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Direct Synthesis of Pyrrolo[1,2-α]quinoxalines *via* Iron-Catalyzed Transfer Hydrogenation between 1-(2-Nitrophenyl)pyrroles and Alcohols

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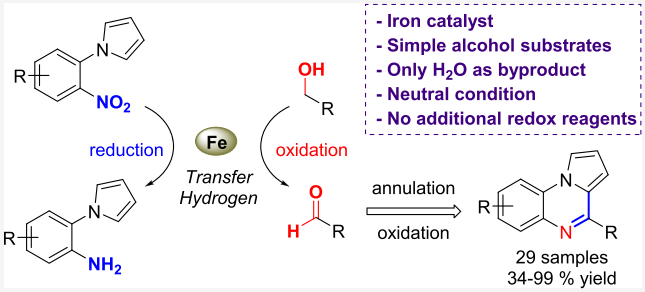
ABSTRACT: Herein, we describe novel iron-catalyzed transfer hydrogenation between alcohols and 1-(2-nitrophenyl)pyrroles for the synthesis of pyrrolo[1,2-α]quinoxalines. The tricarbonyl (η^4-cyclopentadienone) iron complex catalyzed the oxidation of alcohols and the reduction of nitroarenes, and the corresponding aldehydes and aniline were generated *in situ*. The resulting Pictet–Spengler-type annulation/oxidation completed the quinoxaline structure formation. The protocol tolerated various kinds of functional groups and provided 29 samples of 4-substituted pyrrolo[1,2-α]quinoxalines. The developed method was also applied for the synthesis of additional polyheterocycles.



INTRODUCTION

The transfer hydrogenation strategy has become an attractive tool in organic synthesis. Based on this strategy, the borrowing hydrogen process has provided a convenient method for new bond formation between nucleophiles and alcohol substrates.[1] In the borrowing hydrogen process, this bond formation usually proceeds in the following sequence (Figure 1 top): (i) the dehydrogenation of alcohol generates a more reactive carbonyl intermediate, (ii) the more reactive intermediate can undergo further transformations with a nucleophile to give an unsaturated intermediate, and (iii) the unsaturated intermediate will be hydrogenated to produce alkylated products. The catalyst mediates the hydrogen transfer from the alcohol to the unsaturated bond during the process. According to this strategy, bench-stable and inexpensive alcohol can be applied as an alkylating reagent, and only water is liberated as a stoichiometric byproduct during the intermediate reaction. Thus, the borrowing hydrogen reaction is an atom-efficient and environmentally benign method. Many kinds of transition metals have been employed as catalysts in C–C or C–N bond formations by the borrowing hydrogen strategy. In addition to commonly used precious metal catalysts,[1c,2] considerable progress has also been made recently with base metal catalysts,[1a] such as Fe,[3] Co,[4] Mn,[5] Ni,[6] and Cu.[7] Among those, iron is the most abundant transition metal with low price and toxicity; thus, it has received significant attention as a catalyst in transfer hydrogenation.

The representative catalyst, tricarbonyl (η^4-cyclopentadienone) iron complex, was originally described by Knölker in 1999.[8] Several pioneering studies by Casey and Guan revealed

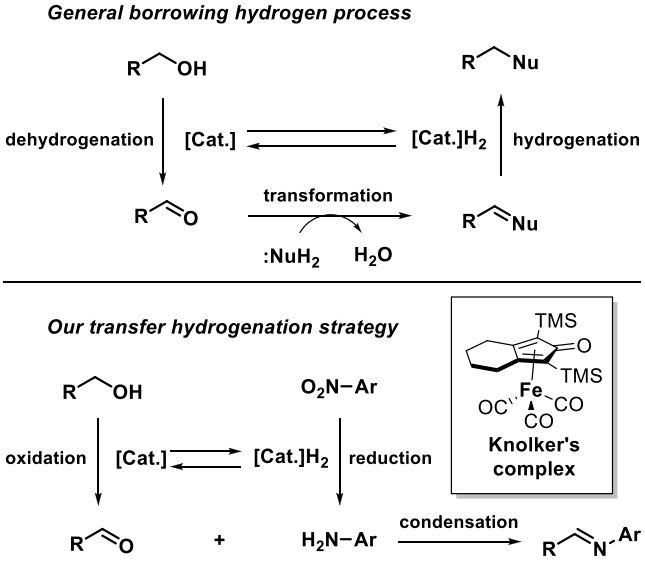


Figure 1. New bond formation through transfer hydrogenation and the representative iron catalyst.

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its catalytic activity for hydrogen transfer from alcohol to carbonyl compound.[9] Subsequently, Feringa and Barta discovered that this iron complex could mediate the transfer hydrogenation from alcohol to imine during the reductive amination process,[10a] and it has been widely applied in C−N bond formation using alcohol through the borrowing hydrogen strategy.[10] Although C−N bond formation was successfully achieved using Knölker's complex, previous borrowing hydrogen studies have applied nucleophilic amines directly. We envisioned the feasibility of nitroarene as a pronucleophile to form C−N bonds with alcohol based on the transfer hydrogenation mechanism. In our strategy, nucleophilic amine and electrophilic aldehyde can be generated *in situ* from nitroarene and alcohol, respectively, through transfer hydrogenation processes. Followed by the condensation of these two intermediates, a new C−N bond was constructed (Figure 1 bottom). To the best of our knowledge, this iron complex has not been explored for the reduction of nitro groups *via* the transfer hydrogenation reaction, and no study on C−N bond formation by directly employing nitroarene has been reported.

Pyrrolo[1,2-α]quinoxalines are important components found in many biologically active molecules.[11] In addition to their various biological activities, their fluorescence and photophysical properties have generated interest in the synthesis of biomarkers, dyes, and materials.[12] Therefore, much attention has been devoted to the synthesis of pyrrolo[1,2-α]quinoxaline derivatives until now. The most common method is the Pictet−Spengler-type condensation of aldehydes with 1-(2-aminophenyl)pyrroles which is usually obtained by the reduction of 1-(2-nitrophenyl)pyrroles.[13]

Although the one-pot synthesis of pyrrolo[1,2-α]-quinoxalines from 1-(2-nitrophenyl)pyrroles provides a shortcut synthetic route, only a few examples have been reported (Scheme 1). In 2012, iron-mediated reduction of nitroarene and alcohol oxidation followed by cyclization to pyrrolo[1,2-*a*]quinoxaline was reported by Pereira.[14] Sanz's group developed a molybdenum-catalyzed redox reaction between nitroarenes and 1,2-diol substrates.[15] Recently, an activated carbon/water catalytic system between 1-(2-nitrophenyl)-pyrroles and arylamines was also reported by Wang.[16] Although these one-pot approaches provided a shortcut synthesis of pyrrolo[1,2-α]quinoxaline and employed bench-stable alcohols or amines, they still suffer from several drawbacks, such as excess amounts of metal and alcohol, strong acidic conditions, limitation of substrate scope, and the generation of additional stoichiometric byproducts. Considering the limitations of the previous procedures, a simpler, milder, affordable, and environmentally friendly system for the synthesis of pyrrolo[1,2-*a*]quinoxalines is still desirable. As part of our process for developing a synthetic method for the *N*-heterocycle, we examined the direct pyrrolo[1,2-α]quinoxaline synthesis between a simple alcohol and 1-(2-nitrophenyl)-pyrrole using Knölker's complex (Scheme 1 bottom).

RESULTS AND DISCUSSION

In the beginning, we selected commercially or readily available 1-(2-nitrophenyl) pyrrole (**1a**) and benzyl alcohol (**2a**) as model substrates for testing our initial hypothesis. A standard Knölker complex (**Fe I**) and trimethylamine *N*-oxide (TMAO), which was used to activate **Fe I** and liberate a vacant site *in situ*, were applied in cyclopentyl methyl ether (CPME) at 140 °C under Ar for 40 h. As shown in Table 1, only trace amounts of the desired product (**3aa**) were obtained in the first trial (5%, entry 1). However, this result showed that it was possible to reduce the nitro group by transfer hydrogenation using the iron complex **Fe I**. Next, the reaction

Scheme 1. Synthesis of Pyrrolo[1,2-α]quinoxaline from 1-(2-Nitrophenyl)pyrrole

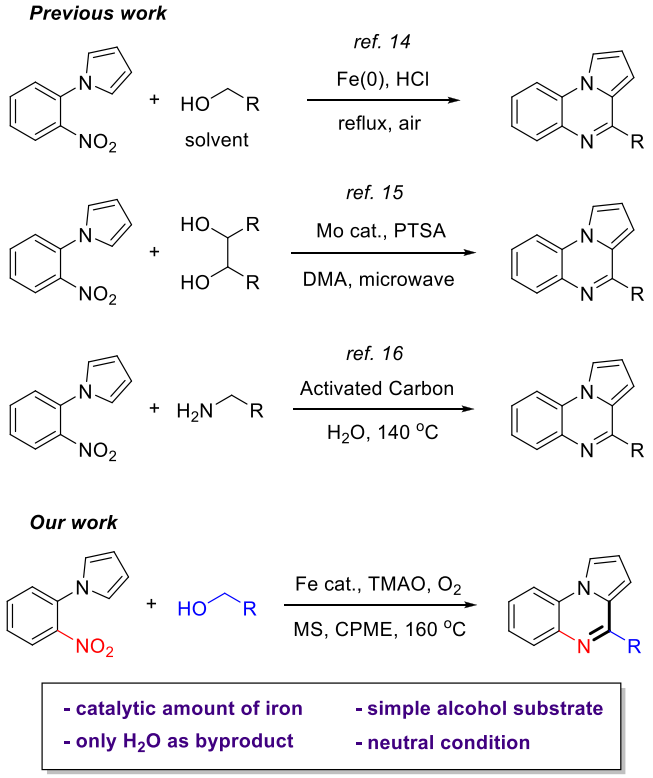
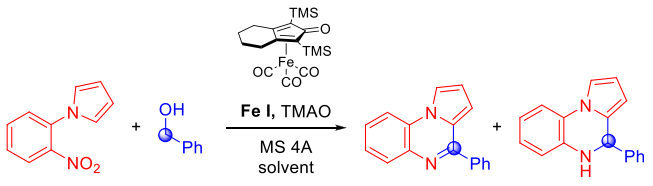


Table 1. Optimization of the Reaction Conditions[a]



entry	solvent	T (°C)	time (h)	**3aa** (%)[b]	**3aa′** (%)[b]	gas
1	CPME	140	40	5	0	Ar
2	CPME	150	40	27	0	Ar
3	CPME	160	40	21	27	Ar
4	CPME	160	40	33	44	air
5	CPME	160	24	93 (90)	0	O_2
6	toluene	160	24	66 (68)	31 (24)	O_2
7	xylene	160	24	40	0	O_2
8[c]	CPME	160	24	79	0	O_2
9[d]	CPME	160	24	74	9	O_2
10[e]	CPME	160	24	0	0	O_2
11[f]	CPME	160	40	(96)	0	O_2

[a]Reaction condition: **1a** (0.3 mmol), **2a** (0.9 mmol), **Fe I** (6 mol %), TMAO (12 mol %), and molecular sieve (50 mg) in solvent (0.3 mL). The reaction vessel was recharged with gas and sealed. [b]NMR yield using dimethyl sulfone as the internal standard. Isolated yield in parentheses. [c]**2a** (0.6 mmol). [d]Without a molecular sieve. [e]Without **Fe I** and TMAO. [f]1 mmol scale reaction of **1a** and **Fe I** (15 mol %) and TMAO (30 mol %) were used.

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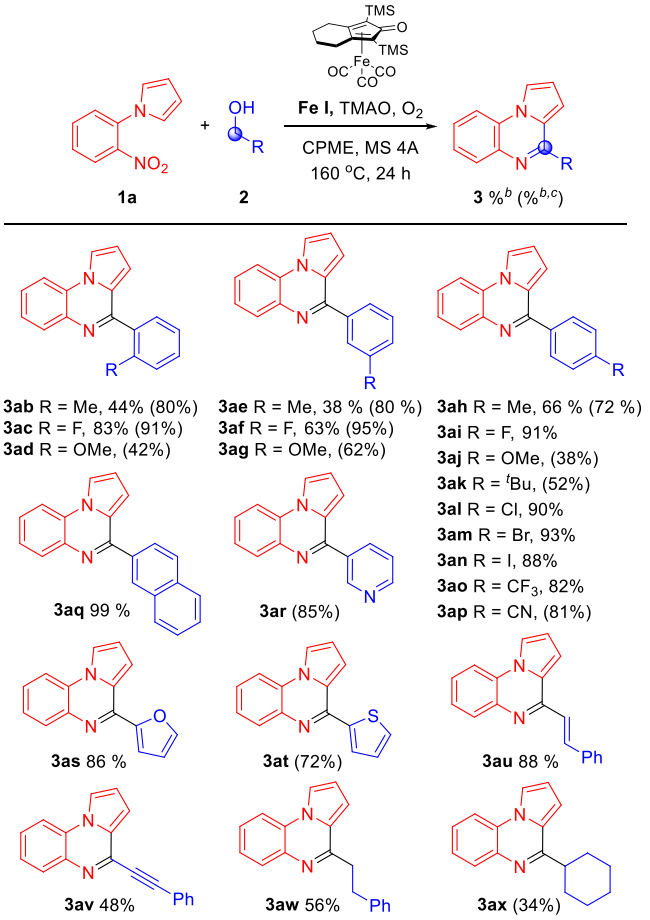
temperature was increased to achieve a higher conversion (entries 2−3). Even when **1a** was consumed completely at 160 °C, the desired product **3aa** was formed along with an unoxidized product **3aa′**. To improve selectivity for **3aa**, the reaction vessel was charged with air and O_2 gas (entries 4−5). We hypothesized that O_2 may help the final oxidation from **3aa′** to **3aa**, which was not favored under Ar. The reaction proceeded quickly and reached full conversion within 24 h with O_2 gas, and quinoxaline product **3aa** was obtained selectively in high yield (90% isolated yield, entry 5). To examine the solvent effect, we employed different types of solvents. However, low selectivity between **3aa** and **3aa′** was observed in toluene, and low conversion was observed in xylene (entries 6−7). At this time, we detected that a small amount of **3aa′** was converted to **3aa** in silica gel during column chromatography. Additionally, we reduced the amount of alcohol **2a** in the reaction; however, lower conversion was observed, and nitroarene **1a** remained in the mixture (entry 8). We speculate that at least 3 equivalents of alcohol are required to reduce 1 equivalent of nitroarene. The reaction without the molecular sieve was slow and not completed in 24 h, indicating that the reaction was retarded by water which is generated *in situ* (entry 9). To demonstrate the crucial role of the iron complex in the transfer hydrogenation process, a control experiment was also performed in the absence of **Fe I** (entry 10). As we expected, no products were formed and most of **1a** and **2a** were remained. Various types of iron complexes have also been explored to estimate their activity. Among the explored iron complexes, **Fe I** showed the best efficiency in the reaction system, and the results of each complex are included in the Supporting Information. These results also suggested that TMAO is essential to activate **Fe I**. We carried out 1 mmol scale reaction to demonstrate the practical utility of the method, and **3aa** was obtained in high yield (96% isolated yield, entry 11).

After optimization of the reaction conditions, a wide range of alcohol **2** was employed for annulation with **1a** to explore the reaction scope (Table 2). Benzylic alcohols containing various substituents reacted with **1a** to the corresponding quinoxaline products **3ab**−**3ap**. In general, benzylic alcohols containing electron-donating groups, such as methyl, *t*-butyl, and methoxy groups, were less reactive than those with electron-withdrawing groups. All of the methoxy benzyl alcohols resulted in low yields even with longer reaction times (**3ad**, **3ag**, and **3aj**). In the case of more electron-enriched 4-(dimethylamino) benzyl alcohol, no desired product was obtained. These electronic effects of benzyl alcohol suggest that the annulation process shows more influence on the product formation than the transfer hydrogenation process. Although electron-rich benzylic alcohols can act as strong reductants in the transfer hydrogenation process, they can act as less-active electrophiles in the annulation process. The steric effect of substituents did not directly influence the formation of the product (**3ab**−**3aj**). The electron density of benzylic carbon according to the position of the substituent showed more influence than the steric effect. The electron-donating methoxy group on ortho- and para-position gave the desired products **3ad** and **3aj** in poor yields. In contrast with the methoxy group, benzyl alcohols containing *ortho*- and *para*-fluorine afforded the annulated product in higher yield than that of *meta*-fluoro benzyl alcohol (**3ac**, **3ai** *vs* **3af**). Various heteroaromatic groups and naphthalene could also be employed at the 4-position of the pyrrolo[1,2-

Table 2. Scope of Alcohols[a]



[a]Reaction condition: **1a** (0.3 mmol), **2** (0.9 mmol), **Fe I** (6 mol %), TMAO (12 mol %), molecular sieve (50 mg), and CPME (0.3 mL) at 160 °C for 24 h under O_2 in sealed tubes. [b]Isolated yield. [c]Reaction time: 40 h.

α]quinoxalines (**3aq**−**3at**). For further expansion of the alcohol scope, allylic, propargylic, and aliphatic alcohols were also investigated. Cinnamyl alcohol reacted with **1a**, and the desired product **3au** was obtained in good yield. However, in the case of geraniol, partial hydrogenation of olefin occurred, and the messy reaction mixture was observed in TLC. Comparing reactions with cinnamyl alcohol and geraniol, highly conjugated olefin of **3au** was inactive in hydrogenation, but it could be assumed that nonconjugated olefin in geraniol can be affected by hydrogenation under the reaction condition. In addition, 3-phenylpropargyl alcohol and aliphatic alcohols could participate in the reaction, even if the products **3av**−**3ax** were obtained in low yields.

Next, we employed various types of 2-pyrrole nitroarenes for further extension of the substrate scope (Table 3). In the case of 1-(2-nitrophenyl) pyrroles, electron-withdrawing substituents on benzene (chloro and trifluoromethyl groups, **3da**−**3ea**/**3ha**) generally afforded the corresponding products in higher yields than electron-donating substituents (methyl and methoxy groups, **3ba**−**3ca**/**3fa**−**3ga**). Interestingly, the position of the substituent played a crucial role in the reaction, regardless of the electron density. The 4-substituted 1-(2-nitrophenyl) pyrroles were more reactive than the 5- or 6-substituted analogues (**3ba**−**3ea** *vs* **3fa**−**3ia**). Additionally, 3-nitro-2-(1*H*-pyrrol-1-yl)pyridine could also be applied in the

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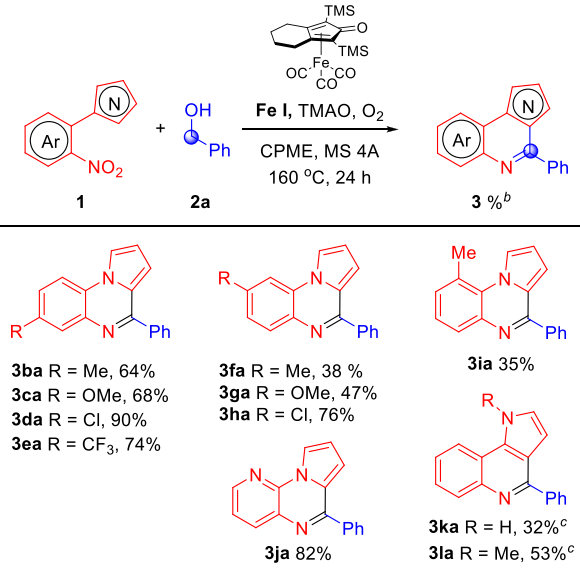
Table 3. Scope of 2-Pyrrole Nitroarenes[a]

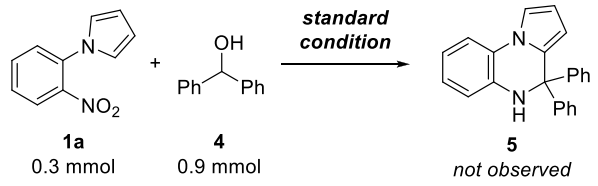


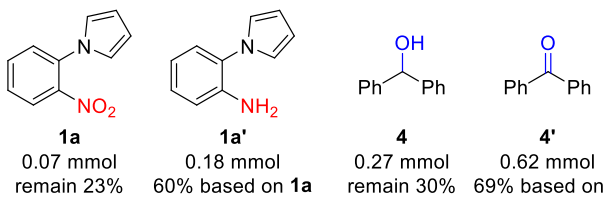
[a]Reaction condition: **1** (0.3 mmol), **2a** (0.9 mmol), **Fe I** (6 mol %), TMAO (12 mol %), molecular sieve (50 mg), and CPME (0.3 mL) at 160 °C for 24 h under O_2 in sealed tubes. [b]Isolated yield. [c]The reaction proceeded at 170 °C for 40 h.

reaction and yielded annulated product **3ja**. In addition to the 2-position of pyrrole, we hypothesized that the 3-position of pyrrole can also participate in the annulation. Accordingly, 2-(2-nitrophenyl)-pyrrole substrates were also subjected to the reaction conditions. Although longer reaction times and higher temperatures were required, pyrrolo[3,2-*c*]quinoline products **3ka** and **3la** were obtained in moderate yields.

We also attempted the annulation using a secondary alcohol to synthesize a dihydropyrrolo[1,2-*α*]quinoxaline structure (Scheme 2). Although the desired product **5** could not be

Scheme 2. Trial to Synthesize Dihydropyrrolo[1,2-*α*]quinoxaline Using Secondary Alcohol 4



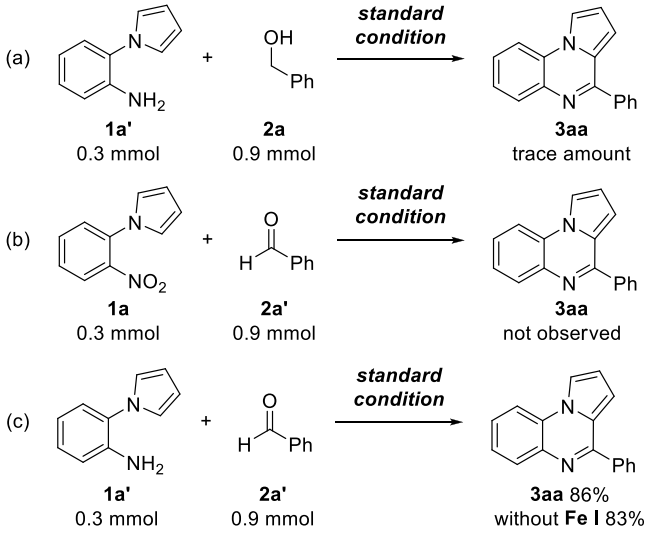


obtained, both 2-(1*H*-pyrrol-1-yl)aniline **1a′** and ketone **4′** were observed in the reaction mixture. This result confirmed our hypothesis that nitroarene is reduced as a hydrogen acceptor and that alcohol is oxidized as a hydrogen donor in the transfer hydrogenation mechanism. Notably, almost 3 equivalents of alcohol were consumed to reduce one nitro functionality.

NMR yield using dimethyl sulfone as the internal standard.

Further control experiments were performed to evaluate the mechanism of hydrogen transfer (Scheme 3). As shown in

Scheme 3. Mechanistic Studies



Scheme 3a, when 2-(1*H*-pyrrol-1-yl)aniline **1a′** was directly treated with benzyl alcohol **2a** under the standard reaction conditions, only negligible product formation occurred in the absence of the nitro functionality. Similarly, the nitro reduction did not occur in the absence of alcohol when benzaldehyde **2a′** was used instead of benzyl alcohol **2a** (Scheme 3b). These results indicated that both the hydrogen acceptor nitro group and the hydrogen donor alcohol are required for the balance of hydrogen transfer. When prereduced **1a′** was reacted with preoxidized **2a′** under the standard conditions, **3aa** was obtained regardless of the presence of **Fe I**. Therefore, the iron complex was determined to be a hydrogen mediator between the nitro and alcohol groups but was not involved in the final oxidation of intermediate **3aa′** to form **3aa**. According to the results in Table 1, O_2 gas could accelerate this final oxidation process.

Based on the abovementioned results, a plausible mechanism of hydrogen transfer and the cyclization process are depicted in Scheme 4. Iron-mediated oxidation of alcohol **2a** leads to aldehydes **2a′** and [**Fe**]−$\mathbf{H_2}$, which reduce nitrobenzene **1a** to aniline **1a′**. For the balance of hydrogen, [**Fe**] transfers six hydrogens from 3 equivalent of alcohols to one nitro group. After the hydrogen transfer process, condensation between aniline **1a′** and aldehyde **2a′** forms imine intermediate **6**, followed by a nucleophilic attack of pyrrole that produces cyclized intermediate **3aa′**. The imine intermediate **6** was directly observed in the NMR spectrum of the crude reaction mixture (see details in the Supporting Information). The final oxidative aromatization occurs with the assistance of O_2 gas. Thus, a total of 4 equiv of H_2O are generated as a byproduct, including the reduction of the nitro group and the condensation step. In addition, 3 equivalents of alcohol are required as a hydrogen donor to reduce the nitro functionality. Although the 16-electron iron complex [**Fe**] has been proposed as an active species in the mechanism, the possibility that another active species can be generated under O_2 gas could not be ruled out.

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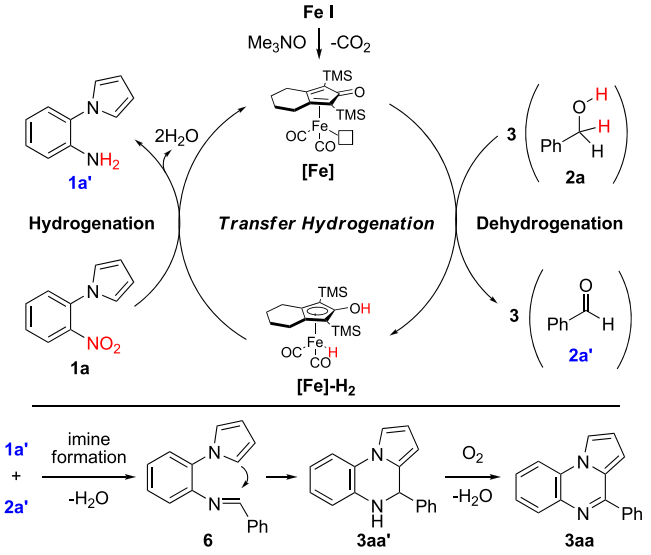
Scheme 4. Proposed Mechanism



CONCLUSIONS

In conclusion, we described the iron-catalyzed synthesis of pyrrolo[1,2-α]quinoxalines by the economical transfer hydrogenative coupling of 1-(2-nitrophenyl)pyrroles and alcohols. The developed transfer hydrogenation process allows for reduction of nitroarene and oxidation of alcohol in the presence of the tricarbonyl (η^4-cyclopentadienone) iron complex. It is the first discovery that this iron catalyst has potential to reduce nitro functionality *via* hydrogen transfer. Iron is an earth-abundant and low-toxicity metal, and only water is liberated as the reaction byproduct. Additionally, alcohol is readily available and used in the reaction both as a reductant and coupling reagent; thus, any external redox reagent is not required. Therefore, this methodology provides an ecofriendly alternative for the synthesis of pyrrolo[1,2-α]quinoxalines. Further expansion of the iron-catalyzed transfer hydrogenation strategy to access other types of *N*-heterocycles is currently investigated by our research group.

EXPERIMENTAL SECTION

General Information. All commercially available reagents and solvents (purchased from Sigma-Aldrich, TCI, Alfa-Aesar, and Acros) were used without further purification unless otherwise noted. All reactions were carried out in an oven-dried round-bottom flask or sealed tube purchased from Fishcer Scientific (Fisherbrand disposable borosilicate glass tubes with threaded end and Qorpak Green Thermoset Cap with F217 and PTFE Liner). Reactions were monitored by thin layer chromatography on a silica gel 60 F254 plate (Merck, Darmstadt, Germany) using UV illumination at 254 and 365 nm (VL-4.LC, Vilber Lourmat, Eberhardzell, Germany). Column chromatography was performed on silica gel (230−400 mesh; Zeochem, Lake Zurich, Switzerland), using hexane and EtOAc as eluents. Nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR, and ^{19}F NMR) spectra were measured on a JEOL JNM-ECZ400s [400 MHz (^{1}H), 100 MHz (^{13}C), and 376 MHz (^{19}F)] spectrometer. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^{1}H NMR: $CDCl_3$ = 7.26 ppm; for ^{13}C NMR: $CDCl_3$ = 77.16 ppm. Coupling constants (J) are expressed in hertz (Hz). All high-resolution mass spectra (HR-MS) were acquired using a fast atom bombardment (FAB) ionization method on a JMS-700 MStation mass spectrometer (JEOL, Tokyo, Japan). Melting points were measured on a Büchi B-540 melting point apparatus. Starting compounds **1a−1j** were synthesized through known procedures and characterization data were consistent with the literature.[13f]

Synthesis of 2-(2-nitrophenyl)-1*H*-pyrrole (1k).[15] 1-Bromo-2-nitrobenzene (2 mmol, 404 mg), cesium carbonate (4 mmol, 1.3 g), and pyrrole (4 mmol, 0.28 mL) were added to anhydrous acetonitrile (20 mL) and the mixture was refluxed at 92 °C in an oil bath. After 12 h, pyrrole (4 mmol, 0.28 mL) was added to the reaction mixture. After 1 day, the reaction mixture was cooled to room temperature, diluted with water (25 mL), and extracted with EtOAc (15 mL) three times. The organic layer was dried over anhydrous $MgSO_4$ and concentrated. After purification by flash column chromatography (hexane/EtOAc = 50:1 to 10:1), **1k** was obtained as a red solid (189 mg, 50% yield); mp 44−46 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (s, 1H), 7.72 (dd, J = 8.6, 1.2 Hz, 2H), 7.52−7.61 (m, 4H), 7.33−7.37 (m, 2H), 6.91−6.93 (m, 2H), 6.48−6.50 (m, 2H), 6.31−6.33 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.1, 132.4, 130.8, 127.2, 127.0, 126.3, 124.5, 120.6, 111.0, 110.1; HRMS (FAB) m/z: calcd for $C_{10}H_8N_2O_2$ $[M]^+$, 188.0586; found, 188.0588.

Synthesis of 1-Methyl-2-(2-nitrophenyl)-1*H*-pyrrole (1l).[15] 1-Iodo-2-nitrobenzene (20 mmol), lithium hydroxide (80 mmol, 1.92 g), and 1-methyl pyrrole (60 mmol, 5.3 mL) were added to anhydrous DMSO (11 mL) and the mixture was refluxed at 100 °C in an oil bath. After 2 h, 1-methyl pyrrole was added (60 mmol, 5.3 mL) to the reaction mixture and stirred for overnight at 110 °C. The reaction mixture was cooled to room temperature, diluted with water (100 mL), and extracted with EtOAc (30 mL) three times. The organic layer was dried over anhydrous $MgSO_4$ and concentrated. After purification by flash column chromatography (hexane/EtOAc = 50:1 to 10:1), **1l** was obtained as a red solid (3.64 g, 90% yield); mp 58−60 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 7.9 Hz, 1H), 7.62 (dd, J = 7.3, 6.1 Hz, 1H), 7.46−7.53 (m, 2H), 6.76 (t, J = 2.4 Hz, 1H), 6.21 (t, J = 3.1 Hz, 1H), 6.15 (q, J = 1.8 Hz, 1H), 3.45 (s, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$): δ 150.0, 133.5, 132.4, 128.8, 128.4, 128.0, 124.2, 123.8, 109.7, 108.2, 34.4; HRMS (FAB) m/z: calcd for $C_{11}H_{11}N_2O_2$ $[M + H]^+$, 203.0821; found, 203.0816.

Synthesis of Pyrrolo[1,2-α]quinoxalines. *Optimized Condition.* To a mixture of 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg), iron catalyst (0.018 mmol), trimethylamine *N*-oxide (0.036 mmol, 2.7 mg), and 50 mg molecular sieve (4 Å, powder), benzyl alcohol **2a** (0.9 mmol, 93 μL) and solvent (0.3 mL) were added in O_2-charged borosilicate glass tubes. The reaction tube was sealed and stirred at 160 °C in a heating block. After stirring for 24 h, the reaction mixture was cooled to room temperature, diluted with DCM (1 mL), and filtered. Then, the reaction mixture was concentrated *in vacuo*. The crude reaction mixture was analyzed using dimethyl sulfone (0.03 mmol) as an internal standard. In the case of entry 5 in Table 1, the residue was purified by flash column chromatography on silica gel, using hexane/EtOAc (50:1) as the eluent. After purification, **3aa** was obtained as a pale-yellow solid (66 mg, 90%). In the case of entry 6 in Table 1, **3aa** (50 mg, 68%) and **3aa′** (18 mg, 24%) were obtained.

For 1 mmol Scale Reaction (Entry 11 in Table 1). To a mixture of 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (1.0 mmol, 188.2 mg), **Fe I** (0.15 mmol), trimethylamine *N*-oxide (0.3 mmol, 22.5 mg), and 300 mg molecular sieve (4 Å, powder), benzyl alcohol **2a** (3.0 mmol, 309 μL) and CPME (1 mL) were added in an O_2-charged Ace pressure tube. The reaction tube was sealed and stirred at 160 °C in an oil bath. After stirring for 40 h, the reaction mixture was cooled to room temperature, diluted with DCM (3 mL), and filtered. Then, the reaction mixture was concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel, using hexane/EtOAc (50:1) as the eluent. After purification, **3aa** was obtained as a pale-yellow solid (181 mg, 96%).

*4-Phenylpyrrolo[1,2-a]quinoxaline (**3aa**).* Pale-yellow solid; mp 85−86 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (dd, J = 8.0, 1.6 Hz, 1H), 8.01 (dd, J = 7.8, 1.8 Hz, 3H), 7.88 (d, J = 8.3 Hz, 1H), 7.44−7.58 (m, 5H), 7.00 (t, J = 2.1 Hz, 1H), 6.90 (t, J = 3.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.6, 138.6, 136.4, 130.4, 129.9, 128.7, 127.6, 127.3, 125.5, 125.4, 114.7, 114.1, 113.8, 108.8;

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HRMS (FAB) m/z: calcd for $C_{17}H_{13}N_2$ $[M + H]^+$, 245.1079; found, 245.1075.

*4-Phenyl-4,5-dihydropyrrolo[1,2-a]quinoxaline (**3aa'**).* Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (dd, J = 8.0, 1.6 Hz, 2H), 7.34−7.41 (m, 4H), 7.20 (t, J = 2.1 Hz, 1H), 6.98 (td, J = 7.6, 1.4 Hz, 1H), 6.86 (td, J = 7.7, 1.2 Hz, 1H), 6.76 (dd, J = 7.8, 1.4 Hz, 1H), 6.25 (t, J = 3.2 Hz, 1H), 5.58 (t, J = 1.6 Hz, 1H), 5.55 (s, 1H), 4.17 (s, 1H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$): δ 141.5, 136.3, 130.1, 128.8, 128.5, 128.4, 128.0, 125.6, 124.8, 119.5, 115.5, 114.9, 114.5, 110.3, 106.0, 56.3; HRMS (FAB) m/z: calcd for $C_{17}H_{14}N_2$ $[M]^+$, 246.1157; found, 246.1161.

General Procedure of Pyrrolo[1,2-α]quinoxalines. To a mixture of 2-pyrrole nitroarene **1** (0.3 mmol), **Fe I** (0.018 mmol, 7.5 mg), trimethylamine *N*-oxide (0.036 mmol, 2.7 mg), and 50 mg molecular sieve (4 Å, powder), alcohol **2** (0.9 mmol) and CPME (0.3 mL) were added in O_2-charged borosilicate glass tubes. The reaction tube was sealed and stirred at 160 °C in a heating block. After stirring for 24 h, the reaction mixture was cooled to room temperature, diluted with DCM (1 mL), and filtered. Then, the reaction mixture was concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel, using hexane/EtOAc (50:1) as the eluent.

*4-(o-Tolyl)pyrrolo[1,2-a]quinoxaline (**3ab**).* Following the general procedure, 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg) and 2-methylbenzyl alcohol **2b** (0.9 mmol, 110 mg) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3ab** was obtained as a pale-yellow solid (34 mg, 44% yield for 24 h; 62 mg, 80% yield for 40 h); mp 105−106 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 8.0 Hz, 1H), 7.99 (s, 1H), 7.91 (d, J = 7.4 Hz, 1H), 7.46−7.57 (m, 3H), 7.30−7.40 (m, 3H), 6.84−6.86 (m, 1H), 6.58 (d, J = 2.8 Hz, 1H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.8, 137.6, 136.6, 136.2, 130.9, 130.3, 129.1, 129.0, 127.6, 127.4, 126.4, 125.8, 125.4, 114.6, 114.0, 113.8, 108.8, 19.9; HRMS (FAB) m/z: calcd for $C_{18}H_{15}N_2$ $[M + H]^+$, 259.1235; found, 259.1239.

*4-(2-Fluorophenyl)pyrrolo[1,2-a]quinoxaline (**3ac**).* Following the general procedure, 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg) and 2-fluorobenzyl alcohol **2c** (0.9 mmol, 97 μL) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3ac** was obtained as a white solid (65 mg, 83% yield for 24 h; 72 mg, 91% yield for 40 h); mp 124−127 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (dd, J = 8.0, 1.4 Hz, 1H), 7.98 (q, J = 1.3 Hz, 1H), 7.89 (dd, J = 8.2, 1.3 Hz, 1H), 7.74 (td, J = 7.4, 1.6 Hz, 1H), 7.45−7.56 (m, 3H), 7.31−7.34 (m, 1H), 7.24−7.28 (m, 1H), 6.88 (dd, J = 3.9, 2.8 Hz, 1H), 6.75−6.76 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.5 (d, $^1J_{C-F}$ = 249.2 Hz), 159.0 (d, $^1J_{C-F}$ = 249.2 Hz), 150.6, 136.1, 131.3 (d, $^5J_{C-F}$ = 11.5 Hz), 131.2, 131.2 (d, $^5J_{C-F}$ = 11.5 Hz), 130.4, 128.0, 127.4, 126.3 (d, $^4J_{C-F}$ = 15.4 Hz), 126.2 (d, $^4J_{C-F}$ = 15.4 Hz), 125.9, 125.4, 124.5 (d, $^6J_{C-F}$ = 3.8 Hz), 124.5 (d, $^6J_{C-F}$ = 3.8 Hz), 116.5 (d, $^3J_{C-F}$ = 21.1 Hz), 116.3 (d, $^3J_{C-F}$ = 21.1 Hz), 114.7, 114.1 (d, $^2J_{C-F}$ = 33.6 Hz), 113.8 (d, $^2J_{C-F}$ = 33.6 Hz), 108.7 (d, $^7J_{C-F}$ = 3.8 Hz), 108.6 (d, $^7J_{C-F}$ = 3.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −112.99 ppm; HRMS (FAB) m/z: calcd for $C_{17}H_{12}FN_2$ $[M + H]^+$, 263.0985; found, 263.0992.

*4-(2-Methoxyphenyl)pyrrolo[1,2-a]quinoxaline (**3ad**).* Following the general procedure, 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg) and 2-methoxylbenzyl alcohol **2d** (0.9 mmol, 124 mg) were used as the starting material. After column chromatography (hexane/EtOAc = 10:1), **3ad** was obtained as a yellow liquid (35 mg, 42% yield for 40 h); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (dd, J = 8.0, 1.8 Hz, 1H), 7.93 (q, J = 1.4 Hz, 1H), 7.86 (dd, J = 8.3, 1.5 Hz, 1H), 7.54 (dd, J = 7.4, 1.8 Hz, 1H), 7.42−7.52 (m, 3H), 7.05−7.13 (m, 2H), 6.82 (q, J = 2.2 Hz, 1H), 6.60 (q, J = 1.8 Hz, 1H), 3.77 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.4, 153.6, 136.3, 130.6, 130.3, 127.5, 126.6, 125.2, 120.8, 114.1, 113.8, 113.7, 111.6, 108.6, 55.7; HRMS (FAB) m/z: calcd for $C_{18}H_{15}N_2O$ $[M + H]^+$, 275.1184; found, 275.1183.

*4-(m-Tolyl)pyrrolo[1,2-a]quinoxaline (**3ae**).* Following the general procedure, 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg) and 3-methylbenzyl alcohol **2e** (0.9 mmol, 110 mg) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3ae** was obtained as a pale-yellow solid (30 mg, 38% yield for 24 h; 62 mg, 80% yield for 40 h); mp 86−87 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (dd, J = 7.8, 1.8 Hz, 1H), 7.98 (q, J = 1.4 Hz, 1H), 7.87 (dd, J = 7.8, 1.4 Hz, 1H), 7.79−7.82 (m, 2H), 7.41−7.53 (m, 3H), 7.34 (d, J = 7.3 Hz, 1H), 7.00 (dd, J = 3.9, 1.1 Hz, 1H), 6.89 (q, J = 2.3 Hz, 1H), 2.48 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.7, 138.5, 136.4, 130.7, 130.3, 129.3, 128.5, 127.5, 127.3, 125.8, 125.6, 125.4, 114.7, 114.0, 113.7, 108.9, 21.7; HRMS (FAB) m/z: calcd for $C_{18}H_{15}N_2$ $[M + H]^+$, 259.1235; found, 259.1241.

*4-(3-Fluorophenyl)pyrrolo[1,2-a]quinoxaline (**3af**).* Following the general procedure, 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg) and 3-fluorobenzyl alcohol **2f** (0.9 mmol, 102 μL) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3af** was obtained as a white solid (50 mg, 63% yield for 24 h; 75 mg, 95% yield for 40 h); mp 103−105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (dd, J = 8.0, 1.6 Hz, 1H), 8.01 (q, J = 1.3 Hz, 1H), 7.88 (dd, J = 8.2, 1.3 Hz, 1H), 7.81 (dt, J = 7.7, 1.2 Hz, 1H), 7.73 (ddd, J = 9.8, 2.4, 1.6 Hz, 1H), 7.45−7.56 (m, 3H), 7.23 (tdd, J = 8.4, 2.6, 0.9 Hz, 1H), 7.00 (dd, J = 4.0, 1.3 Hz, 1H), 6.91 (dd, J = 4.1, 2.8 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.2 (d, $^1J_{C-F}$ = 245.3 Hz), 161.7 (d, $^1J_{C-F}$ = 245.3 Hz), 153.0 (d, $^6J_{C-F}$ = 2.9 Hz), 153.0 (d, $^6J_{C-F}$ = 2.9 Hz), 140.7 (d, $^5J_{C-F}$ = 7.7 Hz), 140.6 (d, $^5J_{C-F}$ = 7.7 Hz), 136.1, 130.4, 130.3 (d, $^4J_{C-F}$ = 8.6 Hz), 130.2 (d, $^4J_{C-F}$ = 8.6 Hz), 127.9, 127.2, 125.5, 125.1, 124.4 (d, $^7J_{C-F}$ = 2.9 Hz), 124.4 (d, $^7J_{C-F}$ = 2.9 Hz), 116.9 (d, $^3J_{C-F}$ = 21 Hz), 116.7 (d, $^3J_{C-F}$ = 21 Hz), 115.9 (d, $^2J_{C-F}$ = 23 Hz), 115.7 (d, $^2J_{C-F}$ = 23 Hz), 114.9, 114.2, 113.7, 108.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ −112.47 ppm; HRMS (FAB) m/z: calcd for $C_{17}H_{12}FN_2$ $[M + H]^+$, 263.0985; found, 263.0983.

*4-(3-Methoxyphenyl)pyrrolo[1,2-a]quinoxaline (**3ag**).* Following the general procedure, 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg) and 3-methoxylbenzyl alcohol **2g** (0.9 mmol, 112 μL) were used as the starting material. After column chromatography (hexane/EtOAc = 10:1), **3ag** was obtained as a pale-yellow solid (51 mg, 62% yield for 40 h); mp 129−131 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (dd, J = 7.8, 1.4 Hz, 1H), 7.99 (t, J = 1.4 Hz, 1H), 7.87 (d, J = 8.3 Hz, 1H), 7.44−7.60 (m, 5H), 7.08 (dd, J = 7.8, 2.3 Hz, 1H), 7.02 (q, J = 1.7 Hz, 1H), 6.89 (t, J = 3.2 Hz, 1H), 3.91 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.9, 154.3, 139.9, 136.3, 130.4, 129.7, 127.6, 127.3, 125.5, 125.4, 121.2, 116.0, 114.7, 114.1, 113.8, 113.7, 108.9, 55.5; HRMS (FAB) m/z: calcd for $C_{18}H_{15}N_2O$ $[M + H]^+$, 275.1184; found, 275.1183.

*4-(p-Tolyl)pyrrolo[1,2-a]quinoxaline (**3ah**).* Following the general procedure, 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg) and 4-methylbenzyl alcohol **2h** (0.9 mmol, 110 mg) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3ah** was obtained as a pale-yellow solid (51 mg, 66% yield for 24 h; 56 mg, 72% yield for 40 h); mp 80−82 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (dd, J = 8.0, 1.2 Hz, 1H), 7.99 (q, J = 1.2 Hz, 1H), 7.87−7.92 (m, 3H), 7.48 (tdd, J = 15.3, 7.4, 1.2 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.00 (q, J = 1.6 Hz, 1H), 6.89 (q, J = 2.2 Hz, 1H), 2.46 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.5, 140.0, 136.4, 135.8, 130.3, 129.4, 128.7, 127.4, 127.3, 125.5, 125.4, 114.6, 114.0, 113.7, 108.8, 21.6; HRMS (FAB) m/z: calcd for $C_{18}H_{15}N_2$ $[M + H]^+$, 259.1235; found, 259.1238.

*4-(4-Fluorophenyl)pyrrolo[1,2-a]quinoxaline (**3ai**).* Following the general procedure, 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg) and 4-fluorobenzyl alcohol **2i** (0.9 mmol, 98 μL) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3ai** was obtained as a white solid (72 mg, 91% yield); mp 155−157 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99−8.04 (m, 4H), 7.89 (dd, J = 8.0, 1.2 Hz, 1H), 7.51−7.55 (m, 1H), 7.45−7.49 (m, 1H), 7.21−7.26 (m, 2H), 6.97 (q, J = 1.6 Hz, 1H), 6.91 (t, J = 3.4 Hz, 1H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$): δ 165.2 (d, $^1J_{C-F}$ = 247.3 Hz), 162.7 (d, $^1J_{C-F}$ = 247.3 Hz), 153.4, 136.3, 134.7 (d, $^4J_{C-F}$ = 3.8 Hz), 134.7 (d, $^4J_{C-F}$ = 3.8 Hz), 130.7 (d, $^3J_{C-F}$ = 6.6 Hz), 130.7 (d, $^3J_{C-F}$ = 6.6 Hz), 130.3, 127.7, 127.2, 125.5, 125.3, 115.9 (d, $^2J_{C-F}$ = 22.0 Hz), 115.6 (d, $^2J_{C-F}$ = 22.0 Hz), 114.9, 114.2, 113.8, 108.7; ^{19}F NMR (376

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MHz, $CDCl_3$): δ −110.98 ppm; HRMS (FAB) m/z: calcd for $C_{17}H_{12}FN_2$ $[M + H]^+$, 263.0985; found, 263.0986.

*4-(4-Methoxyphenyl)pyrrolo[1,2-a]quinoxaline (**3aj**).* Following the general procedure, 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg) and 4-methoxylbenzyl alcohol **2j** (0.9 mmol, 124 mg) were used as the starting material. After column chromatography (hexane/EtOAc = 10:1), **3aj** was obtained as a pale-yellow solid (31 mg, 38% yield for 40 h); mp 112−114 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97−8.04 (m, 4H), 7.86 (dd, J = 8.0, 1.6 Hz, 1H), 7.43−7.51 (m, 2H), 7.07 (dt, J = 9.3, 2.5 Hz, 2H), 7.01 (dd, J = 4.1, 0.9 Hz, 1H), 6.89 (dd, J = 3.7, 2.7 Hz, 1H), 3.90 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.1, 153.9, 136.4, 131.2, 130.2, 130.1, 127.2, 127.1, 125.4, 125.3, 114.6, 114.0, 113.9, 113.6, 108.7, 55.5; HRMS (FAB) m/z: calcd for $C_{18}H_{15}N_2O$ $[M + H]^+$, 275.1184; found, 275.1184.

*4-(4-(tert-Butyl)phenyl)pyrrolo[1,2-a]quinoxaline (**3ak**).* Following the general procedure, 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg) and 4-*tert*-butylbenzyl alcohol **2k** (0.9 mmol, 148 mg) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3ak** was obtained as a yellow liquid (47 mg, 52% yield for 40 h); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03−8.06 (m, 1H), 7.99 (t, J = 1.5 Hz, 1H), 7.95−7.97 (m, 2H), 7.87 (d, J = 7.7 Hz, 1H), 7.56−7.58 (m, 2H), 7.49−7.52 (m, 1H), 7.44−7.47 (m, 1H), 7.04 (q, J = 1.8 Hz, 1H), 6.90 (t, J = 3.4 Hz, 1H), 1.40 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.5, 153.2, 136.5, 135.8, 130.3, 128.4, 127.4, 127.3, 125.7, 125.5, 125.4, 114.6, 114.0, 113.7, 108.9, 35.0, 31.4; HRMS (FAB) m/z: calcd for $C_{21}H_{21}N_2$ $[M + H]^+$, 301.1705; found, 301.1706.

*4-(4-Chlorophenyl)pyrrolo[1,2-a]quinoxaline (**3al**).* Following the general procedure, 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg) and 4-chlorobenzyl alcohol **2l** (0.9 mmol, 128 mg) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3al** was obtained as a pale-yellow solid (76 mg, 90% yield); mp 176−178 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.0 Hz, 2H), 7.96 (d, J = 8.5 Hz, 2H), 7.89 (d, J = 8.0 Hz, 1H), 7.45−7.56 (m, 4H), 6.96 (d, J = 4.1 Hz, 1H), 6.91−6.92 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.3, 137.1, 136.3, 136.0, 130.4, 130.1, 129.0, 127.9, 127.3, 125.6, 125.3, 114.9, 114.3, 113.8, 108.6; HRMS (FAB) m/z: calcd for $C_{17}H_{12}ClN_2$ $[M + H]^+$, 279.0689; found, 279.0695.

*4-(4-Bromophenyl)pyrrolo[1,2-a]quinoxaline (**3am**).* Following the general procedure, 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg) and 4-bromobenzyl alcohol **2m** (0.9 mmol, 168 mg) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3am** was obtained as a white solid (90 mg, 93% yield); mp 160−162 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02−8.04 (m, 2H), 7.89−7.91 (m, 3H), 7.67−7.69 (m, 2H), 7.54 (t, J = 7.7 Hz, 1H), 7.45−7.49 (m, 1H), 6.96 (dd, J = 4.1, 1.1 Hz, 1H), 6.92 (dd, J = 3.8, 2.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.2, 137.5, 136.2, 131.9, 130.4, 130.3, 127.8, 127.2, 125.5, 125.1, 124.3, 114.9, 114.2, 113.8, 108.6; HRMS (FAB) m/z: calcd for $C_{17}H_{12}BrN_2$ $[M + H]^+$, 323.0184; found, 323.0189.

*4-(4-Iodophenyl)pyrrolo[1,2-a]quinoxaline (**3an**).* Following the general procedure, 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg) and 4-iodobenzyl alcohol **2n** (0.9 mmol, 210 mg) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3an** was obtained as a pale-yellow solid (97 mg, 88% yield); mp 129−130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03−8.04 (m, 1H), 8.01−8.02 (m, 2H), 7.87−7.90 (m, 3H), 7.75 (dt, J = 8.7, 2.1 Hz, 2H), 7.52−7.56 (m, 1H), 7.47 (td, J = 7.7, 1.4 Hz, 1H), 6.96 (dd, J = 4.1, 1.4 Hz, 1H), 6.91 (dd, J = 4.1, 2.7 Hz, 1H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$): δ 153.3, 138.0, 137.8, 136.2, 130.4, 130.3, 127.8, 127.2, 125.5, 125.0, 114.9, 114.2, 113.7, 108.5, 96.3; HRMS (FAB) m/z: calcd for $C_{17}H_{12}IN_2$ $[M + H]^+$, 371.0045; found, 371.0051.

*4-(4-(Trifluoromethyl)phenyl)pyrrolo[1,2-a]quinoxaline (**3ao**).* Following the general procedure, 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg) and 4-(trifluoromethyl)benzyl alcohol **2o** (0.9 mmol, 158 mg) were used as the starting material. After column chromatography (hexane/EtOAc = 100:1), **3ao** was obtained as a yellow solid (77 mg, 82% yield for 24 h); mp 150−153 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, J = 8.0 Hz, 2H), 8.02−8.06 (m, 2H), 7.90 (dd, J = 8.1, 0.8 Hz, 1H), 7.81 (d, J = 8.0 Hz, 2H), 7.54−7.58 (m, 1H), 7.48 (td, J = 7.5, 1.1 Hz, 1H), 6.96−6.97 (m, 1H), 6.93 (dd, J = 4.0, 2.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.0, 142.0, 136.2, 132.3 (q, $^2J_{C-F}$ = 33.5 Hz), 131.9 (q, $^2J_{C-F}$ = 33.5 Hz), 131.6 (q, $^2J_{C-F}$ = 33.5 Hz), 131.3 (q, $^2J_{C-F}$ = 33.5 Hz), 130.5, 129.1, 128.1, 127.3, 125.8 (q, $^3J_{C-F}$ = 3.8 Hz), 125.7 (q, $^3J_{C-F}$ = 3.8 Hz), 125.7 (q, $^3J_{C-F}$ = 3.8 Hz), 125.7 (q, $^3J_{C-F}$ = 3.8 Hz), 125.6 (d, $^1J_{C-F}$ = 275.9 Hz), 125.6, 125.1, 122.9 (d, $^1J_{C-F}$ = 275.9 Hz), 115.1, 114.4, 113.9, 108.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.55 ppm; HRMS (FAB) m/z: calcd for $C_{18}H_{12}F_3N_2$ $[M + H]^+$, 313.0953; found, 313.0963.

*4-(Pyrrolo[1,2-a]quinoxalin-4-yl)benzonitrile (**3ap**).* Following the general procedure, 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg) and 4-cyanobenzyl alcohol **2p** (0.9 mmol, 120 mg) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3ap** was obtained as a yellow solid (47 mg, 58% yield for 24 h; 66 mg, 81% yield for 40 h); mp 227−229 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 8.6 Hz, 2H), 8.03−8.05 (m, 2H), 7.92 (d, J = 8.6 Hz, 1H), 7.85 (d, J = 8.6 Hz, 2H), 7.58 (t, J = 7.0 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 6.94−6.95 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.3, 142.8, 136.1, 132.6, 130.6, 129.5, 128.4, 127.3, 125.7, 124.9, 118.8, 115.3, 114.5, 113.9, 113.5, 108.4; HRMS (FAB) m/z: calcd for $C_{18}H_{12}N_3$ $[M + H]^+$, 270.1031; found, 270.1032.

*4-(Naphthalen-2-yl)pyrrolo[1,2-a]quinoxaline (**3aq**).* Following the general procedure, 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg) and 2-naphtalenemethanol **2q** (0.9 mmol, 142 mg) were used as the starting material. After column chromatography (hexane/EtOAc = 100:1), **3aq** was obtained as a yellow solid (88 mg, 99%); mp 107−109 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (s, 1H), 8.10−8.17 (m, 2H), 7.93−8.04 (m, 4H), 7.87 (dd, J = 7.9, 1.5 Hz, 1H), 7.46−7.60 (m, 4H), 7.09 (dd, J = 4.0, 1.3 Hz, 1H), 6.91 (dd, J = 3.9, 2.8 Hz, 1H);^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.5, 136.5, 136.0, 134.2, 133.3, 130.4, 128.9, 128.5, 128.5, 127.9, 127.7, 127.3, 127.0, 126.5, 126.2, 125.7, 125.5, 114.8, 114.2, 113.8, 108.9; HRMS (FAB) m/z: calcd for $C_{21}H_{15}N_2$ $[M + H]^+$, 295.1235; found, 295.1237.

*4-(Pyridin-3-yl)pyrrolo[1,2-a]quinoxaline (**3ar**).* Following the general procedure, 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg) and 3-pyridinemethanol **2r** (0.9 mmol, 98 mg) were used as the starting material. After column chromatography (hexane/EtOAc = 10:1), **3ar** was obtained as a yellow solid (63 mg, 85% yield for 40 h); mp 153−155 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.25 (s, 1H), 8.76 (d, J = 4.9 Hz, 1H), 8.30 (d, J = 7.9 Hz, 1H), 8.02 (d, J = 7.9 Hz, 2H), 7.86 (d, J = 7.9 Hz, 1H), 7.44−7.54 (m, 3H), 6.97 (t, J = 2.1 Hz, 1H), 6.90 (t, J = 3.1 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 151.6, 150.8, 149.6, 136.2, 134.4, 130.4, 128.1, 127.2, 125.6, 125.2, 123.6, 115.1, 114.4, 113.8, 108.4; HRMS (FAB) m/z: calcd for $C_{16}H_{12}N_3$ $[M + H]^+$, 246.1031; found, 246.1036.

*4-(Furan-2-yl)pyrrolo[1,2-a]quinoxaline (**3as**).* Following the general procedure, 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg) and furfuryl alcohol **2s** (0.9 mmol, 78 μL) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3as** was obtained as a yellow solid (60 mg, 86% yield); mp 99−100 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (dd, J = 7.7, 1.5 Hz, 1H), 7.95 (q, J = 1.2 Hz, 1H), 7.82 (dd, J = 7.7, 1.5 Hz, 1H), 7.72 (d, J = 1.8 Hz, 1H), 7.40−7.48 (m, 4H), 6.92 (q, J = 2.2 Hz, 1H), 6.64 (q, J = 1.6 Hz, 1H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$): δ 152.4, 144.6, 143.5, 135.8, 130.1, 127.5, 127.2, 125.4, 123.2, 114.6, 114.2, 113.7, 112.9, 112.1, 108.5; HRMS (FAB) m/z: calcd for $C_{15}H_{11}N_2O$ $[M + H]^+$, 235.0871; found, 235.0875.

*4-(Thiophen-2-yl)pyrrolo[1,2-a]quinoxaline (**3at**).* Following the general procedure, 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg) and 2-thiophenemethanol **2t** (0.9 mmol, 85 μL) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3at** was obtained as a yellow solid (54 mg, 72% yield for 40 h); mp 116−118 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97−8.01 (m, 3H), 7.86−7.88 (m, 1H), 7.44−7.56 (m, 3H), 7.29 (t, J = 2.5 Hz, 1H), 7.23 (q, J = 2.9 Hz, 1H), 6.94 (q, J = 2.2 Hz, 1H); ^{13}C{^{1}H}

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NMR (100 MHz, $CDCl_3$): δ 147.4, 142.5, 135.9, 130.0, 128.8, 128.3, 127.9, 127.5, 127.1, 125.4, 124.1, 114.8, 114.2, 113.6, 107.9; HRMS (FAB) m/z: calcd for $C_{15}H_{11}N_2S$ $[M + H]^+$, 251.0643; found, 251.0639.

*(E)-4-Styrylpyrrolo[1,2-a]quinoxaline (**3au**).* Following the general procedure, 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg) and cinnamyl alcohol **2u** (0.9 mmol, 121 mg) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3au** was obtained as a yellow solid (71 mg, 88% yield); mp 128−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 15.6 Hz, 1H), 8.00 (d, J = 6.9 Hz, 1H), 7.97−7.97 (m, 1H), 7.86 (dd, J = 8.0, 1.6 Hz, 1H), 7.70−7.72 (m, 2H), 7.41−7.55 (m, 5H), 7.36 (t, J = 7.3 Hz, 1H), 7.12 (d, J = 3.2 Hz, 1H), 6.93 (dd, J = 3.7, 2.7 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.9, 136.6, 136.5, 136.3, 129.9, 129.1, 128.9, 127.8, 127.4, 127.2, 126.2, 125.5, 123.3, 114.6, 113.9, 113.8, 106.0; HRMS (FAB) m/z: calcd for $C_{19}H_{15}N_2$ $[M + H]^+$, 271.1235; found, 271.1230.

*4-(Phenylethynyl)pyrrolo[1,2-a]quinoxaline (**3av**).* Following the general procedure, 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg) and 3-phenyl-2-propyn-1-ol **2v** (0.9 mmol, 110 μL) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3av** was obtained as a yellow liquid (39 mg, 48% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (dd, J = 8.2, 1.4 Hz, 1H), 7.95 (q, J = 1.2 Hz, 1H), 7.85 (dd, J = 8.2, 0.9 Hz, 1H), 7.71−7.73 (m, 2H), 7.39−7.56 (m, 5H), 7.15 (dd, J = 3.9, 1.1 Hz, 1H), 6.93 (q, J = 2.3 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.7, 136.0, 132.4, 130.1, 129.6, 128.5, 128.2, 127.3, 127.1, 125.5, 121.7, 114.6, 114.1, 113.7, 107.7, 93.2, 85.8; HRMS (FAB) m/z: calcd for $C_{19}H_{13}N_2$ $[M + H]^+$, 269.1079; found, 269.1078.

*4-Phenethylpyrrolo[1,2-a]quinoxaline (**3aw**).* Following the general procedure, 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg) and 3-phenyl-1-propanol **1w** (0.9 mmol, 122 μL) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3aw** was obtained as a thick brown liquid (45 mg, 56% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91−7.96 (m, 2H), 7.84 (dd, J = 8.0, 1.6 Hz, 1H), 7.49 (td, J = 7.7, 1.5 Hz, 1H), 7.44 (td, J = 7.4, 1.5 Hz, 1H), 7.29−7.35 (m, 4H), 7.19−7.23 (m, 1H), 6.90 (dd, J = 3.9, 1.1 Hz, 1H), 6.84 (dd, J = 3.7, 2.7 Hz, 1H), 3.29−3.35 (m, 2H), 3.20−3.26 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.4, 141.9, 136.1, 129.6, 128.6, 127.4, 127.2, 126.2, 126.0, 125.3, 125.0, 114.4, 113.8, 113.7, 106.3, 37.7, 34.3; HRMS (FAB) m/z: calcd for $C_{19}H_{16}N_2$ $[M + H]^+$, 273.1392; found, 273.1398.

*4-Cyclohexylpyrrolo[1,2-a]quinoxaline (**3ax**).* Following the general procedure, 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg) and cyclohexanemethanol **2x** (0.9 mmol, 110 μL) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3ax** was obtained as a yellow solid (47 mg, 58% yield for 24 h; 66 mg, 81% yield for 40 h); mp 75−77 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (t, J = 8.0 Hz, 2H), 7.81−7.83 (m, 1H), 7.39−7.47 (m, 2H), 6.93 (d, J = 3.7 Hz, 1H), 6.84 (t, J = 3.4 Hz, 1H), 3.13 (t, J = 11.7 Hz, 1H), 2.02 (d, J = 12.8 Hz, 2H), 1.78−1.94 (m, 5H), 1.33−1.54 (m, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$): δ 161.2, 136.3, 129.8, 127.3, 126.9, 125.7, 125.1, 114.1, 113.7, 113.3, 105.9, 43.7, 31.4, 26.7, 26.2; HRMS (FAB) m/z: calcd for $C_{17}H_{19}N_2$ $[M + H]^+$, 251.1548; found, 251.1551.

*7-Methyl-4-phenylpyrrolo[1,2-a]quinoxaline (**3ba**).* Following the general procedure, 1-(4-methyl-2-nitrophenyl)-1*H*-pyrrole **1b** (0.3 mmol, 61 mg) and benzyl alcohol **2a** (0.9 mmol, 93 μL) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3ba** was obtained as a pale-yellow solid (50 mg, 64% yield); mp 96−97 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 1.4 Hz, 1H), 7.44 (dd, J = 8.2, 1.8 Hz, 1H), 7.35 (d, J = 8.2 Hz, 1H), 6.77 (t, J = 2.1 Hz, 2H), 6.35 (t, J = 2.1 Hz, 2H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.4, 138.7, 136.3, 135.2, 130.2, 129.8, 128.7, 128.7, 125.4, 125.2, 114.5, 113.8, 113.5, 108.5, 21.2; HRMS (FAB) m/z: calcd for $C_{18}H_{15}N_2$ $[M + H]^+$, 259.1235; found, 259.1233.

*7-Methoxy-4-phenylpyrrolo[1,2-a]quinoxaline (**3ca**).* Following the general procedure, 1-(4-methoxyl-2-nitrophenyl)-1*H*-pyrrole **1c** (0.3 mmol, 65 mg) and benzyl alcohol **2a** (0.9 mmol, 93 μL) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3ca** was obtained as a pale-yellow solid (56 mg, 68% yield); mp 129−130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (dd, J = 7.6, 2.1 Hz, 2H), 7.94 (t, J = 1.2 Hz, 1H), 7.80 (d, J = 8.6 Hz, 1H), 7.50−7.57 (m, 4H), 7.14 (dd, J = 9.2, 3.1 Hz, 1H), 6.97 (d, J = 4.3 Hz, 1H), 6.87 (q, J = 2.2 Hz, 1H), 3.93 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.2, 154.6, 138.5, 137.3, 129.8, 128.6, 128.6, 125.1, 121.4, 116.6, 114.5, 114.3, 113.6, 111.3, 108.4, 55.7; HRMS (FAB) m/z: calcd for $C_{18}H_{15}N_2O$ $[M + H]^+$, 275.1184; found, 275.1188.

*7-Chloro-4-phenylpyrrolo[1,2-a]quinoxaline (**3da**).* Following the general procedure, 1-(4-chloro-2-nitrophenyl)-1*H*-pyrrole **1d** (0.3 mmol, 66 mg) and benzyl alcohol **2a** (0.9 mmol, 93 μL) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3da** was obtained as a yellow solid (75 mg, 90% yield); mp 154−155 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97−8.00 (m, 2H), 7.95 (d, J = 8.7 Hz, 1H), 7.90 (q, J = 1.2 Hz, 1H), 7.84 (d, J = 2.3 Hz, 1H), 7.53−7.56 (m, 3H), 7.39 (dd, J = 8.5, 2.1 Hz, 1H), 7.00 (dd, J = 3.9, 1.1 Hz, 1H), 6.90 (q, J = 2.3 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.6, 138.2, 137.3, 130.5, 130.3, 129.7, 128.8, 128.8, 127.6, 126.0, 125.4, 115.1, 114.9, 114.6, 109.5; HRMS (FAB) m/z: calcd for $C_{17}H_{12}ClN_2$ $[M + H]^+$, 279.0689; found, 79.0685.

*4-Phenyl-7-(trifluoromethyl)pyrrolo[1,2-a]quinoxaline (**3ea**).* Following the general procedure, 1-(2-nitro-4-(trifluoromethyl)-phenyl)-1*H*-pyrrole **1e** (0.3 mmol, 77 mg) and benzyl alcohol **2a** (0.9 mmol, 93 μL) were used as the starting material. After column chromatography (hexane/EtOAc = 100:1), **3ea** was obtained as a yellow solid (69 mg, 74% yield); mp 96−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, J = 0.9 Hz, 1H), 8.00−8.04 (m, 3H), 7.97 (d, J = 8.7 Hz, 1H), 7.74 (dd, J = 8.7, 1.8 Hz, 1H), 7.54−7.58 (m, 3H), 7.07 (d, J = 4.1 Hz, 1H), 6.96 (t, J = 3.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.9, 138.0, 136.1, 130.4, 129.4, 128.8 (d, $^2J_{C-F}$ = 8.6 Hz), 128.7 (d, $^2J_{C-F}$ = 8.6 Hz), 128.0 (q, $^3J_{C-F}$ = 3.8 Hz), 127.9 (q, $^3J_{C-F}$ = 3.8 Hz), 127.9 (q, $^3J_{C-F}$ = 3.8 Hz), 127.9 (q, $^3J_{C-F}$ = 3.8 Hz), 127.8, 127.5, 125.7, 125.5 (d, $^1J_{C-F}$ = 270.0 Hz), 124.0 (q, $^4J_{C-F}$ = 3.8 Hz), 123.9 (q, $^4J_{C-F}$ = 3.8 Hz), 123.9 (q, $^4J_{C-F}$ = 3.8 Hz), 123.9 (q, $^4J_{C-F}$ = 3.8 Hz), 122.8 (d, $^1J_{C-F}$ = 270.0 Hz), 115.5, 115.1, 114.5, 110.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ −61.83 ppm; HRMS (FAB) m/z: calcd for $C_{18}H_{12}F_3N_2$ $[M + H]^+$, 313.0953; found, 313.0951.

*8-Methyl-4-phenylpyrrolo[1,2-a]quinoxaline (**3fa**).* Following the general procedure, 1-(5-methyl-2-nitrophenyl)-1*H*-pyrrole **1f** (0.3 mmol, 61 mg) and benzyl alcohol **2a** (0.9 mmol, 93 μL) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3fa** was obtained as a pale-yellow solid (30 mg, 38% yield); mp 76−77 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (dd, J = 7.6, 1.6 Hz, 2H), 7.86 (q, J = 1.2 Hz, 1H), 7.83 (d, J = 8.3 Hz, 1H), 7.57 (s, 1H), 7.41−7.47 (m, 3H), 7.17 (dd, J = 8.7, 1.8 Hz, 1H), 6.87 (dd, J = 3.9, 1.1 Hz, 1H), 6.78 (q, J = 2.3 Hz, 1H), 2.46 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.6, 138.7, 138.1, 134.4, 130.1, 129.8, 128.7, 128.7, 127.0, 126.7, 125.6, 114.4, 114.0, 113.8, 108.5, 22.0; HRMS (FAB) m/z: calcd for $C_{18}H_{15}N_2$ $[M + H]^+$, 259.1235; found, 259.1225.

*8-Methoxy-4-phenylpyrrolo[1,2-a]quinoxaline (**3ga**).* Following the general procedure, 1-(5-methoxyl-2-nitrophenyl)-1*H*-pyrrole **1g** (0.3 mmol, 65 mg) and benzyl alcohol **2a** (0.9 mmol, 93 μL) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3ga** was obtained as a yellow solid (39 mg, 47% yield); mp 95−96 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (dt, J = 8.1, 2.3 Hz, 3H), 7.89 (d, J = 1.4 Hz, 1H), 7.53 (q, J = 6.4 Hz, 3H), 7.29 (d, J = 2.7 Hz, 1H), 7.06 (dd, J = 9.1, 2.7 Hz, 1H), 6.97 (q, J = 1.8 Hz, 1H), 6.90 (q, J = 2.3 Hz, 1H), 3.97 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.3, 152.0, 138.8, 131.6, 130.9, 129.6, 128.7, 128.0, 125.5, 121.8, 114.2, 114.2, 113.0, 109.6, 108.3, 97.7, 56.0; HRMS (FAB) m/z: calcd for $C_{18}H_{15}N_2O$ $[M + H]^+$, 275.1184; found, 275.1193.

*8-Chloro-4-phenylpyrrolo[1,2-a]quinoxaline (**3ha**).* Following the general procedure, 1-(5-chloro-2-nitrophenyl)-1*H*-pyrrole **1h** (0.3 mmol, 66 mg) and benzyl alcohol **2a** (0.9 mmol, 93 μL) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3ha** was obtained as a pale-yellow solid (63 mg, 76% yield); mp

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187−189 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (t, *J* = 2.5 Hz, 1H), 7.97−8.00 (m, 2H), 7.93 (q, *J* = 1.4 Hz, 1H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.53−7.56 (m, 3H), 7.44 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.01 (dd, *J* = 3.9, 1.1 Hz, 1H), 6.90 (q, *J* = 2.3 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.6, 138.2, 134.9, 132.9, 131.5, 130.1, 128.7, 128.7, 127.8, 125.8, 125.4, 114.9, 114.6, 113.9, 109.3; HRMS (FAB) *m*/*z*: calcd for $C_{17}H_{12}ClN_2$ [M + H]$^+$, 279.0689; found, 279.0685.

*9-Methyl-4-phenylpyrrolo[1,2-a]quinoxaline (**3ia**).* Following the general procedure, 1-(2-methyl-6-nitrophenyl)-1*H*-pyrrole **1i** (0.3 mmol, 61 mg) and benzyl alcohol **2a** (0.9 mmol, 93 μL) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3ia** was obtained as a pale-yellow solid (27 mg, 35% yield); mp 122−124 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (t, *J* = 1.5 Hz, 1H), 7.92−8.00 (m, 3H), 7.50−7.57 (m, 3H), 7.30−7.37 (m, 2H), 7.00 (q, *J* = 1.8 Hz, 1H), 6.87 (q, *J* = 2.2 Hz, 1H), 2.97 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.4, 131.1, 129.9, 128.8, 128.7, 127.6, 126.9, 125.4, 124.9, 120.5, 113.4, 108.4, 24.1; HRMS (FAB): *m*/*z* calcd for $C_{18}H_{15}N_2$ [M + H]$^+$, 259.1235; found, 259.1229.

*6-Phenylpyrido[3,2-e]pyrrolo[1,2-a]pyrazine (**3ja**).* Following the general procedure, 3-nitro-2-(1*H*-pyrrol-1-yl)pyridine **1j** (0.3 mmol, 57 mg) and benzyl alcohol **2a** (0.9 mmol, 93 μL) were used as the starting material. After column chromatography (hexane/EtOAc = 50:1), **3ja** was obtained as a brown solid (60 mg, 82% yield); mp 144−146 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.48 (q, *J* = 1.4 Hz, 1H), 8.32 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.99−8.02 (m, 2H), 7.55 (td, *J* = 5.1, 3.4 Hz, 3H), 7.46 (q, *J* = 4.3 Hz, 1H), 7.07 (q, *J* = 1.8 Hz, 1H), 6.94 (dd, *J* = 3.7, 2.7 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.4, 146.8, 139.4, 138.1, 137.5, 131.2, 130.3, 128.8, 128.8, 126.9, 121.8, 116.1, 114.6, 110.5; HRMS (FAB) *m*/*z*: calcd for $C_{16}H_{12}N_3$ [M + H]$^+$, 246.1031; found, 246.1029.

*4-Phenyl-1H-pyrrolo[3,2-c]quinoline (**3ka**).* Following the general procedure, 2-(2-nitrophenyl)-1*H*-pyrrole **1k** (0.3 mmol, 57 mg) and benzyl alcohol **2a** (0.9 mmol, 93 μL) were used as the starting material. The reaction was proceeded at 170 °C for 40 h. After column chromatography (hexane/EtOAc = 10:1 to 5:1), **3ka** was obtained as a brown solid (24 mg, 32% yield); mp 184−185 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.11 (s, 1H), 8.27 (d, *J* = 8.3 Hz, 1H), 8.08 (q, *J* = 7.6 Hz, 3H), 7.55 (q, *J* = 7.2 Hz, 3H), 7.48 (q, *J* = 6.5 Hz, 2H), 7.35 (s, 1H), 6.92 (d, *J* = 3.1 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.3, 142.9, 139.2, 136.4, 129.4, 129.3, 129.0, 128.8, 127.3, 125.9, 124.1, 119.9, 119.0, 116.9, 105.3; HRMS (FAB) *m*/*z*: calcd for $C_{17}H_{13}N_2$ [M + H]$^+$, 245.1079; found, 245.1084.

*1-Methyl-4-phenyl-1H-pyrrolo[3,2-c]quinoline (**3la**).* Following the general procedure, 1-methyl-2-(2-nitrophenyl)-1*H*-pyrrole **1l** (0.3 mmol, 61 mg) and benzyl alcohol **2a** (0.9 mmol, 93 μL) were used as the starting material. The reaction was proceeded at 170 °C for 40 h. After column chromatography (hexane/EtOAc = 10:1 to 5:1), **3la** was obtained as a pale-yellow solid (41 mg, 53% yield); mp 129−130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (d, *J* = 6.7 Hz, 1H), 8.32 (d, *J* = 8.6 Hz, 1H), 8.05 (d, *J* = 6.7 Hz, 2H), 7.62−7.64 (m, 1H), 7.54−7.57 (m, 3H), 7.49−7.50 (m, 1H), 7.11 (d, *J* = 3.1 Hz, 1H), 6.84 (d, *J* = 3.1 Hz, 1H), 4.30 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.9, 144.9, 140.4, 135.0, 130.9, 129.8, 129.3, 128.9, 128.7, 126.4, 125.5, 120.6, 120.3, 118.5, 103.2, 38.3; HRMS (FAB) *m*/*z*: calcd for $C_{18}H_{15}N_2$ [M + H]$^+$, 259.1235; found, 259.1239.

Transfer Hydrogenation of 1a with Secondary Alcohol 4. To a mixture of 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg), **Fe I** (0.018 mmol, 7.5 mg), trimethylamine *N*-oxide (0.036 mmol, 2.7 mg), and 50 mg molecular sieve (4 Å, powder), benzhydrol **4** (0.9 mmol, 166 mg) and CPME (0.3 mL) were added in O_2-charged borosilicate glass tubes. The reaction tube was sealed and stirred at 160 °C in a heating block. After stirring for 40 h, the reaction mixture was cooled to room temperature, diluted with DCM (1 mL), and filtered. Then, the reaction mixture was concentrated *in vacuo*. The crude reaction mixture was analyzed using dimethyl sulfone (0.03 mmol) as an internal standard.

Mechanistic Studies. *Reaction between **1a**′ and **2a**.* To a mixture of 2-(1*H*-pyrrol-1-yl)aniline **1a**′ (0.3 mmol, 47.5 mg), **Fe I** (0.018 mmol, 7.5 mg), trimethylamine *N*-oxide (0.036 mmol, 2.7 mg), and 50 mg molecular sieve (4 Å, powder), benzyl alcohol **2a** (0.9 mmol, 93 μL) and CPME (0.3 mL) were added in O_2-charged borosilicate glass tubes. The reaction tube was sealed and stirred at 160 °C using a heating block. After stirring for 24 h, only trace amount of the **3aa** was observed in TLC.

*Reaction between **1a** and **2a**′.* To a mixture of 1-(2-nitrophenyl)-1*H*-pyrrole **1a** (0.3 mmol, 56.4 mg), **Fe I** (0.018 mmol, 7.5 mg), trimethylamine *N*-oxide (0.036 mmol, 2.7 mg), and 50 mg molecular sieve (4 Å, powder), benzaldehyde **2a**′ (0.9 mmol, 92 μL) and CPME (0.3 mL) were added in O_2-charged borosilicate glass tubes. The reaction tube was sealed and stirred at 160 °C in a heating block. After stirring for 24 h, **3aa** was not observed in TLC.

*Reaction between **1a**′ and **2a**′.* To a mixture of 2-(1*H*-pyrrol-1-yl)aniline **1a**′ (0.3 mmol, 47.5 mg), **Fe I** (0.018 mmol, 7.5 mg), trimethylamine *N*-oxide (0.036 mmol, 2.7 mg), and 50 mg molecular sieve (4 Å, powder), benzaldehyde **2a**′ (0.9 mmol, 92 μL) and CPME (0.3 mL) were added in O_2-charged borosilicate glass tubes. The reaction tube was sealed and stirred at 160 °C in a heating block. After stirring for 24 h, the reaction mixture was cooled to room temperature, diluted with DCM (1 mL), and filtered. Then, the reaction mixture was concentrated *in vacuo*. After purification by flash column chromatography (hexane/EtOAc = 50:1), **3aa** was obtained as a pale-yellow solid (63 mg, 86% yield).

*Reaction between **1a**′ and **2a**′ without Fe I.* To a mixture of 2-(1*H*-pyrrol-1-yl)aniline **1a**′ (0.3 mmol, 47.5 mg) and 50 mg molecular sieve (4 Å, powder), benzaldehyde **2a**′ (0.9 mmol, 92 μL) and CPME (0.3 mL) were added in O_2-charged borosilicate glass tubes. The reaction tube was sealed and stirred at 160 °C in a heating block. After stirring for 24 h, the reaction mixture was cooled to room temperature, diluted with DCM (1 mL), and filtered. Then, the reaction mixture was concentrated *in vacuo*. After purification by flash column chromatography (hexane/EtOAc = 50:1), **3aa** was obtained as a pale-yellow solid (61 mg, 83% yield).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02145.

^{1}H and ^{13}C NMR spectra, results of catalyst screening, and details for detection of intermediates (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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