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A Green Aerobic Oxidative Synthesis of Pyrrolo[1,2-*a*]quinoxalines from Simple Alcohols without Metals and Additives

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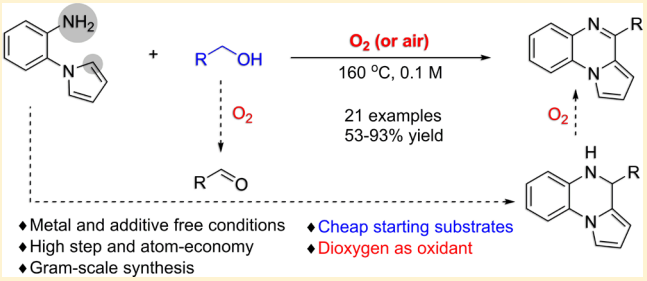
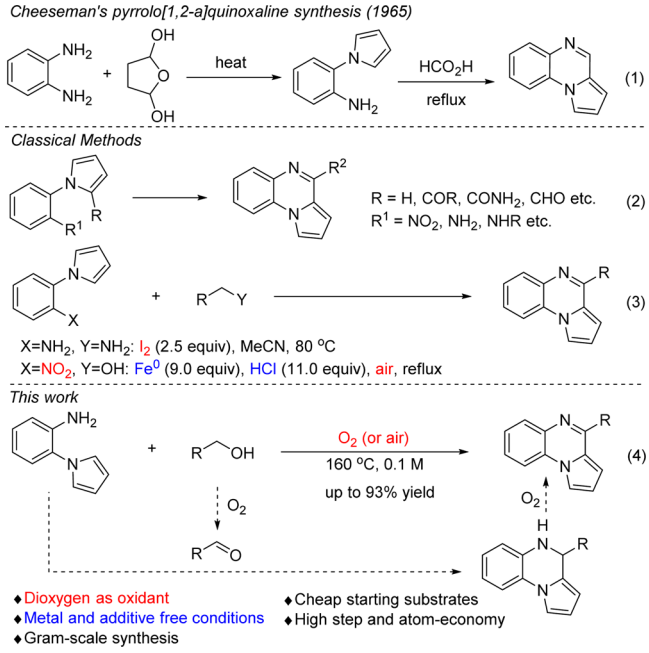
Supporting Information

ABSTRACT: A practical and concise protocol for the efficient preparation of pyrrolo[1,2-*a*]quinoxalines through a cascade of alcohol oxidation/imine formation/intramolecular cyclization/oxidative dehydrogenation has been established. A series of substituted pyrrolo[1,2-*a*]quinoxaline derivatives were constructed readily in yields of 53−93% from the cheap primary alcohols by using dioxygen as the terminal oxidant. Remarkably, the fact that no extra metals and additives were necessary makes this unprecedented aerobic oxidation process highly step- and atom-economical. The usefulness of this transformation was further demonstrated with the gram-scale synthesis of compound **3aa** under standard conditions.



As an important family of heterocyclic compounds, the pyrrolo[1,2-*a*]quinoxaline skeleton is ubiquitous in a wide range of natural products and synthetic molecules.[1] In most cases, the functionalized pyrrolo[1,2-*a*]quinoxalines possess a wide range of bioactivities and pharmaceutical effects, especially as antimalarial,[2] antileishmania,[3] and antitumor,[4] as well as behave as adenosine A3 receptor modulators[5] and human protein kinase CK2 inhibitors.[6] Hence, developing diverse methodologies available for the efficient synthesis of these compounds continues to attract considerable attention from synthetic chemists.[7] In 1965, the Cheesman and Tuck groups reported the first synthesis of the pyrrolo[1,2-*a*]quinoxaline nucleus from 2-(1*H*-pyrrol-1-yl)aniline and formic acid under reflux conditions (Scheme 1, reaction 1).[8] Afterward, many protocols for the pyrrolo[1,2-*a*]quinoxaline synthesis involving the cyclization of substituted *N*-phenyl pyrroles have been developed by other groups.[9] Commonly, a nitro or amino group at the 2-position in phenyl rings and carbonyl groups in pyrroles are of great necessity for the successful cyclization and aromatization, which undoubtedly lead to more synthetic steps and limited functional tolerance (Scheme 1, reaction 2). Over the past decades one-pot multicomponent reactions[10] and cascade transformations[11] have emerged as the most promising alternative access to the synthesis of pyrrolo[1,2-*a*]quinoxaline compounds. Among these methodologies, the redox process can serve this synthetic purpose utilizing commercially available primary alcohols and amines in a step- and atom-economic fashion. In 2012, the Pereira group realized the aerobic oxidative synthesis of pyrrolo[1,2-*a*]quinoxalines from primary alcohols under redox reaction conditions with iron (9 equiv) and 12 M hydrochloric acid (11 equiv).[12] In 2015, an iodine

Scheme 1. Synthesis of Pyrrolo[1,2-*a*]quinoxaline Derivatives



(2.5 equiv) promoted oxidative pathway utilizing primary aromatic amines as the substrates was reported by Jayaprakash

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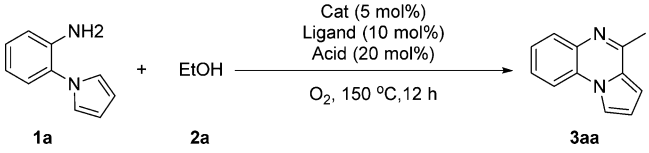
and co-workers (Scheme 1, reaction 3).[13] However, these synthetic routes usually suffered from either the excess use of toxic oxidants or an overstoichiometric amount of catalyst and additives. Recently, an oxidative route to installation of the pyrrolo[1,2-*a*]quinoxalines from both aromatic and aliphatic aldehydes under mild reaction conditions was presented by the Zhai group, featuring metal-free and dioxygen oxidation.[15] Despite the advances made in this field, further exploration of more efficient and environmental-benign strategies that allow the preparation of this fused heterocyclic motif is in high demand. The transition metal catalyzed aerobic oxidation of alcohols to aldehydes with dioxygen or other oxidants employed for a number of chemical transformations is well-documented.[14] Nevertheless, the direct oxidation of alcohols to aldehydes using molecular oxygen as the only oxidant in the absence of metals and additives remains elusive to date. Herein, we report a green aerobic oxidative method access to various substituted pyrrolo[1,2-*a*]quinoxalines in moderate to excellent yields from simple primary alcohols without additions of any metals and acidic additives (Scheme 1, reaction 4).

Initially, the reaction of 2-(1*H*-pyrrol-1-yl)aniline **1a** in ethanol **2a** solvent with a concentration of 0.1 M for 12 h under a O_2 atmosphere was chosen as the model reaction to optimize the reaction conditions (Table 1). The screening of metal catalysts revealed that a satisfactory result of up to 99% conversion was obtained using $Pd(OAc)_2$ as the catalyst (entries 1−5). The addition of ligand 2,4,6-collidine and CF_3CO_2H to the reaction system had no obvious influences on

Table 1. Optimization of the Reaction Conditions[a]



1a **2a** **3aa**

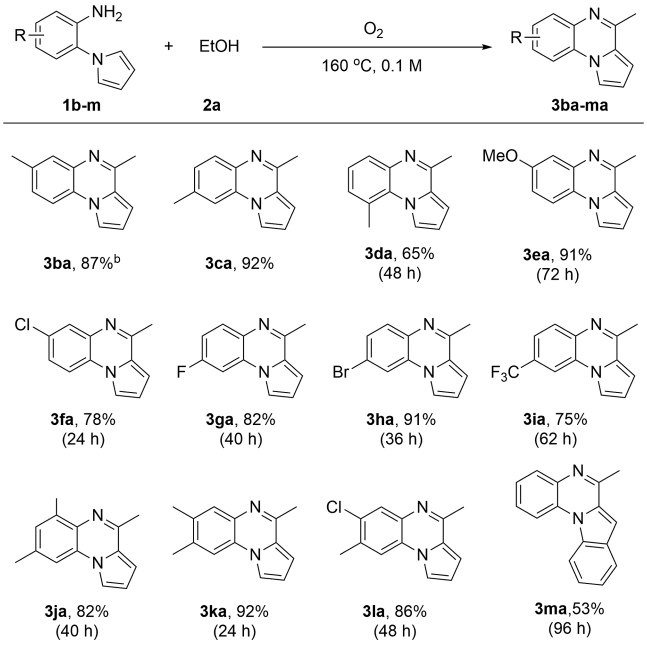
entry	cat. (5 mol %)	additive (10 mol %)	*T* (°C)	conversion (%)[b]
1	$FeCl_3$	–	150	75
2	$FeCl_2$	–	150	30
3	$CuBr_2$	–	150	20
4	CuBr	–	150	25
5	$Pd(OAc)_2$	–	150	>99
6[c]	$Pd(OAc)_2$	TFA	150	>99
7	–	TFA	150	85
8	–	–	150	(78)[d]
9	–	–	140	(76)[d]
10	–	–	130	(34)[d]
11	–	–	160	(93)[d]
12[e] (0.05 M)	–	–	160	21
13[f] (0.2 M)	–	–	160	63
14	–	1,10-Phenanthroline	160	91
15[g] (air)	–	–	160	(70)[d]
16[h] (N_2)	–	–	160	no reaction

[a]Reaction conditions: substrate **1a** (0.3 mmol, 0.1 M), cat. (5 mol %), and additive (10 mol %) in ethanol (3 mL) was stirred for appropriate time under a dioxygen atmosphere. [b]The conversion was determined by GC-MS. [c]The reaction was conducted with 2,4,6-collidine as ligand of palladium catalyst. [d]Isolated yield was in parentheses. [e]The reaction was performed with a concentration of 0.05 M. [f]The reaction was performed with a concentration of 0.2 M. [g]The reaction was performed under an air atmosphere. [h]The reaction was performed under a N_2 atmosphere

the reaction outcomes (entry 6). Under the metal-free conditions, an 85% conversion was achieved employing CF_3CO_2H as the only reaction promotor to facilitate the reaction process (entry 7). Incredibly, further optimization of the reaction conditions demonstrated that the desired product can be isolated in a yield of 78% in the absence of any metals and additives (entry 8). The yields declined to 76% and 34% if the reaction was conducted at a lower temperature of 140 and 130 °C, respectively (entries 9−10). To our delight, a satisfactory yield of 93% was obtained at 160 °C (entry 11). A further decrease of the reaction concentration to 0.05 M or increase to 0.2 M was detrimental to the reaction results (entries 12−13). To exclude the possibility that trace metals might be involved in the reaction process, a chelating agent of 1,10-phenanthroline was added to the reaction mixture and the same high yield of 91% was detected (entry 14). GC-MS investigation confirmed that the aldehyde heptanal was formed by using heptan-1-ol under the conditions. Additionally, under an air atmosphere, a 70% isolated yield was acquired (entry 15). As expected, under a nitrogen atmosphere no reaction occurred, indicating that the existence of dioxygen was vital for the alcohol oxidation and final dehydrogenation process (entry 16).

With the optimized reaction conditions in hand (Table 1, entry 11), we started to examine the reaction scope of the present transformation utilizing ethanol **2a** as the reaction solvent at 160 °C (Scheme 2). In total, the results illustrated

Scheme 2. Scope of the Aromatic Amine Substrates



that electron-donating substituents in aromatic rings delivered relatively high yields in contrast to electron-withdrawing groups. Accordingly, the methyl group in meta- and para-positions of the aryl rings provided the desired products **3ba** and **3ca** in 87% and 92% yields, respectively. The methyl group at the ortho-position in the aromatic ring gave rise to **3da** in a lower yield of 65%, likely caused by the steric hindrance effect of the methyl group. Readily, the **3ea** was synthesized in 91% yield after 48 h if the methoxyl substituted reactant was treated to the reaction conditions. Electron-withdrawing groups, such

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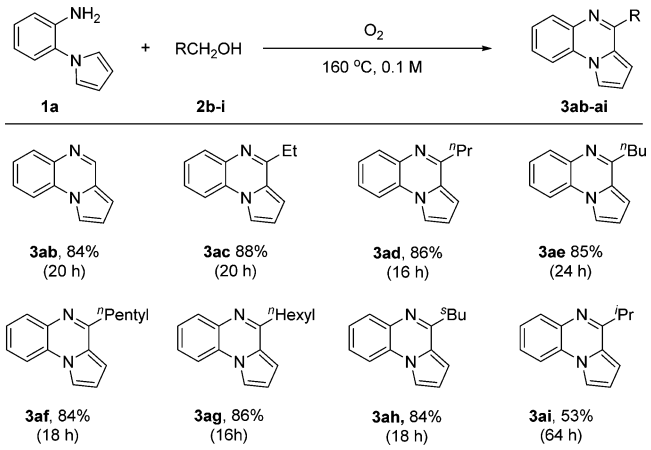
as halogen atoms and the CF_3 group, were also amenable to the current conditions, exclusively affording the products **3fa–ia** in 75–91% yields. In addition, the bis-substituted aromatic amines were also appropriate substrates to deliver the compounds **3fa–la** in 82–86% yields. Besides pyrrolylanilines, the indolylaniline **1m** can be applied into this reaction as well, and the molecule **3ma** in 53% yield was produced after 96 h.

Next, a range of aliphatic alcohols was utilized to standard reaction conditions (Scheme 3). In all cases, the reactions

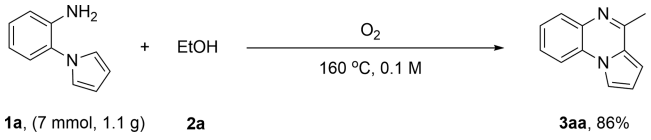
Scheme 3. Scope of the Alcohol Reactants



proceeded smoothly to provide alkyl group substituted pyrrolo[1,2-*a*]quinoxalines **3ab–ag** in more than 80% yields in terms of both short- and long-chain linear alcohols. In addition, the branched alcohols 3-methylbutan-1-ol **2h** and 2-methylpropan-1-ol **2i** also worked well in the annulation and converted to **3ha** and **3ia** in 84% and 53% yields, respectively. For the long-chain alcohol substrates just a trace amount of self-condensation products of aldehydes was detected by GC-MS, by virtue of the faster speed of the reaction between nucleophilic **1a** with in situ formed aldehydes than self-condensation of a small amount of aldehydes themselves.

Notably, this novel aerobic oxidative method can be easily scaled up with a slightly decreased yield. As an example, the desired compound **3aa** was conveniently synthesized in 86% yield when using 1.1 g (7 mmol) of **1a** as the starting material (Scheme 4).

Scheme 4. Gram-Scale Synthesis of 3aa



In conclusion, we have developed a novel and concise oxidative strategy for the synthesis of pyrrolo[1,2-*a*]quinoxaline derivatives from simple primary alcohols under a dioxygen atmosphere. It is worth noting that this unprecedented protocol can serve as a green alternative methodology without the use of any metal catalysts and additives, providing the desired products in a step- and atom-economic fashion. Moreover, the gram-scale synthesis with satisfactory yields enforced its practical application.

EXPERIMENTAL SECTION

General Information. All nonaqueous manipulations utilized standard Schlenk techniques. Reactions were monitored using thin-layer chromatography (TLC) on silica gel plates. Visualization of the developed plates was performed under UV light (254 nm) or $KMnO_4$ stain. Silica gel flash column chromatography was performed on 40–63 μm silica gel. Moreover, commercially available reagents were used without additional purification. All NMR spectra were run at 400 MHz (^{1}H NMR) or 100 MHz (^{13}C NMR) or 377 MHz (^{19}F NMR) in $CDCl_3$ solution. ^{1}H NMR spectra were internally referenced to TMS. ^{13}C NMR spectra were internally referenced to the residual solvent signal. High resolution mass spectra (HRMS) were recorded on a TOF-Q II mass instrument (ESI).

General Procedures for the Products 3aa–ma and 3ab–ai. Aniline **1** (0.3 mmol) was added to a flame-dried Schlenk tube which was charged with a magnetic stir bar in 3.0 mL of alcohols. The resulting suspension was stirred at 160 °C under O_2 for an appropriate time. After a Celite filtration and evaporation of the solvents in vacuo, the crude products were purified by column chromatography on silica gel to providing the desired products (petroleum and ethyl acetate = 100:1).

4-Methylpyrrolo[1,2-a]quinoxaline[12] (***3aa***). A light yellow solid, mp 132–133 °C. Yield: 50.8 mg (93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (d, J = 8.0 Hz, 1H), 7.91 (s, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.35–7.42 (m, 2H), 6.79–6.84 (m, 2H), 2.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.6, 135.8, 129.2, 126.9, 126.2, 125.1, 114.2, 113.6, 113.5, 106.5, 22.0.

4,8-Dimethylpyrrolo[1,2-a]quinoxaline1[17] (***3ba***). A light yellow solid, mp 128–124 °C. Yield: 51.2 mg (87%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.83 (s, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.59 (s, 1H), 7.21 (d, J = 8.0 Hz, 1H), 6.81–6.84 (m, 2H), 2.70 (s, 3H), 2.51 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 152.5, 144.7,137.2, 133.7, 128.8, 126.9, 126.3, 126.2, 113.8, 113.6, 113.3, 106.1, 21.8, 21.6.

4,7-Dimethylpyrrolo[1,2-a]quinoxaline[16] (***3ca***). A light yellow solid, mp 134–135 °C. Yield: 54.1 mg (92%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.91 (s, 1H), 7.64–68 (m, 2H), 7.25 (d, J = 8.0 Hz, 1H), 6.79–6.84 (m, 2H), 2.70 (s, 3H), 2.64 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 153.4, 135.6, 134.7, 128.9, 127.9, 126.0, 125.0, 113.9, 113.2, 113.1, 106.1, 21.8, 21.0.

4,9-Dimethylpyrrolo[1,2-a]quinoxaline[18] (***3da***). A yellow solid, mp 89–90 °C. Yield: 38.2 mg (65%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.26 (s, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.23–318 (m, 2H), 6.89–6.91 (m, 1H), 6.80–6.82 (m, 1H), 2.90 (s, 3H), 2.70 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 153.1, 137.4, 130.4, 127.6, 127.4, 127.48, 125.2, 124.4, 119.8, 112.7, 105.9, 23.8, 21.8.

8-Methoxy-4-methylpyrrolo[1,2-a]quinoxaline[18] (***3ea***). A yellow solid, mp 83–84 °C. Yield: 57.9 mg (91%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.90 (d, J = 8.0 Hz, 1H), 7.74 (s, 1H), 7.17 (s, 1H), 6.98 (dd, J_1= 8.0 Hz, J_2 = 4.0 Hz,1H), 6.81 (m, 2H), 3.90 (s, 3H), 2.68 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 158.4, 150.8, 130.1, 130.1, 127.8, 126.1, 113.7, 113.4, 112.4, 105.9, 97.5, 55.6, 21.6.

8-Chloro-4-methylpyrrolo[1,2-a]quinoxaline[17] (***3fa***). A light yellow solid, mp 175–178 °C. Yield: 50.7 mg (78%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.76 (d, J = 8.0 Hz, 1H), 7.71 (s, 1H), 7.31 (d, J = 8.0 Hz, 1H), 6.91–6.95 (m, 2H), 2.68 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 153.7, 134.3, 132.0, 130.2, 127.7, 126.0, 125.3, 114.3, 113.9, 113.6, 106.9, 21.8.

7-Fluoro-4-methylpyrrolo[1,2-a]quinoxaline[17] (***3ga***). A light yellow solid, mp 167–168 °C. Yield: 49.2 mg (82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (s, 1H), 7.70–7.73 (m, 1H), 7.54 (d, J = 8.0 Hz, 1H),7.16 (t, J = 8.0 Hz, 1H), 6.81–6.87 (m, 2H), 2.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.9, 158.5, 154.8, 146.6 (d, $^1J_{C-F}$ = 40.6 Hz), 137.0, 136.9, 125.9, 114.7, 114.6, 114.4, 114.3, 113.5, 106.9, 21.9. HRMS (ESI) calcd for $C_{12}H_{10}FN_2$ [M + H]: 201.0828, found: 201.0823. HRMS (ESI) calcd for $C_{12}H_{10}FN_2$ [M + H]: 201.0828, found: 201.0823.

8-Bromo-4-methylpyrrolo[1,2-a]quinoxaline[17] (***3ha***). A light yellow solid, mp 159–160 °C. Yield: 71.3 mg (91%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.95 (d, J = 8.0 Hz, 1H), 7.75 (s, 1H), 7.54 (d,

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J = 8.0 Hz, 1H), 7.43−7.46 (m, 1H), 6.79−6.84 (m, 2H), 2.66 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 154.6, 136.9, 131.5, 129.4, 126.1, 125.9, 117.4, 114.8, 114.4, 113.8, 107.0, 21.9. HRMS (ESI) calcd for $C_{12}H_{10}BrN_2$ [M + H]: 261.0027, found: 261.0022.

4-Methyl-7-(trifluoromethyl)pyrrolo[1,2-a]quinoxaline (**3ia**). A light yellow solid, mp 125−127 °C. Yield: 56.2 mg (75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.15 (s, 1H), 7.99 (s, 1H),7.65 (d, J = 8.0 Hz, 1H), 6.88−6.93 (m, 2H), 2.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.2, 135.5, 129.4,127.3,126.8, 126.8, 126.7, 126.7, 125.3, 123.3 (q, J = 3.5 Hz), 114.9, 114.4, 114.3, 107.6, 22.0. HRMS (ESI) calcd for $C_{13}H_{10}F_3N_2$ [M + H]: 251.0796, found: 251.0792.

4,7,9-Trimethylpyrrolo[1,2-a]quinoxaline (**3ja**). A light yellow solid, mp 115−116 °C. Yield: 51.7 mg (82%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.12 (s, 1H), 7.53 (s, 1H), 6.99 (s, 1H), 6.81−6.83 (m,1H), 6.72−6.73 (m, 1H), 2.77 (s, 3H), 2.66 (s, 3H), 2.38 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 152.8, 137.2, 133.8, 131.3, 127.4, 127.2, 125.1, 124.7, 119.3, 112.3, 105.4, 23.4, 21.7, 20.4. HRMS (ESI) calcd for $C_{14}H_{15}N_2$ [M + H]: 211.1235, found: 211.1230.

4,7,8-Trimethylpyrrolo[1,2-a]quinoxaline[18] (**3ka**). A light yellow solid, mp 152−153 °C. Yield: 58.0 mg (92%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.77 (s, 1H), 7.63 (s, 1H), 7.50 (s, 1H), 6.77−6.81 (m, 2H), 2.68 (s, 3H), 2.38 (s, 3H), 2.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 152.3, 136.0, 133.9, 133.7, 129.2, 126.1, 125.0, 113.9, 113.6, 112.9, 105.8, 21.8, 20.0, 19.4.

8-Chloro-4,7-dimethylpyrrolo[1,2-a]quinoxaline (**3la**). A light yellow solid, mp 143−144 °C. Yield: 59.5 mg (86%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.63 (s, 1H), 7.60 (s, 1H), 6.74−6.78 (m, 2H), 2.62 (s, 3H), 2.39 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 153.5, 145.5, 134.2, 132.6, 132.3, 130.4, 125.7, 125.6, 114.0, 113.6, 113.4, 106.5, 21.8, 19.7. HRMS (ESI) calcd for $C_{13}H_{12}ClN_2$ [M + H]: 231.0689, found: 231.0686.

6-Methylindolo[1,2-a]quinoxaline[17] (**3ma**). A light yellow solid, mp 102−103 °C. Yield: 36.9 mg (53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.35 (t, J = 8.0 Hz, 2H), 7.91−7.94 (m, 2H), 7.50−7.55 (m, 2H), 7.38−7.43 (m, 2H), 7.09 (s, 1H), 2.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.1, 135.7, 130.1, 129.6, 129.4, 128.9, 127.7, 124.1, 123.9, 122.6, 122.5, 114.5, 114.5, 99.9, 22.3.

Pyrrolo[1,2-a]quinoxaline[12] (**3ab**). A light yellow solid, mp 130−131 °C. Yield: 42.3 mg (84%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.79 (s, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.89 (s, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 8.0 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 6.85−6.89 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 145.7, 145.6, 135.7, 130.0, 127.9, 127.7, 126.3, 125.0, 114.1, 113.9, 113.7, 107.2.

4-Ethylpyrrolo[1,2-a]quinoxaline[12] (**3ac**). A light yellow solid, mp 70−72 °C. Yield: 51.7 mg (88%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.93 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.41−7.47 (m, 1H), 6.84−6.91 (m, 2H), 3.06 (q, 4H), 1.46 (t, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 158.3, 135.9, 129.3, 126.8, 125.0, 114.0, 113.5, 113.3, 106.0, 28.9, 12.6.

4-Propylpyrrolo[1,2-a]quinoxaline[12] (**3ad**). A light yellow solid, mp 48−49 °C. Yield: 54.2 mg (86%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.92 (d, J = 8.0 Hz, 1H), 7.87 (s, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.40−7.46 (m, 2H), 6.84−6.91 (m, 2H), 2.99 (t, 2H), 1.91−1.97 (m, 2H), 1.08 (t, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 157.3, 135.9, 129.3, 127.1, 126.7, 125.9, 124.9, 114.0, 113.5, 113.3, 106.2, 37.8, 21.9, 14.2.

4-Butylpyrrolo[1,2-a]quinoxaline[19] (**3ae**). A light yellow solid, mp 46 °C. Yield: 57.1 mg (85%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.92 (d, J = 8.0 Hz, 1H), 7.87 (s, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.40−7.46 (m, 2H), 6.84−6.91 (m, 2H), 3.02 (t, 2H), 1.85−1.92 (m, 2H), 1.48−1.53 (m, 2H), 0.99 (t, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 157.5, 135.9, 129.3, 126.7, 125.0, 114.0, 113.5, 113.3, 106.2, 35.6, 30.7, 22.9, 13.9.

4-Pentylpyrrolo[1,2-a]quinoxaline[19] (**3af**). A light yellow solid, mp 42 °C. Yield: 59.9 mg (84%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.93 (d, J = 8.0 Hz, 1H), 7.87(s, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.40−7.46 (m, 2H), 6.82−6.90 (m, 2H), 3.01 (t, 2H), 1.86−1.94 (m, 2H), 1.37−1.43 (m, 4H), 0.92 (t, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 157.5, 135.9, 129.4, 127.1, 126.7, 125.9, 124.9, 114.0, 113.5, 113.3, 106.2, 35.9, 31.9, 28.3, 22.5, 14.0.

4-Hexylpyrrolo[1,2-a]quinoxaline[19] (**3ag**). A light yellow solid, mp 40 °C. Yield: 65.1 mg (86%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.93 (d, J = 8.0 Hz, 1H), 7.89 (s, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.40−7.46 (m, 2H), 6.84−6.91 (m, 2H), 3.01 (t, 2H), 1.95−1.99 (m, 2H), 1.30−1.50 (m, 8H), 0.90 (t, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 157.6, 135.9, 129.4, 127.2, 126.8, 125.9, 125.0, 114.0, 113.5, 113.4, 106.2, 36.0, 31.7, 29.5, 28.6, 22.6, 14.1.

4-Isobutylpyrrolo[1,2-a]quinoxaline (**3ah**). A yellow solid, mp 43−44 °C. Yield: 55.1 mg (82%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.92−7.95 (m, 1H), 7.89 (s, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.39−7.47 (m, 2H), 6.82−6.90 (m, 2H), 2.99 (d, 2H), 2.37−2.45 (m, 1H), 1.03 (d, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 156.8, 135.9, 129.4, 127.1, 126.8, 126.5, 125.0, 114.0, 113.5, 113.3, 106.5, 44.6, 28.4, 22.8. HRMS (ESI) calcd for $C_{15}H_{17}N_2$ [M + H]: 225.1392, found: 225.1391.

4-Isopropylpyrrolo[1,2-a]quinoxaline (**3ai**). A yellow solid, mp 57−58 °C. Yield: 33.4 mg (53%). ^{1}H NMR ($CDCl_3$, 400 MHz) = 7.96 (d, J = 8.0 Hz, 1H), 7.90 (s, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.40−7.48 (m, 2H), 6.83−6.89 (m, 2H), 3.44−3.51 (m, 1H), 1.47 (d, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 161.6, 136.0, 129.6, 126.7, 125.4, 124.9, 113.9, 113.5, 113.2, 105.7, 33.2, 21.0. HRMS (ESI) calcd for $C_{14}H_{15}N_2$ [M + H]: 211.1235, found: 211.1231.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02501.

Copy of ^{1}H and ^{13}C NMR spectra of all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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