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Iron-catalyzed one-pot synthesis of quinoxalines: transfer hydrogenative condensation of 2-nitroanilines with vicinal diols†

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Here, we report iron-catalyzed one-pot synthesis of quinoxalines *via* transfer hydrogenative condensation of 2-nitroanilines with vicinal diols. The tricarbonyl (η^4 -cyclopentadienone) iron complex, which is well known as the Knölker complex, catalyzed the oxidation of alcohols and the reduction of nitroarenes, and the corresponding carbonyl and 1,2-diaminobenzene intermediates were generated *in situ*. Trimethylamine N-oxide was used to activate the iron complex. Various unsymmetrical and symmetrical vicinal diols were applied for transfer hydrogenation, resulting in quinoxaline derivatives in 49–98% yields. A plausible mechanism was proposed based on a series of control experiments. The major advantages of this protocol are that no external redox reagents or additional base is needed and that water is liberated as the sole byproduct.

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Introduction

Quinoxaline is a nitrogen-containing heterocyclic compound with both benzene and pyrazine rings. Quinoxaline structures are widely found in natural products and biologically active molecules.¹ Several commercial drugs, such as quinacillin, sulfaquinoxaline, clofazimine and echinomycin, contain quinoxaline moieties. Due to their immense importance for not only medicinal chemistry but also organic semiconductors² and fluorescent dyes,³ diverse synthetic routes have been developed so far. Among such methods, the traditional method involves the double condensation of 1,2-diamines with dicarbonyl compounds.⁴ Alternatively, oxidative annulation of 1,2-diamines with α -hydroxy ketones⁵ or phenacyl bromides⁶ and epoxide opening with 1,2-diamine have also been developed.⁷ However, the use of additional oxidants, harsh reaction conditions, multistep processes and low atom efficiency are the major concerns for these protocols. In the last decade, several research groups have made considerable progress in the synthesis of quinoxalines by employing vicinal diols *via* an acceptorless dehydrogenative coupling strategy (ADC).⁸ In this strategy, alcohol is oxidized to carbonyl compounds *in situ*, and hydrogen gas is liberated as a byproduct. From the viewpoint of

atom economy, the transfer hydrogenation (TH) strategy has emerged as a more attractive method for the construction of C–C and C–N bonds.⁹ In transfer hydrogenative condensation, alcohols can act as hydrogen donors and coupling components at the same time, which are easily handled, renewable and inexpensive. On the other hand, nitroarenes are usually considered precursors of anilines, which can be hydrogenated as hydrogen acceptors in the TH process.¹⁰ Nitroarenes are highly versatile and common synthetic blocks in the organic synthesis and chemical industries. Through the TH process, alcohols could serve as electrophilic carbonyl intermediates and nitroarenes as nucleophilic aniline intermediates (Fig. 1). The main advantage of this protocol is that no additional oxidant and reductant are required and water is generated as the only byproduct. Thus, it is considered an environmentally benign process and a green alternative.

In 2012, Climent *et al.* developed the synthesis of quinoxalines by using a Au-heterogeneous catalyst from 1,2-dinitrobenzenes and vicinal diols.¹¹ However, an external high-

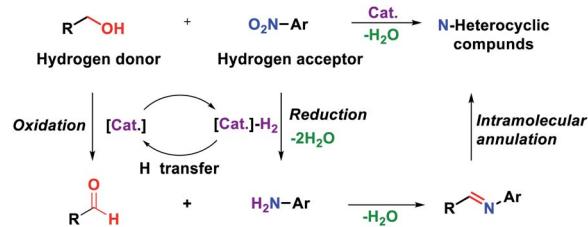


Fig. 1 Transfer hydrogenation process between nitroarenes and alcohols.

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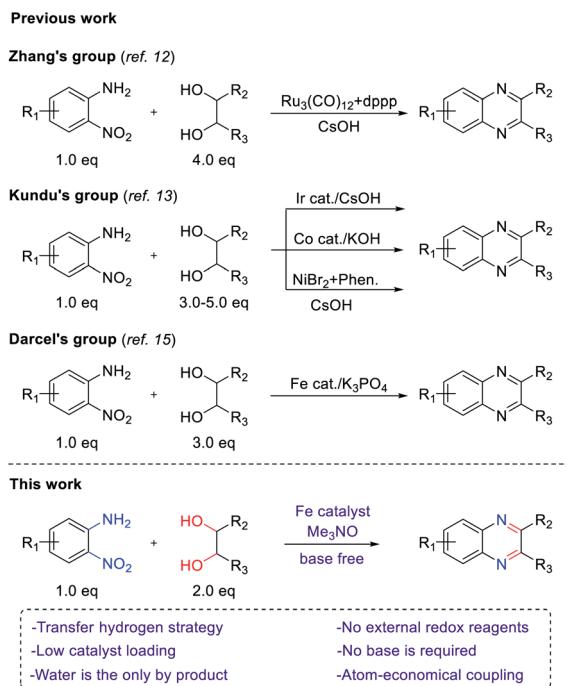


pressure hydrogen source was used for the reduction of 1,2-dinitrobenzenes. Inspired by that work, Zhang's group reported ruthenium- and dppp-catalyzed transfer hydrogenative condensation to synthesize quinoxalines from 2-nitroanilines and vicinal diols (Scheme 1).¹² Later, Kundu's group employed Ir, Co and NiBr₂/1,10-phenanthroline catalysts in the transfer hydrogenation between 2-nitroanilines and vicinal diols to afford quinoxalines.¹³ Nevertheless, these reaction systems required an additional base and excess amount of alcohols to achieve satisfactory yields. Therefore, it is still highly desirable to develop new methods using nonprecious, earth-abundant catalysts without an additional base. Among transition metals, iron is the most abundant metal with a low price and low toxicity. For these reasons, the reduction of nitro arene using an iron-based catalyst and the synthesis of N-heterocycles through redox annulation have been reported.¹⁴ More recently, we reported the synthesis of N-heterocycles from nitroarenes and alcohols *via* a transfer hydrogenative condensation catalyzed by cyclopentadienyl iron complex, which is well known as Knölker complex.¹⁵ Based on this work, we reasoned that the transfer hydrogenative condensation of 2-nitroanilines with vicinal diols might be possible, leading to the formation of quinoxalines. During the preparation of this manuscript, transfer hydrogenative synthesis of quinoxaline using same iron catalyst was reported by Darcel's group.¹⁶ However, they still used excess amounts of base and alcohol in their method. Herein, we report the iron-catalyzed one-pot synthesis of quinoxalines from 2-nitroanilines with vicinal diols by a transfer hydrogenative condensation strategy. No additional base or external redox agents were required, and water was generated as the sole byproduct (Scheme 1).

Results and discussion

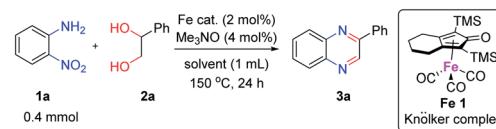
To determine the optimal condition of transfer hydrogenative condensation for the quinoxalines, we chose 2-nitroaniline **1a** and 1-phenylethane-1,2-diol **2a** as model substrates (Table 1). Initially, 2 mol% FeCl₂ as the catalyst and *o*-xylene (1 mL) as the solvent were employed, and the reaction mixture was heated at 150 °C for 24 h (entry 1). Unfortunately, desired 2-phenyl quinoxaline **3a** was observed in low yield. To find more efficient catalysts, various iron complexes were screened (entries 1–4). Cyclopentadienyl iron complex **Fe 1** exhibited the highest activity in the formation of desired product **3a**. Trimethylamine N-oxide (Me₃NO) was used to oxidize CO ligand and liberate a vacant site on iron carbonyl complex. Next, we applied different kinds of solvents, such as toluene, CPME, chlorobenzene and 1,4-dioxane (entries 5–8). Toluene showed the best result, affording **3a** in 84% isolated yield (entry 5). Both decreasing and increasing the amount of alcohol (1.0 eq. or 3.0 eq.) showed lower conversion to the desired product (entries 9 and 10). When the catalyst loading was increased from 2 to 3 mol%, an increased yield for the desired product **3a** was obtained (87%, entry 11). Hence, we chose the optimal reaction conditions as indicated in Table 1, entry 11. It is worth mentioning that trace amounts of 2-phenyl-benzimidazole were observed as byproducts, which could be generated *via* annulation of 1,2-diaminobenzene with benzaldehyde. We supposed that some **2a** might undergo C–C bond cleavage to form benzaldehyde during the dehydrogenative process.

With the optimized reaction conditions, we explored the versatility and limitations of the synthetic method. First, we explored the scope of unsymmetrical vicinal diols **2** with a variety of 2-nitroanilines **1** for transfer hydrogenative



Scheme 1 Quinoxaline synthesis from 2-nitroanilines and vicinal diols *via* transfer hydrogenative condensation.

Table 1 Optimization of the reaction conditions^a



Entry	2a (equiv.)	Fe cat.	Solvent	Yield ^b (%)
1	2.0	FeCl ₂	<i>o</i> -Xylene	13
2	2.0	FeCl ₃ ·6H ₂ O	<i>o</i> -Xylene	<5
3	2.0	Fe ₂ (CO) ₉	<i>o</i> -Xylene	40
4	2.0	Fe 1	<i>o</i> -Xylene	62
5	2.0	Fe 1	Toluene	84
6	2.0	Fe 1	CPME	41
7	2.0	Fe 1	Chlorobenzene	66
8	2.0	Fe 1	1,4-Dioxane	30
9	1.0	Fe 1	Toluene	73
10	3.0	Fe 1	Toluene	67
11 ^c	2.0	Fe 1	Toluene	87

^a Reaction conditions: **1a** (0.4 mmol), **2a** (0.8 mmol), catalyst (2 mol%), Me₃NO (4 mol%) and solvent (1 mL) in a sealed tube at 150 °C for 24 h.

^b Isolated yield. ^c 3 mol% of **Fe 1** and 6 mol% of Me₃NO.



condensation (Table 2). Alkyl-substituted unsymmetrical vicinal diols also underwent smooth condensation followed by cyclization with 2-nitroaniline **1a**, affording 2-alkyl-substituted quinoxalines **3b–d** in good yields. 4,5-Dimethyl-2-nitroaniline **1b** reacted well with aryl- and alkyl-substituted unsymmetrical vicinal diols, resulting in 2-substituted quinoxalines **3e–h** with excellent yields (82–94%). Reaction of 4-chloro-2-nitroaniline **1c** with **2a** gave the two regioisomers **3i** and **3i'** in a 1 : 1.5 ratio. Similarly, 4-methoxy-2-nitroaniline **1d** and 5-methoxy-2-nitroaniline **1e** were annulated with **2a**, resulting in a mixture of regioisomers **3j** and **3j'** in 1 : 1.9 and 1 : 1.6 ratios, respectively. In addition, the reaction of 3-nitropyridin-4-amine **1f** with **2a** also gave an inseparable mixture of regioisomers **3k** and **3k'**.

Table 2 Scope of reaction with unsymmetrical vicinal diols

1	2	3	Yield ^a (%)
1a	2a	3a	87
1a	2b	3b	81
1a	2c	3c	78
1a	2d	3d	80
1b	2a	3e	94
1b	2b	3f	87
1b	2c	3g	82
1b	2d	3h	83
1c	2a	3i 29 3i' 45	
1d	2a	3j 34 3j' 64	
1e	2a	3j 38 3j' 60	
1f	2a	3k 3k'	79 ^b 3k : 3k' (1 : 4.3)

^a Isolated yield. ^b Mixture was not separated. ^c NMR ratio.

3k'. Even if the regioselectivities are not good, it was found that more 2,7-disubstituted quinoxalines are produced than 2,6-disubstituted quinoxalines, regardless of the substituent position on the starting materials. Generally, aryl-substituted vicinal diols **2a** showed better yields than alkyl-substituted vicinal diols **2b–2d**. Moreover, electron-donating groups (Me and OMe) containing nitroanilines **1b** and **1d–1e** afforded quinoxalines in higher yields than electron-deficient groups (Cl) containing substrate **1c**.

After investigating the scope of the unsymmetrical diols, we turned our attention toward the transfer hydrogenative condensation of symmetrical diols **2** with 2-nitroanilines **1**, as illustrated in Table 3. The reaction of (*R,R*)-1,2-diphenylethane-1,2-diol **2e** with 2-nitroaniline **1a** afforded a low yield of the

Table 3 Scope of reaction with symmetrical vicinal diols

1	2	3	Yield ^a (%)
1a	2e	3l	50 ^b
1a	2e'	3l	52 ^c
1a	2f	3m	80
1a	2g	3n	0
1b	2f	3o	81
1d	2f	3p	83
1g	2f	3q	79
1h	2f	3r	77
1i	2f	3s	71
1j	2f	3t	59
1k	2f	3u	61
1l	2f	3v	66
1f	2f	3w	0
1f	2e	3x	49

^a Isolated yield. ^b 24 h, 2-phenyl benzimidazole was obtained in 18%.

^c 24 h, 2-phenyl benzimidazole was obtained in 20%.



desired product **3l** along with a significant amount of 2-phenyl benzimidazole as a side product. In addition, when meso **2e'** was applied to the reaction, the similar result was obtained. This result implies that the stereocenter of diol does not affect the reaction. In the case of 1,2-dimethylethane-1,2-diol **2f**, the corresponding quinoxaline product **3m** was obtained in 80% yield, even if a longer reaction time was needed for full conversion. On the other hand, cyclohexane-1,2-diol **2g** failed to produce desired product **3n** under the reaction conditions. This result was in contrast to previous Darcel's conditions using bases.¹⁶ We expected that the base influences the imine condensation or the annulation process rather than transfer hydrogenation. Therefore, we thought the ring strain of fused tricyclic product **3n** retards the annulation process. Because 1,2-diaminobenzene and cyclic ketone could be observed in this reaction, that are supposed as intermediates went through transfer hydrogenation. Based on the above results, we chose **2f** as a coupling partner to explore the reaction scope of 2-nitroaniline with a symmetrical diol. Various substituted 2-nitroanilines **1** reacted well with **2f**, resulting in the corresponding products with moderate to good yields **3o–3v** (61–80%). In particular, 2-nitroanilines bearing electron-donating groups (Me and OMe) afforded the respective products **3o–3q** in good yields. Although 2-nitroanilines with electron-withdrawing groups (Cl, Br, I and CF₃) were less efficient than electron-rich 2-nitroanilines (**3r–3v** vs. **3o–3q**), the halogen groups were tolerated well under the reaction conditions. No dehalogenated products were observed in the reaction with 2-nitroanilines containing halogen substituents (Cl, Br and I), which could be affected in Darcel's conditions.¹⁶ The tolerance of halogen groups opens up a pathway for further modification of the quinoxaline products. 3-Nitropyridin-4-amine **1f** underwent smooth cyclization with **2e**, leading to desired product **3x**, whereas no desired product was observed with **2f**.

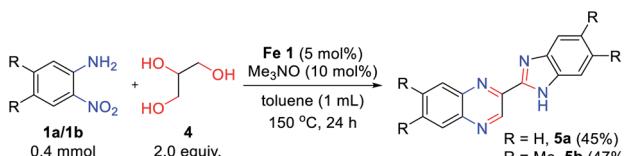
Encouraged by the above results, 1,2,3-triol **4** (glycerol) was applied in this reaction system instead of vicinal diol (Scheme 2). Interestingly, 2-benzimidazoyl quinoxaline product **5a** was obtained by the reaction of 2-nitroaniline **1a** with glycerol **4**, and no other products were observed. We expected that the quinoxaline ring might be formed at first and that the benzimidazole moiety can be formed followed by cyclocondensation of another 2-nitroaniline with a quinoxaline-2-aldehyde intermediate. The reaction of 4,5-dimethyl-2-nitroaniline **1b** also affords the desired product **5b** in moderate yield. However, in the case of 4-methoxy-2-nitroaniline **1d**, a messy products were observed in TLC, which are expected as a mixture of regioisomers. And only trace

amount of product was observed in the reaction of 3-nitropyridin-4-amine **1f**. Although the scope of the reaction is somewhat limited, this result opens up a new route for the synthesis of 2-benzimidazoyl quinoxaline derivatives *via* one-pot transfer hydrogenative condensation.

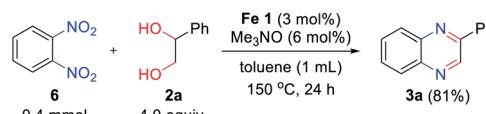
To further extend the scope of the reaction system, we employed 1,2-dinitrobenzene **6** instead of 2-nitroaniline **1** as a coupling partner to explore the possibility of quinoxaline formation (Scheme 3). Under the reaction with twice the amount of hydrogen donor **2a**, 1,2-dinitrobenzene **6** resulted in the desired product **3a** with high yield (81%).

To investigate the mechanism for the developed reaction, few control experiments were performed, as shown in Scheme 4. First, we examined the reaction without a catalyst to investigate the role of the iron complex (Scheme 4a). No reaction was observed in the absence of catalyst, and most of the starting materials remained, which indicates the vital role of iron catalysts in transfer hydrogenation. Next, to determine the intermediates, the reaction of **1b** with **2a** was interrupted after 12 h (Scheme 4b). Unfortunately, no intermediates were observed; only product **3e** was observed in 38% yield, and the starting materials remained. Thus, we can expect that the cyclization step occurs very quickly after transfer hydrogenation. Furthermore, an acceptorless dehydrogenative coupling (ADC) strategy has been applied to determine the feasibility of the formation of quinoxaline. For this purpose, we examined the reaction between 1,2-diaminobenzene **7** and **2a**; however, a lower yield of the desired product **3a** was observed (31%, Scheme 4c). Based on these results, we speculate that sufficient diol oxidation does not proceed well without a hydrogen acceptor or nitro group. We also suppose that the formation of an imine intermediate from 2-nitroanilines is favored over the formation of a 1,2-diaminobenzene intermediate in the whole reaction process.

Based on these results and the related literature,^{12,13b,15} a plausible mechanism for the transfer hydrogenative condensation of 2-nitroanilines with vicinal diols was proposed, as depicted in Scheme 5. Initially, Me₃NO oxidizes a CO ligand on Knölker complex **Fe 1** and liberate CO₂. The activated catalyst **[Fe]** is formed and mediates the oxidation of diols **2** to afford the corresponding carbonyl intermediate and **[Fe]–H₂**. Followed by the condensation of carbonyl compounds with 2-nitroanilines **1** produce the α -hydroxyimine intermediate (**I** or **II**). Then, α -keto amine intermediates **III** or **IV** can be formed by the hydrogenation of nitro groups and oxidation of the remaining alcohol *via* an iron-mediated transfer hydrogenation process. Finally, the α -keto amine intermediate (**III** or **IV**) undergoes intramolecular condensation followed by aromatization and produces the desired products **3** or **3'**. Throughout the whole TH

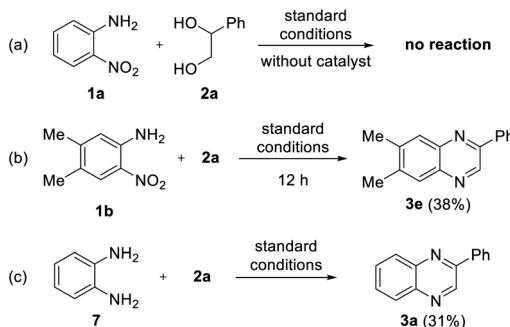


Scheme 2 Transfer hydrogenative condensation of 2-nitroaniline with glycerol.

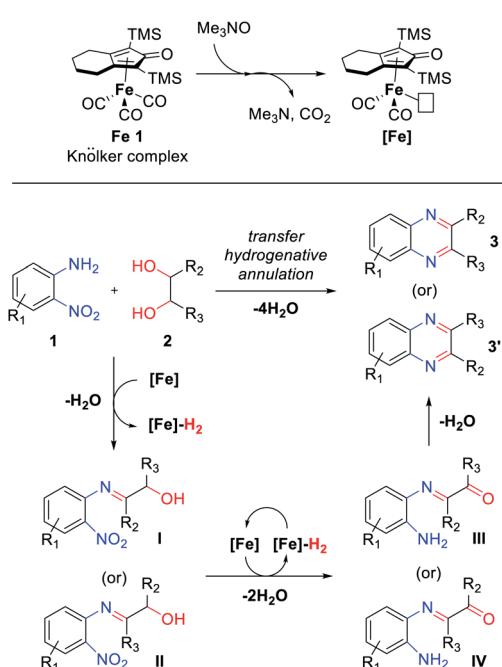


Scheme 3 Transfer hydrogenative condensation of 1,2-dinitrobenzene with vicinal diol.





Scheme 4 Control experiments.



Scheme 5 Plausible mechanism for the formation of quinoxalines.

process, at least 1.5 equivalents of diol are required as hydrogen donors to reduce one nitro functionality.

Conclusions

In summary, we have developed an iron-catalyzed transfer hydrogenative condensation process for the one-pot synthesis of quinoxalines from 2-nitroanilines and vicinal diols. A cyclopentadienyl iron complex has been applied to a hydrogen transfer strategy between nitro and alcohol functionalities. In this protocol, alcohols serve as hydrogen donors, and nitroarenes act as hydrogen acceptors. Various unsymmetrical and symmetrical vicinal diols underwent efficient cyclization and produced quinoxaline derivatives in 49–98% yields. A plausible mechanism for quinoxaline formation was proposed based on a series of control experiments. Furthermore, glycerol was successfully employed in the reaction system, leading to a 2-benzimidazoyl quinoxaline product. This result opens up a new

route for the synthesis of 2-benzimidazoyl quinoxaline derivatives *via* the one-pot condensation of 2-nitroaniline with glycerol. Additionally, a hydrogen transfer strategy was applied in the reaction of 1,2-dinitrobenzene with a vicinal diol, resulting in the desired quinoxaline in 81% yield. This hydrogen transfer process can proceed smoothly without the use of external redox reagents and an additional base. Utilization of a nonprecious iron metal catalyst and the generation of water as the sole byproduct make this reaction an eco-friendly method for synthesizing quinoxalines. Further application of this transfer hydrogen protocol in the synthesis of N-heterocycles is ongoing in our laboratory.

Author contributions

R. R. Putta – investigation (reaction scope), methodology, writing-original draft. S. Chun – conceptualization, project administration, investigation (preparation of catalyst). S. B. Lee – investigation (reaction scope), resources. J. Hong – investigation (mechanism), formal analysis, validation. D.-C. Oh – data curation, funding acquisition, writing-review & editing. S. Hong – conceptualization, supervision, funding acquisition, writing-review & editing.

Conflicts of interest

There are no conflicts to declare.

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