stirred at room temperature for 15 min. Upon completion of the reaction, the mixture was filtered through a short pad of silica gel and the solvent was evaporated. The product was dissolved in CH_2Cl_2 (75 mL), precipitated ammonium formate was filtered off and the solvent was evaporated under reduced pressure. The crude residue was purified by flash column chromatography (petroleum ether/EtOAc, 20:1) to afford methyl 3-amino-4-(indolin-1-yl)benzoate.

Methyl 3-Amino-4-(indolin-1-yl)benzoate

Yield: 1.85 g (86%); off-white solid; mp 102–103 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 1.6 Hz, 1 H), 7.45 (dd, *J* = 8.4, 2.0 Hz, 1 H), 7.22 (d, *J* = 8.0 Hz, 1 H), 7.19 (d, *J* = 7.2 Hz, 1 H), 7.03 (dd, *J* = 7.6, 7.6 Hz, 1 H), 6.76 (dd, *J* = 6.8, 6.8 Hz, 1 H), 6.35 (d, *J* = 7.6 Hz, 1 H), 3.89 (m, 5 H), 3.80 (br s, 2 H), 3.14 (t, *J* = 8.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 149.0, 142.5, 135.9, 130.7, 127.7, 127.2, 124.8, 123.1, 120.4, 119.2, 117.0, 109.5, 53.8, 52.0, 28.9.

Methyl 3-Amino-4-(1*H*-indol-1-yl)benzoate (2e) (Scheme 13)

Scheme 13

A mixture of methyl 3-amino-4-(indolin-1-yl)benzoate (1.00 g, 3.7 mmol) and DDQ (1.70 g, 7.5 mmol) in EtOAc (15 mL) was stirred at room temperature for 4 h. Upon completion of the reaction, the mixture was partitioned between 1 M NaOH and EtOAc. The aqueous layer was extracted with EtOAc (3 × 20 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether/EtOAc, 20:1) to furnish methyl 3-amino-4-(1*H*-indol-1-yl)benzoate (**2e**).

Yield: 542 mg (55%); off-white solid; mp 63–64 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.55 (d, *J* = 1.6 Hz, 1 H), 7.49 (dd, *J* = 8.0, 1.6 Hz, 1 H), 7.24–7.11 (m, 5 H), 6.70 (d, *J* = 3.2 Hz, 1 H), 3.91 (s, 3 H), 3.54 (br s, 2 H).

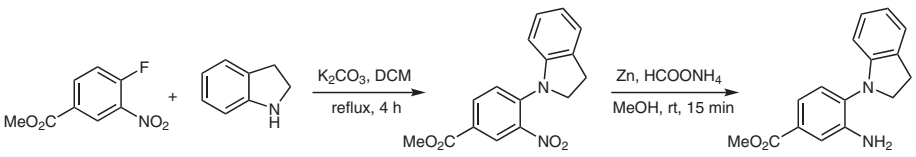
^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 142.8, 136.0, 130.6, 128.8, 128.7, 128.4, 128.1, 122.6, 121.2, 120.6, 119.6, 117.5, 110.8, 104.0, 52.3.

4,5-Dihydroquinoxalines 4; General Procedure

A mixture of arylamine **2** (0.5 mmol) and aldehyde **3** (0.6 mmol) in CH_3CN (2.5 mL, 0.2 M) was stirred for 15 min at room temperature. TEMPO oxoammonium salt **1b** (1.0 mol%) was then introduced. The mixture was stirred at room temperature and the reaction progress was monitored by TLC. Upon completion, the mixture was directly purified by flash column chromatography (petroleum ether/EtOAc, 80:1–20:1) to afford the desired 4,5-dihydroquinoxaline **4**.

4-Phenyl-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (4aa)[9d]

Yield: 115 mg (93%); pale yellow solid; mp 89–90 °C.



Scheme 12

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IR (KBr): 3433, 3346, 3059, 2923, 1605, 1512, 1487, 1384, 1332, 1281, 1059, 1029, 752, 702, 627 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.44 (dd, *J* = 8.0, 1.6 Hz, 2 H), 7.38–7.29 (m, 4 H), 7.17 (dd, *J* = 2.4, 1.2 Hz, 1 H), 6.94 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1 H), 6.82 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1 H), 6.69 (dd, *J* = 7.6, 1.2 Hz, 1 H), 6.23 (dd, *J* = 3.2, 3.2 Hz, 1 H), 5.57–5.56 (m, 1 H), 5.49 (s, 1 H), 4.12 (br s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.5, 136.2, 130.0, 128.7, 128.3, 128.0, 125.5, 124.7, 119.4, 115.4, 114.8, 114.4, 110.2, 105.9, 56.2.

4-(*p*-Tolyl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (4ab)

Yield: 116 mg (90%); colorless oil.

IR (KBr): 3447, 3345, 2924, 2854, 1743, 1655, 1626, 1597, 1384, 1216, 1160, 1117, 1034, 636, 507 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.26 (m, 3 H), 7.15–7.12 (m, 3 H), 6.91 (dd, *J* = 7.6, 7.6 Hz, 1 H), 6.79 (dd, *J* = 7.6, 7.6 Hz, 1 H), 6.64 (d, *J* = 8.0 Hz, 1 H), 6.21 (dd, *J* = 3.2, 3.2 Hz, 1 H), 5.56 (dd, *J* = 2.0, 1.2 Hz, 1 H), 5.42 (s, 1 H), 4.05 (br s, 1 H), 2.33 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.6, 138.0, 136.4, 130.3, 129.4, 127.9, 125.6, 124.7, 119.4, 115.4, 114.8, 114.4, 110.3, 105.9, 56.0, 21.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{17}N_2$: 261.1386; found: 261.1381.

4-(4-Methoxyphenyl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (4ac)[9d]

Yield: 130 mg (94%); white solid; mp 125–126 °C.

IR (KBr): 3431, 3332, 2932, 2801, 1606, 1511, 1484, 1336, 1287, 1238, 1173, 1155, 1022, 778, 751, 708, 674, 603 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 8.8 Hz, 2 H), 7.31 (dd, *J* = 7.6, 1.2 Hz, 1 H), 7.17 (dd, *J* = 2.4, 1.2 Hz, 1 H), 6.95 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1 H), 6.89 (d, *J* = 8.8 Hz, 2 H), 6.82 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1 H), 6.70 (dd, *J* = 7.6, 1.2 Hz, 1 H), 6.23 (dd, *J* = 3.2, 3.2 Hz, 1 H), 5.56 (dd, *J* = 1.6, 0.8 Hz, 1 H), 5.44 (s, 1 H), 4.09 (br s, 1 H), 3.79 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 136.4, 133.5, 130.5, 129.2, 125.6, 124.7, 119.3, 115.4, 114.8, 114.3, 114.0, 110.2, 105.8, 55.7, 55.3.

4-(4-Chlorophenyl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (4ad)[9k]

Yield: 121 mg (86%); white crystalline solid; mp 176–177 °C.

IR (KBr): 3433, 3343, 3044, 2923, 2853, 1592, 1473, 1421, 1340, 1088, 1039, 826, 749, 712, 595 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.29 (m, 5 H), 7.17–7.16 (m, 1 H), 6.97–6.93 (m, 1 H), 6.86–6.81 (m, 1 H), 6.71 (dd, *J* = 7.6, 1.2 Hz, 1 H), 6.24–6.22 (m, 1 H), 5.55–5.54 (m, 1 H), 5.47 (s, 1 H), 4.09 (br s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.0, 135.9, 134.1, 129.4, 129.3, 128.9, 125.5, 124.8, 119.6, 115.4, 114.8, 114.5, 110.3, 106.0, 55.6.

4-(4-Nitrophenyl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (4ae)[9d]

Yield: 128 mg (88%); yellow solid; mp 132–133 °C.

IR (KBr): 3340, 3133, 3102, 3070, 1601, 1514, 1487, 1344, 1286, 1154, 783, 751, 704, 660 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 8.4 Hz, 2 H), 7.55 (d, *J* = 8.4 Hz, 2 H), 7.30 (dd, *J* = 7.6, 0.8 Hz, 1 H), 7.18 (dd, *J* = 2.8, 1.2 Hz, 1 H), 6.97 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1 H), 6.85 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1 H), 6.75 (dd, *J* = 8.0, 1.2 Hz, 1 H), 6.24 (dd, *J* = 3.2, 3.2 Hz, 1 H), 5.61 (s, 1 H), 5.56–5.55 (m, 1 H), 4.25 (br s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.9, 147.7, 135.3, 128.6, 128.0, 125.2, 125.0, 123.9, 119.9, 115.6, 114.9, 110.5, 106.3, 55.4.

4-(3-Methoxyphenyl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (4af)[9o]

Yield: 127 mg (92%); white solid; mp 129–130 °C.

IR (KBr): 3326, 3060, 2960, 1600, 1513, 1485, 1467, 1336, 1263, 1028, 755, 714, 635, 555 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.0 Hz, 1 H), 7.26 (dd, *J* = 8.4, 8.4 Hz, 1 H), 7.16 (dd, *J* = 2.4, 1.2 Hz, 1 H), 7.02–7.00 (m, 2 H), 6.94 (ddd, *J* = 7.6, 7.6, 0.8 Hz, 1 H), 6.87–6.79 (m, 2 H), 6.69 (dd, *J* = 8.0, 0.8 Hz, 1 H), 6.23 (dd, *J* = 3.2, 3,2 Hz, 1 H), 5.61–5.60 (m, 1 H), 5.47 (s, 1 H), 4.14 (br s, 1 H), 3.75 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 143.1, 136.1, 129.8, 129.7, 125.5, 124.7, 120.3, 119.4, 115.4, 114.8, 114.4, 114.0, 113.2, 110.3, 105.9, 56.2, 55.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{17}N_2O$: 277.1335; found: 277.1361.

4-(2,4-Dichlorophenyl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (4ag)[9d]

Yield: 145 mg (92%); white solid; mp 138–139 °C.

IR (KBr): 3438, 3312, 3134, 2924, 2830, 1588, 1513, 1469, 1384, 1332, 1041, 778, 748, 714, 665, 578 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.39 (s, 1 H), 7.33 (dd, *J* = 8.0, 0.8 Hz, 1 H), 7.22 (dd, *J* = 2.8, 1.6 Hz, 1 H), 7.11 (d, *J* = 1.2 Hz, 2 H), 6.93 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1 H), 6.83 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1 H), 6.67 (dd, *J* = 7.6, 1.2 Hz, 1 H), 6.30 (dd, *J* = 3.2, 3.2 Hz, 1 H), 6.02 (s, 1 H), 5.81–5.80 (m, 1 H), 4.33 (br s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.3, 134.9, 134.2, 133.3, 130.2, 129.3, 127.7, 126.9, 125.3, 124.9, 119.7, 115.7, 114.7, 114.6, 110.5, 106.1, 51.5.

4-(Benzo[*d*][1,3]dioxol-5-yl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (4ah)[9p]

Yield: 129 mg (89%); colorless oil.

IR (KBr): 3362, 3139, 3066, 2893, 1609, 1512, 1484, 1444, 1336, 1248, 1038, 932, 746, 705 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.20 (d, *J* = 6.8 Hz, 1 H), 7.07–7.06 (m, 1 H), 6.86–6.82 (m, 2 H), 6.78 (dd, *J* = 8.0, 1.6 Hz, 1 H), 6.74–6.70 (m, 1 H), 6.67 (d, *J* = 8.0 Hz, 1 H), 6.60 (d, *J* = 8.0 Hz, 1 H), 6.14 (dd, *J* = 3.2, 3.2 Hz, 1 H), 5.82 (s, 2 H), 5.52 (d, *J* = 3.2 Hz, 1 H), 5.32 (s, 1 H), 4.02 (br s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.0, 147.6, 136.1, 135.5, 130.0, 125.4, 124.7, 121.3, 119.4, 115.4, 114.7, 114.4, 110.2, 108.3, 108.1, 105.9, 101.2, 55.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{15}N_2O_2$: 291.1128; found: 291.1158.

4-(Naphthalen-1-yl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (4ai)

Yield: 137 mg (93%); white crystalline solid; mp 114–115 °C.

IR (KBr): 3415, 3333, 3053, 2869, 1597, 1514, 1475, 1331, 1290, 1231, 1160, 806, 771, 702, 671, 636, 566, 519 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.4 Hz, 1 H), 7.88–7.85 (m, 1 H), 7.81 (d, *J* = 8.0 Hz, 1 H), 7.60 (d, *J* = 6.8 Hz, 1 H), 7.46–7.39 (m, 3 H), 7.35 (dd, *J* = 8.0, 0.8 Hz, 1 H), 7.20 (dd, *J* = 2.8, 1.6 Hz, 1 H), 6.93 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1 H), 6.83 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1 H), 6.65 (dd, *J* = 7.6, 1.2 Hz, 1 H), 6.24 (s, 1 H), 6.18 (dd, *J* = 3.2, 3.2 Hz, 1 H), 5.49–5.48 (m, 1 H), 4.14 (br s, 1 H).

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^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.7, 136.4, 134.2, 131.3, 129.3, 128.90, 128.86, 126.2, 125.83, 125.78, 125.6, 125.5, 124.8, 124.1, 119.5, 115.6, 114.8, 114.3, 110.3, 106.3, 53.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{17}N_2$: 297.1386; found: 297.1390.

4-(Furan-2-yl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (4aj)

Yield: 113 mg (96%); pale yellow oil.

IR (KBr): 3364, 3116, 2920, 2805, 1613, 1516, 1482, 1425, 1337, 1289, 1177, 1011, 742, 710, 602, 531 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (d, *J* = 0.8 Hz, 1 H), 7.28–7.27 (m, 1 H), 7.16 (dd, *J* = 2.8, 1.2 Hz, 1 H), 6.91 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1 H), 6.80 (dd, *J* = 7.6, 1.2 Hz, 1 H), 6.69–6.66 (m, 1 H), 6.29 (dd, *J* = 3.2, 3.2 Hz, 1 H), 6.22 (dd, *J* = 3.2, 2.0 Hz, 1 H), 6.04 (d, *J* = 3.2 Hz, 1 H), 5.99 (d, *J* = 2.8 Hz, 1 H), 5.65 (s, 1 H), 4.32 (br s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.6, 142.4, 134.9, 125.9, 125.4, 124.8, 119.6, 115.8, 114.7, 114.6, 110.4, 110.3, 107.1, 105.8, 49.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{13}N_2O$: 237.1022; found: 237.1031.

4-(Pyridin-2-yl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (4ak)[16]

Yield: 112 mg (91%); pale yellow solid; mp 125–126 °C.

IR (KBr): 3455, 3267, 3059, 2985, 2929, 1611, 1589, 1513, 1469, 1429, 1338, 1288, 752, 712, 684, 648 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52–8.50 (m, 1 H), 7.48 (ddd, *J* = 7.6, 7.6, 2.0 Hz, 1 H), 7.26 (dd, *J* = 7.6, 1.2 Hz, 1 H), 7.19 (dd, *J* = 3.2, 1.2 Hz, 1 H), 7.11 (d, *J* = 8.0 Hz, 1 H), 7.07 (ddd, *J* = 7.6, 5.2, 1.2 Hz, 1 H), 6.88 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1 H), 6.75 (ddd, *J* = 8.0, 8.0, 1.2 Hz, 1 H), 6.68 (dd, *J* = 7.6, 1.2 Hz, 1 H), 6.30 (dd, *J* = 3.2, 3.2 Hz, 1 H), 5.92–5.91 (m, 1 H), 5.67 (s, 1 H), 4.93 (br s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.3, 149.2, 137.0, 135.2, 126.8, 125.3, 124.8, 122.7, 121.6, 119.2, 115.9, 114.6, 114.5, 110.4, 106.5, 56.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{14}N_3$: 248.1182; found: 248.1174.

4-Phenethylpyrrolo[1,2-*a*]quinoxaline (4al)[17]

Yield: 98 mg (72%); yellow solid; mp 48–49 °C.

IR (KBr): 3434, 3138, 3026, 2926, 2858, 1608, 1528, 1480, 1452, 1424, 1376, 1100, 1036, 753, 705 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.87 (dd, *J* = 2.8, 1.2 Hz, 1 H), 7.79 (dd, *J* = 8.0, 1.6 Hz, 1 H), 7.47–7.39 (m, 2 H), 7.34–7.28 (m, 4 H), 7.23–7.18 (m, 1 H), 6.88 (dd, *J* = 4.0, 1.2 Hz, 1 H), 6.82 (dd, *J* = 3.6, 2.4 Hz, 1 H), 3.34–3.29 (m, 2 H), 3.25–3.20 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.3, 141.8, 136.0, 129.5, 128.5, 127.3, 127.0, 126.1, 125.9, 125.1, 114.3, 113.7, 113.6, 106.2, 37.5, 34.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{17}N_2$: 273.1386; found: 273.1413.

4-Ethyl-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (4am)[9d]

Yield: 75 mg (76%); white solid; mp 54–55 °C.

IR (KBr): 3368, 3060, 2964, 2929, 1612, 1516, 1483, 1424, 1342, 1295, 1175, 1090, 743, 701 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8.0 Hz, 1 H), 7.13–7.12 (m, 1 H), 6.94–6.90 (m, 1 H), 6.79–6.75 (m, 1 H), 6.70 (dd, *J* = 7.6, 1.2 Hz, 1 H), 6.29 (dd, *J* = 3.2, 3.2 Hz, 1 H), 5.98–5.97 (m, 1 H), 4.36 (dd, *J* = 6.4, 5.6 Hz, 1 H), 3.96 (br s, 1 H), 1.94–1.83 (m, 1 H), 1.81–1.70 (m, 1 H), 1.02 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.0, 129.6, 125.5, 124.6, 119.0, 115.3, 114.6, 114.1, 110.0, 104.0, 52.3, 28.3, 9.9.

1,4-Bis(4,5-dihydropyrrolo[1,2-*a*]quinoxalin-4-yl)benzene (4an)[9d]

Yield: 165 mg (80%); white solid; mp >300 °C.

IR (KBr): 3463, 3340, 3266, 3136, 2926, 2788, 1607, 1513, 1471, 1418, 1335, 1286, 1215, 1157, 1049, 1021, 765, 745, 704, 624, 507 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.48 (d, *J* = 7.6 Hz, 2 H), 7.42 (s, 2 H), 7.31 (s, 4 H), 6.91 (dd, *J* = 7.2, 7.2 Hz, 2 H), 6.85 (d, *J* = 7.2 Hz, 2 H), 6.70 (dd, *J* = 7.2, 7.2 Hz, 2 H), 6.60 (s, 2 H), 6.17 (dd, *J* = 3.2, 3.2 Hz, 2 H), 5.62 (d, *J* = 2.0 Hz, 2 H), 5.54 (s, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 142.6, 137.0, 129.4, 127.6, 125.1, 124.7, 118.1, 115.5, 115.0, 110.4, 105.5, 54.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{23}N_4$: 415.1917; found: 415.1889.

6-Phenyl-5,6-dihydroindolo[1,2-*a*]quinoxaline (4ba)[9d]

Yield: 124 mg (84%); yellow solid; mp 118–119 °C.

IR (KBr): 3446, 3335, 3057, 2924, 2853, 1685, 1654, 1598, 1508, 1454, 1386, 1214, 1156, 765, 744, 702, 648, 506 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.4 Hz, 1 H), 7.93–7.89 (m, 1 H), 7.51–7.48 (m, 3 H), 7.42–7.37 (m, 3 H), 7.25 (dd, *J* = 7.6, 7.6 Hz, 1 H), 7.13 (dd, *J* = 7.6, 7.6 Hz, 1 H), 7.02–6.98 (m, 2 H), 6.84–6.79 (m, 1 H), 5.86 (s, 1 H), 5.47 (s, 1 H), 4.13 (br s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.1, 139.3, 137.7, 134.2, 129.7, 128.8, 128.6, 128.4, 127.4, 124.0, 122.5, 121.1, 120.9, 120.2, 116.9, 116.1, 111.7, 100.2, 57.2.

7-Methyl-6-phenyl-5,6-dihydroindolo[1,2-*a*]quinoxaline (4ca)[9d]

Yield: 142 mg (92%); yellow crystalline solid; mp 152–153 °C.

IR (KBr): 3453, 3378, 3032, 2908, 1624, 1593, 1505, 1451, 1384, 1358, 1320, 1283, 1253, 1229, 1202, 1155, 746, 693, 618, 518 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.4 Hz, 1 H), 7.81–7.78 (m, 1 H), 7.47 (d, *J* = 7.6 Hz, 1 H), 7.21–7.17 (m, 1 H), 7.16–7.08 (m, 6 H), 6.88–6.81 (m, 2 H), 6.65–6.60 (m, 1 H), 5.55 (s, 1 H), 4.18 (s, 1 H), 1.93 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.8, 135.7, 133.5, 132.7, 130.8, 128.8, 128.0, 127.4, 127.2, 123.7, 122.6, 120.4, 119.9, 119.0, 116.5, 116.2, 111.8, 107.5, 55.2, 8.4.

7-Methyl-6-(*p*-tolyl)-5,6-dihydroindolo[1,2-*a*]quinoxaline (4cb)[9f]

Yield: 156 mg (96%); yellow solid; mp 55–56 °C.

IR (KBr): 3437, 3369, 3048, 2920, 2856, 1627, 1510, 1455, 1384, 1363, 1226, 1156, 738, 633, 507 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.4 Hz, 1 H), 7.88–7.86 (m, 1 H), 7.56 (d, *J* = 8.0 Hz, 1 H), 7.27 (dd, *J* = 7.6, 7.6 Hz, 1 H), 7.18 (dd, *J* = 7.6, 7.6 Hz, 1 H), 7.09 (d, *J* = 8.0 Hz, 2 H), 7.03 (d, *J* = 8.0 Hz, 2 H), 6.93–6.90 (m, 2 H), 6.71–6.68 (m, 1 H), 5.61 (s, 1 H), 4.23 (br s, 1 H), 2.26 (s, 3 H), 2.02 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.9, 137.7, 135.8, 133.5, 132.9, 130.8, 129.5, 127.5, 127.1, 123.7, 122.5, 120.4, 119.8, 119.0, 116.4, 116.2, 111.8, 107.3, 54.9, 21.2, 8.4.

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HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{21}N_2$: 325.1699; found: 325.1723.

6-(4-Methoxyphenyl)-7-methyl-5,6-dihydroindolo[1,2-*a*]quinoxaline (4cc)[9f]

Yield: 161 mg (95%); pale yellow crystalline solid; mp 130–131 °C.

IR (KBr): 3447, 3326, 3052, 2910, 2841, 1607, 1511, 1457, 1383, 1363, 1282, 1240, 1179, 1021, 790, 741, 601, 539 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.4 Hz, 1 H), 7.89–7.86 (m, 1 H), 7.55 (d, *J* = 7.6 Hz, 1 H), 7.27 (dd, *J* = 7.6, 7.6 Hz, 1 H), 7.18 (dd, *J* = 7.6, 7.6 Hz, 1 H), 7.12 (d, *J* = 8.4 Hz, 2 H), 6.95–6.89 (m, 2 H), 6.75 (d, *J* = 8.8 Hz, 2 H), 6.70–6.68 (m, 1 H), 5.57 (s, 1 H), 4.20 (br s, 1 H), 3.70 (s, 3 H), 1.99 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 135.9, 134.0, 133.5, 133.1, 130.8, 128.5, 127.4, 123.7, 122.6, 120.4, 119.8, 119.0, 116.4, 116.2, 114.1, 111.8, 107.3, 55.3, 54.7, 8.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{21}N_2O$: 341.1648; found: 341.1625.

6-(4-Chlorophenyl)-7-methyl-5,6-dihydroindolo[1,2-*a*]quinoxaline (4cd)[9d]

Yield: 167 mg (97%); pale yellow solid; mp 59–60 °C.

IR (KBr): 3415, 3370, 3052, 2920, 2856, 1598, 1509, 1487, 1455, 1384, 1362, 1227, 1156, 1089, 739, 627, 509 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.4 Hz, 1 H), 7.90–7.87 (m, 1 H), 7.57 (d, *J* = 8.0 Hz, 1 H), 7.30 (dd, *J* = 8.0, 8.0 Hz, 1 H), 7.23–7.19 (m, 3 H), 7.14 (d, *J* = 8.4 Hz, 2 H), 6.98–6.92 (m, 2 H), 6.75–6.73 (m, 1 H), 5.64 (s, 1 H), 4.26 (br s, 1 H), 2.04 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.3, 135.2, 133.7, 133.5, 132.2, 130.6, 129.0, 128.5, 127.4, 123.8, 122.8, 120.5, 120.1, 119.1, 116.5, 116.3, 111.8, 107.5, 54.4, 8.4.

7-Methyl-6-(4-nitrophenyl)-5,6-dihydroindolo[1,2-*a*]quinoxaline (4ce)[9f]

Yield: 174 mg (98%); yellow solid; mp 102–103 °C.

IR (KBr): 3421, 3369, 3053, 2921, 2855, 1597, 1512, 1344, 1227, 1156, 741, 705, 506 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02–7.98 (m, 3 H), 7.88–7.85 (m, 1 H), 7.58 (d, *J* = 7.6 Hz, 1 H), 7.33–7.27 (m, 3 H), 7.22 (dd, *J* = 7.6, 7.6 Hz, 1 H), 6.98–6.92 (m, 2 H), 6.75–6.73 (m, 1 H), 5.72 (s, 1 H), 4.26 (br s, 1 H), 2.10 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.9, 147.4, 134.5, 133.6, 131.1, 130.5, 127.8, 127.3, 124.1, 123.1, 120.8, 120.5, 119.2, 116.6, 116.5, 111.9, 107.9, 53.8, 8.4.

6-(3-Methoxyphenyl)-7-methyl-5,6-dihydroindolo[1,2-*a*]quinoxaline (4cf)

Yield: 162 mg (95%); pale yellow solid; mp 138–139 °C.

IR (KBr): 3449, 3373, 3052, 2922, 2855, 1597, 1509, 1488, 1454, 1384, 1361, 1224, 1155, 1041, 737, 703, 637, 508 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.0 Hz, 1 H), 7.80–7.77 (m, 1 H), 7.47 (d, *J* = 7.6 Hz, 1 H), 7.19 (dd, *J* = 7.6, 7.6 Hz, 1 H), 7.12–7.04 (m, 2 H), 6.86–6.81 (m, 2 H), 6.71 (d, *J* = 7.6 Hz, 1 H), 6.68–6.64 (m, 2 H), 6.64–6.61 (m, 1 H), 5.51 (s, 1 H), 4.14 (br s, 1 H), 3.55 (s, 3 H), 1.96 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 143.4, 135.8, 133.5, 132.6, 130.8, 129.8, 127.4, 123.8, 122.6, 120.4, 119.9, 119.5, 119.0, 116.5, 116.3, 113.3, 112.8, 111.8, 107.5, 55.2, 55.1, 8.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{21}N_2O$: 341.1648; found: 341.1672.

6-(2,4-Dichlorophenyl)-7-methyl-5,6-dihydroindolo[1,2-*a*]quinoxaline (4cg)

Yield: 184 mg (97%); pale yellow crystalline solid; mp 135–136 °C.

IR (KBr): 3448, 3377, 2922, 2854, 1628, 1593, 1510, 1458, 1384, 1229, 1157, 1041, 862, 818, 796, 746, 690, 639, 542 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.4 Hz, 1 H), 7.89 (d, *J* = 7.6 Hz, 1 H), 7.61 (d, *J* = 7.6 Hz, 1 H), 7.38 (d, *J* = 1.6 Hz, 1 H), 7.32 (dd, *J* = 7.6, 7.6 Hz, 1 H), 7.23 (dd, *J* = 7.6, 7.6 Hz, 1 H), 7.94–6.86 (m, 3 H), 6.66 (d, *J* = 7.2 Hz, 1 H), 6.59 (d, *J* = 8.4 Hz, 1 H), 6.10 (s, 1 H), 4.71 (br s, 1 H), 2.11 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.0, 134.5, 134.3, 133.6, 133.0, 130.9, 130.5, 130.1, 129.6, 127.5, 127.3, 124.0, 122.9, 120.7, 120.3, 119.3, 116.7, 116.4, 111.9, 107.9, 50.7, 8.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{17}Cl_2N_2$: 379.0763; found: 379.0790.

6-(Benzo[*d*][1,3]dioxol-5-yl)-7-methyl-5,6-dihydroindolo[1,2-*a*]quinoxaline (4ch)

Yield: 154 mg (87%); yellow solid; mp 144–145 °C.

IR (KBr): 3446, 3375, 3049, 2902, 2782, 1599, 1500, 1454, 1391, 1367, 1291, 1236, 1157, 1037, 929, 861, 797, 734, 699, 609, 528 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.4 Hz, 1 H), 7.88–7.86 (m, 1 H), 7.56 (d, *J* = 7.6 Hz, 1 H), 7.29–7.25 (m, 1 H), 7.20–7.16 (m, 1 H), 6.95–6.89 (m, 2 H), 6.71–6.64 (m, 4 H), 5.83 (s, 2 H), 5.54 (s, 1 H), 4.18 (br s, 1 H), 2.03 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.1, 147.3, 135.9, 135.6, 133.5, 132.7, 130.8, 127.3, 123.8, 122.6, 120.6, 120.5, 119.9, 119.0, 116.5, 116.2, 111.9, 108.3, 107.7, 107.4, 101.1, 54.9, 8.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{19}N_2O_2$: 355.1441; found: 355.1413.

7-Methyl-6-(naphthalen-1-yl)-5,6-dihydroindolo[1,2-*a*]quinoxaline (4ci)

Yield: 173 mg (96%); yellow solid; mp 134–135 °C.

IR (KBr): 3447, 3376, 3047, 2917, 2853, 1623, 1597, 1508, 1454, 1385, 1362, 1227, 1157, 780, 738, 697, 634, 536 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 8.0 Hz, 1 H), 8.07 (d, *J* = 8.4 Hz, 1 H), 7.95 (d, *J* = 8.0 Hz, 1 H), 7.88 (d, *J* = 7.6 Hz, 1 H), 7.73 (d, *J* = 8.0 Hz, 1 H), 7.56–7.48 (m, 3 H), 7.31 (dd, *J* = 7.6, 7.6 Hz, 1 H), 7.23–7.18 (m, 2 H), 7.06 (d, *J* = 6.8 Hz, 1 H), 6.93 (dd, *J* = 7.6, 7.6 Hz, 1 H), 6.83 (dd, *J* = 7.6, 7.6 Hz, 1 H), 6.55 (d, *J* = 7.6 Hz, 1 H), 6.45 (s, 1 H), 4.31 (br s, 1 H), 1.82 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.0, 135.8, 134.3, 133.5, 132.5, 130.9, 130.8, 129.4, 128.8, 127.3, 126.8, 126.3, 125.9, 125.5, 123.7, 123.0, 122.6, 120.5, 120.1, 119.1, 116.5, 116.4, 111.9, 107.8, 52.7, 8.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{21}N_2$: 361.1699; found: 361.1691.

6-(Furan-2-yl)-7-methyl-5,6-dihydroindolo[1,2-*a*]quinoxaline (4cj)[8b]

Yield: 147 mg (98%); brilliant yellow solid; mp 95–96 °C.

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IR (KBr): 3451, 2924, 2854, 1635, 1458, 1384, 1215, 1157, 1039, 843, 743, 640, 506 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.4 Hz, 1 H), 7.84–7.81 (m, 1 H), 7.60 (d, *J* = 7.6 Hz, 1 H), 7.30–7.26 (m, 2 H), 7.20 (dd, *J* = 7.6, 7.6 Hz, 1 H), 6.95–6.91 (m, 2 H), 6.79–6.77 (m, 1 H), 6.12 (dd, *J* = 3.2, 2.0 Hz, 1 H), 5.80 (d, *J* = 3.2 Hz, 1 H), 5.75 (s, 1 H), 4.49 (br s, 1 H), 2.24 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.9, 142.3, 135.3, 133.6, 130.5, 130.2, 127.4, 123.7, 122.7, 120.5, 120.2, 119.2, 116.5, 111.8, 110.4, 107.7, 107.2, 48.3, 8.1.

7-Methyl-6-(pyridin-2-yl)-5,6-dihydroindolo[1,2-*a*]quinoxaline (4ck)

Yield: 143 mg (92%); white solid; mp 156–157 °C.

IR (KBr): 3450, 3263, 3066, 2925, 1628, 1591, 1507, 1460, 1388, 1362, 1322, 1282, 1228, 1157, 1042, 997, 840, 792, 743, 671, 624 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.55 (d, *J* = 4.4 Hz, 1 H), 8.00 (d, *J* = 8.0 Hz, 1 H), 7.82–7.80 (m, 1 H), 7.62 (d, *J* = 7.6 Hz, 1 H), 7.36–7.27 (m, 2 H), 7.22 (dd, *J* = 7.6, 7.6 Hz, 1 H), 7.02 (dd, *J* = 7.2, 5.6 Hz, 1 H), 6.88–6.83 (m, 2 H), 6.79–6.73 (m, 2 H), 5.79 (s, 1 H), 5.30 (br s, 1 H), 2.23 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.2, 149.6, 136.9, 135.7, 133.8, 130.8, 130.5, 127.5, 123.8, 122.8, 122.5, 121.4, 120.5, 119.8, 119.2, 116.9, 116.3, 111.9, 108.5, 55.1, 8.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{18}N_3$: 312.1495; found: 312.1469.

3-(7-Methyl-5,6-dihydroindolo[1,2-*a*]quinoxalin-6-yl)-4*H*-chromen-4-one (4cl)

Yield: 163 mg (86%); pale yellow solid; mp 117–118 °C.

IR (KBr): 3349, 3060, 2920, 1636, 1607, 1509, 1459, 1389, 1351, 1231, 1154, 762, 734, 700, 540 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 7.6 Hz, 1 H), 8.02 (d, *J* = 8.4 Hz, 1 H), 7.87–7.84 (m, 1 H), 7.64 (d, *J* = 8.0 Hz, 1 H), 7.58 (dd, *J* = 7.6, 7.6 Hz, 1 H), 7.39–7.30 (m, 2 H), 7.28–7.22 (m, 2 H), 7.13 (s, 1 H), 6.92–6.85 (m, 2 H), 6.77–6.74 (m, 1 H), 6.04 (s, 1 H), 5.44 (br s, 1 H), 2.26 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.9, 156.5, 154.0, 135.2, 134.0, 133.9, 130.3, 128.9, 126.9, 125.7, 125.4, 124.1, 123.8, 122.9, 122.4, 120.6, 120.0, 119.3, 118.3, 117.1, 116.4, 111.8, 107.7, 47.1, 8.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{19}N_2O_2$: 379.1441; found: 379.1440.

6-Isopropyl-7-methyl-5,6-dihydroindolo[1,2-*a*]quinoxaline (4cm)

Yield: 111 mg (80%); pale yellow oil.

IR (KBr): 3386, 3052, 2959, 2921, 2866, 1625, 1598, 1509, 1456, 1383, 1363, 1287, 1232, 1049, 738, 702 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.0 Hz, 1 H), 7.79 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.58–7.56 (m, 1 H), 7.26–7.16 (m, 2 H), 6.96–6.88 (m, 2 H), 6.75–6.72 (m, 1 H), 4.26 (br s, 1 H), 4.05 (d, *J* = 9.2 Hz, 1 H), 2.25 (s, 3 H), 1.93–1.84 (m, 1 H), 0.89 (d, *J* = 6.8 Hz, 3 H), 0.84 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.1, 133.7, 133.4, 130.7, 127.9, 123.8, 122.4, 120.3, 119.5, 118.9, 116.8, 116.0, 111.4, 106.8, 56.4, 32.6, 19.6, 19.1, 9.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{21}N_2$: 277.1699; found: 277.1703.

1,4-Bis(7-methyl-5,6-dihydroindolo[1,2-*a*]quinoxalin-6-yl)benzene (4cn)

Yield: 254 mg (93%); pale yellow solid.

IR (KBr): 3388, 3049, 2912, 2857, 1629, 1599, 1510, 1454, 1386, 1364, 1325, 1289, 1252, 1230, 1202, 1156, 1049, 1017, 735, 624, 532 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 8.00 (d, *J* = 8.0 Hz, 2 H), 7.83–7.80 (m, 2 H), 7.55 (d, *J* = 7.6 Hz, 2 H), 7.23 (dd, *J* = 7.6, 7.6 Hz, 2 H), 7.15 (dd, *J* = 7.6, 7.6 Hz, 2 H), 7.10 (d, *J* = 3.2 Hz, 4 H), 6.90–6.89 (m, 4 H), 6.81 (s, 4 H), 5.74 (d, *J* = 3.2 Hz, 2 H), 2.12 (d, *J* = 3.6 Hz, 6 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 142.1, 137.1, 133.33, 133.31, 133.27, 130.5, 127.1, 126.6, 124.3, 122.9, 120.7, 119.3, 118.8, 116.5, 116.3, 112.0, 106.3, 52.2, 8.49, 8.47.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{38}H_{31}N_4$: 543.2543; found: 543.2518.

7-Methyl-6-phenyl-6,7-dihydro-5*H*-indolo[2,3-*c*]quinoline (4da)

Yield: 132 mg (85%); pale yellow solid; mp 159–160 °C.

IR (KBr): 3421, 3057, 3030, 2925, 2852, 1603, 1580, 1547, 1503, 1471, 1453, 1374, 1325, 1281, 1238, 1160, 743, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.56 (dd, *J* = 7.6, 1.2 Hz, 1 H), 7.34–7.32 (m, 2 H), 7.21–7.14 (m, 4 H), 7.07–7.02 (m, 1 H), 6.93 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1 H), 6.86–6.80 (m, 2 H), 6.67 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1 H), 6.47 (d, *J* = 8.0 Hz, 1 H), 5.91 (s, 1 H), 4.21 (br s, 1 H), 3.91 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.6, 144.4, 139.4, 131.9, 128.7, 128.2, 127.9, 127.4, 124.7, 122.5, 121.9, 119.6, 118.8, 117.9, 115.7, 114.4, 111.2, 109.2, 57.3, 32.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{19}N_2$: 311.1543; found: 311.1545.

Methyl 6,6-Dimethyl-5,6-dihydroindolo[1,2-*a*]quinoxaline-3-carboxylate (4ea)[11]

Yield: 131 mg (86%); yellow solid; mp 151–152 °C.

IR (KBr): 3441, 3339, 3044, 2957, 2853, 1710, 1620, 1601, 1492, 1452, 1386, 1315, 1289, 1228, 1111, 1006, 892, 766, 732, 649 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.4 Hz, 1 H), 7.85 (d, *J* = 8.4 Hz, 1 H), 7.61 (dd, *J* = 8.4, 2.0 Hz, 1 H), 7.55 (d, *J* = 8.0 Hz, 1 H), 7.48 (d, *J* = 2.0 Hz, 1 H), 7.23–7.19 (m, 1 H), 7.14 (d, *J* = 7.6 Hz, 1 H), 6.34 (s, 1 H), 3.84 (s, 3 H), 1.51 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 143.0, 135.8, 134.1, 130.6, 130.1, 125.4, 122.8, 121.8, 121.5, 121.1, 117.3, 116.0, 111.9, 97.4, 52.1, 51.9, 28.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{19}N_2O_2$: 307.1441; found: 307.1441.

Quinoxalines 5; General Procedure

A mixture of arylamine **2** (0.5 mmol) and aldehyde **3** (0.6 mmol) in CH_3CN (2.5 mL, 0.2 M) was treated with TEMPO oxoammonium salt **1b** (1.0 mol%). The resulting mixture was stirred at room temperature for 12–18 h until the reaction was complete (as indicated by TLC). Next, additional salt **1b** (0.5 mmol) was added and the mixture was stirred for 6 h at room temperature. The mixture was dissolved in DCM (50 mL) and washed with saturated Na_2CO_3, water, dried over sodium sulfate. The solvent was evaporated and the residue was purified by flash column chromatography (petroleum ether/EtOAc, 20:1) to afford the product **5**.

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4-Phenylpyrrolo[1,2-*a*]quinoxaline (5aa)[9d]

Yield: 110 mg (90%); brilliant yellow solid; mp 98–99 °C.

IR (KBr): 3136, 3061, 1603, 1595, 1522, 1472, 1444, 1414, 1368, 1319, 1244, 1165, 1094, 1071, 1032, 1006, 931, 910, 880, 751, 710, 695, 620 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.04 (dd, *J* = 7.6, 1.2 Hz, 1 H), 8.01–7.98 (m, 3 H), 7.86 (dd, *J* = 8.0, 0.8 Hz, 1 H), 7.56–7.51 (m, 3 H), 7.50 (dd, *J* = 8.0, 1.6 Hz, 1 H), 7.45 (ddd, *J* = 8.0, 8.0, 1.6 Hz, 1 H), 6.99 (dd, *J* = 4.0, 1.2 Hz, 1 H), 6.88 (dd, *J* = 4.0, 2.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4, 138.5, 136.3, 130.3, 129.8, 128.7, 128.6, 127.5, 127.2, 125.4, 125.3, 114.6, 114.0, 113.6, 108.7.

4-(*p*-Tolyl)pyrrolo[1,2-*a*]quinoxaline (5ab)[10a]

Yield: 107 mg (83%); pale yellow oil.

IR (KBr): 3138, 3062, 3032, 2920, 1612, 1529, 1511, 1476, 1445, 1422, 1367, 1347, 1320, 1250, 1211, 1183, 1162, 1100, 1041, 931, 824, 755, 722, 652, 618 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.05 (dd, *J* = 7.6, 1.2 Hz, 1 H), 7.99–7.98 (m, 1 H), 7.93 (d, *J* = 8.0 Hz, 2 H), 7.87 (d, *J* = 8.0 Hz, 1 H), 7.52–7.43 (m, 2 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.01 (dd, *J* = 4.0, 0.8 Hz, 1 H), 6.89 (dd, *J* = 3.6, 2.8 Hz, 1 H), 2.47 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4, 139.9, 136.3, 135.7, 130.2, 129.3, 128.6, 127.3, 127.2, 125.4, 125.2, 114.5, 113.9, 113.6, 108.7, 21.5.

4-(4-Methoxyphenyl)pyrrolo[1,2-*a*]quinoxaline (5ac)[9l]

Yield: 103 mg (75%); white crystalline solid; mp 111–112 °C.

IR (KBr): 3147, 3102, 3063, 3037, 2993, 2965, 2834, 1610, 1532, 1509, 1476, 1423, 1371, 1324, 1298, 1249, 1180, 1098, 1032, 935, 830, 807, 787, 756, 737, 706, 652, 620 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.04–7.98 (m, 4 H), 7.87 (d, *J* = 7.6 Hz, 1 H), 7.52–7.43 (m, 2 H), 7.07 (d, *J* = 8.4 Hz, 2 H), 7.01 (dd, *J* = 4.0, 1.2 Hz, 1 H), 6.90 (dd, *J* = 3.6, 2.8 Hz, 1 H), 3.91 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.0, 153.9, 136.3, 131.1, 130.1, 127.2, 127.1, 125.4, 125.2, 114.5, 114.0, 113.9, 113.6, 108.6, 55.4.

4-(4-Chlorophenyl)pyrrolo[1,2-*a*]quinoxaline (5ad)[10a]

Yield: 128 mg (92%); pale yellow solid; mp 174–175 °C.

IR (KBr): 3142, 3105, 3078, 3045, 1613, 1595, 1531, 1475, 1445, 1422, 1398, 1371, 1348, 1319, 1275, 1245, 1166, 1090, 1039, 1011, 933, 849, 827, 788, 749, 714, 648, 613 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.03 (dd, *J* = 8.0, 0.8 Hz, 1 H), 8.00–7.95 (m, 3 H), 7.87 (d, *J* = 8.0 Hz, 1 H), 7.54–7.51 (m, 3 H), 7.47 (ddd, *J* = 8.0, 8.0, 0.8 Hz, 1 H), 6.96–6.95 (m, 1 H), 6.91–6.89 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.1, 136.9, 136.1, 135.9, 130.3, 123.0, 128.8, 127.7, 127.1, 125.4, 125.1, 114.8, 114.1, 113.7, 108.5.

4-(4-Nitrophenyl)pyrrolo[1,2-*a*]quinoxaline (5ae)[9l]

Yield; 126 mg (87%); brilliant yellow solid; mp 220–221 °C.

IR (KBr): 3150, 3105, 3079, 1601, 1512, 1476, 1424, 1373, 1350, 1318, 1249, 1173, 1102, 1038, 1009, 938, 858, 835, 752, 721, 698, 648, 609 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, *J* = 8.8 Hz, 2 H), 8.20 (d, *J* = 8.8 Hz, 2 H), 8.06–8.04 (m, 2 H), 7.92 (d, *J* = 8.0 Hz, 1 H), 7.61–7.56 (m, 1 H), 7.53–7.49 (m, 1 H), 6.97–6.95 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.8, 148.6, 144.5, 136.0, 130.5, 129.7, 128.4, 127.2, 125.7, 124.8, 123.8, 115.2, 114.5, 113.8, 108.3.

6-Phenylindolo[1,2-*a*]quinoxaline (5ba)[9l]

Yield: 127 mg (86%); yellow solid; mp 170–171 °C.

IR (KBr): 3106, 3058, 2957, 1604, 1517, 1480, 1426, 1380, 1342, 1318, 1285, 1250, 1211, 1174, 1090, 1042, 979, 925, 887, 861, 751, 719, 641 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.51–8.46 (m, 2 H), 8.09 (dd, *J* = 8.0, 1.2 Hz, 1 H), 8.03–8.00 (m, 2 H), 7.91 (d, *J* = 8.0 Hz, 1 H), 7.62–7.52 (m, 5 H), 7.46–7.40 (m, 2 H), 7.24 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.3, 138.2, 136.2, 133.1, 130.5, 130.2, 130.1, 129.2, 129.1, 128.68, 128.66, 128.4, 124.4, 124.2, 122.8, 122.7, 114.7, 114.6, 102.6.

7-Methyl-6-phenylindolo[1,2-*a*]quinoxaline (5ca)[9d]

Yield: 142 mg (92%); yellow solid; mp 159–160 °C.

IR (KBr): 3042, 3029, 2921, 2855, 1611, 1540, 1479, 1447, 1399, 1372, 1332, 1313, 1255, 1207, 1122, 1105, 1072, 988, 941, 913, 848, 732, 967, 645, 608 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.47 (dd, *J* = 8.4, 3.6 Hz, 2 H), 8.02–8.00 (m, 1 H), 7.89 (d, *J* = 8.4 Hz, 1 H), 7.66–7.61 (m, 2 H), 7.57 (dd, *J* = 7.6, 7.6 Hz, 2 H), 7.54–7.52 (m, 3 H), 7.44 (dd, *J* = 7.6, 7.6 Hz, 1 H), 7.39 (dd, *J* = 7.6, 7.6 Hz, 1 H), 2.05 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.7, 139.5, 135.6, 132.1, 130.6, 130.3, 130.1, 129.3, 128.6, 128.5, 128.3, 125.7, 124.8, 123.8, 122.1, 120.8, 114.4, 111.0, 11.1.

7-Methyl-6-(*p*-tolyl)indolo[1,2-*a*]quinoxaline (5cb)[9d]

Yield: 143 mg (89%); brilliant yellow solid; mp 156–157 °C.

IR (KBr): 3273, 3226, 3063, 2919, 1615, 1543, 1480, 1452, 1400, 1379, 1328, 1325, 1225, 1213, 1187, 1158, 1120, 1083, 1033, 994, 815, 782, 747, 635, 610 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 8.72 (d, *J* = 8.4 Hz, 2 H), 8.00 (d, *J* = 8.0 Hz, 1 H), 7.91 (d, *J* = 7.6 Hz, 1 H), 7.73–7.65 (m, 2 H), 7.59 (d, *J* = 8.0 Hz, 2 H), 7.53–7.47 (m, 2 H), 7.43 (d, *J* = 7.6 Hz, 2 H), 2.46 (s, 3 H), 2.04 (s, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 157.2, 140.3, 132.4, 130.2, 130.1, 129.9, 129.4, 129.2, 128.0, 126.8, 125.1, 124.9, 123.1, 121.6, 115.6, 115.3, 21.6, 11.6.

6-(4-Methoxyphenyl)-7-methylindolo[1,2-*a*]quinoxaline (5cc)[10a]

Yield: 137 mg (81%); brilliant yellow solid; mp 202–203 °C.

IR (KBr): 3279, 3227, 3175, 3069, 2923, 2840, 1607, 1579, 1534, 1511, 1479, 1452, 1395, 1330, 1310, 1255, 1211, 1180, 1118, 1081, 1029, 992, 946, 835, 762, 742, 678, 608 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 8.79 (d, *J* = 8.4 Hz, 2 H), 8.09 (d, *J* = 8.0 Hz, 1 H), 7.96 (d, *J* = 8.0 Hz, 1 H), 7.79–7.72 (m, 4 H), 7.59–7.53 (m, 2 H), 7.23 (d, *J* = 8.4 Hz, 2 H), 3.91 (s, 3 H), 2.15 (s, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.0, 156.8, 133.1, 131.5, 130.5, 130.3, 123.0, 128.1, 125.3, 124.9, 123.6, 122.0, 116.0, 115.4, 114.5, 56.0, 11.9.

6-(4-Chlorophenyl)-7-methylindolo[1,2-*a*]quinoxaline (5cd)

Yield: 161 mg (94%); orange-yellow solid; mp 226–227 °C.

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IR (KBr): 3271, 3225, 3176, 3068, 2913, 1616, 1596, 1533, 1483, 1455, 1400, 1330, 1255, 1214, 1192, 1159, 1086, 1017, 994, 942, 860, 824, 786, 749, 728, 678, 612 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 8.75–8.71 (m, 2 H), 8.01 (d, *J* = 8.0 Hz, 1 H), 7.93 (dd, *J* = 8.0, 1.6 Hz, 1 H), 7.73–7.63 (m, 6 H), 7.54–7.47 (m, 2 H), 2.06 (s, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 156.2, 137.9, 134.9, 134.7, 132.0, 131.1, 130.12, 130.07, 129.74, 129.72, 128.9, 126.0, 125.2, 124.7, 122.9, 121.3, 115.4, 115.2, 11.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{16}N_2Cl$: 343.0997; found: 343.1006.

7-Methyl-6-(4-nitrophenyl)indolo[1,2-*a*]quinoxaline (5ce)

Yield: 159 mg (90%); red solid; mp 259–260 °C.

IR (KBr): 3151, 3097, 3066, 2946, 2905, 2861, 1597, 1566, 1542, 1520, 1479, 1450, 1408, 1379, 1347, 1312, 1256, 1214, 1194, 1158, 1104, 1016, 993, 932, 873, 850, 749, 718, 702, 674, 653, 609 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 8.75 (dd, *J* = 8.4, 6.0 Hz, 2 H), 8.44 (d, *J* = 8.8 Hz, 2 H), 8.03–7.93 (m, 4 H), 7.75–7.70 (m, 1 H), 7.66 (dd, *J* = 7.6, 7.6 Hz, 1 H), 7.54–7.47 (m, 2 H), 2.05 (s, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.7, 157.4, 145.7, 135.3, 133.1, 131.9, 130.8, 130.3, 130.2, 130.0, 125.9, 124.7, 124.0, 123.0, 121.3, 115.5, 115.2, 110.4, 11.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{16}N_3O_2$: 354.1237; found: 354.1252.

7-Methyl-6-phenyl-7*H*-indolo[2,3-*c*]quinoline (5da)

Yield: 139 mg (90%); white solid; mp 112–113 °C.

IR (KBr): 3053, 2925, 2854, 1611, 1557, 1512, 1489, 1472, 1442, 1419, 1377, 1333, 1306, 1262, 1227, 1199, 1157, 1128, 1088, 1024, 999, 943, 918, 856, 796, 761, 741, 701, 642, 611 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.73 (d, *J* = 8.0 Hz, 1 H), 8.60 (d, *J* = 8.0 Hz, 1 H), 8.32 (d, *J* = 8.0 Hz, 1 H), 7.71–7.62 (m, 4 H), 7.59 (dd, *J* = 7.6, 7.6 Hz, 1 H), 7.55–7.51 (m, 3 H), 7.49 (d, *J* = 8.4 Hz, 1 H), 7.41 (dd, *J* = 7.6, 7.6 Hz, 1 H), 3.45 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.0, 142.2, 141.8, 140.2, 132.3, 130.3, 129.4, 128.8, 128.5, 126.9, 125.9, 124.2, 123.3, 122.9, 122.5, 121.9, 120.7, 110.4, 33.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{17}N_2$: 309.1386; found: 309.1392.

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Supporting Information

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