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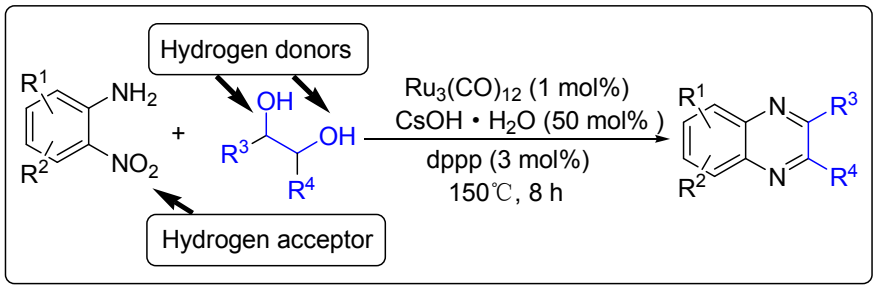

An efficient synthesis of quinoxalines from 2-nitroanilines and biomass-derived vicinal diols has been demonstrated via hydrogen transfer strategy.

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ARTICLE

Efficient Synthesis of Quinoxalines from 2-Nitroanilines and Vicinal Diols via a Ruthenium-Catalyzed Hydrogen Transfer Strategy

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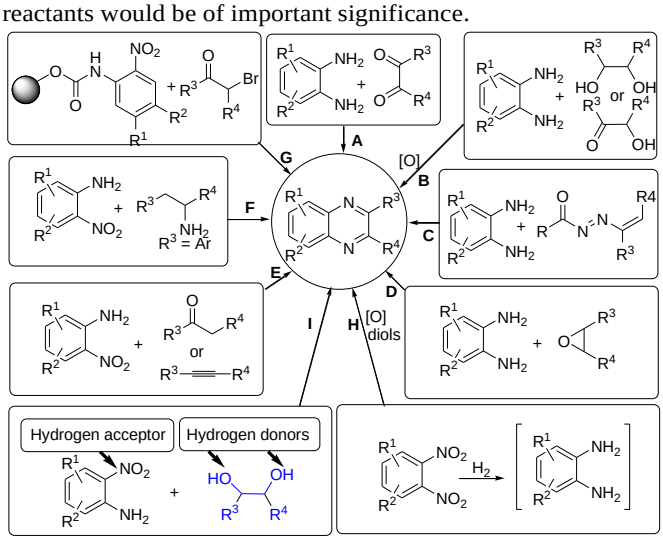
Feng Xie,[a,b] Min. Zhang,[*a] Huanfeng Jiang,[a] Mengmeng Chen,[a,b] Wan Lv,[a] Aibin Zheng,[a] and Xiujuan Jian[a]

Via a ruthenium-catalyzed hydrogen transfer strategy, we have demonstrated a one-pot method for efficient synthesis of quinoxalines from 2-nitroanilines and biomass-derived vicinal diols for the first time. In such a synthetic protocol, the diols and the nitro group serve as the hydrogen suppliers and acceptors, respectively. Hence, there is no need for the use of external reducing agents. Moreover, it has the advantages of operational simplicity, broad substrate scope and the use of renewable reactants, offering an important basis for accessing various quinoxaline derivatives.

Introduction

Concerning the gradual depletion of fossil resources, the utilization of renewable reactants for chemical production has become a key issue of sustainable chemistry. As a result, the biomass-derived alcohols have emerged as desirable candidates for various synthetic purposes: 1) Condensation reactions with the use of *in-situ* formed carbonyl intermediates via transition-metal catalysed alcohol dehydrogenation;[1] 2) Reduction reactions using alcohols as alternative hydrogen sources for reducing a number of organic chemicals;[2] 3) In line with the principles of green chemistry, the application of alcohols as both hydrogen suppliers and coupling components for benign construction of carbon-carbon and carbon-heteroatom bonds is, in synthetic chemistry, of particular importance.[3-5] In these processes, the screening of suitable catalyst system that is compatible to both dehydrogenation of alcohols and hydrogen transfer processes is considered as the main challenging point.

Quinoxaline derivatives constitute an important class of N-containing heterocycles that exhibit diverse biological activities such as antitumor,[6] antiviral,[7] antibacterial,[8] anti-inflammatory,[9] anti-HIV,[10] and anticancer[11]. Moreover, quinoxalines have been widely applied as building blocks for the preparation of dyes,[12] cavitands,[13] luminescent materials,[14] semiconductors,[15] chemically controllable switches,[16] dehydroannulenes[17] and etc. Due to the interesting functions, the development of efficient methods for accessing quinoxalines has long been a subject of synthetic chemists. Conventionally, quinoxalines could be prepared via a double condensation of 1,2-phenylenediamines with 1,2-diketones (Scheme 1, method–**A**).[18] Other elegant contributions mainly involve the oxidative trapping of vicinal diols or α-hydroxy ketones with 1,2-diamines (method–**B**),[19,20] 1,4-addition of 1,2-diamines to diazenylbutenes (method-**C**),[21] the coupling of epoxides with ene-1,2-diamines (method–**D**),[22] 2-nitroanilines with phenethylamines (method–**E**),[23] alkynes or ketones with 1,2-diamines via a key oxidation process (method–**F**),[24] and the sequential reductive coupling and cyclization of polymer-linked 2-nitrophenyl carbamate with α-bromoketones (method–**G**).[25] Nevertheless, many of these methods require the addition of excessive additives, the use of special pre-functionalized or less environmentally benign halogenated reagents, which could constantly result in preparation difficulties and/or a detrimental influence on the environment. In 2012, the Corma and Iborra group demonstrated an interesting synthesis of quinoxalines from glycols with 1,2-phenylenediamines or 1,2-dinitrobenzenes by employing heterogeneous catalysis.[26] However, the use of 1,2-dinitrobenzenes need to undergo the nitro group reduction using external high-pressure hydrogen source and the oxidative cyclization processes (method–**H**). From the viewpoint of step-economy concern, the development of environmentally friendly shortcuts for the synthesis of quinoxalines from renewable reactants would be of important significance.

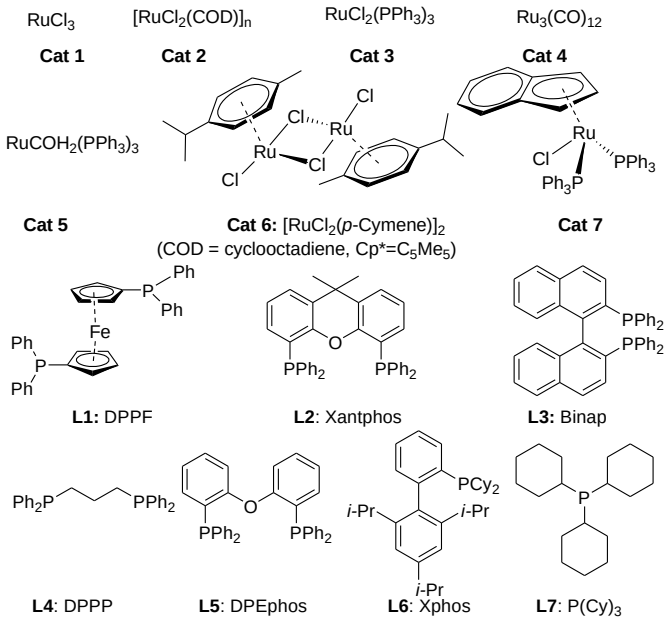


Scheme 1 Various methods for accessing quinoxalines

Herein, via a ruthenium-catalyzed hydrogen transfer strategy, we report a straightforward method for efficient synthesis of quinoxalines from biomass-derived glycols[27] and stable 2-nitroanilines for the first time. In such a synthetic protocol, the vicinal diols and the nitro group of 2-nitroanilines serve as the hydrogen donors and hydrogen acceptor, respectively. Hence, there is no need for the use of external reducing agents (Scheme 1, method–**I**).

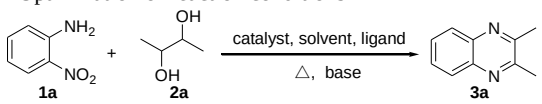
Results and discussion

We initiated our investigations by choosing the synthesis of 2,3-dimethylquinoxaline **3a** from 2-nitroaniline **1a** and butane-2,3-diol **2a** as a model reaction to determine different reaction parameters. First, 7 ruthenium catalysts (Scheme 2, see **Cat 1**-**Cat 7**) were tested by performing the reaction at 150 ^{o}C for 8 h using *t*-BuOK as the base and *t*-amyl alcohol as the solvent (Table 1, entries 1–7). $Ru_3(CO)_{12}$ (**Cat 4**) exhibited the highest activity in the formation of product **3a**. The absence of ruthenium catalyst failed to give any desired product (Table 1, entry 8). Further investigation showed that the ligand played an important role in the reaction yield (Table 1, entry 9). By using **Cat 4**, the diphosphine **L4** was proven to be the most effective one among various phosphine ligands tested (Scheme 2: **L1**-**L7** and Table 1: entries 10–15). Subsequently, several inorganic and organic bases were examined, CsOH·H_2O was the best choice (Table 1, entries 16–20). Other polar and less-polar solvents were proven to be inferior to *t*-amyl alcohol (Table 1, entry 21). Finally, we employed the combination of **Cat 4**, **L4**, CsOH·H_2O and *t*-amyl alcohol, a decrease of reaction temperature led to a decreased product yield (Table 1, entry 22). And 50 mol% of base was sufficient to obtain a desirable yield (Table 1, entry 23). An increase diol amount to 2 mmol resulted in the best product yield (Table 1, entry 24). Hence, the optimal reaction condition can be as indicated in entry 24 of Table 1 (Table 1, entry 24).



Scheme 2 Catalysts and ligands employed for the optimization of reaction conditions

Table 1 Optimization of reaction conditions[a]



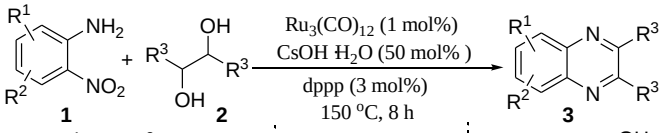
Entry	Catalyst	Ligand	Base	**3a**, Yield%[b]
1	**Cat 1**	**L1**	*t*-BuOK	12
2	**Cat 2**	**L1**	*t*-BuOK	16
3	**Cat 3**	**L1**	*t*-BuOK	25
4	**Cat 4**	**L1**	*t*-BuOK	62
5	**Cat 5**	**L1**	*t*-BuOK	45
6	**Cat 6**	**L1**	*t*-BuOK	31
7	**Cat 7**	**L1**	*t*-BuOK	14
8	-	**L1**	*t*-BuOK	-
9	**Cat 4**	-	*t*-BuOK	8
10	**Cat 4**	**L2**	*t*-BuOK	23
11	**Cat 4**	**L3**	*t*-BuOK	57
12	**Cat 4**	**L4**	*t*-BuOK	68
13	**Cat 4**	**L5**	*t*-BuOK	61
14	**Cat 4**	**L6**	*t*-BuOK	16
15	**Cat 4**	**L7**	*t*-BuOK	<10
16	**Cat 4**	**L4**	K_2CO_3	64
17	**Cat 4**	**L4**	Cs_2CO_3	75
18	**Cat 4**	**L4**	CsOH·H_2O	79
19	**Cat 4**	**L4**	KOH	63
20	**Cat 4**	**L4**	NEt_3	22
21	**Cat 4**	**L4**	CsOH·H_2O	[65, 45, 72][c]
22	**Cat 4**	**L4**	CsOH·H_2O	62[d]
23	**Cat 4**	**L4**	CsOH·H_2O	83[e], 83[f]
24	**Cat 4**	**L4**	CsOH·H_2O	87[g]

[a] Reaction conditions: all reactions were carried out under nitrogen atmosphere by using **1a** (0.5 mmol), **2a** ((3 equiv), catalyst (1 mol%), ligand (3 mol%), solvent (1.5 mL), temperature (150 ℃), base (20 mol%), reaction time (8 h). [b] GC Yield using hexadecane as internal standard. [c] Yields are with respect to toluene, DMSO and diglyme used as the reaction solvents, respectively. [d] Reaction temperature (140 ℃). [e] base (50 mol%). [f] base (70 mol%). [g] **2a**: (4 equiv), base (50 mol%).

With the availability of optimized reaction conditions, we then examined the generality of the synthetic protocol. First, we focused on the synthesis of quinoxaline **3** by testing a variety of 2-nitroanilines **1** with symmetrical vicinal diols **2**. As shown in Table 2, both alkyl (i.e. **2a**, **2b**) and aryl (i.e. **2c**) substituted vicinal diols underwent smooth cyclization to afford the 2,3-dialkyl and 2,3-diaryl quinoxalines in moderate to excellent yields upon isolation (Table 2, entries 1–16). The *ortho*-substitutent of 2-nitroaniline **1d** has little influence in affording the desired product **3d** (Table 2, entry 4).Cyclohexane-1,2-diol **2b** resulted in the tricyclic products efficiently (entries 8–12), these examples demonstrate the potential of the methodology for further construction of polycyclic products. Interestingly, ethylene glycol can also be applied for the preparation of 2,3-non-substituted products in reasonable yields (entries 17–19). Among all the examples examined, it was found that the electronic property of the substituents on the aryl ring of substrate **1** influenced the product yields significantly. Specially, the electron-donating groups (i.e., -Me, -OMe) containing 2-nitroanilines (Table 2, entries 2-4, 9, 10, 14, 17 and 18) afforded the products in higher yield than the electron-deficient ones (i.e., -Cl, -F) (Table 2, entries 5, 6, 11, 15 and 19). This

phenomenon can be rationalized as the electron-donating groups could enhance the nucleophilicity of the anilines **1**, thus favoring the imination step of the annulation process. Noteworthy, owing to the aryl groups are *ortho* to the nitrogen atom of the quinoxalines, the 2,3-diaryl quinoxalines could be applied as the C^N ligands for the preparation of organometallic complexes or materials[28] (Table 2, entries 13–16).

Table 2 Ruthenium-catalyzed synthesis of Quinoxaline from Nitroaniline and symmetrical vicinal diols[a]



1

1a: R^1 = H, R^2 = H;
1b: R^1 = 4-OMe, R^2 = H;
1c: R^1 = 4-Me, R^2 = 5-Me;
1d: R^1 = 2-Me, R^2 = H;
1e: R^1 = 4-Cl, R^2 = H;
1f: R^1 = 4-F, R^2 = H;

2

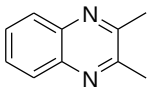
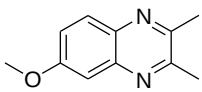
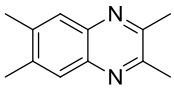
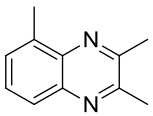
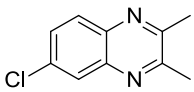
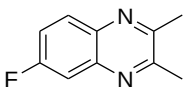
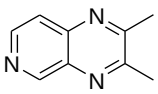
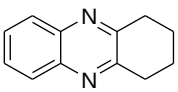
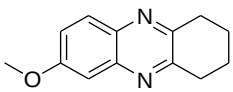
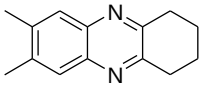
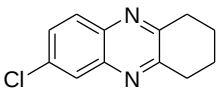
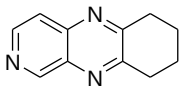
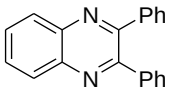
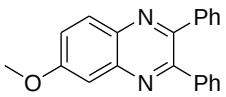
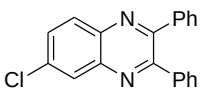
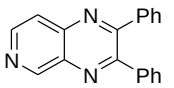
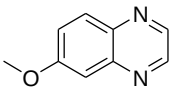
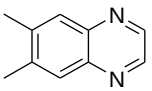
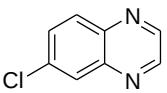
1g:

2a: R^3 = Me;

3

2b:

2c: R^3 = Ph;
2d: R^3 = H;

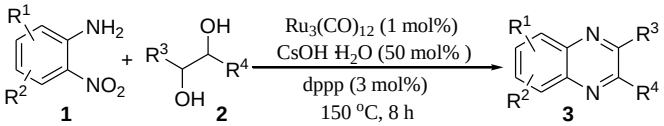
Entry	1	2	Product 3	Yield%[b]
1	**1a**	**2a**		**3a**, 82
2	**1b**	**2a**		**3b**, 86
3	**1c**	**2a**		**3c**, 71
4	**1d**	**2a**		**3d**, 80
5	**1e**	**2a**		**3e**, 68
6	**1f**	**2a**		**3f**, 61
7	**1g**	**2a**		**3g**, 45[c]
8	**1a**	**2b**		**3h**, 79
9	**1b**	**2b**		**3i**, 83
10	**1c**	**2b**		**3j**, 84
11	**1e**	**2b**		**3k**, 56
12	**1g**	**2b**		**3l**, 43[c]
13	**1a**	**2c**		**3m**, 84
14	**1b**	**2c**		**3n**, 87
15	**1e**	**2c**		**3o**, 70
16	**1g**	**2c**		**3p,** 63[c]
17	**1b**	**2d**		**3q,** 65
18	**1c**	**2d**		**3r,** 68
19	**1e**	**2d**		**3s,** 58

[a] Reaction conditions: all reactions were carried out under nitrogen atmosphere by using **1a** (0.5 mmol), **2a** (4 equiv), catalyst (1 mol%), ligand (3 mol%), solvent (1.5 mL), temperature (150 ℃), base (50 mol%), reaction time (8 h). [b] Isolated yield.

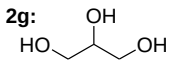
Subsequently, we turned our attention to employ unsymmetrical vicinal diols with our synthetic protocol. Representative substrates such as 1-phenylethane-1,2-diol **2e** and propane-1,2-diol **2f** in combination with various 2-nitroanilines were tested. All the reactions underwent efficient cyclization to afford the desired products in moderate to good isolated yields (Table 3, entries 1–9). Similar to the results described in Table 2, the electron-rich 2-nitroanilines could give the products in relatively higher yields (Table 3, entries 2, 4 and 7) than the electron-poor ones (Table 3, entries 3 and 5). Based on ^{1}H-NMR analysis, the reactions of 4-methoxy-2-nitrobenzenamine **1b** and 4-chloro-2-nitrobenzenamine **1e** with **2e** gave two regionisomers in ratios of 43 : 57 and 52 : 48, respectively (Table 3, entries 4 and 5). Interestingly, glycerol **2g** could also be transformed in combination with 2-

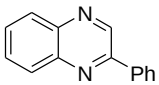
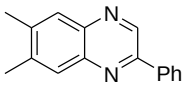
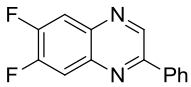
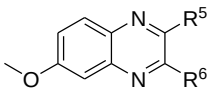
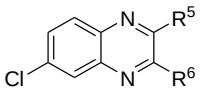
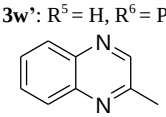
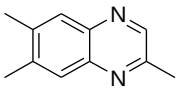
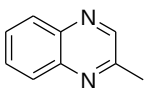
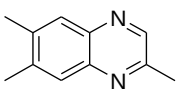
nitroanilines into the 2-methyl quinoxalines in reasonable yields (Table 3, entries 8 and 9), indicating glycerol can be utilized as the alternative of propane-1,2-diol **2f**.

Table 3 Synthesis of quinoxaline using unsymmetrical vicinal diols[a]



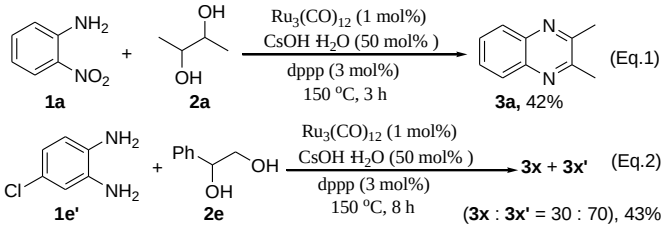
1 **2** **3**

1h: R^1 = 4-F, R^2 = 5-F; **2e**: R^3 = Ph, R^4 = H; **2f**: R^3 = Me, R^4 = H; **2g:** 

Entry	1	2	Product 3	Yield (%)[b]
1	**1a**	**2e**		**3t**, 78
2	**1c**	**2e**		**3u**, 70
3	**1h**	**2e**		**3v**, 40[c]
4	**1b**	**2e**	 **3v**: R^5 = Ph, R^6 = H **3v'**: R^5 = H, R^6 = Ph	**(3w : 3w'** = 43 : 57), 75
5	**1e**	**2e**	 **3w**: R^5 = Ph, R^6 = H **3w'**: R^5 = H, R^6 = Ph	**(3x : 3x'** = 52 : 48), 61
6	**1a**	**2f**		**3y**, 74
7	**1c**	**2f**		**3z**, 69
8	**1a**	**2g**		**3y,** 36[c]
9	**1c**	**2g**		**3z,** 38[c]

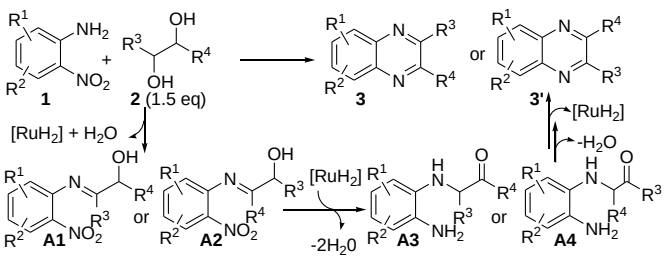
[a] Reaction conditions: all reactions were carried out under nitrogen atmosphere by using **1a** (0.5 mmol), **2a** (4 equiv), catalyst (1 mol%), ligand (3 mol%), solvent (1.5 mL), temperature (150 ℃), base (50 mol%), reaction time (8 h). [b] Isolated yield. [c] Reaction time (12 h).

Upon the GC and GC-MS analyses, it was found that the vicinal diols undergo partial decomposition to form aldehydes under the standard reaction conditions. It is noteworthy that the aldehydes can be easily trapped by 1,2-phenylenediamine to form benzimidazoles.[24] Interestingly, in all of our tested examples (Table 2 and Table 3), we did not observe any benzimidazole by-products. Further, the reaction of **1a** and **2a** was interrupted after 3h to analyze the reaction intermediates. We detected only the product **3a** in 42% yield without observation of any 1,2-phenylenediamine (Scheme 3, Eq.1). Moreover, the reaction of 4-chlorobenzene-1,2-diamine **1e'** with **2e** gave products **3x** and **3x'** in a ratio of 30 : 70 upon ^{1}H-NMR analysis (Scheme 3, Eq.2), which is inconsistent with the result of the reaction of **1e** with **2e** (Table 3, entry 5). These results suggest that the reactions involving 1,2-phenylenediamine intermediates are less likely, and the imination of the amino group of 2-nitroanilines should occur prior to the reduction of the nitro group.



Scheme 3 Verification experiments

On the basis of the above-described results as well as the related processes,[19, 20, 24] a possible reaction pathway is depicted in Scheme 4, which comprises the following tandem sequences: 1) The reaction initiates with the dehydrogenation of vicinal diol **2** via cooperative actions of ruthenium catalyst and base;[3] 2) Then, the imination of 2-nitroaniline **1** gave *α*-hydroxy imine **A1** or **A2**; 3) The transfer hydrogenation of the nitro group and tautomerization result in intermediate **A3** or **A4**; 4) Finally, the intramolecular condensation of **A3** or **A4** and dehydrogenative aromatization would afford desired product **3** or **3'** (Scheme 4).



Scheme 4 Possible pathway for the formation of quinoxalines

Experimental

General information

All the obtained products were characterized by melting points (m.p), ^{1}H-NMR, ^{13}C-NMR, infrared spectra (IR), and mass spectra (MS), the NMR spectra of the known compounds were found to be identical with the ones reported in the literatures. Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and are uncorrected; IR spectra were recorded on a FTLA2000 spectrometer; ^{1}H-NMR，^{13}C-NMR spectra were obtained on Bruker-400; Mass spectra were recorded on Trace DSQ GC/MS. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was

performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; All the reagents were purchased from commercial sources (J&KChemic, TCI, Fluka, Acros, SCRC), and used without further purification.

Typical procedure for synthesis of 2,3-dimethylquinoxaline 3a

$[Ru_3(CO)_{12}]$ (3.2 mg, 0.005 mmol), dppp (6.2 mg, 0.015 mmol), CsOH·H_2O (37 mg, 0.25 mmol), and 2-nitroaniline (**1a**; 69 mg, 0.5 mmol) were added successively to schlenk tube (50 mL) equipped with a magnetic stirrer bar, and the pressure tube was then purged. Under nitrogen atmosphere 2, 3-butanediol (**2a**; 180 mg, 2.0 mmol), and *tert*-amyl alcohol (1.5 mL) were added. The reaction mixture was heated at 150 ℃ for 8 h in a sealed tube under nirogen atmosphere. After cooling to room temperature, the solvent was removed under vacuum, then it was directly purified by preparative TLC on silica, eluting with petroleum ether (60-90 ℃): ethyl acetate (12 : 1) to give 2,3-dimethylquinoxaline (**3a**) as a brown solid (62 mg, 82%).

Conclusions

In conclusion, we have demonstrated a new and straightforward method for efficient synthesis of quinoxalines via a ruthenium-catalyzed hydrogen-transfer strategy. By employing a commercially available catalyst system $[Ru_3(CO)_{12}$/dppp/CsOH·$H_2O]$, different 2-nitroanilines were efficiently converted in combination with a variety of biomass-derived glycols into various substituted products in moderate to excellent isolated yields. The synthetic protocol has the advantages of no need for the use of external reducing agents, operational simplicity, broad substrate scope and the utilization of renewable reactants, offering an important basis for accessing quinoxaline derivatives.

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Notes and references

[a] School of Chemistry & Chemical Engineering, South China University of Technology, Wushan Rd-381, Guangzhou 510641, People's Republic of China.
Fax: (+86)-020-39925999; Phone: (+86)-13424037838; e-mail: minzhang@scut.edu.cn
[b] School of Chemical & Material Engineering, Jiangnan University, Wuxi 214122, People's Republic of China.
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