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Copper-catalyzed oxidative cyclization of α-hydroxyketones with *o*-phenylenediamines leading to quinoxalines

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Abstract

α-Hydroxyketones are oxidatively cyclized with *o*-phenylenediamines in toluene at 120 °C under an atmosphere of air in the presence of a catalytic amount of a copper catalyst along with powdered 4A molecular sieves to afford the corresponding quinoxalines in high yields. The reaction is applicable to a wide range of α-hydroxyketones which have various aryl and alkyl groups attached to carbonyl carbon.

Keywords: Copper catalyst; α-Hydroxyketones; Oxidative cyclization; *o*-Phenylenediamines; Quinoxalines

1. Introduction

The transition metal-catalyzed oxidative cyclization process has been recognized as an easy and useful synthetic tool for heterocycles, which play an important role as a basic unit for the design of many pharmacologically and biologically active compounds. Thus, in connection with this report, in contrast to conventional quinoxaline synthesis, which frequently suffers from the handling of highly reactive dicarbonyl compounds, several transition metal-catalyzed oxidative cyclization methods have also been developed as alternative routes for the construction of the quinoxaline framework. It is known that α-hydroxyketones are oxidatively cyclized with *o*-phenylenediamines in the presence of transition metals such as Mn and Ru to give quinoxalines [1–4]. As another substitute for the conventional method, Antonitti and Duñach also have reported on the synthesis of quinoxalines via bismuth-catalyzed oxidative coupling of epoxides and 1,2-diamines [5]. On the other hand, during the course of our ongoing studies on transition metal-catalyzed oxidative coupling and cyclization reactions [6–11], we also recently reported on the synthesis of quinoxalines via a ruthenium-catalyzed oxidative cyclization of vicinal-diols with *o*-phenylenediamines in the presence of a base [12]. Theses circumstances led us to seek for a new elegant catalyst alternative for the synthesis of N-heterocycles using such an intrinsic transition metal-catalyzed oxidative cyclization. As an example, we recently developed a copper-catalyzed oxidative cyclization of 2-aminobenzyl alcohol with ketones as well as aldehydes leading to quinolines (modified Friedländer quinoline synthesis [13–15]), which is superior to the reported transition metal-catalyzed oxidative cyclization versions for Friedländer quinoline synthesis in a sense of the price of a catalyst and the unnecessity of a hydrogen acceptor [16–20]. Herein, as another example for such a purpose, we describe a copper-catalyzed oxidative cyclization of α-hydroxyketones with *o*-phenylenediamines leading to quinoxalines.

2. Experimental

2.1. General

^{1}H and ^{13}C NMR (400 and 100 MHz) spectra were recorded on a Bruker Avance Digital 400 spectrometer using TMS as an internal standard. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and were uncorrected. The isolation of pure products was carried out via thin layer (silica gel 60 GF_{254}, Merck) chromatography. α-Hydroxyketones **2b–2l** were prepared by the reported method [21]. Commercially

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available organic and inorganic compounds were used without further purification except for toluene, which was distilled by the known method before use.

2.2. General experimental procedure for copper-catalyzed synthesis of quinoxalines from o-phenylenediamines and α-hydroxyketones on a small scale

To a 50 mL organic reactor were added *o*-phenylenediamine (0.5 mmol), α-hydroxyketone (0.5 mmol), $CuCl_2$ (0.007 g, 0.05 mmol) and dry toluene (5 mL). The pale yellow brown solution was stirred at 100 °C for 3 h under air atmosphere. The deep brown reaction mixture was passed through a short silica gel column (ethyl acetate–hexane mixture) to eliminate inorganic salts. Removal of the solvent left a crude mixture, which was separated by thin layer chromatography (silica gel, ethyl acetate–hexane mixture) to give quinoxalines. All products prepared by the above procedure were characterized spectroscopically as shown below.

2-Phenylquinoxaline (***3a***): Solid; m.p. 75–76 °C (hexane–chloroform) (lit. [22] 73–75 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.59 (m, 3H), 7.72–7.81 (m, 2H), 8.11–8.21 (m, 4H), 9.33 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.52, 129.09, 129.12, 129.51, 129.60, 130.16, 130.25, 136.75, 141.55, 142.27, 143.33, 151.82.

2-(4-Methylphenyl)quinoxaline (***3b***): Solid; m.p. 90–91 °C (hexane–chloroform) (lit. [23] 94 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 7.35 (d, J = 8.0 Hz, 2H), 7.69–7.77 (m, 2H), 8.08–8.14 (m, 4H), 9.29 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.82, 127.81, 129.48, 129.67, 129.93, 130.27, 130.57, 134.36, 140.88, 141.83, 142.71, 143.69, 152.20.

2-(3-Methylphenyl)quinoxaline (***3c***): Solid; m.p. 82–83 °C (hexane–chloroform); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H), 7.27 (d, J = 7.5 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.67–7.75 (m, 2H), 7.89 (d, J = 7.5 Hz, 1H), 7.95 (s, 1H), 8.07–8.13 (m, 2H), 9.24 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.94, 125.11, 128.62, 129.09, 129.48, 129.89, 130.15, 130.92, 131.57, 136.79, 139.41, 141.21, 142.68, 143.28, 152.48. Anal. Calcd for $C_{15}H_{12}N_2$: C 81.79; H 5.49; N 12.72. Found: C 81.44; H 5.66; N 12.47.

2-(2-Methylphenyl)quinoxaline (***3d***): Solid; m.p. 91–92 °C (hexane–chloroform) (lit. [23] 93–94 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 7.27–7.36 (m, 3H), 7.47–7.49 (m, 1H), 7.70–7.76 (m, 2H), 8.10–8.12 (m, 2H), 8.94 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.76, 126.78, 129.31, 129.88, 129.94, 130.39, 130.44, 130.44, 130.87, 131.66, 137.03, 137.28, 140.98, 142.40, 145.89, 155.37.

2-(4-Methoxyphenyl)quinoxaline (***3e***): Solid; m.p. 99–100 °C (hexane–chloroform) (lit. [23] 99 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H), 7.06–7.10 (m, 2H), 7.69–7.79 (m, 2H), 8.08–8.13 (m, 2H), 8.16–8.20 (m, 2H), 9.29 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.84, 114.99, 129.38, 129.46 (×2), 129.69, 129.78, 130.58, 141.60, 142.71, 143.48, 151.85, 161.86.

2-(3-Methoxyphenyl)quinoxaline (***3f***): Solid; m.p. 87–88 °C (hexane–chloroform) ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 7.01 (dd, J = 2.5 and 8.5 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.67–7.75 (m, 4H), 8.08–8.13 (m, 2H), 9.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.88, 113.07, 116.84, 120.33, 129.13, 129.94, 130.28, 130.61, 130.96, 138.22, 141.37, 142.61, 143.25, 152.05, 160.74. Anal. Calcd for $C_{15}H_{12}N_2O$: C 76.25; H 5.12; N 11.86. Found: C 76.11; H 5.17; N 11.91.

2-(2-Methoxyphenyl)quinoxaline (***3g***): Solid; m.p. 109–110 °C (hexane–chloroform) (lit. [23] 112 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.99 (d, J = 8.0 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 7.39–7.42 (m, 1H), 7.66–7.72 (m, 2H), 7.83 (d, J = 7.5 Hz, 1H), 8.07–8.11 (m, 2H), 9.27 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.84, 114.99, 129.38, 129.46 (×2), 129.69, 129.78, 130.58, 141.60, 142.71, 143.48, 151.85, 161.86.

2-(4-Fluorophenyl)quinoxaline (***3h***): Solid; m.p. 120–121 (hexane–chloroform) (lit. [24] 121.8–122.3 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17–7.21 (m, 2H), 7.68–7.76 (m, 2H), 8.07–8.11 (m, 4H), 9.23 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 116.7 (d, J = 22.2 Hz), 129.21, 129.89, 129.97 (d, J = 8.7 Hz), 130.27, 131.07, 133.10 (d, J = 2.9 Hz), 141.30, 142.63, 142.84, 151.22, 164.74 (d, J = 249.2 Hz).

6,7-Dimethyl-2-phenylquinoxaline (***3i***): Solid; m.p. 128–129 °C (hexane–chloroform) (lit. [25] 127.5–128.5 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.50 (s, 6H), 7.47–7.57 (m, 3H), 7.85 (s, 1H), 7.90 (s, 1H), 8.14–8.17 (m, 2H), 9.22 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.73, 20.76, 127.77, 128.54, 129.05, 129.46, 130.22, 137.53, 140.51, 140.96, 141.19, 141.62, 142.80, 151.40.

6,7-Dimethyl-2-(4-methylphenyl)quinoxaline (***3j***): Solid; m.p. 128–129 °C (hexane–chloroform); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 2.50 (s, 6H), 7.35 (d, J = 8.0 Hz, 2H), 7.83 (s, 1H), 7.88 (s, 1H), 8.06 (d, J = 8.0 Hz, 2H), 9.20 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.73, 20.77, 21.79, 127.63, 128.51, 128.97, 130.21, 134.71, 140.23, 140.45, 140.80, 141.09, 141.62, 142.75, 151.40. Anal. Calcd for $C_{17}H_{16}N_2$: C 82.22; H 6.49; N 11.28. Found: C 82.11; H 6.74; N 11.16.

2-(2-Naphthyl)quinoxaline (***3k***): Solid; m.p. 140–142 °C (hexane–chloroform) (lit. [26] 137 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.57 (m, 2H), 7.73–7.81 (m, 2H), 7.89–7.91 (m, 1H), 7.99–8.03 (m, 2H), 8.14 (dd, J = 1.0 and 8.0 Hz, 1H), 8.19 (dd, J = 1.5 and 8.3 Hz, 1H), 8.36 (dd, J = 1.5 and 8.8 Hz, 1H), 8.65 (s, 1H), 9.47 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.88, 127.09, 127.70, 127.90, 128.21, 129.31, 129.45, 129.55, 129.97, 130.02, 130.75, 133.79, 134.47, 134.53, 141.96, 142.78, 143.91, 152.10.

2-(2-Furanyl)quinoxaline (***3l***): Solid; m.p. 97–98 °C (hexane–chloroform) (lit. [2] 101 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.62–6.63 (m, 1H), 7.32 (d, J = 3.5 Hz, 1H), 7.68–7.77 (m, 3H), 8.05–8.11 (m, 2H), 9.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.19, 112.86, 129.56 (×2), 129.69, 130.84, 141.63, 142.40, 142.44, 144.20, 145.46, 151.93.

2-Butylquinoxaline (***3m***) [27]: Oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, J = 7.3 Hz, 3H), 1.34–1.43 (m, 2H), 1.72–1.80 (m, 2H), 2.95 (t, J = 7.8 Hz, 2H), 7.61–7.68 (m, 2H), 7.98-8.02 (m, 2H), 8.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.26, 22.94, 32.00, 36.52, 129.08, 129.37, 129.51, 130.40, 141.55, 142.34, 146.18, 157.98.

*1,2,3,4-Tetrahydrophenazine (**3n**)*: Solid; m.p. 91–92 °C (hexane–chloroform) (lit. [28] 93–95 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.02–2.06 (m, 4H), 3.16–3.18 (m, 4H), 7.64–7.68 (m, 2H), 7.95–7.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.16, 33.57, 128.69, 129.29, 141.57, 154.51.

2.3. Typical experimental procedure for copper-catalyzed synthesis of quinoxalines from o-phenylenediamines and α-hydroxyketones on a large scale

To a stirred mixture of *o*-phenylenediamine (2.433 g, 22.5 mmol), $CuCl_2$ (0.202 g, 1.5 mmol) and powdered 4A molecular sieves (9.000 g) in dry toluene (100 mL) was added a solution of α-hydroxyacetophenone (2.042 g, 15 mmol) in dry toluene (50 mL) using a dropping funnel over 3 h at 120 °C (oil bath temperature). The system was stirred at 120 °C for 12 h under air atmosphere. The reaction mixture was filtered through a Büchner funnel and evaporation of the filtrate left a crude mixture, which was separated by column chromatography (silica gel, ethyl acetate/hexane = 3:10) to give 2-phenylquinoxaline (**3a**) (2.568 g, 83%).

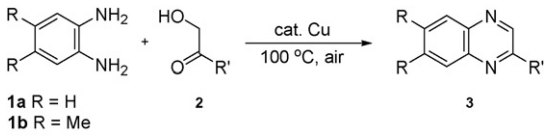
3. Results and discussion

The results of several oxidative cyclization of 2-hydroxyacetophenone (**2a**) with *o*-phenylenediamine (**1a**) under a variety of conditions are listed in Table 1 (Scheme 1). Treatment of equimolar amount of **1a** and **2a** (0.5 mmol) in toluene at 100 °C for 5 h under an atmosphere of air afforded 2-phenylquinoxaline (**3a**) in 53% yield (run 1). Performing the reaction for a longer time (20 h) gave a slightly increased yield of **3a** (60%) with incomplete conversion of **2a** (68% conversion) (run 2). However, when the reaction was carried out in the presence of a catalytic amount of $CuCl_2$ (10 mol%), the reaction rate was remarkably enhanced toward the formation of **3a** with complete conversion of **2a** (run 3). Among the copper catalysts examined, $CuCl_2$ in terms of product **3a** yield revealed to be the catalyst of choice (runs 3–5). On the other hand, when the reaction was carried out under argon, **3a** was formed in only 55% yield (run 6). Based on these results, **1a** was subjected to the reaction with **2a** on a larger scale to show the scope of the current methodology. However, performing the reaction on a larger scale (30 times) resulted in a lower yield of **3a** (70%) with concomitant formation of a considerable amount of 2-phenyl-1,2,3,4-tetrahydroquinoxaline (13% yield) (run 7) [29]. Thus, the variation of reaction conditions was required for the effective formation of **3a** along with suppressed formation of 2-phenyl-1,2,3,4-tetrahydroquinoxaline. As a result, when the reaction was carried out under modified conditions such as molar ratio of [**1a**]/[**2a**] = 1.5, dropwise addition of **2a** and addition of 4A molecular sieves, **3a** was obtained nearly as the sole product (**3a**, 83%; 2-phenyl-1,2,3,4-tetrahydroquinoxaline, <1%) (see Section 2) (run 8).

Table 1
Optimization of conditions for the reaction of **1a** with **2a**

Run	[**1a**]/[**2a**]	Cu catalyst	Time (h)	Isolated yield (%)
1	1	–	5	53
2	1	–	20	60
3	1	$CuCl_2$	3	94
4	1	CuCl	3	54
5	1	$Cu(OAc)_2{\cdot}H_2O$	3	84
6[a]	1	$CuCl_2$	3	55
7[b]	1	$CuCl_2$	3	70
8[b]	1.5	$CuCl_2$	15	83

All reactions were carried out with **2a** (0.5 mmol) and copper catalyst (0.05 mmol) in toluene (5 mL) at 100 °C under air unless otherwise stated.
[a] Under argon.
[b] Thirty times scale (see Section 2).



Scheme 1.

Having optimized reaction conditions, various α-hydroxyketones **2** were subjected to the reaction with *o*-phenylenediamines (**1a** and **1b**) under two sets of reaction conditions, small scale (run 3 of Table 1, condition A) and large scale (run 6 of Table 1, condition B) in order to investigate the reaction scope and several representative results are summarized in Table 2. An array of α-hydroxyketones (**2a**–**2h**) having electron-donating and -withdrawing substituents on the aromatic ring attached to carbonyl carbon reacted with **1a** and the corresponding 2-aryl substituted quinoxalines (**3a**–**3h**) were produced in the ranges of 72–94% and 78–91% yields, respectively, under conditions A and B. The position and electronic nature of the substituents on the aromatic ring of **2a**–**2h** had no significant relevance to the product yield. 4,5-Dimethyl-1,2-phenylenediamine (**1b**) reacts similarly with **2a** and **2b** to afford 6,7-dimethyl-2-phenylquinoxaline (**3i**) and 6,7-dimethyl-2-(4-methylphenyl)quinoxaline (**3j**), respectively. 2-Hydroxy-2′-acetonaphthone (**2i**) was also readily oxidatively cyclized with **1a** to give 2-(2-naphthyl)quinoxaline (**3k**) in similar yields under both reaction conditions. The reaction proceeds likewise with α-hydroxyketone **2j** having heteroaryl group attached to carbonyl carbon to give the corresponding 2-heteroaryl substituted quinoxaline **3l** in 79% and 85% yields, respectively, under conditions A and B. The reaction of α-hydroxyketone **2k**, which has an alkyl group attached to carbonyl carbon, with **1a** also proceeds to give 2-alkyl substituted quinoxaline **3m**. From the reaction between **1a** and cyclic α-hydroxyketone **2l**, 6,7,8,9-tetrahydrophenazine (**3n**) was also produced in 75% and 70% yields, respectively, under conditions A and B.

The reaction seems to proceed via the initial oxidation of **2a** to a di-carbonyl **4** under the $CuCl_2$/air system, which in turn triggers condensation with **1a** to give **3a** (Scheme 2). Alternatively, **3a** seems to be formed by the route via ketimine **5** formation, which is formed by the condensation between **1a** and **2a**, followed by oxidation to **6** and cyclization. It is reported by us that *o*-phenylenediamines react with vicinal-diols in the presence of a ruthenium catalyst along with KOH and a sacrificial

Table 2
Copper-catalyzed synthesis of quinoxalines **3** from *o*-phenylenediamines **1** and α-hydroxyketones **2**

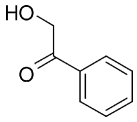
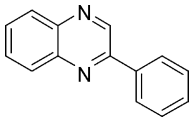
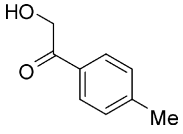
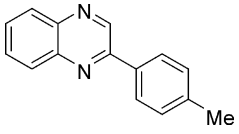
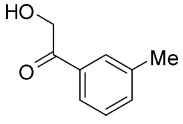
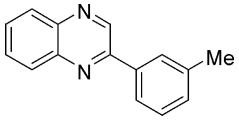
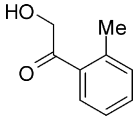
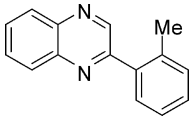
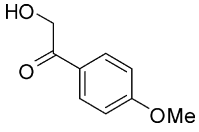
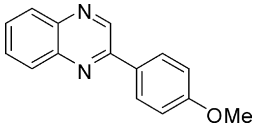
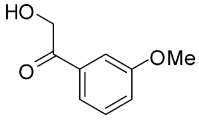
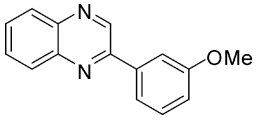
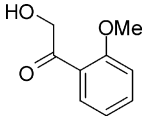
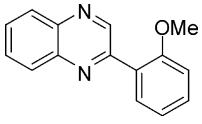
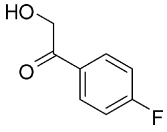
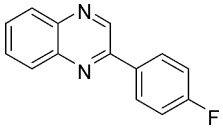
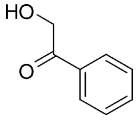
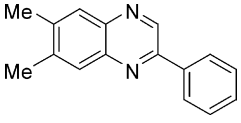
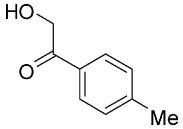
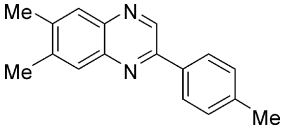
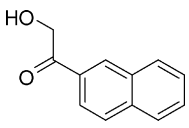
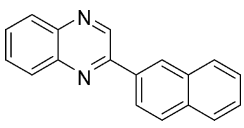
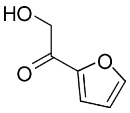
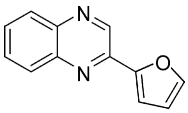
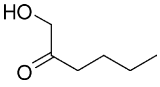
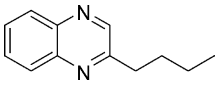
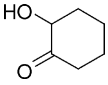
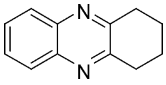
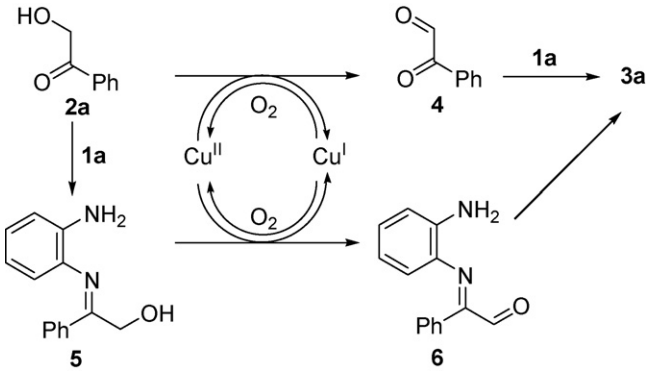
1	α-Hydroxyketones **2**	Quinoxalines **3**		Isolated yield (%)	
				Condition A[a]	Condition B[b]
1a		**2a**		**3a**	94	83
1a		**2b**		**3b**	85	78
1a		**2c**		**3c**	72	81
1a		**2d**		**3d**	77	80
1a		**2e**		**3e**	87	91
1a		**2f**		**3f**	85	85
1a		**2g**		**3g**	83	86
1a		**2h**		**3h**	88	82
1b		**2a**		**3i**	95	80
1b		**2b**		**3j**	83	79
1a		**2i**		**3k**	86	80

Table 2 (*Continued*)

1	α-Hydroxyketones **2**		Quinoxalines **3**		Isolated yield (%)	
					Condition A[a]	Condition B[b]
1a		**2j**		**3l**	79	85
1a		**2k**		**3m**	76	65
1a		**2l**		**3n**	75	70

[a] All reactions were carried out with **1** (0.5 mmol), **2** (0.5 mmol) and $CuCl_2$ (0.05 mmol) in toluene (5 mL) at 100 °C for 3 h.

[b] Dropwise addition of a solution of **2** (15 mmol) in toluene (50 mL) over 3 h to a mixture of **1** (22.5 mmol), $CuCl_2$ (1.5 mmol) and powdered 4A molecular sieves (9.000 g) in toluene (100 mL) at 120 °C and stirring for 12 h at 120 °C.



Scheme 2.

hydrogen acceptor to afford quinoxalines and the presence of KOH is essential for the effective formation of quinoxalines [12,31]. However, a similar treatment of **1a** (0.5 mmol) with 2 equiv. of 1-phenyl-1,2-ethanediol under $CuCl_2$ (5 mol%)/KOH (1 equiv.)/toluene/20 h afforded **3a** in only 32% yield.

4. Conclusion

In summary, we have demonstrated that an array of α-hydroxyketones undergoes an oxidative cyclization with *o*-phenylenediamines in the presence of a copper catalyst to afford the corresponding quinoxalines in high yields. The present reaction provides an alternative catalytic approach for quinoxalines from *o*-phenylenediamines and α-hydroxyketones and further elaborated synthetic application using this protocol is currently under investigation.

Acknowledgement

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[31] The present reaction is superior to the reported ruthenium-catalyzed synthesis of quinoxalines from *o*-phenylenediamines and vicinal-diols in a sense of the price of a catalyst, reaction temperature and the unnecessity of additives.