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Graphical Abstract

One-pot synthesis of pyrrolo[1,2-a]quinoxaline and pyrrolo[1,2-a]pyrazine derivatives *via* the three-component reaction of 1,2-diamines, ethyl pyruvate and *α*-bromo ketones

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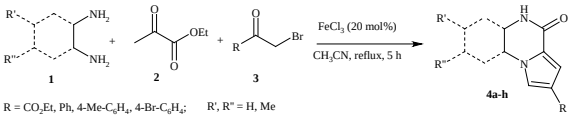

R = CO_2Et, Ph, 4-Me-C_6H_4, 4-Br-C_6H_4; R', R'' = H, Me

A simple synthetic protocol has been developed involving the one-pot three-component reaction between 1,2-diamines, ethyl pyruvate and *α*-bromo ketones in the presence of $FeCl_3$ as a catalyst. A number of pyrrolo[1,2-a]quinoxaline and pyrrolo[1,2-a]pyrazine derivatives were synthesized in excellent yields using this protocol.

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Original article

One-pot synthesis of pyrrolo[1,2-a]quinoxaline and pyrrolo[1,2-a]pyrazine derivatives *via* the three-component reaction of 1,2-diamines, ethyl pyruvate and α-bromo ketones

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ABSTRACT

A simple synthetic protocol has been developed involving the three-component reaction between 1,2-diamines, ethyl pyruvate and α-bromo ketones in the presence of $FeCl_3$ as a catalyst. A number of pyrrolo[1,2-a]quinoxaline and pyrrolo[1,2-a]pyrazine derivatives were synthesized in excellent yields using this protocol.

1. Introduction

Multicomponent reactions (MCRs) are economically and environmentally advantageous as three or more starting materials can be reacted in a one-pot procedure to give a single product [1-3].

The quinoxaline nucleus is present in many biologically and pharmaceutically active compounds. Quinoxalines show anti-inflammatory [4], antiviral [5], antiglucoma [6], herbicidal [7], and anticancer [8] activities. Furthermore, the synthesis of quinoxalines and their derivatives has received much attention from organic and medicinal chemists. Nevertheless, most of the reported methods for the synthesis of pyrrolo[1,2-a]quinoxalines suffer from one or more disadvantages which limit their use, such as: difficulties in product isolation, the use of highly expensive and detrimental metal precursors, unsatisfactory yields, and longer reaction times [9-12].

Iron(III) chloride has been used as an efficient catalyst for the manufacture of carbon-heteroatom and heteroatom-heteroatom bonds with considerable advantages [13]. It has been used previously by us for the synthesis of pyrrolo[2,1-c]benzoxazines [14]. As part of our current studies on the development of new routes to synthesize heterocyclic systems [15-17], the syntheses of pyrrolo[1,2-a]quinoxaline and pyrrolo[1,2-a] pyrazine derivatives from 1,2-diamines (**1**), ethyl pyruvate (**2**) and α-bromo ketones (**3**) in the presence of $FeCl_3$ as a catalyst are reported herein (Scheme 1).

2. Experimental

Melting point (mp) was measured on a microscopic melting point apparatus. The IR spectra were recorded on a Shimadzu 460 FT-IR spectrometer with a KBr disk. ^{1}H NMR and ^{13}C NMR spectra were taken on a Bruker DRX-250 Avance spectrometer at 250 MHz and 62.5 MHz in DMSO-d_6, chemical shift are given in part per million (ppm) relative to TMS as an internal standard. Mass spectra and high resolution mass spectra were performed on Finnigan-MAT-8430 mass spectrometer with electron spray ionization (ESI) as the ionization mode. Elemental analyses were obtained using Heraeus CHN-O-Rapid analyzer.

Typical procedure for the preparation of compounds **4a**-**h**, exemplified by **4a**: In a round-bottom flask equipped with a magnetic stirrer, 1,2 phenylenediamine (2 mmol) and ethyl pyruvate (2 mmol) in MeCN (3 mL) were added, and the mixture was stirred vigorously at room temperature. Ethyl bromopyruvate (2 mmol) in MeCN (2 mL) and $FeCl_3$ (20 mol%) were added to the mixture, which was refluxed for 5 h. After completion of the reaction, as indicated by TLC (EtOAC/hexane = 1/3, v/v), the mixture was cooled to room temperature. The solvent was evaporated and the residue was purified by column chromatography using *n*-hexane/EtOAc (3/1, v/v) as the eluent. The solvent was removed and the product was obtained.

Ethyl 4-oxo-4,5-dihydropyrrolo[1,2-a]quinoxaline-2-carboxylate (**4a**): Yield (0.20 g, 78%), grey crystals; mp 240-242 ^{o}C. IR (KBr, cm^{-1}): ν_{max} 3419 (NH), 1721 (C=O), 1669 (C=O). ^{1}H NMR (250.1 MHz, DMSO-d_6): δ 1.30 (t, 3H, ^3J = 7.0 Hz, CH_3), 4.27 (q, 2H, ^3J = 7.0 Hz, OCH_2), 7.19-7.35 (m, 4H, 4CH), 8.22 (d, 1H, ^3J = 8.0 Hz, CH), 8.75 (s, 1H, CH), 11.45 (br s, 1H, NH). ^{13}C NMR (62.9 MHz,

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DMSO-d_6): δ 14.7 (CH_3), 60.5 (OCH_2), 111.9 (CH), 116.3 (CH), 117.1 (CH), 119.4 (C), 121.8 (CH), 122.5 (C), 123.4 (CH), 124.7 (C), 127.3 (C), 129.4 (CH), 155.2 (C=O), 163.6 (C=O). MS: *m/z* (%): 256 (M^+, 100), 241 (8), 228 (44), 211 (100), 183 (47), 155 (42), 77 (15). Anal. Calcd. for $C_{14}H_{12}N_2O_3$ (256.26): C, 65.62; H, 4.72; N, 10.93; found: C, 65.57; H, 4.69; N, 10.96.

2-Phenylpyrrolo[1,2-a]quinoxaline-4(5*H*)-one (**4b**): Yield (0.18 g, 70%), yellow oil. IR (KBr, cm^{-1}): ν_{max} 3423 (NH), 1662 (C=O), ^{1}H NMR (250.1 MHz, DMSO-d_6): δ 7.21-7.53 (m, 9H, 9CH), 8.12 (d, 1H, ^3J = 8.0 Hz, CH), 8.62 (s, 1H, CH), 11.47 (br s, 1H, NH). ^{13}C NMR (62.9 MHz, DMSO-d_6): δ 111.9 (CH), 116.0 (C), 117.1 (CH), 117.2 (C), 121.6 (C), 122.2 (CH), 123.4 (CH), 126.5 (CH), 126.9 (CH), 127.3 (2CH), 127.8 (CH), 129.0 (C), 129.3 (2CH), 133.1 (C), 154.3 (C=O). MS: *m/z* (%): 260 (M^+, 100), 232 (13), 218 (24), 183 (86), 77 (35). Anal. Calcd. for $C_{17}H_{12}N_2O$ (260.30): C, 78.44; H, 4.65; N, 10.76; found: C, 78.57; H, 4.61; N, 10.79.

2-(4-Bromophenyl)pyrrolo[1,2-a]quinoxalin-4(5*H*)-one (**4c**): Yield (0.25 g, 73%), pink crystals; mp 119-121 ^{o}C. IR (KBr, cm^{-1}): ν_{max} 3315 (NH), 1667 (C=O). ^{1}H NMR (250.1 MHz, DMSO-d_6): δ 7.17-7.48 (m, 8 H, 8 CH), 8.09 (d, 1H, ^3J = 8.1 Hz, CH), 8.65 (s, 1H, CH), 11.42 (br s, 1H, NH). ^{13}C NMR (62.9 MHz, DMSO-d_6): δ 116.8 (CH), 118.2 (CH), 123.1 (C), 123.8 (CH), 124.4 (CH), 125.1 (CH), 125.8 (2CH), 126.3 (C), 129.8 (C), 132.2 (2CH), 132.9 (C), 135.4 (CH), 136.6 (C), 139.2 (C), 154.1 (C=O). MS: *m/z* (%): 339 (M^+, 9), 297 (28), 218 (91), 183 (96), 157 (38), 76 (62), 57 (100). Anal. Calcd. for $C_{17}H_{11}BrN_2O$ (339.19): C, 60.20; H, 3.27; N, 8.26; found: C, 60.27; H, 3.21; N, 8.32.

1-Methyl-2-*p*-tolylpyrrolo[1,2-a]quinoxalin-4(5*H*)-one (**4d**): Yield (0.20 g, 72%), yellow powder; mp 60-61 ^{o}C. IR (KBr, cm^{-1}): ν_{max} 3200 (NH), 1663 (C=O). ^{1}H NMR (250.1 MHz, DMSO-d_6): δ 2.29 (s, 3H, CH_3), 7.21-7.39 (m, 5H, 5CH), 7.64-7.67(m, 3H, 3CH), 8.07 (s, 1H, CH), 8.64 (s, 1H, CH), 11.23 (br s, 1H, NH). ^{13}C NMR (62.9 MHz, DMSO-d_6): δ 22.3 (CH_3), 116.1 (CH), 116.6 (CH), 118.1 (CH), 124.0 (C), 124.4 (CH), 125.8 (CH), 126.9 (2CH), 127.3 (C), 129.4 (C), 130.1 (CH), 130.5 (C), 131.0 (2CH), 132.5 (C), 137.5 (C), 156.5 (C=O). MS: *m/z* (%): 274 (M^+, 100), 246 (6), 232 (41), 183 (81), 91 (32), 76 (18). Anal. Calcd. for $C_{18}H_{14}N_2O$ (274.33): C, 78.81; H, 5.14; N, 7.63; found: C, 78.94; H, 5.19; N, 7.69.

Ethyl 7,8-diamethy1-4-oxo-4,5-dihydroptrrolo[1,2-a]quinoxaline-1-carboxylate (**4e**): Yield (0.24 g, 84%), grey crystals; mp 237-239 ^{o}C. IR (KBr, cm^{-1}): ν_{max} 3305 (NH), 1731 (C=O), 1623 (C=O). ^{1}H NMR (250.1 MHz, DMSO-d_6): δ 1.23 (t, 3H, ^3J = 7.1 Hz, CH_3), 2.24 (s, 3H, CH_3) , 2.47 (s, 3H, CH_3), 4.27 (q, 2H, ^3J = 7.0 Hz, OCH_2), 7.08 (s, 1H, CH), 7.32 (s, 1H, CH), 7.75 (s, 1H, CH), 8.33 (s, 1H, CH) , 11.45 (br s, 1H, NH). ^{13}C NMR (62.9 MHz, DMSO-d_6): δ 14.3 (CH_3), 21.2 (CH_3), 22.4(CH_3), 61.8 (OCH_2), 115.6 (CH), 118.5 (C), 121.0 (CH), 123.8 (CH), 125.2 (C), 128.3 (C), 129.4 (CH), 133.6 (C), 135.3 (CH), 136.2 (CH), 155.2 (C=O), 162.4 (C=O). MS: *m/z* (%): 284 (M^+, 100), 269 (10), 256 (45), 239 (100), 211 (45), 183 (38), 169 (25). Anal. Calcd. for $C_{14}H_{16}N_2O_3$ (284.32): C, 67.59; H, 5.67; N, 9.85; found: C, 67.62; H, 5.69; N, 9.81.

2-(4-Bromophenyl)-7,8-dimethylpyrrolo[1,2-a]quinoxalin-4(5*H*)-one (**4f**): Yield (0.27 g, 74%), grey crystals; mp 235-237 ^{o}C. IR (KBr, cm^{-1}): ν_{max} 3335 (NH), 1653 (C=O). ^{1}H NMR (250.1 MHz, DMSO-d_6): δ 2.29 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 6.85(s, 1H, CH), 7.23-7.39 (m, 3H, 3CH), 7.48-7.59 (m, 2H, 2CH), 7.71-7.75 (m, 1H, CH), 8.22 (s, 1H, CH), 11.45 (br s, 1H, NH). ^{13}C NMR (62.9 MHz, DMSO-d_6): δ 22.3 (CH_3), 22.8 (CH_3), 109.9 (CH), 116.4 (CH), 117.1 (C), 118.6 (CH), 122.8 (C), 124.1 (C), 124.3 (C), 126.1 (2CH), 127.2 (CH), 129.3 (C), 132.9 (C), 130.0 (C), 131.1 (2CH), 136.4 (C), 155.6 (C=O). MS: *m/z* (%): 367 (M^+, 12), 325 (28), 246 (94), 76 (63), 57 (100). Anal. Calcd. for $C_{19}CH_{15}BrN_2O$ (367.25): C, 62.14; H, 4.12; N, 7.63; found: C, 62.11; H, 4.15; N, 7.59.

Ethyl 4-oxo-4,5,5a,6,7,8,9,9a-octahydropyrrolo[1,2-a]quinoxalin-1-carboxylate (**4g**): Yield (0.18 g, 68%), yellow oil. IR (KBr, cm^{-1}): ν_{max} 3280 (NH), 1725 (C=O), 1656 (C=O). ^{1}H NMR (250.1 MHz, DMSO-d_6): δ 1.22-1.46 (m, 7H, $2CH_2$ and CH_3), 1.75-1.94 (m, 4H, $2CH_2$), 3.38-3.54 (m, 2H, 2CH), 4.23 (q, 2H, ^3J = 7.1 Hz, OCH_2), 6.76 (d, 1H, ^4J = 1.5 Hz, CH), 7.69 (d, 1H, ^4J = 1.5 Hz, CH), 11.28 (1H, br s, NH). ^{13}C NMR (62.9 MHz, DMSO-d_6): δ 14.3 (CH_3), 23.2 (CH_2), 24.8 (CH_2), 31.2 (CH_2), 31.8 (CH_2), 54.7 (CH), 60.5 (CH_2), 61.2 (OCH_2), 111.3 (C), 118.6 (CH), 126.3 (C), 132.2 (CH) 158.4, 164.7 (2 C=O). MS: *m/z* (%): 262 (M^+, 100), 247 (15), 217 (51), 189 (100), 161 (39). Anal. Calcd. for $C_{14}H_{18}N_2O_3$ (262.31): C, 64.11; H, 6.92; N, 10.68; found: C, 64.05; H, 6.88; N, 10.76.

Ethyl 1-oxo-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine-7-carboxylate (**4h**): Yield (0.15 g, 72%), yellow crystals; mp 236-238 ^{o}C. IR (KBr, cm^{-1}): ν_{max} 3330 (NH), 1727 (C=O), 1647 (C=O). ^{1}H NMR (250.1 MHz, DMSO-d_6): δ 1.27 (t, 3H, ^3J = 7.1 Hz, CH_3), 3.46-3.51 (m, 2H, CH_2), 4.11-4.13 (m, 2H, CH_2), 4.21 (q, 2H, ^3J = 7.0 Hz, OCH_2), 6.90 (d, 1H, ^4J = 1.4 Hz, CH), 7.62 (d, 1H, ^4J = 1.4 Hz, CH), 11.21 (s, 1H, NH).^{13}C NMR (62.9 MHz, DMSO-d_6): δ 14.8 (CH_3), 43.1 (CH_2), 43.9 (CH_2), 60.9 (OCH_2), 114.2 (CH), 116.7 (C), 118.3 (C), 134.6 (CH), 156.0 (C=O), 163.7 (C=O). MS: *m/z* (%): 208 (M^+, 100), 193 (82), 180 (27), 163 (100), 135 (20), 120 (57), 107 (26), 77 (27). Anal. Calcd. for $C_{10}H_{12}N_2O_3$ (208.22): C, 57.69; H, 5.8; N, 13.45; found: C, 57.73; H, 5.78; N, 13.41.

3. Results and discussion

The reaction of 1, 2 phenylenediamine, ethyl pyruvate, and ethyl bromopyruvate in the presence of $FeCl_3$ (20 mol%) was selected as a model system (Scheme 2).

Initially, we thought of varying the nature of solvent to increase the product yield, so we carried out the reactions in dichloromethane, dichloroethane, ethanol, ethyl acetate, acetonitrile, and methanol at reflux temperature (Table 1). When the reaction mixture was refluxed for 5 h in acetonitrile, the yield of **4a** was improved significantly (78%), Next the catalytic amount of the Iron (III) chloride catalyst was examined in the model reaction. In the presence of 10, 15, 20, and 25 mol% of $FeCl_3$, the yields of pyrrolo[1,2-a]quinoxaline **4a** obtained were 42%, 55%, 78%, and 78%, respectively. This shows the important role of $FeCl_3$ in this reaction. Thus, to verify that this is generally the case, we optimized the conditions for the other reactions. The results are presented in Table 2.

The ^{1}H NMR, ^{13}C NMR, IR spectra and MS of the products clearly indicated the formation of compounds **4a-h**. For example, the ^{1}H NMR spectrum of **4a** exhibited a triplet at 1.21 ppm and a quartet at 4.20 ppm for the ethoxy group, along with multiplets (7.19–8.75

ppm) for the aromatic region, and a broad singlet at 11.45 ppm due to the NH group. The ^{1}H-decoupled ^{13}C NMR spectrum of **4a** showed 14 distinct resonances in agreement with the proposed structure. The IR spectrum of **4a** exhibited absorption bands due to carbonyl groups at 1721 and 1669 cm^{-1}. The ^{1}H NMR and ^{13}C NMR spectra of products **4b-h** were similar to those of **4a**, except for the ester moieties, which exhibited characteristic resonances in the appropriate parts of the spectrum.

On the basis of these results, a possible mechanism for the formation of pyrrolo[1,2-a]quinoxaline **4a** is shown in Scheme 3. The reaction between 1,2-diaminobenzene (**1a**) and ethyl pyruvate (**2**) affords quinoxaline **5**, then ethyl bromopyruvate (**3**) could be activated by $FeCl_3$ and undergo the nucleophilic addition. The subsequent intermediate **6** by the elimination of the HBr leads to intermediate **7**, which undergoes a series of cyclization and elimination reactions to generate product **4a**.

4. Conclusion

In conclusion, we have described a simple and efficient method for the synthesis of pyrrolo[1,2-a]quinoxaline and pyrrolo[1,2-a]pyrazine derivatives of potential synthetic and pharmacological interest. This method is characterized by several unique advantages, such as simplicity in operation under neutral conditions, high yields of products, and relatively short reaction time.

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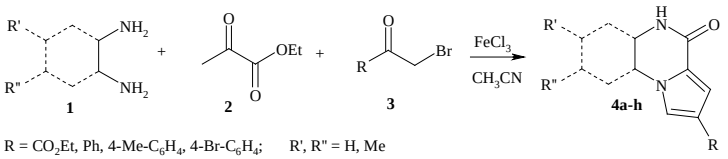
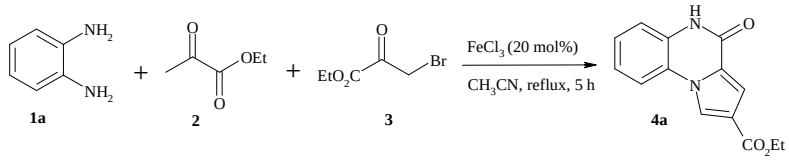


R = CO_2Et, Ph, 4-Me-C_6H_4, 4-Br-C_6H_4; R', R" = H, Me

Scheme 1. Three-component synthesis of pyrrolo[1,2-a]quinoxaline and pyrrolo[1,2-a]pyrazine derivatives.



Scheme 2. The model system for the synthesis of **4a**.

Table 1

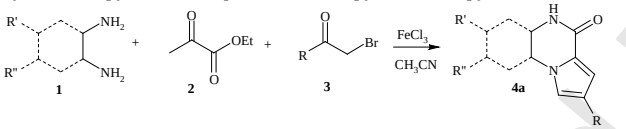
The effect of solvent on the reaction time and yield.[a]

Entry	1	2	3	4	5	6	7
Solvent	DCM	EtOAC	DCE	MeCN	MeCN	EtOH	MeOH
Time (h)	8	8	8	5	8	8	8
Yield (%)[b]	64	60	61	78	77	68	65

[a] Reaction conditions: 1,2-phenylenediamine (2 mmol), ethyl pyruvate (2 mmol), ethyl bromopyruvate (2 mmol), and $FeCl_3$ (20 mol %).
[b] Isolated yield.

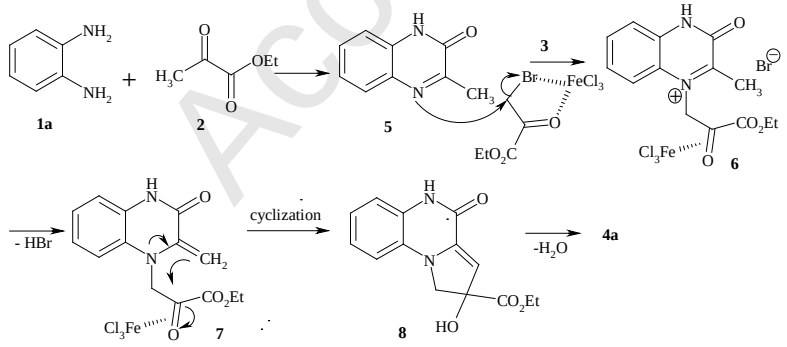
Table 2

Synthesis of pyrrolo[1,2-a]quinoxaline and pyrrolo[1,2-a]pyrazine derivatives **4.**



Entry	Diamine	R	Product	Yield (%)[a]
1	benzene-1,2-diamine	CO_2Et	**4a**	78
2	benzene-1,2-diamine	Ph	**4b**	70
3	benzene-1,2-diamine	4-Br-C_6H_4	**4c**	73
4	benzene-1,2-diamine	4-Me-C_6H_4	**4d**	72
5	4,5-dimethylbenzene-1,2-diamine	CO_2Et	**4e**	84
6	4,5-dimethylbenzene-1,2-diamine	4-Br-C_6H_4	**4f**	74
7	cyclohexyl diamine	CO_2Et	**4g**	68
8	ethylenediamine	CO_2Et	**4h**	72

[a] Isolated yield.



Scheme 3. Possible mechanism for the synthesis of pyrrolo[1,2-a]quinoxaline **4a**.