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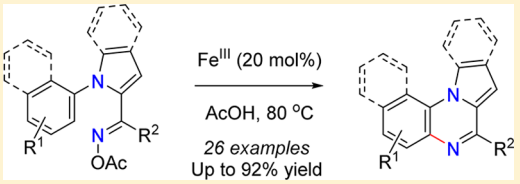
Iron-Catalyzed Intramolecular C(sp^2)−N Cyclization of 1-(*N*-Arylpyrrol-2-yl)ethanone *O*-Acetyl Oximes toward Pyrrolo[1,2-*a*]quinoxaline Derivatives

Zhiguo Zhang,* Junlong Li, Guisheng Zhang,* Nana Ma, Qingfeng Liu, and Tongxin Liu

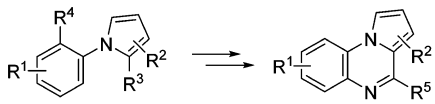
Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, P. R. China

Supporting Information

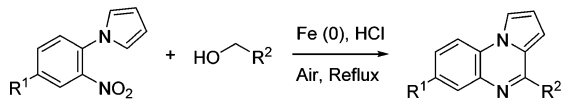
ABSTRACT: An efficient and convenient iron-catalyzed protocol has been developed for the synthesis of substituted pyrrolo[1,2-*a*]quinoxalines from 1-(*N*-arylpyrrol-2-yl)ethanone *O*-acetyl oximes through N−O bond cleavage and intramolecular directed C−H arylation reactions in acetic acid.



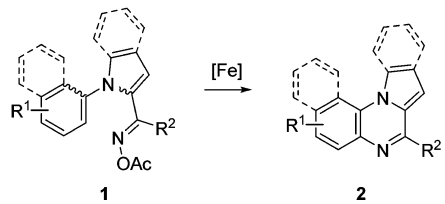
Pyrrolo[1,2-*a*]quinoxalines are an important class of heterocyclic compounds that possess a wide variety of interesting biological activities. Furthermore, substituted pyrrolo[1,2-*a*]quinoxaline derivatives have been reported to behave as human protein kinase CK2 inhibitors[1] and adenosine A3 receptor modulators,[2] as well as exhibiting anti-HIV,[3] antiparasitic,[4] antipsychotic,[5] antiproliferative[6] and antitumor[7] activities. Pyrrolo[1,2-*a*]quinoxalines can be assembled by a one-pot multicomponent reaction[8] or the cyclization of quinoxaline derivatives via a single or multistep reaction process.[1,9] The most commonly used strategy for the synthesis of pyrrolo[1,2-*a*]quinoxalines involves the cyclization the functionalized *N*-phenyl pyrroles, which generally have a nitro or amino group at the 2-position of their phenyl group (eq 1).[1,6a,10] However, the application of this approach has been limited by the lack of suitable substrates for diverse synthesis because the phenyl group must be decorated with a nitrogen-containing group prior to the reaction. A review of the literature in this area revealed a lack of robust alternatives for the synthesis of pyrrolo[1,2-*a*]quinoxalines, with the exception of the Fe-catalyzed[11] method established by Pereira's group[10a] in 2012. In this particular study, Pereira's group reported the development of a one-pot procedure for the synthesis of pyrrolo[1,2-*a*]quinoxalines via a redox reaction/imine formation/intramolecular cyclization cascade. Notably, this procedure tolerated a broad range of readily available substituted 1-(2-nitrophenyl)pyrrole derivatives and aliphatic or benzylic alcohols as starting materials using iron powder under acidic conditions (eq 2). In this paper, we present our efforts toward the Fe(III)-catalyzed intramolecular directed aromatic C(sp^2)-N cross-coupling reaction of 1-(*N*-arylpyrrol-2-yl)ethanone *O*-acetyl oximes (**1**) for the synthesis of pyrrolo[1,2-*a*]-quinoxalines (**2**) (eq 3).



(1)



(2)



(3)

O-Substituted oximes play an important role in organic synthesis because they can undergo a variety of different reactions,[12] including ortho functionalization,[13] addition,[14] rearrangement[15] as well as serving as protecting group.[16] *O*-Substituted oxime derivatives can also undergo *N*-arylation reactions, which generally proceed via photocatalytic[17] or metallocatalytic[18] pathways, and this strategy has been widely used for the construction of numerous *N*-containing heterocycles, including phenanthridines,[18a] indolo[3,2-*c*]isoquinolines, thieno[3,2-*c*]isoquinolines, pyrido[2,3-*b*]indoles and quinazolines.[12]

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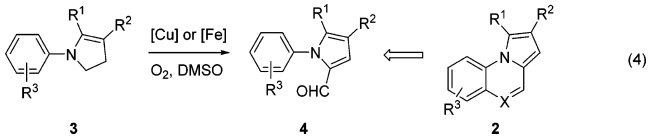
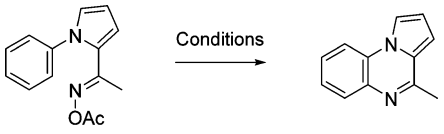
We recently reported the Cu(I) and Fe(III)-catalyzed tandem oxidation/α-formylation reactions of readily available 2,3-dihydro-1*H*-pyrroles (**3**) in dimethyl sulfoxide (DMSO) for the construction of α-formyl pyrroles (**4**), where DMSO acted as a formyl donor and the oxygen acted as an oxidant (eq 4).[19]



(4)

We are continuously interested in the feasibility of **4** further to cyclization to other heterocycles, such as pyrrolo[1,2-*a*]-quinoxalines (**2**). With this in mind, we prepared 1-(1-phenyl-1*H*-pyrrol-2-yl)ethan-1-one *O*-acetyl oxime (**1a**) as a model substrate[18a,20] and evaluated its ability to undergo a ring-closure reaction to give the corresponding pyrrolo[1,2-*a*]quinoxaline (**2a**). Pleasingly, the desired compound **2a** was obtained in 91% yield when the starting material was heated for 2 h in AcOH at 80 °C in the presence of $Fe(acac)_3$ (20 mol %)[18a] (Table 1, entry 1). A longer reaction time of 10 h was required to reach an acceptable level of conversion when the reaction was performed at a slightly lower temperature (60 °C) (Table 1, entry 2). The use of 20 mol % $Fe(acac)_3$ was found to be optimal in terms of the yield of **2a**, with increases and decreases in the amount of the $Fe(acac)_3$ leading to a decrease in the yield (Table 1, entries 3−6). Several other iron salts were screened against the reaction, including $FeCl_3$, $FeCl_3·6H_2O$, $Fe_2(SO_4)_3·xH_2O$, $FeBr_3$, Fe_2O_3, $FeCl_2$, $FeSO_4·7H_2O$, $Fe(acac)_2$, $Fe(OTf)_2$ and $Fe(OAc)_2$, but they were all found to be less effective than $Fe(acac)_3$ for the desired reaction (Table 1, entries 7−16). The reaction was also screened against a variety of different solvents, including DMF, xylene, DMSO, toluene and 1,4-dioxane, but they were all found to be much less efficient than AcOH for the desired conversion process (Table 1, entries 17−21).

Table 1. Survey of the Reaction Conditions[a]



entry	cat. (equiv)	solvent	time (h)	yield (%)
1	$Fe(acac)_3$ (0.2)	AcOH	2	91
2[b]	$Fe(acac)_3$ (0.2)	AcOH	10	78
3	$Fe(acac)_3$ (0.5)	AcOH	3	82
4	$Fe(acac)_3$ (0.1)	AcOH	1.5	80
5	$Fe(acac)_3$ (0.05)	AcOH	1	77
6	$Fe(acac)_3$ (0)	AcOH	4	66
7	$FeCl_3$ (0.2)	AcOH	2	74
8	$FeCl_3·6H_2O$ (0.2)	AcOH	2	81
9	$Fe_2(SO_4)_3·xH_2O$ (0.2)	AcOH	2	65
10	$FeBr_3$ (0.2)	AcOH	2	84
11	Fe_2O_3 (0.2)	AcOH	2	53
12	$FeCl_2$ (0.2)	AcOH	2	82
13	$FeSO_4·7H_2O$ (0.2)	AcOH	2	67
14	$Fe(acac)_2$ (0.2)	AcOH	2	80
15	$Fe(OTf)_2$ (0.2)	AcOH	2	63
16	$Fe(OAc)_2$ (0.2)	AcOH	2	76
17	$Fe(acac)_3$ (0.2)	DMF	27	83
18	$Fe(acac)_3$ (0.2)	Xylene	24	82
19	$Fe(acac)_3$ (0.2)	DMSO	30	80
20	$Fe(acac)_3$ (0.2)	Toluene	24	68
21	$Fe(acac)_3$ (0.2)	1,4-Dioxane	24	76

[a]Unless otherwise indicated, all reactions were carried with **1a** (0.2 mmol) in 2 mL of solvent at 80 °C. [b]Reaction was performed at 60 °C.

With the optimized conditions in hand (Table 1, entry 1), we proceeded to investigate the scope of this intramolecular C(sp^2)-N bond forming reaction using a series of different *O*-acetyl oximes **1** (Table 2). As shown in Table 2, the scope of the R^1 group was examined first, and the results revealed that the reaction was tolerant toward a wide variety of electron-donating groups (EDG's) (e.g., −Me and −OMe) and electron-withdrawing groups (EWG's) (e.g., −Cl, $-CF_3$, $-NO_2$ and $-CO_2Et$) at the *ortho*-, *meta*- or *para*-position on the phenyl ring, with the desired fused tricyclic compounds **2b−p** being formed in moderate to good yields (47−86%). Starting materials bearing the R^1 group(s) at the *meta*-position generally afforded the desired compounds in higher yields than those bearing the R^1 group at the *para*- or *ortho*-position (e.g., **2d** vs **2b** and **2c**; **2g** vs **2e** and **2f**; **2k** vs **2i** and **2j**; **2n** vs **2l** and **2m**). It is noteworthy that the cyclization pathways of starting materials **1d**, **1g**, **1h**, **1k** and **1n** bearing the R^1 group(s) at the *meta*-position showed interesting regioselectivity.[21] Furthermore, the results indicated that cyclization to the *para*-position relative to R^1 was preferable to the *ortho*-position, based on the ratio of the isolated regioisomers.[17a,22] Similar results were also observed for the *N*-containing heterocycles (e.g., **2t** vs **2q** and **2r**). A comparison of these experimental results suggested that the regioselectivity of this cyclization reaction could be attributed not only to the steric hindrance of R^1, but also to the electronic effects of the phenyl ring.[18a,22,23] Pleasingly, compounds **1u** (R^1 = −Ph) and **1v** (with a naphthyl moiety attached to the nitrogen atom of the pyrrole) also reacted smoothly under the optimized conditions to afford **2u** and **2v** in 73 and 34% yields, respectively.[17b] It is noteworthy that compounds **1c**, **1j** and **1m** bearing an *ortho*-substituent (i.e., −OMe, −Cl and $-CF_3$, respectively) on the phenyl ring underwent an unusual C−O, C−Cl or C−C bond cleavage reaction during the transformation.[24] Interestingly, compounds **1b**, **1h**, **1i**, **1l** and **1u** bearing the R^1 group(s) at the *para*-position gave the byproducts **3b**, **3h**, **3i**, **3l** and **3u**, as well as the desired products **2b**, **2h**, **2i**, **2l** and **2u**, via the cleavage of oxime group.[13a,b] Fewer experiments were conducted toward varying the R^2 group because of the limited number of available substrates bearing different groups at this position. Three representative materials **1w** (R^2 = H), **1x** (R^2 = −Et) and **1y** (R^2 = −Ph) afford the corresponding cyclization products in 26, 56 and 81% yields, respectively. To our delight, the cyclization of **1z** proceeded smoothly to provide the 6-methylindolo[1,2-*a*]quinoxaline **2z** in 72% yield, whose analogues have been identified possession variety of bio-activity.[25]

Radical trapping experiments were conducted to determine whether a radical process was involved in this reaction using four different kinds of radical scavenger (100 mol %), including 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), diphenylethylene, galvinoxyl and 2,3,5,6-tetramethylbenzo-1,4-quinone (duroquinone) (Table 3). The results of these experiments revealed that the reaction proceed smoothly in the presence of the radical scavengers, which suggested that a radical process

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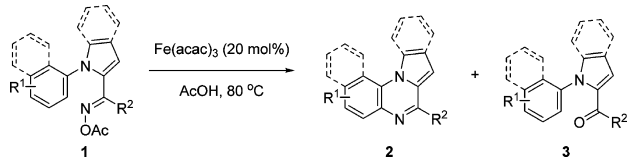
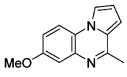
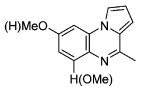
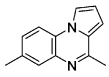
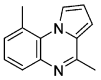
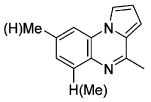
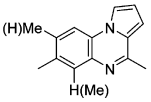
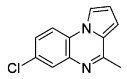
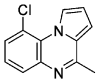
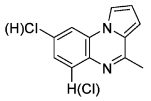
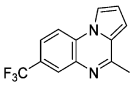
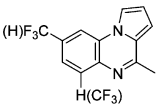
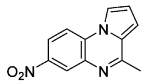
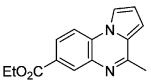
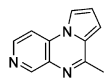
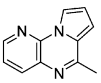
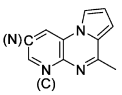
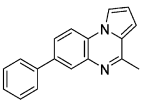
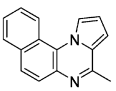
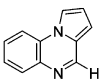
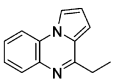
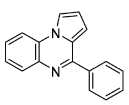
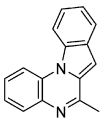
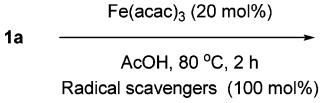
Table 2. Extension of the Reaction Scope[a]



 **2a**: 2 h, 91%	 **2b**: 2 h, 55%[b]	 **2c**: 2 h, 47%[c]	 **2da**+**2db**: 3 h, 84% (5:3)
 **2e**: 2 h, 84%	 **2f**: 2.5 h, 59%	 **2ga**+**2gb**: 2 h, 86% (3:2)	 **2ha**+**2hb**: 2h, 56% (2:1)[d]
 **2i**: 2 h, 65%[e]	 **2j**: 2 h, 50%[f]	 **2ka**+**2kb**: 1 h, 85% (1:1)	 **2l**: 2 h, 56%[g]
 **2m**: 2 h, 52%[h]	 **2na**+**2nb**: 2 h, 84% (2:1)	 **2o**: 6 h, 61%	 **2p**: 2 h, 84%
 **2q**: 10 h, 78%	 **2r**: 3 h, 37%	 **2s**: 0.5 h, 67%	 **2ta**+**2tb**: 4 h, 92% (3:1)
 **2u**: 2 h, 73%[i]	 **2v**: 2 h, 34%[j]	 **2w**: 2 h, 26%[j]	 **2x**: 0.25 h, 56%
 **2y**: 1.5 h, 81%	 **2z**: 12 h, 72%[k]		

[a]Unless otherwise indicated, all of the reactions were carried out with **1** (0.3 mmol) and $Fe(acac)_3$ (0.06 mmol) in AcOH (2 mL) at 80 °C, and the ratios of the regioisomers (i.e., **2da** to **2db**, **2ga** to **2gb**, **2ha** to **2hb**, **2ka** to **2kb** and **2na** to **2nb**) provided in the brackets were determined on the basis of the isolated yields. [b]21% of **3b** was obtained. [c]8% of **2a** was obtained. [d]32% of **3h** was obtained. [e]19% of **3i** was obtained. [f]6% of **2a** was obtained. [g]27% of **3l** was obtained. [h]12% of **2a** was obtained. [i]14% of **3u** was obtained. [j]Along with an unidentified complex mixture. [k]13% **3z** was obtained.

Table 3. Radical Trapping Experiments



radical scavengers	no scavenger	TEMPO	diphenylethylene	galvinoxyl	duroquinone
yield of **2a** (%)	91	81	76	74	69

was not involved in the transformation. Furthermore, the equipment was covered with tin foil to determine whether a photochemical process was involved in the conversion of **1** to **2**.[17a−c,22a] When the reaction was performed under the optimized conditions in the absence of light (Table 1, entry 1), the desired product **2a** was formed in 88% yield (eq 5). Furthermore, compound **2a** was isolated in 61% yield together with recovered **1a** (21%) when the reaction was conducted in the absence of both $Fe(acac)_3$ catalyst and light in AcOH at 80 °C (eq 6). The result of these control experiments therefore demonstrated that this newly developed reaction is mechanistically distinct from a photochemical cyclization reaction and does not involve the formation of an iminyl radical. A plausible mechanism for this reaction was proposed based on the results of the current study and information from the literature (Scheme 1).[18a,22,23] The reaction most likely begins with the coordination of **1** to Fe(III) to allow for the activation of the

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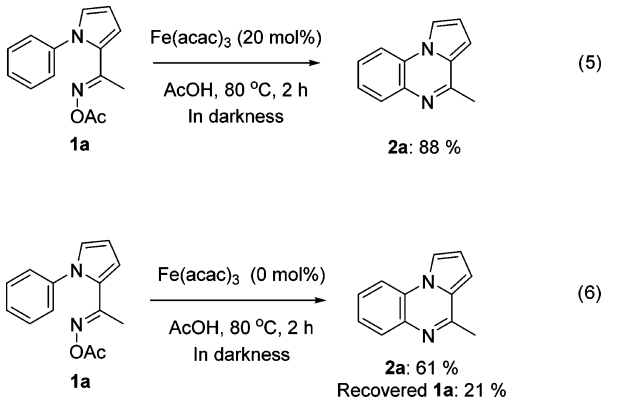
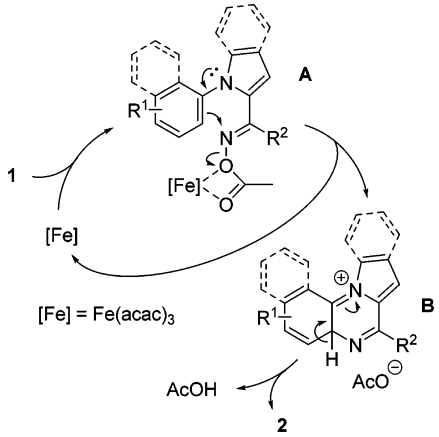


Scheme 1. Proposed Mechanism



acetoxy group and the formation of intermediate **A**, which would undergo an intramolecular cyclization to give intermediate **B** with the help of the lone pair of electrons on the nitrogen atom of the pyrrole moiety. Product **2** would then be released by the deprotonation of intermediate **B**.

In summary, an alternative route has been developed for the facile and efficient synthesis of pyrrolo[1,2-*a*]quinoxalines from 1-(*N*-arylpyrrol-2-yl)ethanone *O*-acetyl oximes in the presence of $Fe(acac)_3$. This reaction occurs under mild conditions and provides rapid, highly modular and flexible access to a wide range of fused pyrrolo[1,2-*a*]quinoxaline ring systems.

EXPERIMENTAL SECTION

General Information. All reactions were carried out at room temperature, unless otherwise indicated. All reagents were purchased from commercial sources and used without further treatment, unless otherwise indicated. Petroleum ether (PE) used refers to the 60−90 °C boiling point fraction of petroleum. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded on a 400 MHz NMR spectrometer (^{1}H: 400 MHz, ^{13}C{^{1}H}: 100 MHz at 25 °C). Coupling constants are reported in Hertz (Hz). All high-resolution mass spectra (HRMS) were measured on a mass spectrometer by using electrospray ionization (ESI-oa-TOF). Melting points were measured on a melting point apparatus equipped with a thermometer and were uncorrected. IR spectra were recorded on a FT-IR spectrophotometer as KBr pellets. All reactions were monitored by TLC with GF254 silica gel coated plates. Flash chromatography was carried out on SiO_2 (silica gel 200−300 mesh).

General Procedure for the Synthesis of 2-Acetyl-*N*-phenylpyrroles. Under N_2 atmosphere, to a round-bottom flask (25 mL) was charged K_2CO_3 (830 mg, 6.0 mmol), CuI (58 mg, 0.3 mmol), NH-containing heterocycle (3.0 mmol), aryl or heteroaryl iodide (3.6 mmol) and DMF (9 mL). The reaction mixture was stirred for 1 h at room temperature, and then the mixture was heated at 130 °C for 12−48 h (monitored by TLC). After cooling, the mixture was directly through a plug of 200−300 mesh silica gel and rinsed with EtOAc (ca. 20 mL). The combined filtrate was washed with saturated brine (3 × 10 mL) and dried over anhydrous Na_2SO_4. After being filtered, the organic solvent was concentrated in vacuo. The residue was purified by column chromatography on silica gel to provide the desired 2-acetyl-*N*-phenylpyrroles.

General Procedure for the Synthesis of 1. To a round-bottom flask (25 mL) was added ketone (2.0 mmol) in EtOH (6.0 mL), hydroxylamine hydrochloride (4.0 mmol, 2.0 equiv) and NaOAc (4.0 mmol, 2.0 equiv). The mixture was heated at 100 °C for 4−12 h. After cooling off, the reaction was quenched by water, the mixture was extracted with dichloromethane (DCM) (3 × 4.0 mL), the organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, and then DCM (6.0 mL) and triethylamine (TEA, 4.0 mmol, 2.0 equiv) were added at 0 °C. A solution of acetyl chloride (4.6 mmol, 2.3 equiv) in DCM (2.0 mL) was added dropwise to this stirred cooled solution. The reaction mixture was stirred at rt for 1−4 h. After the reaction was quenched by water, the mixture was extracted with DCM (3 × 5.0 mL), and the combined extracts were washed with $NaHCO_3$(aq.) (5.0 mL) and brine (5.0 mL). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel to provide the desired product **1**.

General Procedure for the Synthesis of 2. A solution of *O*-acetyl oximes **1** (0.3 mmol) and $Fe(acac)_3$ (20 mol %) in acetic acid (4.0 mL, 0.22 M) was heated at 80 °C for 2 h. The reaction mixture was then allowed to room temperature, neutralized with $NaHCO_3$ (saturated solution), and extracted with EtOAc (3 × 5 mL). The organic extracts were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, hexane:EtOAc).

General Procedure for the Radical Trapping Experiments. A solution of *O*-acetyl oximes **1a** (0.3 mmol), $Fe(acac)_3$ (20 mol %) and radical scavenger (0.3 mmol) in acetic acid (4.0 mL, 0.22 M) was heated at 80 °C for 2 h. The reaction mixture was then allowed to reach room temperature, neutralized with $NaHCO_3$ (saturated solution), and extracted with EtOAc (3 × 5 mL). The organic extracts were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, hexane:EtOAc).

(*E*)-1-(1-Phenyl-1*H*-pyrrol-2-yl)ethan-1-one *O*-acetyl oxime (1a). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:10) as a white solid (411 mg, 85%): mp 54−56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (t, J = 7.4 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.29 (d, J = 7.2 Hz, 2H), 6.92 (t, J = 2 Hz, 1H), 6.72 (dd, J = 3.6, 1.6 Hz, 1H), 6.32 (t, J = 3.2 Hz, 1H), 2.17 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 154.5, 141.1, 128.8, 128.0, 127.1, 125.7, 115.41, 109.1, 19.3, 15.1; HRMS (ESI), m/z calcd. for $C_{14}H_{14}N_2O_2$ ([M + Na]$^+$) 265.0947, found 265.0952; IR (KBr, neat) ν 3104, 1759, 1720, 1600, 1500, 1371, 1221, 1114, 1049, 873, 694.

(*E*)-1-(1-(4-Methoxyphenyl)-1*H*-pyrrol-2-yl)ethan-1-one *O*-acetyl oxime (1b). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:12) as a white solid (425 mg, 78%): mp 58−60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 6.87 (t, J = 1.6 Hz, 1H), 6.69 (dd, J = 3.6, 1.6 Hz, 1H), 6.29 (t, J = 3.2 Hz, 1H), 3.83 (s, 3H), 2.14 (s, 3H), 1.88 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.8, 158.6, 154.9, 134.2, 128.3, 127.4, 126.9, 115.0, 113.9, 108.9, 55.4, 19.5, 15.3; HRMS (ESI), m/z calcd. for $C_{15}H_{16}N_2O_3$ ([M + Na]$^+$) 295.1053, found 295.1060; IR (KBr, neat) ν 3106, 2838, 1766, 1697, 1613, 1514, 1364, 1253, 1115, 962, 834, 739.

(*E*)-1-(1-(2-Methoxyphenyl)-1*H*-pyrrol-2-yl)ethan-1-one *O*-acetyl oxime (1c). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:10) as a white solid (392 mg, 72%): mp 62−64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, J = 7.8 Hz, 1H), 7.27 (d, J = 8.0 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H), 6.99 (d, J = 8.4 Hz, 1H), 6.84 (s, 1H), 6.74 (d, J = 3.6 Hz, 1H), 6.36 (t, J = 3.0 Hz, 1H), 3.77 (s, 3H), 2.26 (s, 3H), 1.73 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ

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171.9, 154.4, 154.1, 130.8, 128.8, 128.2, 128.0, 127.8, 120.6, 114.7, 111.7, 109.0, 55.7, 19.5, 14.5; HRMS (ESI), m/z calcd. for $C_{15}H_{16}N_2O_3$ ([M + Na]$^+$) 295.1053, found 295.1055; IR (KBr, neat) ν 3003, 2835, 1760, 1692, 1598, 1505, 1365, 1238, 962, 759, 749.

(*E*)-1-(1-(3-Methoxyphenyl)-1*H*-pyrrol-2-yl)ethan-1-one *O*-acetyl oxime (1d). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:10) as a pale yellow oil (398 mg, 73%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, J = 8.0 Hz, 1H), 6.88 (t, J = 2.0 Hz, 1H), 6.86−6.82 (m, 3H), 6.68 (dd, J = 3.6, 1.6 Hz, 1H), 6.26 (t, J = 3.6 Hz, 1H), 3.76 (s, 3H), 2.12 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 159.7, 154.6, 141.9, 129.3, 127.7, 127.0, 117.7, 115.2, 112.5, 111.4, 108.9, 55.0, 19.2, 15.0; HRMS (ESI), m/z calcd. for $C_{15}H_{16}N_2O_3$ ([M + Na]$^+$) 295.1053, found 295.1034; IR (KBr, neat) ν 3109, 2838, 1768, 1606, 1491, 1316, 1228, 1197, 928, 733, 693.

(*E*)-1-(1-(*p*-Tolyl)-1*H*-pyrrol-2-yl)ethan-1-one *O*-acetyl oxime (1e). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:10) as a white solid (384 mg, 75%): mp 94−96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23−7.15 (m, 4H), 6.89 (dd, J = 2.4, 1.6 Hz, 1H), 6.70 (dd, J = 4.0, 2.0 Hz, 1H), 6.29 (dd, J = 4.0, 2.8 Hz, 1H), 2.38 (s, 3H), 2.14 (s, 3H), 1.85 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.0, 154.9, 138.6, 137.1, 129.4, 128.1, 127.3, 125.5, 115.2, 109.0, 20.9, 19.5, 15.4; HRMS (ESI), m/z calcd. for $C_{15}H_{16}N_2O_2$ ([M + Na]$^+$) 279.1104, found 279.1097; IR (KBr, neat) ν 3110, 1758, 1742, 1605, 1516, 1451, 1366, 1234, 1042, 924, 823, 730.

(*E*)-1-(1-(*o*-Tolyl)-1*H*-pyrrol-2-yl)ethan-1-one *O*-acetyl oxime (1f). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:10) as a white solid (410 mg, 80%): mp 61−62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.27 (m, 2H), 7.24 (t, J = 3.2 Hz, 1H), 7.20 (d, J = 7.2 Hz, 1H), 6.81−6.71 (m, 2H), 6.35 (t, J = 3.4 Hz, 1H), 2.26 (s, 3H), 2.02 (s, 3H), 1.63 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.9, 153.3, 141.0, 135.4, 130.2, 127.8, 127.2, 127.1, 126.2, 115.0, 109.0, 19.3, 17.1, 14.0; HRMS (ESI), m/z calcd. for $C_{15}H_{16}N_2O_2$ ([M + Na]$^+$) 279.1104, found 279.1102; IR (KBr, neat) ν 3022, 1760, 1741, 1602, 1531, 1496, 1366, 1232, 1088, 923, 787, 737.

(*E*)-1-(1-(*m*-Tolyl)-1*H*-pyrrol-2-yl)ethan-1-one *O*-acetyl oxime (1g). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:8) as a yellow oil (374 mg, 73%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, J = 7.8 Hz, 1H), 7.12 (d, J = 7.6 Hz, 1H), 7.10 (s, 1H), 7.05 (d, J = 7.6 Hz, 1H), 6.87 (t, J = 2.0 Hz, 1H), 6.69 (dd, J = 3.6, 1.6 Hz, 1H), 6.27 (t, J = 3.4 Hz, 1H), 2.36 (s, 3H), 2.13 (s, 3H), 1.81 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.8, 154.6, 141.0, 138.7, 128.5, 128.0, 127.8, 127.1, 126.3, 122.7, 115.2, 109.0, 21.0, 19.3, 15.1; HRMS (ESI), m/z calcd. for $C_{15}H_{16}N_2O_2$ ([M + Na]$^+$) 279.1104, found 279.1103; IR (KBr, neat) ν 3109, 1768, 1609, 1536, 1493, 1455, 1366, 1231, 1191, 928, 730, 696.

(*E*)-1-(1-(3,4-Dimethylphenyl)-1*H*-pyrrol-2-yl)ethan-1-one *O*-acetyl oxime (1h). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:15) as a white solid (362 mg, 67%): mp 89−91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 7.6 Hz, 1H), 7.08 (d, J = 2.0 Hz, 1H), 6.99 (dd, J = 8.0, 2.4 Hz, 1H), 6.85 (dd, J = 2.8, 2.0 Hz, 1H), 6.50 (dd, J = 3.6, 2.0 Hz, 1H), 6.26 (dd, J = 3.6, 2.8 Hz, 1H), 2.29 (s, 6H), 1.94 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.1, 138.6, 137.5, 135.4, 130.0, 129.5, 126.1, 126.0, 122.6, 112.3, 108.7, 19.8, 19.3, 14.2; HRMS (ESI), m/z calcd. for $C_{16}H_{18}N_2O_2$ ([M + Na]$^+$) 293.1260, found 293.1266; IR (KBr, neat) ν 3104, 1768, 1655, 1615, 1508, 1453, 1271, 1130, 921, 820, 723.

(*E*)-1-(1-(4-Chlorophenyl)-1*H*-pyrrol-2-yl)ethan-1-one *O*-acetyl oxime (1i). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:10) as a yellow oil (437 mg, 79%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 6.87 (t, J = 1.6 Hz, 1H), 6.72 (dd, J = 3.6, 1.2 Hz, 1H), 6.31 (t, J = 3.4 Hz, 1H), 2.19 (s, 3H), 1.87 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.4, 154.6, 139.8, 133.0, 129.0, 128.2, 127.3, 127.2, 116.0, 109.6, 19.4, 15.2; HRMS (ESI), m/z calcd. for $C_{14}H_{13}ClN_2O_2$ ([M + Na]$^+$) 299.0558, found 299.0570; IR (KBr, neat) ν 3109, 1766, 1666, 1494, 1366, 1229, 1196, 1090, 838, 733.

(*E*)-1-(1-(2-Chlorophenyl)-1*H*-pyrrol-2-yl)ethan-1-one *O*-acetyl oxime (1j). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:15) as a white solid (387 mg, 70%): mp 54−56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, J = 6.0, 2.8 Hz, 1H), 7.36−7.31 (m, 3H), 6.78 (d, J = 2.0 Hz, 1H), 6.75 (d, J = 3.6 Hz, 1H), 6.37 (t, J = 3.2 Hz, 1H), 2.28 (s, 3H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 153.5, 139.7, 132.2, 129.9, 129.0, 128.9, 127.9, 127.8, 127.3, 115.3, 109.6, 19.5, 14.1; HRMS (ESI), m/z calcd. for $C_{14}H_{13}ClN_2O_2$ ([M + Na]$^+$) 299.0558, found 299.0559; IR (KBr, neat) ν 3110, 1767, 1663, 1489, 1366, 1230, 1198, 1071, 925, 763, 740.

(*E*)-1-(1-(3-Chlorophenyl)-1*H*-pyrrol-2-yl)ethan-1-one *O*-acetyl oxime (1k). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:15) as a yellow oil (421 mg, 76%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.30 (m, 3H), 7.22−7.14 (m, 1H), 6.88 (dd, J = 2.4, 1.6 Hz, 1H), 6.73 (dd, J = 3.6, 1.6 Hz, 1H), 6.32 (dd, J = 3.6, 2.8 Hz, 1H), 2.21 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 154.1, 142.2, 134.1, 129.7, 128.1, 127.3, 127.0, 126.2, 124.2, 116.1, 109.6, 19.3, 14.9; HRMS (ESI), m/z calcd. for $C_{14}H_{13}ClN_2O_2$ ([M + Na]$^+$) 299.0558, found 299.0532; IR (KBr, neat) ν 3068, 1768, 1595, 1484, 1366, 1230, 1196, 1092, 927, 731, 689.

(*E*)-1-(1-(4-(Trifluoromethyl)phenyl)-1*H*-pyrrol-2-yl)ethan-1-one *O*-acetyl oxime (1l). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:15) as a white solid (478 mg, 77%): mp 71−73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 6.92 (t, J = 2.0 Hz, 1H), 6.76 (dd, J = 3.6, 1.2 Hz, 1H), 6.36 (t, J = 3.2 Hz, 1H), 2.22 (s, 3H), 1.81 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.3, 154.5, 144.2, 129.5, 129.1, 128.1, 127.3, 126.3, 126.1 (q, J = 3.6 Hz), 125.5, 125.1, 122.4, 116.6, 110.1, 19.3, 15.2; HRMS (ESI), m/z calcd. for $C_{15}H_{13}F_3N_2O_2$ ([M + Na]$^+$) 333.0821, found 333.0822; IR (KBr, neat) ν 3071, 1774, 1615, 1454, 1367, 1327, 1180, 1123, 1067, 852, 725.

(*E*)-1-(1-(2-(Trifluoromethyl)phenyl)-1*H*-pyrrol-2-yl)ethan-1-one *O*-acetyl oxime (1m). The product was isolated by flash chromatography (eluent EtOAc:PE = 2:15) as a white solid (484 mg, 78%): mp 64−66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 7.6 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 6.83 (s, 1H), 6.75 (dd, J = 3.6, 1.6 Hz, 1H), 6.34 (dd, J = 3.6, 2.8 Hz, 1H), 2.25 (s, 3H), 1.63 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.0, 153.3, 140.0, 132.4, 130.5, 129.3, 128.5, 128.3, 127.4, 127.1, 126.7 (q, J = 5.0 Hz), 124.4, 121.6, 115.6, 109.2, 19.4, 14.1; HRMS (ESI), m/z calcd. for $C_{15}H_{13}F_3N_2O_2$ ([M + Na]$^+$) 333.0821, found 333.0826; IR (KBr, neat) ν 3062, 1771, 1653, 1599, 1498, 1364, 1196, 1098, 764, 695.

(*E*)-1-(1-(3-(Trifluoromethyl)phenyl)-1*H*-pyrrol-2-yl)ethan-1-one *O*-acetyl oxime (1n). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:20) as a yellow oil (503 mg, 81%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.6 Hz, 1H), 7.57 (d, J = 2.0 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 6.91 (dd, J = 2.8, 1.6 Hz, 1H), 6.76 (dd, J = 3.6, 1.6 Hz, 1H), 6.35 (dd, J = 3.6, 2.8 Hz, 1H), 2.25 (s, 3H), 1.78 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.3, 154.1, 141.9, 131.6, 131.2, 129.6, 129.5, 128.4, 127.3, 124.9, 124.0 (q, J = 3.7 Hz), 123.2(q, J = 3.7 Hz), 116.5, 110.0, 19.3, 14.9; HRMS (ESI), m/z calcd. for $C_{15}H_{13}F_3N_2O_2$ ([M + Na]$^+$) 333.0821, found 333.0824; IR (KBr, neat) ν 3116, 1769, 1599, 1496, 1367, 1336, 1129, 1070, 929, 802, 699.

(*E*)-1-(1-(4-Nitrophenyl)-1*H*-pyrrol-2-yl)ethan-1-one *O*-acetyl oxime (1o). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:5) as a yellow solid (437 mg, 76%): mp 103−105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28−8.23 (m, 2H), 7.47−7.40 (m, 2H), 6.93 (dd, J = 2.8, 1.6 Hz, 1H), 6.78 (dd, J = 4.0, 1.6 Hz, 1H), 6.37 (dd, J = 3.6, 2.8 Hz, 1H), 2.25 (s, 3H), 1.90 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.0, 154.6, 146.4, 146.1, 128.1, 127.1, 126.3, 124.3, 117.4, 110.6, 19.3, 15.1; HRMS (ESI), m/z calcd. for $C_{14}H_{13}N_3O_4$ ([M + Na]$^+$) 310.0798, found 310.0824; IR (KBr, neat) ν 3072, 1767, 1598, 1513, 1346, 1218, 1187, 1106, 855, 730.

Ethyl (*E*)-4-(2-(1-(acetoxyimino)ethyl)-1*H*-pyrrol-1-yl)-benzoate (1p). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:10) as a yellow oil (503 mg, 80%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 6.91 (dd, J = 2.8, 2.0 Hz, 1H), 6.72 (dd, J = 4.0, 1.6 Hz, 1H), 6.31 (t, J = 3.4 Hz, 1H), 4.36 (q, J = 7.2 Hz, 2H), 2.16 (s, 3H), 1.81 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.2, 165.6, 154.6, 144.7, 130.3, 128.9, 127.8, 127.1, 125.3, 116.3,

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109.9, 61.0, 19.4, 15.3, 14.1; HRMS (ESI), m/z calcd. for $C_{17}H_{18}N_2O_4$ ([M + Na]$^+$) 337.1159, found 337.1179; IR (KBr, neat) ν 3116, 2984, 1770, 1716, 1608, 1512, 1455, 1367, 1278, 1193, 1099, 925, 774, 700.

(*E*)-1-(1-(Pyridin-4-yl)-1*H*-pyrrol-2-yl)ethan-1-one *O*-acetyl oxime (1q). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:2) as a yellow solid (360 mg, 74%): mp 65−67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, J = 6.0 Hz, 2H), 7.20 (d, J = 6.0 Hz, 2H), 6.92 (t, J = 2.2 Hz, 1H), 6.73 (dd, J = 3.6, 1.2 Hz, 1H), 6.34 (t, J = 3.2 Hz, 1H), 2.21 (s, 3H), 1.85 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.5, 154.2, 150.3, 147.7, 127.3, 126.6, 119.8, 117.1, 110.4, 19.0, 15.0; HRMS (ESI), m/z calcd. $C_{13}H_{13}N_3O_2$ for ([M + Na]$^+$) 266.0900, found 266.0891; IR (KBr, neat) ν 3017, 1762, 1653, 1593, 1502, 1456, 1365, 1214, 927, 831, 689.

(*E*)-1-(1-(Pyridin-2-yl)-1*H*-pyrrol-2-yl)ethan-1-one *O*-acetyl oxime (1r). The product was isolated by flash chromatography (eluent EtOAc:PE = 3:10) as a yellow oil (370 mg, 76%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46−8.41 (m, 1H), 7.79−7.70 (m, 1H), 7.24 (d, J = 8.4 Hz, 1H), 7.20 (m, 1H), 7.13 (dd, J = 2.8, 1.6 Hz, 1H), 6.67 (dd, J = 3.6, 1.6 Hz, 1H), 6.29 (dd, J = 3.6, 2.8 Hz, 1H), 2.17 (s, 3H), 1.89 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.7, 155.3, 152.4, 148.5, 137.9, 126.7, 126.6, 121.9, 118.9, 116.3, 109.9, 19.4, 15.6; HRMS (ESI), m/z calcd. $C_{13}H_{13}N_3O_2$ for ([M + Na]$^+$) 266.0900, found 266.0893; IR (KBr, neat) ν 3110, 1766, 1590, 1474, 1443, 1366, 1200, 926, 787, 736.

(*E*)-1-(1-(Pyrazin-2-yl)-1*H*-pyrrol-2-yl)ethan-1-one *O*-acetyl oxime (1s). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:2) as a yellow solid (376.2 mg, 77%): mp 59−61 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 1.6 Hz, 1H), 8.42 (d, J = 2.4 Hz, 1H), 8.37 (dd, J = 2.4, 1.6 Hz, 1H), 7.11 (dd, J = 2.8, 1.6 Hz, 1H), 6.71 (dd, J = 3.6, 1.6 Hz, 1H), 6.31 (t, J = 3.2 Hz, 1H), 2.21 (s, 3H), 1.84 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.5, 154.3, 149.0, 142.2, 142.0, 141.4, 127.0, 126.5, 117.4, 110.7, 19.1, 14.7; HRMS (ESI), m/z calcd. for $C_{12}H_{12}N_4O_2$ ([M + Na]$^+$) 267.0852, found 267.0853; IR (KBr, neat) ν 3105, 1770, 1652, 1612, 1452, 1359, 1217, 1187, 1016, 743, 704.

(*E*)-1-(1-(Pyridin-3-yl)-1*H*-pyrrol-2-yl)ethan-1-one *O*-acetyl oxime (1t). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:5) as a yellow oil (341 mg, 70%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54−8.45 (m, 2H), 7.63 (d, J = 8.0 Hz, 1H), 7.33 (dd, J = 8.0, 4.8 Hz, 1H), 6.84 (s, 1H), 6.73 (d, J = 2.0 Hz, 1H), 6.32 (t, J = 3.2 Hz, 1H), 2.22 (s, 3H), 1.76 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.9, 153.9, 148.1, 147.0, 137.9, 133.6, 128.4, 127.1, 123.2, 116.5, 110.0, 19.3, 14.7; HRMS (ESI), m/z calcd. $C_{13}H_{13}N_3O_2$ for ([M + Na]$^+$) 266.0900, found 266.0898; IR (KBr, neat) ν 3110, 1766, 1662, 1484, 1431, 1366, 1232, 1199, 926, 735, 708.

(*E*)-1-(1-([1,1′-Biphenyl]-4-yl)-1*H*-pyrrol-2-yl)ethan-1-one *O*-acetyl oxime (1u). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:2) as a white solid (484 mg, 76%): mp 94−96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.61 (m, 4H), 7.48 (t, J = 7.6 Hz, 2H), 7.39 (t, J = 8.6 Hz, 3H), 6.98 (dd, J = 2.8, 2.0 Hz, 1H), 6.79 (dd, J = 3.6, 1.6 Hz, 1H), 6.37 (dd, J = 3.6, 2.8 Hz, 1H), 2.23 (s, 3H), 1.85 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.8, 154.5, 140.2, 140.1, 139.8, 128.7, 128.0, 127.4, 127.4, 127.1, 126.8, 126.0, 115.6, 109.3, 19.2, 15.2; HRMS (ESI), m/z calcd. for $C_{20}H_{18}N_2O_2$ ([M + Na]$^+$) 341.1260, found 341.1253; IR (KBr, neat) ν 3026, 1761, 1686, 1602, 1519, 1486, 1447, 1362, 1225, 1084, 924, 769, 702.

(*E*)-1-(1-(Naphthalen-1-yl)-1*H*-pyrrol-2-yl)ethan-1-one *O*-acetyl oxime (1v). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:2) as a yellow solid (368 mg, 63%): mp 73−75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92−7.88 (m, 2H), 7.56−7.49 (m, 2H), 7.47−7.43 (m, 2H), 7.30 (d, J = 8.4 Hz, 1H), 6.94 (dd, J = 2.8, 2.0 Hz, 1H), 6.88 (dd, J = 3.6, 1.6 Hz, 1H), 6.44 (dd, J = 4.0, 2.8 Hz, 1H), 2.23 (s, 3H), 1.13 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.2, 153.1, 138.7, 133.9, 131.0, 129.4, 128.5, 128.2, 127.8, 127.0, 126.4, 125.1, 124.3, 122.7, 115.3, 109.2, 19.0, 14.2; HRMS (ESI), m/z calcd. for $C_{18}H_{16}N_2O_2$ ([M + Na]$^+$) 315.1104, found 315.1101; IR (KBr, neat) ν 3056, 1764, 1652, 1596, 1508, 1448, 1362, 1216, 1083, 947, 778, 739.

(*E*)-1-Phenyl-1*H*-pyrrole-2-carbaldehyde *O*-acetyl oxime (1w). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:10) as a yellow solid (183 mg, 40%): mp 65−67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.51−7.44 (m, 3H), 7.30 (d, J = 6.8 Hz, 2H), 7.09 (dd, J = 3.6, 1.2 Hz, 1H), 7.02 (dd, J = 2.4, 1.2 Hz, 1H), 6.38 (t, J = 3.2 Hz, 1H), 2.09 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.1, 147.2, 138.5, 129.4, 128.2, 127.5, 126.2, 123.4, 120.6, 114.1, 110.7, 19.5; HRMS (ESI), m/z calcd. for $C_{13}H_{12}N_2O_2$ ([M + Na]$^+$) 251.0791, found 251.0802; IR (KBr, neat) ν 3066, 2216, 1765, 1672, 1592, 1500, 1449, 1324, 1202, 1039, 765, 696.

(*E*)-1-(1-Phenyl-1*H*-pyrrol-2-yl)propan-1-one *O*-acetyl oxime (1x). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:15) as a white solid (400 mg, 78%): mp 56−58 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, J = 7.4 Hz, 2H), 7.28 (t, J = 7.4 Hz, 1H), 7.24−7.20 (m, 2H), 6.87 (t, J = 2.2 Hz, 1H), 6.66 (dd, J = 4.0, 1.6 Hz, 1H), 6.27 (t, J = 3.2 Hz, 1H), 2.57 (q, J = 7.6 Hz, 2H), 1.71 (s, 3H), 1.10 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.5, 159.4, 141.4, 129.0, 128.3, 127.2, 126.3, 125.9, 115.6, 109.3, 22.8, 19.5, 11.7; HRMS (ESI), m/z calcd. for $C_{15}H_{16}N_2O_2$ ([M + Na]$^+$) 279.1104, found 279.1106; IR (KBr, neat) ν 3106, 2987, 2937, 1765, 1594, 1499. 1448, 1366, 1237, 1095, 943, 738, 703.

(*E*)-Phenyl(1-phenyl-1*H*-pyrrol-2-yl)methanone *O*-acetyl oxime (1y). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:5) as a pale yellow oil (257 mg, 42%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69−7.66 (m, 2H), 7.45−7.41 (m, 1H), 7.36−7.29 (m, 4H), 7.25−7.19 (m, 3H), 7.13 (dd, J = 2.8, 1.6 Hz, 1H), 6.47 (dd, J = 3.6, 1.6 Hz, 1H), 6.43 (dd, J = 3.7, 2.8 Hz, 1H), 1.86 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.1, 156.7, 140.4, 134.9, 130.8, 129.3, 129.3, 128.8, 128.2, 127.7, 126.9, 126.0, 125.4, 123.6, 123.0, 117.2, 109.8, 19.4; HRMS (ESI), m/z calcd. for $C_{19}H_{16}N_2O_2$ ([M + Na]$^+$) 327.1104, found 327.1100; IR (KBr, neat) ν 3114, 1762, 1746, 1605, 1504, 1463, 1369, 1321, 1235, 1119, 1066, 930, 787, 737.

(*E*)-1-(1-Phenyl-1*H*-indol-2-yl)ethan-1-one *O*-acetyl oxime (1z). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:10) as a white solid (421 mg, 72%): mp 102−104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.6 Hz, 1H), 7.52 (t, J = 7.4 Hz, 2H), 7.46−7.40 (m, 1H), 7.35 (m, 2H), 7.25−7.22 (m, 1H), 7.21−7.16 (m, 1H), 7.15−7.11 (m, 1H), 7.09 (s, 1H), 2.26 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 155.1, 140.4, 139.3, 133.7, 129.4, 127.8, 127.7, 126.8, 124.4, 121.4, 121.0, 110.9, 108.6, 19.5, 15.4; HRMS (ESI), m/z calcd. for $C_{18}H_{16}N_2O_2$ ([M + Na]$^+$) 315.1104, found 315.1113; IR (KBr, neat) ν 3057, 1765, 1717, 1527, 1498, 1367, 1274, 1223, 1117, 934, 810, 700.

4-Methylpyrrolo[1,2-*a*]quinoxaline (2a).[26] The product was isolated by flash chromatography (eluent EtOAc:PE = 1:5) as a yellow solid (50 mg, 91%): mp 129−130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.0 Hz, 1H), 7.86 (s, 1H), 7.77 (d, J = 7.9 Hz, 1H), 7.47−7.36 (m, 2H), 6.88−6.80 (m, 2H), 2.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 135.6, 129.0, 127.1, 126.9, 126.1, 125.0, 114.2, 113.5, 113.5, 106.6, 21.8; HRMS (ESI), m/z calcd. for $C_{12}H_{10}N_2$ ([M + H]$^+$) 183.0917, found 183.0919; IR (KBr, neat) ν 3099, 2917, 1716, 1611, 1529, 1480, 1417, 1361, 1529, 1042, 761, 732.

7-Methoxy-4-methylpyrrolo[1,2-*a*]quinoxaline (2b).[26] The product was isolated by flash chromatography (eluent EtOAc:PE = 1:5) as a white solid (35 mg, 55%): mp 86−87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 0.8 Hz, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.39 (d, J = 2.8 Hz, 1H), 7.06 (dd, J = 9.2, 2.8 Hz, 1H), 6.87 (d, J = 3.6 Hz, 1H), 6.81 (t, J = 3.4 Hz, 1H), 3.89 (s, 3H), 2.72 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.1, 153.8, 136.5, 125.8, 121.4, 116.0, 114.5, 114.1, 113.3, 110.3, 106.5, 55.6, 21.7; HRMS (ESI), m/z calcd. for $C_{13}H_{12}N_2O$ ([M + H]$^+$) 213.1022, found 213.1026; IR (KBr, neat) ν 3086, 2993, 2834, 1716, 1617, 1594, 1491, 1351, 1246, 1161, 1048, 802, 719.

9-Methoxy-4-methylpyrrolo[1,2-*a*]quinoxaline (2c). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:7) as a yellow solid (30 mg, 47%): mp 90−92 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (dd, J = 2.8, 1.2 Hz, 1H), 7.54 (dd, J = 8.0, 1.2 Hz, 1H), 7.34 (t, J = 8.2 Hz, 1H), 7.01 (dd, J = 8.0, 0.8 Hz, 1H), 6.93 (dd, J = 4.0, 1.2 Hz, 1H), 6.80 (dd, J = 4.0, 2.8 Hz, 1H), 4.06 (s, 3H), 2.73 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.8, 149.8, 137.8,

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126.6, 124.3, 122.1, 121.1, 118.6, 112.5, 108.5, 106.1, 56.1, 21.8; HRMS (ESI), m/z calcd. for $C_{13}H_{12}N_2O$ ($[M + H]^+$) 213.1022, found 213.1031; IR (KBr, neat) ν 3085, 2934, 2836, 1683, 1586, 1534, 1459, 1356, 1268, 1072, 788, 731.

6-Methoxy-4-methylpyrrolo[1,2-*a*]quinoxaline (2da). The product was isolated by flash chromatography (eluent EtOAc:PE = 2:7) as a yellow solid (20 mg, 31%): mp 156−158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 9.2 Hz, 1H), 7.77 (s, 1H), 7.19 (d, J = 2.4 Hz, 1H), 6.99 (dd, J = 9.2, 2.8 Hz, 1H), 6.83 (s, 2H), 3.92 (s, 3H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 150.9, 130.2, 130.1, 127.9, 126.1, 113.8, 113.5, 112.5, 106.1, 97.5, 55.7, 21.6; HRMS (ESI), m/z calcd. for $C_{13}H_{12}N_2O$ ($[M + H]^+$) 213.1022, found 213.1028; IR (KBr, neat) ν 3098, 2943, 2838, 1717, 1606, 1548, 1484, 1416, 1353, 1264, 1076, 781, 742.

8-Methoxy-4-methylpyrrolo[1,2-*a*]quinoxaline (2db). The product was isolated by flash chromatography (eluent EtOAc:PE = 3:7) as a white solid (34 mg, 53%): mp 92−94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, J = 2.8, 1.2 Hz, 1H), 7.44−7.36 (m, 2H), 6.93−6.87 (m, 2H), 6.84 (dd, J = 4.0, 2.8 Hz, 1H), 4.05 (s, 3H), 2.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 152.3, 128.0, 127.1, 126.3, 114.4, 113.6, 106.4, 106.0, 105.8, 56.2, 22.3; HRMS (ESI), m/z calcd. for $C_{13}H_{12}N_2O$ ($[M + H]^+$) 213.1022, found 213.1027; IR (KBr, neat) ν 3010, 2962, 2837, 1747, 1620, 1532, 1489, 1414, 1352, 1238, 1025, 823, 710.

4,7-Dimethylpyrrolo[1,2-*a*]quinoxaline (2e).[27] The product was isolated by flash chromatography (eluent EtOAc:PE = 3:10) as a yellow solid (50 mg, 84%): mp 136−138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, J = 2.8, 1.2 Hz, 1H), 7.69 (s, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.27−7.23 (m, 1H), 6.85 (dd, J = 4.0, 1.2 Hz, 1H), 6.80 (dd, J = 4.0, 2.8 Hz, 1H), 2.70 (s, 3H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.4, 135.6, 134.8, 128.9, 127.9, 126.1, 125.0, 114.0, 113.3, 113.2, 106.2, 21.9, 21.1; HRMS (ESI), m/z calcd. for $C_{13}H_{12}N_2$ ($[M + H]^+$) 197.1073, found 197.1088; IR (KBr, neat) ν 3095, 2911, 1713, 1588, 1493, 1415, 1380, 1303, 1038, 813, 732.

4,9-Dimethylpyrrolo[1,2-*a*]quinoxaline (2f). The product was isolated by flash chromatography (eluent EtOAc:PE = 3:10) as a white solid (35 mg, 59%): mp 99−101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, J = 2.8, 1.2 Hz, 1H), 7.78 (dd, J = 7.6, 1.2 Hz, 1H), 7.29 (t, J = 7.8 Hz, 1H), 7.24 (d, J = 6.8 Hz, 1H), 6.89 (dd, J = 4.0, 1.2 Hz, 1H), 6.81 (dd, J = 4.0, 3.2 Hz, 1H), 2.89 (s, 3H), 2.70 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.1, 137.3, 130.4, 127.5, 127.5, 127.4, 125.2, 124.5, 119.9, 112.7, 105.9, 23.8, 21.7; HRMS (ESI), m/z calcd. for $C_{13}H_{12}N_2$ ($[M + H]^+$) 197.1073, found 197.1072; IR (KBr, neat) ν 3111, 2913, 1716, 1603, 1536, 1467, 1353, 1244, 1098, 790, 742.

4,8-Dimethylpyrrolo[1,2-*a*]quinoxaline (2ga). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:8) as a yellow solid (27 mg, 45%): mp 106−108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, J = 2.8, 1.6 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.56 (s, 1H), 7.20 (dd, J = 8.4, 1.2 Hz, 1H), 6.83 (dd, J = 4.0, 1.2 Hz, 1H), 6.80 (dd, J = 3.6, 2.4 Hz, 1H), 2.69 (s, 3H), 2.50 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.5, 137.2, 133.6, 128.7, 126.9, 126.3, 126.2, 113.8, 113.6, 113.3, 106.1, 21.8, 21.6; HRMS (ESI), m/z calcd. for $C_{13}H_{12}N_2$ ($[M + H]^+$) 197.1073, found 197.1065; IR (KBr, neat) ν 3095, 2917, 1705, 1620, 1532, 1471, 1415, 1353, 1256, 1085, 1042, 820, 742.

4,6-Dimethylpyrrolo[1,2-*a*]quinoxaline (2gb). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:10) as a white solid (18 mg, 31%): mp 137−139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, J = 2.8, 1.6 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 7.8 Hz, 1H), 7.28 (d, J = 7.2 Hz, 1H), 6.85 (dd, J = 4.0, 1.2 Hz, 1H), 6.82 (dd, J = 3.6, 2.4 Hz, 1H), 2.77 (s, 3H), 2.74 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.0, 137.7, 134.5, 127.1, 126.2, 126.1, 126.1, 114.0, 113.2 111.4, 105.7, 22.2, 18.2; HRMS (ESI), m/z calcd. for $C_{13}H_{12}N_2$ ($[M + H]^+$) 197.1073, found 197.1072; IR (KBr, neat) ν 3106, 2921, 1716, 1662, 1607, 1531, 1482, 1419, 1379, 1177, 1062, 747, 725.

4,7,8-Trimethylpyrrolo[1,2-*a*]quinoxaline (2ha). The product was isolated by flash chromatography (eluent EtOAc:PE = 2:7) as a yellow solid (23 mg, 36%): mp 116−118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 2.4, 1.2 Hz, 1H), 7.66 (s, 1H), 7.58 (s, 1H), 6.85 (dd, J = 4.0, 1.2 Hz, 1H), 6.81 (dd, J = 4.0, 2.8 Hz, 1H), 2.71 (s, 3H), 2.43 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 136.3, 133.9, 129.3, 126.2, 125.2, 114.1, 113.8, 113.1, 106.0, 21.8, 20.2, 19.6; HRMS (ESI), m/z calcd. for $C_{14}H_{14}N_2$ ($[M + H]^+$) 211.1230, found 211.1252; IR (KBr, neat) ν 3100, 2921, 1713, 1625, 1524, 1490, 1414, 1353, 1244, 1024, 852, 717.

4,6,7-Trimethylpyrrolo[1,2-*a*]quinoxaline (2hb). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:7) as a yellow solid (13 mg, 20%): mp 126−128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.26 (t, J = 4.0 Hz, 1H), 6.85−6.79 (m, 2H), 2.74 (s, 3H), 2.71 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 135.7, 133.2, 128.1, 125.9, 125.3, 113.8, 113.1, 110.4, 105.4, 22.3, 20.3, 13.8; HRMS (ESI), m/z calcd. for $C_{14}H_{14}N_2$ ($[M + H]^+$) 211.1230, found 211.1252; IR (KBr, neat) ν 3106, 2910, 1715, 1529, 1480, 1417, 1358, 1287, 1065, 780, 712.

7-Chloro-4-methylpyrrolo[1,2-*a*]quinoxaline (2i).[26] The product was isolated by flash chromatography (eluent EtOAc:PE = 1:4) as a white solid (42 mg, 65%): mp 172−174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85−7.76 (m, 2H), 7.65 (d, J = 8.8 Hz, 1H), 7.35 (dd, J = 8.8, 2.0 Hz, 1H), 6.87 (d, J = 4.0 Hz, 1H), 6.82 (t, J = 3.2 Hz, 1H), 2.69 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.7, 136.5, 130.1, 128.4, 126.8, 125.9, 125.7, 114.6, 114.6, 113.9, 107.2, 21.8; HRMS (ESI), m/z calcd. for $C_{12}H_9ClN_2$ ($[M + H]^+$) 217.0527, found 217.0527; IR (KBr, neat) ν 3098, 1716, 1684, 1578, 1526, 1482, 1418, 1360, 1295, 1039, 781, 739.

9-Chloro-4-methylpyrrolo[1,2-*a*]quinoxaline (2j). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:8) as a white solid (33 mg, 50%): mp 111−113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (dd, J = 3.2, 1.6 Hz, 1H), 7.83 (dd, J = 8.0, 1.6 Hz, 1H), 7.49 (dd, J = 8.0, 1.6 Hz, 1H), 7.31 (t, J = 8.0 Hz, 1H), 6.97 (dd, J = 4.4, 1.2 Hz, 1H), 6.85 (dd, J = 4.0, 3.2 Hz, 1H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 129.5, 128.3, 127.3, 125.5, 124.7, 121.1, 121.0, 113.1, 107.1, 21.8; HRMS (ESI), m/z calcd. for $C_{12}H_9ClN_2$ ($[M + H]^+$) 217.0527, found 217.0535; IR (KBr, neat) ν 3100, 1716, 1606, 1544, 1462, 1418, 1357, 1271, 1171, 1034, 784, 730.

8-Chloro-4-methylpyrrolo[1,2-*a*]quinoxaline (2ka). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:4) as a white solid (29 mg, 44%): mp 147−149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.79 (d, J = 6.0 Hz, 1H), 7.76 (d, J = 2.0 Hz, 1H), 7.34 (dd, J = 8.4, 2.0 Hz, 1H), 6.88 (dd, J = 4.0, 1.2 Hz, 1H), 6.85 (t, J = 3.2 Hz, 1H), 2.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 134.4, 132.2, 130.3, 127.8, 126.1, 125.4, 114.4, 114.0, 113.7, 107.0, 21.9; HRMS (ESI), m/z calcd. for $C_{12}H_9ClN_2$ ($[M + H]^+$) 217.0527, found 217.0532; IR (KBr, neat) ν 3109, 1663, 1601, 1527, 1473, 1418, 1360, 1192, 1042, 781, 742.

6-Chloro-4-methylpyrrolo[1,2-*a*]quinoxaline (2kb). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:8) as a white solid (27 mg, 41%): mp 166−168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 1.6 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 8.0 Hz, 1H), 6.92 (d, J = 3.2 Hz, 1H), 6.87 (t, J = 3.4 Hz, 1H), 2.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 133.4, 133.0, 128.4, 126.5, 126.2, 125.8, 114.8, 114.2, 112.5, 107.1, 22.3; HRMS (ESI), m/z calcd. for $C_{12}H_9ClN_2$ ($[M + H]^+$) 217.0527, found 217.0530; IR (KBr, neat) ν 3099, 1610, 1529, 1476, 1418, 1351, 1253, 1085, 814, 739.

4-Methyl-7-(trifluoromethyl)pyrrolo[1,2-*a*]quinoxaline (2l). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:7) as a white solid (42 mg, 56%): mp 106−108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.85 (dd, J = 2.8, 1.2 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 6.94−6.83 (m, 2H), 2.70 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.1, 135.2, 129.2, 127.2, 126.9, 126.7 (q, J = 3.8 Hz) 126.2, 125.6, 123.2 (q, J = 3.5 Hz), 122.6, 114.8, 114.4, 114.2, 107.5, 21.9; HRMS (ESI), m/z calcd. for $C_{13}H_9F_3N_2$ ($[M + H]^+$) 251.0791, found 251.0799; IR (KBr, neat) ν 3090, 1770, 1626, 1534, 1458, 1330, 1172, 1096, 892, 720.

4-Methyl-9-(trifluoromethyl)pyrrolo[1,2-*a*]quinoxaline (2m). The product was isolated by flash chromatography (eluent EtOAc:PE = 2:7) as a white solid (39 mg, 52%): mp 108−110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.49 (t, J = 7.8 Hz, 1H), 7.02 (d, J = 3.6 Hz, 1H), 6.91 (t, J =

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3.6 Hz, 1H), 2.76 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 154.4, 134.3, 127.5, 126.0 (q, J = 7.2 Hz), 125.7, 124.1, 123.0, 121.7 (q, J = 1.7 Hz), 117.0, 116.7, 114.1, 107.7, 29.7, 21.7; HRMS (ESI), m/z calcd. for $C_{13}H_9F_3N_2$ ($[M + H]^+$) 251.0791, found 251.0807; IR (KBr, neat) ν 3056, 1756, 1608, 1545, 1461, 1363, 1311, 1185, 1104, 1035, 796, 716.

4-Methyl-8-(trifluoromethyl)pyrrolo[1,2-*a*]quinoxaline (2na). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:7) as a white solid (42 mg, 56%): mp 89−91 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.80 (dd, J = 2.8, 1.2 Hz, 1H), 7.56 (dd, J = 8.4, 1.2 Hz, 1H), 6.85 (dd, J = 4.0, 1.2 Hz, 1H), 7.80 (dd, J = 4.0, 2.8 Hz, 1H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 137.8, 129.6, 128.3, 128.0, 126.8, 125.9, 125.1, 122.4, 121.3 (q, J = 3.6 Hz), 114.8, 114.1, 111.0 (q, J = 4.0 Hz), 107.6, 21.9; HRMS (ESI), m/z calcd. for $C_{13}H_9F_3N_2$ ($[M + H]^+$) 251.0791, found 251.0803; IR (KBr, neat) ν 3035, 1743, 1629, 1536, 1471, 1359, 1318, 1282, 1164, 1108, 1035, 849, 717.

4-Methyl-6-(trifluoromethyl)pyrrolo[1,2-*a*]quinoxaline (2nb). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:14) as a white solid (21 mg, 28%): mp 166−167 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 1.6 Hz, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.48 (t, J = 7.8 Hz, 1H), 7.04−6.76 (m, 2H), 2.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 133.7, 128.4, 127.8, 125.9, 125.6, 125.3, 122.7 (q, J = 5.6 Hz), 122.5, 117.5, 114.5, 114.0, 107.0, 22.5; HRMS (ESI), m/z calcd. for $C_{13}H_9F_3N_2$ ($[M + H]^+$) 251.0791, found 251.0804; IR (KBr, neat) ν 3030, 1759, 1611, 1534, 1469, 1368, 1302, 1118, 1039, 807, 731.

4-Methyl-7-nitropyrrolo[1,2-*a*]quinoxaline (2o). The product was isolated by flash chromatography (eluent EtOAc:PE = 2:7) as a yellow solid (42 mg, 61%): mp 236−238 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.34 (d, J = 7.6 Hz, 1H), 7.97 (s, 1H), 7.92 (d, J = 8.8 Hz, 1H), 6.98 (d, J = 16.4 Hz, 2H), 2.76 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 156.2, 144.6, 135.7, 131.5, 126.4, 125.2, 121.7, 115.5, 115.3, 114.3, 108.4, 22.1; HRMS (ESI), m/z calcd. for $C_{12}H_9N_3O_2$ ($[M + H]^+$) 228.0784, found 228.0768; IR (KBr, neat) ν 3013, 1750, 1622, 1552, 1515, 1488, 1416, 1339, 1034, 824, 742.

Ethyl 4-methylpyrrolo[1,2-*a*]quinoxaline-7-carboxylate (2p). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:7) as a white solid (64 mg, 84%): mp 114−116 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 1.6 Hz, 1H), 8.04 (dd, J = 8.8, 2.0 Hz, 1H), 7.82 (d, J = 1.2 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 6.88−6.78 (m, 2H), 4.38 (q, J = 7.2 Hz, 2H), 2.67 (s, 3H), 1.40 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.8, 154.3, 135.1, 130.9, 130.0, 127.6, 126.9, 126.1, 114.8, 114.2, 113.5, 107.3, 61.0, 21.8, 14.2; HRMS (ESI), m/z calcd. for $C_{15}H_{14}N_2O_2$ ($[M + H]^+$) 255.1128, found 255.1140; IR (KBr, neat) ν 3098, 2986, 1704, 1616, 1419, 1365, 1285, 1196, 1102, 1027, 761, 745.

6-Methylpyrido[3,4-*e*]pyrrolo[1,2-*a*]pyrazine (2q). The product was isolated by flash chromatography (eluent EtOAc:PE = 2:1) as a yellow solid (43 mg, 78%): mp 135−137 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.47 (d, J = 5.6 Hz, 1H), 7.79−7.70 (m, 1H), 7.50 (d, J = 5.2 Hz, 1H), 6.85−6.79 (m, 2H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 151.2, 146.3, 131.9, 131.5, 126.2, 114.9, 114.7, 107.9, 107.7, 21.8; HRMS (ESI), m/z calcd. for $C_{11}H_9N_3$ ($[M + H]^+$) 184.0869, found 184.0857; IR (KBr, neat) ν 3101, 1600, 1493, 1417, 1366, 1283, 1041, 830, 744.

6-Methylpyrido[3,2-*e*]pyrrolo[1,2-*a*]pyrazine (2r).[26] The product was isolated by flash chromatography (eluent EtOAc:PE = 3:7) as a white solid (20 mg, 37%): mp 78−80 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.50 (dd, J = 4.8, 1.6 Hz, 1H), 8.36 (dd, J = 2.8, 1.2 Hz, 1H), 8.18 (dd, J = 8.0, 1.6 Hz, 1H), 7.42 (dd, J = 8.0, 4.8 Hz, 1H), 6.97 (dd, J = 4.0, 1.6 Hz, 1H), 6.89 (dd, J = 3.6, 2.8 Hz, 1H), 2.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 146.2, 139.5, 136.5, 130.8, 127.7, 121.4, 115.6, 114.0, 108.1, 21.9; HRMS (ESI), m/z calcd. for $C_{11}H_9N_3$ ($[M + H]^+$) 184.0869, found 184.0847; IR (KBr, neat) ν 3095, 1597, 1531, 1474, 1417, 1363, 1042, 803, 735.

6-Methylpyrazino[2,3-*e*]pyrrolo[1,2-*a*]pyrazine (2s). The product was isolated by flash chromatography (eluent EtOAc:PE = 5:7) as a yellow solid (37 mg, 67%): mp 137−139 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 2.4 Hz, 1H), 8.35 (d, J = 2.4 Hz, 1H), 8.26 (dd, J = 2.4, 1.2 Hz, 1H), 6.93 (dd, J = 4.0, 1.2 Hz, 1H), 6.83 (dd, J = 4.0, 3.2 Hz, 1H), 2.74 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.2, 143.1, 141.9, 139.9, 135.3, 127.4, 117.0, 115.0, 109.4, 22.2; HRMS (ESI), m/z calcd. for $C_{11}H_8N_4$ ($[M + H]^+$) 185.0822, found 185.0804; IR (KBr, neat) ν 3100, 1741, 1584, 1526, 1479, 1408, 1321, 1197, 1067, 880, 731.

6-Methylpyrido[2,3-*e*]pyrrolo[1,2-*a*]pyrazine (2ta). The product was isolated by flash chromatography (eluent EtOAc:PE = 2:1) as a white solid (39 mg, 70%): mp 170−172 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, J = 4.0 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 1.2 Hz, 1H), 7.37 (dd, J = 8.0, 4.8 Hz, 1H), 6.91 (d, J = 3.6 Hz, 1H), 6.86 (t, J = 3.2 Hz, 1H), 2.76 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.7, 147.5, 146.7, 126.0, 122.9, 121.9, 121.5, 115.4, 114.5, 107.4, 22.3; HRMS (ESI), m/z calcd. for $C_{11}H_9N_3$ ($[M + H]^+$) 184.0869, found 184.0874; IR (KBr, neat) ν 3093, 1596, 1572, 1527, 1474, 1415, 1364, 1303, 1093, 1033, 800, 741.

6-Methylpyrido[4,3-*e*]pyrrolo[1,2-*a*]pyrazine (2tb). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:1) as a white solid (12 mg, 22%): mp 155−157 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.27 (s, 1H), 8.61 (d, J = 5.2 Hz, 1H), 8.07 (dd, J = 2.8, 1.2 Hz, 1H), 7.72 (d, J = 5.6 Hz, 1H), 7.02 (dd, J = 4.0, 1.2 Hz, 1H), 6.91 (dd, J = 3.6, 2.4 Hz, 1H), 2.76 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.9, 145.8, 140.8, 137.2, 126.6, 123.9, 122.0, 114.9, 114.5, 108.5, 22.3; HRMS (ESI), m/z calcd. for $C_{11}H_9N_3$ ($[M + H]^+$) 184.0869, found 184.0872; IR (KBr, neat) ν 3095, 1604, 1571, 1485, 1412, 1368, 1280, 1032, 831, 740.

4-Methyl-7-phenylpyrrolo[1,2-*a*]quinoxaline (2u). The product was isolated by flash chromatography (eluent EtOAc:PE = 5:7) as a yellow solid (57 mg, 73%): mp 138−140 °C;^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 2.0 Hz, 1H), 7.83 (dd, J = 2.4, 0.8 Hz, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.71−7.67 (m, 2H), 7.65 (dd, J = 8.4, 2.0 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H), 6.87 (dd, J = 4.0, 1.2 Hz, 1H), 6.82 (dd, J = 4.0, 2.8 Hz, 1H), 2.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 139.8, 137.8, 135.8, 128.8, 127.3, 126.9, 126.3, 125.9, 125.6, 114.3, 113.9, 113.6, 106.8, 21.7; HRMS (ESI), m/z calcd. for $C_{18}H_{14}N_2$ ($[M + H]^+$) 259.1230, found 259.1239; IR (KBr, neat) ν 3106, 1716, 1615, 1574, 1523, 1481, 1413, 1359, 1300, 1210, 1087, 820, 694.

4-Methylbenzo[*h*]pyrrolo[1,2-*a*]quinoxaline (2v). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:1) as a yellow solid (24 mg, 34%): mp 128−130 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, J = 8.8 Hz, 1H), 8.77 (s, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 8.8 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.75−7.66 (m, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.10−7.00 (m, 2H), 2.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 135.0, 133.0, 129.1, 128.7 127.7, 126.5, 126.1, 125.9, 123.9, 122.8, 122.3, 119.3, 114.3, 105.5, 21.8; HRMS (ESI), m/z calcd. for $C_{16}H_{12}N_2$ ($[M + H]^+$) 233.1073, found 233.1083; IR (KBr, neat) ν 3100, 1716, 1531, 1449, 1386, 1249, 1130, 1034, 820, 723.

Pyrrolo[1,2-*a*]quinoxaline (2w).[28] The product was isolated by flash chromatography (eluent EtOAc:PE = 1:8) as a yellow solid (13 mg, 26%): mp 127−129 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.96 (s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 6.94 (d, J = 3.6 Hz, 1H), 6.91 (t, J = 3.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.7, 135.7, 130.0, 129.4, 127.8, 126.7, 126.4, 125.2, 114.3, 114.1, 113.8, 107.5; HRMS (ESI), m/z calcd. for $C_{11}H_8N_2$ ($[M + H]^+$) 169.0760, found 169.0760; IR (KBr, neat) ν 3092, 1716, 1616, 1589, 1549, 1478, 1338, 1295, 1241, 1033, 867, 745.

4-Ethylpyrrolo[1,2-*a*]quinoxaline (2x).[26] The product was isolated by flash chromatography (eluent EtOAc:PE = 1:7) as a yellow solid (33 mg, 56%): mp 70−72 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, J = 7.6, 1.2 Hz, 1H), 7.89 (d, J = 1.6 Hz, 1H), 7.80 (dd, J = 8.0, 1.6 Hz, 1H), 7.48−7.39 (m, 2H), 6.91 (dd, J = 4.0, 1.2 Hz, 1H), 6.84 (t, J = 3.4 Hz, 1H), 3.06 (q, J = 7.6 Hz, 2H), 1.46 (t, J = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.3, 135.9, 129.3, 127.2, 126.8, 125.6, 125.0, 114.1, 113.5, 113.4, 106.1, 28.9, 12.6; HRMS (ESI), m/z calcd. for $C_{13}H_{12}N_2$ ($[M + H]^+$) 197.1073, found 197.1081; IR (KBr, neat) ν 3104, 2964, 2932, 1712, 1613, 1528, 1481, 1426, 1330, 1208,1085, 1038, 753, 727.

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4-Phenylpyrrolo[1,2-*a*]quinoxaline (2y).[29] The product was isolated by flash chromatography (eluent EtOAc:PE = 1:7) as a white solid (59 mg, 81%): mp 78−80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 7.6 Hz, 1H), 8.02 (d, J = 2.8 Hz, 1H), 8.00 (d, J = 1.2 Hz, 2H), 7.88 (d, J = 8.0 Hz, 1H), 7.58−7.50 (m, 4H), 7.49−7.44 (m, 1H), 7.01 (d, J = 3.2 Hz, 1H), 6.90 (t, J = 3.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.3, 138.3, 136.1, 130.1, 129.8, 128.6, 128.6, 127.6, 127.1, 125.3, 125.3, 114.6, 114.0, 113.6, 108.8; HRMS (ESI), m/z calcd. for $C_{17}H_{12}N_2$ ([M + H]$^+$) 245.1073, found 245.1081; IR (KBr, neat) ν 3065, 1616, 1533, 1475, 1415, 1369, 1320, 1096, 753, 689.

6-Methylindolo[1,2-*a*]quinoxaline (2z). The product was isolated by flash chromatography (eluent EtOAc:PE = 1:7) as a white solid (50 mg, 72%): mp 105−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 2H), 7.90 (dd, J = 16.0, 7.6 Hz, 2H), 7.49 (dd, J = 18.0, 8.8 Hz, 2H), 7.39 (dd, J = 14.0, 6.8 Hz, 2H), 7.05 (s, 1H), 2.75 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.0, 135.3, 132.9, 130.0, 129.4, 129.2, 128.9, 127.7, 124.2, 123.9, 122.5, 122.5, 114.5, 114.4, 100.1, 22.1; HRMS (ESI), m/z calcd. for $C_{16}H_{12}N_2$ ([M + H]$^+$) 233.1073, found 233.1080; IR (KBr, neat) ν 3062, 1615, 1538, 1472, 1401, 1363, 1300, 1207, 1101, 774, 744.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compounds **1** and **2**. CIF file of **2i**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00915.

■ AUTHOR INFORMATION

Corresponding Authors

*Fax: (+86)-373-332-5250. E-mail: zhangzg@htu.edu.cn.
*E-mail: zgs6668@yahoo.com.

Notes

The authors declare no competing financial interest.

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