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Iron-Catalyzed Hydrogen Transfer Reduction of Nitroarenes with Alcohols: Synthesis of Imines and Aza Heterocycles

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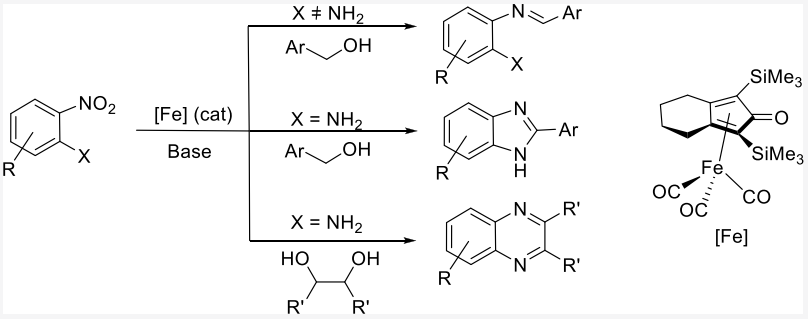

ABSTRACT: A straightforward and selective reduction of nitroarenes with various alcohols was efficiently developed using an iron catalyst via a hydrogen transfer methodology. This protocol led specifically to imines in 30−91% yields, with a good functional group tolerance. Noticeably, starting from *o*-nitroaniline derivatives, in the presence of alcohols, benzimidazoles can be obtained in 64−72% yields when the reaction was performed with an additional oxidant, DDQ, and quinoxalines were prepared from 1,2-diols in 28−96% yields. This methodology, unprecedented at iron for imines, also provides a sustainable alternative for the preparation of quinoxalines and benzimidazoles.

INTRODUCTION

In the beginning of this millennium, with the global climate change concerns associated to the depletion of fossil resources, the utilization of eco-compatible methodologies and abundant sustainable starting materials as the feedstocks for chemical preparation is more than highly desirable. In reduction area, comparing to the classical hydrogenations performed in autoclaves under hydrogen pressure, a hydrogen borrowing methodology is very attractive in terms of convenience and chemoselectivity.[1−3] Thus, alcohols are alternative interesting reductants and coupling partners in acceptorless dehydrogenative processes, such as the formation of C═N bonds in various derivatives such as imines or *N*-heterocycles. On the other hand, quinoxalines[4] and benzimidazoles[5] are among the most important nitrogen-containing heterocycles[6] exploited by the pharmaceutical industry as they exhibit a broad spectrum of biological activities (Figure 1). Additionally, Schiff bases bearing imine moiety also possess numerous potent biological activities such as antibacterial and antimicrobial ones.[7]

In the area of hydrogen transfer reaction, cross-dehydrogenative coupling promoted by first row transition metal-based catalysts is an emerging research area in molecular synthesis.[3] More particularly, iron, being the most abundant and inexpensive transition metal on Earth, the last two decades have seen an impressive growth of its use in homogeneous catalysis.[8] Thus, numerous examples of iron-catalyzed reductive coupling reactions were reported[9] including amination reactions which can be efficiently promoted *via* a hydrogen borrowing pathway at rather high temperatures starting from alcohols,[10] notably using Knölker-type catalysts.[11−13]

On the other hand, the reduction of nitroarenes represents a powerful and widely used technology to access anilines, even if often conducted in drastic conditions.[14] Such reductions were successfully conducted with iron. The most known technology is Béchamps reduction of nitroarenes which was reported using more than a stoichiometric amount of iron powder in acidic conditions.[15] More recently, iron-catalyzed hydrosilylation,[16] hydrogenation,[17] and hydrogen transfer[18] were also reported as efficient and chemoselective reactions. Interestingly, Baran, Cui, Thomas and Driver reported cascade reactions involving reduction of nitroarenes *via* hydrosilylation to anilines and then hydroamination of alkenes yielding to alkylated amines.[19] Iron-catalyzed cascade reduction of nitroarenes leading to imines and *N*-heterocyclic compounds was also described by

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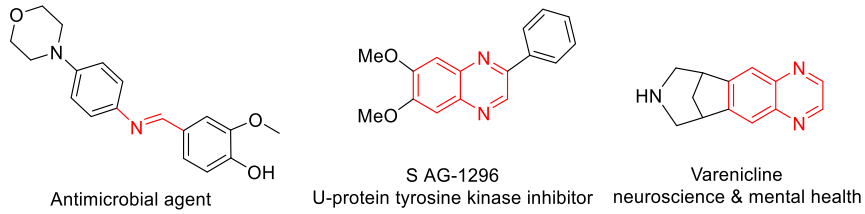


Figure 1. Representative examples of imines and quinoxalines with biological activities.

Scheme 1. Fe-Catalyzed Hydrogen Transfer of Nitroarenes

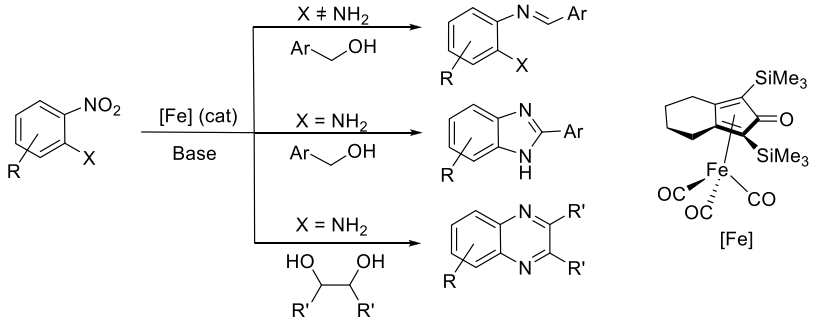
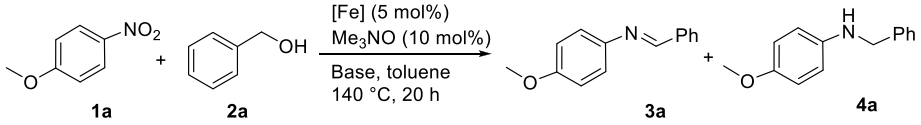


Table 1. Optimizations of Reaction conditions[a]



entry	2a (equiv)	base (equiv)	3a/4a (%)[b]
1	4	Cs_2CO_3 (3)	84/0
2	6	Cs_2CO_3 (3)	87/0
3	2	Cs_2CO_3 (3)	45/0
4[c]	4	Cs_2CO_3 (3)	
5[d]	4	Cs_2CO_3 (3)	64/0
6	4		
7	4	K_2CO_3 (3)	trace
8	4	KOAc (3)	trace
9	4	CsOAc (3)	trace
10	4	EtONa (3)	4/-
11	4	*t*-BuOK (3)	55/10
12	4	KOH (3)	41/22
13	4	NaOH (3)	39/7
14	4	$K_3PO_4·H_2O$ (3)	90/0
15	4	$K_3PO_4·H_2O$ (1)	75/0

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (2−6 equiv), [Fe] (5 mol %), Me_3NO (10 mol %), base (3 equiv), toluene (2 mL), 140 °C, 20 h, under argon. [b]Determined by GC using dodecane as an internal standard. [c]Without [Fe] and Me_3NO. [d]Without Me_3NO.

hydrogenation with carbonyl derivatives using an iron nanocomposite.[20] Additionally, quinoxalines and benzimidazoles can be prepared from nitroarenes by hydrogen transfer catalyzed by sodium sulfide in combination with an iron salt[21] or a ferrocenyldiphosphine.[22] Such cascade reduction can be also performed with other first row metals such as cobalt[23] or manganese.[24]

Following our recent contributions involving iron-catalyzed cascade reactions,[25] we report herein the use of the well-defined Knölker catalyst for the selective hydrogen transfer transformation of nitroarenes, leading to imines and benzimidazoles by reaction with alcohols and to quinoxaline by reaction with diols. To the best of our knowledge, there is no report dealing with the direct formation of imines from nitroarenes at iron under hydrogen transfer conditions (Scheme 1). It should be noticed that the Knölker-type complex was used for two very recent contributions dealing with N-heterocycles synthesis starting from nitroarenes.[26]

RESULTS AND DISCUSSION

Using the Knölker complex [Fe] (5 mol %) associated to 10 mol % Me_3NO, we commenced our study by performing the reaction of 4-nitroanisole (**1a**) with benzylalcohol (**2a**) as a model system in the presence of 3 equiv of Cs_2CO_3 in toluene at 140 °C under argon for 20 h (Table 1). To our delight, the corresponding imine (**3a**) was selectively obtained in 84% GC-yield which demonstrated that the hydrogen transfer reaction transforming nitroarene to aniline derivatives can be performed

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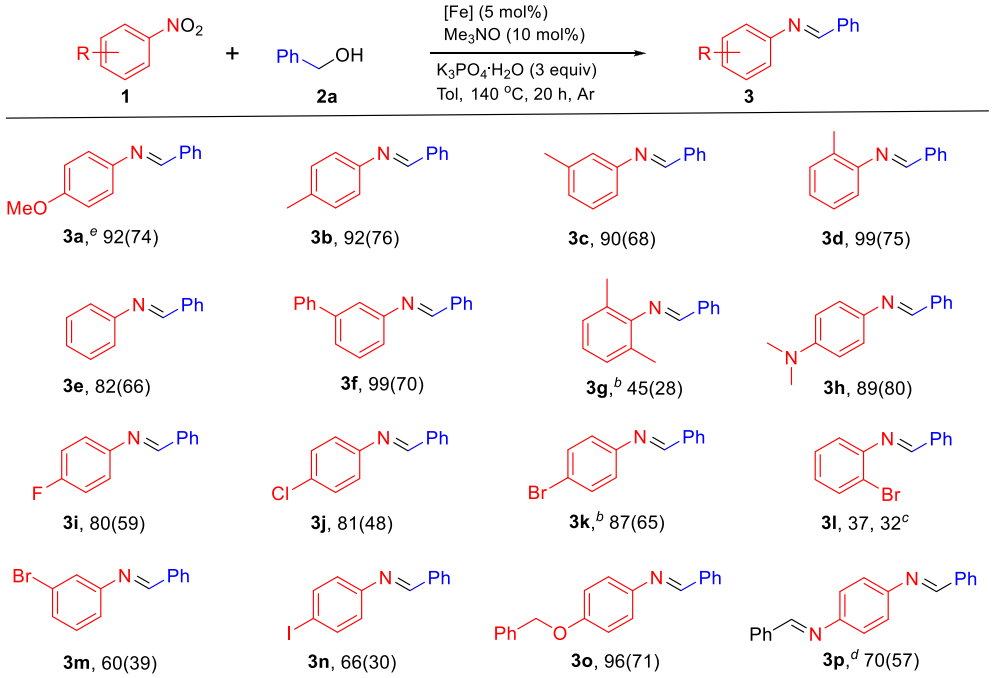
Scheme 2. Scope of the Reaction of Nitroarenes with Benzylalcohol[a]



[a]Reaction conditions: nitroarene **1** (0.5 mmol), benzylalcohol **2a** (4 equiv), [Fe] (5 mol %), Me_3NO (10 mol %), $K_3PO_4{\cdot}H_2O$ (3 equiv), toluene (5 mL), 140 °C, 20 h under argon. ^1H NMR yields were determined by using CH_2Br_2 as an internal standard, yields in parentheses. [b]150 °C. [c]Yield of debrominated product. [d]Benzylalcohol **2a** (10 equiv) for 72 h. [e]Reaction performed in 5 mmol scale, 81% yield.

under such reaction conditions (Table 1, entry 1). Noticeably, no trace amount of the *N*-benzyl-4-methoxyaniline **4a**, resulting from the reduction of **3a** was observed. A similar result was obtained with 6 equiv of benzylalcohol (87%, entry 2), whereas a decrease of the benzylalcohol amount (2 equiv) had a deleterious effect on the activity (45%, entry 3). It is worth mentioning that [Fe], Me_3NO, and base are crucial for the success of the transformation. Indeed, no reaction occurred in the absence of the iron catalyst or base, and the efficiency decreased without the addition of Me_3NO (entries 4−6). Among the different solvent tested, toluene showed a superior catalytic performance (Table S1 in the Supporting Information). Several sources of bases were then examined (Table 1, entries 7−14), with $K_3PO_4{\cdot}H_2O$ found to afford the highest efficiency and selectivity (90% of **3a**). The use of common bases such as K_2CO_3, CsOAc, or KOAc did not lead to any resulting imine, while either *t*-BuOK, NaOH, or KOH led to **3a** in moderate yields, with notable amount of the secondary amine **4a**. Nevertheless, the yield of product was lowered to 75% with decreasing the amount of $K_3PO_4{\cdot}H_2O$ to 1 equiv (entry 15). This protocol represents one of the rare examples of formation of imines from nitroarenes by the hydrogen transfer methodology in homogeneous conditions.[27,28] Noticeably, even if its role is not clearly explained and confirmed by experimental evidences, the use of a base has a crucial consequence on the course of the reaction. Base was necessary to perform the reduction of nitroarenes to anilines, but it inhibited the reduction of the obtained imines to amines and then subsequent alkylation, as already mentioned by Gandon and Bour for the contribution on ethylation of imines with ethanol.[29]

Having the optimized reaction conditions in hand, a variety of nitroarene derivatives were subjected to the reaction with benzylalcohol **2a**, as summarized in Scheme 2. Nitroarenes with electron-donating methoxy, methyl, *N*,*N*-dimethylamino, and benzyloxy substituents reacted nicely with **2a**, providing the resulting imines (**3a**−**3d**, **3h**, and **3o**) in good NMR yields and 68−80% yields. Notably, the reaction proceeded efficiently with *o*,*m*,*p*-nitrotoluene. Nevertheless, when using the more sterically hindered 2,6-dimethyl-1-nitrobenzene **1g**, lower activity was observed even at higher temperature (150 °C); the corresponding imine **3g** was obtained in only 45% NMR yield, thus demonstrating that steric hindrance can hamper the transformation. Additionally, the reaction of nitrobenzene and 3-phenyl-1-nitrobenzene with **2a** gave the corresponding imines **3e** and **3f** in 66 and 70% yields, respectively. Starting from *p*-substituted halogenated nitroarenes, the corresponding imines **3i**-**3k** were obtained in 48−65% yields, showing that fluoro, chloro, and bromo groups can be tolerated. The reaction can be also performed with *p*-iodonitroarene **1n** with a lower efficiency (66% NMR, 30% yields). Whereas 3-bromo-1-nitrobenzene **1m** led to the corresponding imine **3m** in 60%, the reaction of 2-bromonitrobenzene with **2a** gave a mixture of *N*-(2-bromophenyl)benzylideneimine **3l** and the debrominated derivative *N*-phenyl-benzylideneimine **3e** in 37 and 32% NMR yields, respectively. Impressively, 1,4-dinitrobenzene could also undergo this transformation to afford corresponding bis-imine **3p** in 57% yield.

The scope of the reaction with respect to the alcohols was next explored (Scheme 3). Various benzylalcohols substituted with electron-donating groups (MeO, alkyl) reacted efficiently with 4-nitroanisole to furnish the desired products **3q**−**3t** in 68−91% yields. Gratifyingly, halogen substituents (F, Cl, and Br) at the *ortho*- and *para*-positions of benzylalcohols were tolerated and the resulting imines **3u**−**3y** were obtained in modest to good yields up to 88%. It is worth noting that benzylalcohols decorated with electron-deficient trifluoromethyl or cyano moieties were compatible for the reductive

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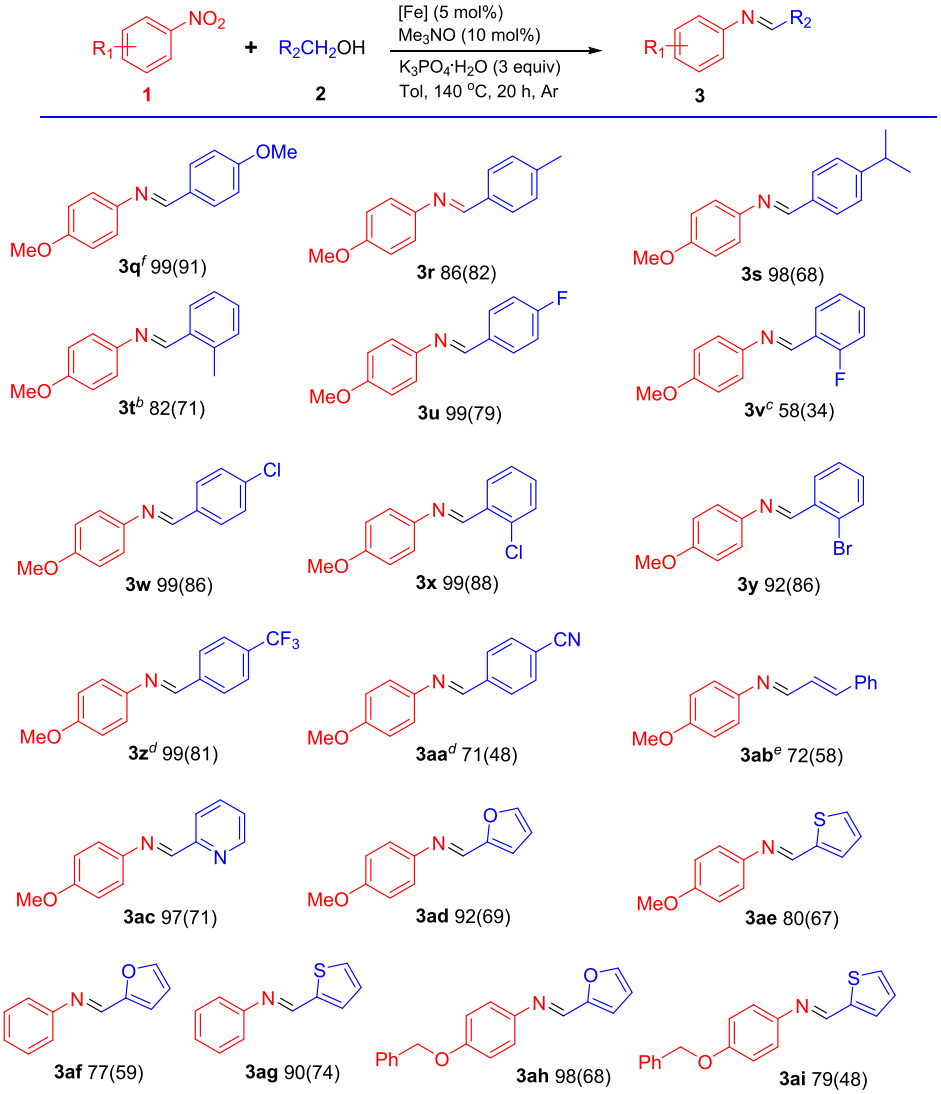
Scheme 3. Scope of the Reaction of Nitroarenes with Various (Hetero)aromatic Methanol[a]



[a]Reaction conditions: nitroarene **1** (0.5 mmol), alcohol **2** (4 equiv), [Fe] (5 mol %), Me_3NO (10 mol %), $K_3PO_4·H_2O$ (3 equiv), toluene (5 mL), 140 °C, 20 h under argon. ^1H NMR yields were determined by using CH_2Br_2 as an internal standard, yields in parentheses. [b]30 h. [c]150 °C, 48 h. [d]150 °C, 24 h. [e]16 h. [f]Reaction performed in 5 mmol scale, 83% yield.

coupling leading to **3z** and **3aa** in 81 and 48% yields, respectively, performing the reaction at 150 °C for 24 h. The reaction conditions were applied to the reaction of the more challenging cinnamyl alcohol with 4-nitroanisole. Nicely the corresponding allylic imine **3ab** was produced in 58% yield. Moreover, various heterocyclic alcohols, such as 2-pyridylmethanol, 2-furfuryl alcohol, and 2-thiophene-methanol were successfully coupled to 4-nitroanisole, nitrobenzene, and 1-(benzyloxy)-4-nitrobenzene, leading to the targeted imines **3ac**−**3ai** in good yields. Noticeably, under standard conditions (140 °C, 20 h), the reaction of 4-nitroanisole with alkyl alcohols such as 3-phenylpropan-1-ol and hexan-1-ol gave the corresponding imine derivatives in low NMR yields (<10%). Additionally, the reaction of nitroalkanes such as 1-nitropropane and 2-nitropropane with benzylalcohol did not lead to the corresponding imines.

The above results led us to further investigate the generality of this reaction, and we then evaluated this hydrogen transfer/coupling methodology for the direct synthesis of aza heterocyclic derivatives from 2-nitroaniline **5**. By reaction with benzylalcohol, benzimidazole[30,31] **6a** can be obtained in 28% yield when performing the reaction with 5 mol % of the Knölker complex, 10 mol % of Me_3NO, and 1 equiv of $K_3PO_4·H_2O$ in mesitylene at 160 °C for 24 h. Noticeably using the (1,4-dimethyl-5,7-diphenyl-3,4-dihydro-1*H*-cyclopenta-[*b*]-pyrazine-6(2*H*)-one)iron tricarbonyl complex developed by Renaud et al.[9d] as the catalyst, only 17% of **6a** was obtained under the same conditions (see Table S2 for details of the optimization). Thus, **6a**−**c** can be obtained with 64−72% yields but an additional step with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone, 0.5 equiv) was required to oxidize the dihydrobenzimidazole intermediate.[32] (Scheme 4).

Finally, we applied this methodology for the direct synthesis of quinoxalines from 2-nitroaniline derivatives and diols (Scheme 4).[33,34] As a benchmark reaction, 2-nitroaniline can react with 1-phenylethane-1,2-diol using similar conditions (5 mol % [Fe]; 10 mol % Me_3NO, 3 equiv $K_3PO_4·H_2O$, toluene, 150 °C, 48 h, see Table S3 in the Supporting Information for details of the optimization) and the corresponding quinoxaline **8a** was isolated in 80% yield. 4,5-Dimethyl-2-nitroaniline

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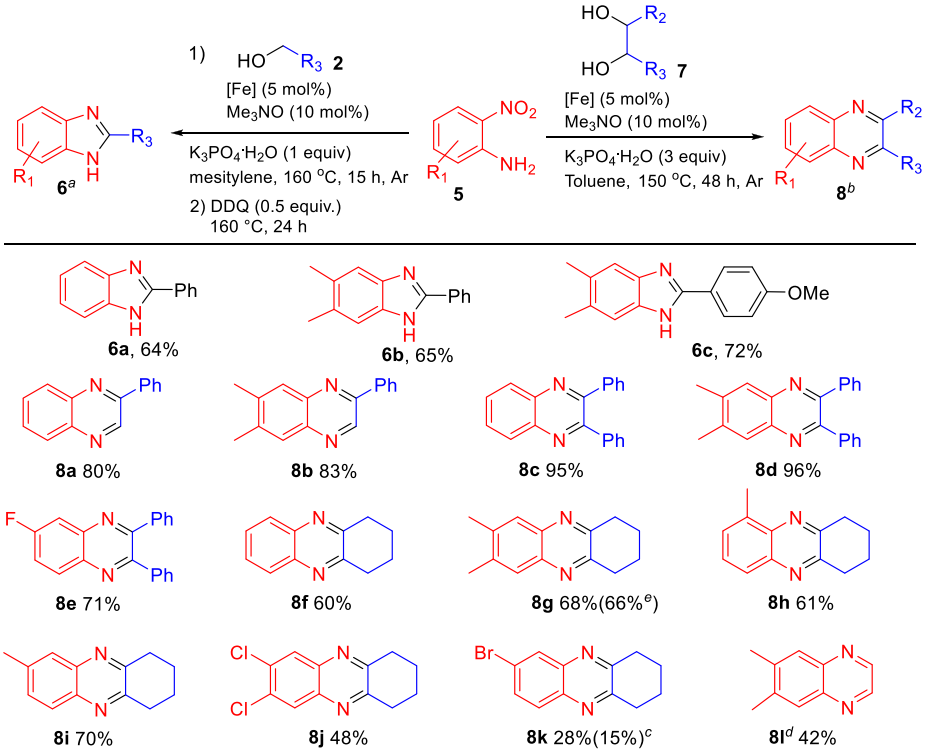
Scheme 4. Scope of the Synthesis of Aza Heterocyclic Derivatives



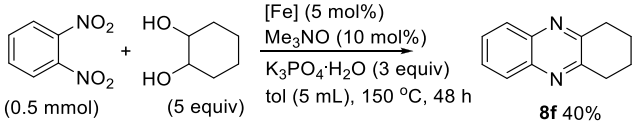
[a]Reaction conditions: (*i*) *ortho*-nitroaniline **5** (0.5 mmol), alcohol **2** (3 equiv), [Fe] (5 mol %), Me_3NO (10 mol %), $K_3PO_4·H_2O$ (1 equiv), mesitylene (3 mL), 160 °C, 15 h under argon; (ii) DDQ (0.5 equiv), 160 °C, 24 h. [b]Reaction conditions: *ortho*-nitroaniline **5** (0.5 mmol), 1,2-diols **7** (3 equiv), [Fe] (5 mol %), Me_3NO (10 mol %), $K_3PO_4·H_2O$ (3 equiv), toluene (2.5 mL), 150 °C, 48 h under argon. [c]In parentheses, the yield of debrominated product **8f**. [d]*t*-BuOK (1 equiv). [e]Reaction performed in 5 mmol scale, 66% yield.

reacted also with 1-phenylethane-1,2-diol, leading to **8b** in 83% yield. Noticeably, 1,2-diphenylethane-1,2-diol was also a good partner for this transformation and the corresponding quinoxalines **8c–e** were obtained in 71–96% yields. Non-activated diols such as cyclohexane-1,2-diol or ethylene glycol are more challenging partners for this transformation. Nevertheless, the corresponding quinoxalines **8f–j** were obtained in 48–70% yields starting from 1,2-cyclohexanediol. Whereas fluoro and chloro substitutions were tolerated on the 2-nitroaniline motif (**8e** and **8j**), 4-bromo-2-nitroaniline led to the expected quinoxaline **8k** (28%) in the mixture with the debrominated derivative **8f** (15%). The reaction can be also conducted with 1,2-ethanediol yielding **8l** in 42%. Noticeably, *t*BuOK was used as the base. Indeed, using optimized conditions with $K_3PO_4·H_2O$, the transformation was not selective.

Even if it is a more expensive starting material than 2-nitroaniline **5**, we also performed the reaction of 1,2-dinitrobenzene with 1,2-cyclohexanediol under the optimized conditions (150 °C, 48 h). The resulting quinoxaline **8f** was obtained in 40% yield, showing that this methodology can be extended to 1,2-dinitroarene derivatives, even if it is less efficient than the one with 2-nitroaniline (Scheme 5).

The Knölker catalyst is known to promote efficiently hydrogen transfer and hydrogen borrowing transformation *via* outer-sphere hydride transfer/protonation-deprotonation fashion.[7−13] The catalytic reduction of nitroarenes to anilines can be evolved along two pathways (Scheme 6). Thus, starting from nitroarenes, the reduced iron species [FeH_2] underwent the reduction of the nitro moiety, leading to an arylnitroso **9**

Scheme 5. Reaction of 1,2-Dinitrobenzene with 1,2-Cyclohexanediol



regenerating the Knölker catalyst [Fe] and aldehyde. Similarly, the arylnitroso is then reduced to *N*-hydoxyaniline **10**. Two competitive pathways can be then envisaged: either the direct reduction route (in blue) of *N*-hydroxyaniline to aniline **14**, or the red pathway *via* the condensation of arylnitroso **9** with *N*-hydroxyarylamine **10**, leading to azoxyarene **11** and then azoarene **12**. Noticeably, when the reaction of 4-nitroanisole **1a** was conducted with 2 equiv of benzylalcohol under the optimized conditions (140 °C, 20 h), the corresponding azoxyarene **11a** and 4-methoxyaniline **14a** were detected in GC–MS analysis (Scheme S1 in the Supporting Information). Additionally, during the reaction with 4-bromo-1-nitrobenzene with benzylalcohol, under the optimized conditions, 4-bromoazobenzene **12k** was also observed in GC–MS and isolated (10%). Both observations seem to suggest that this iron-catalyzed process might proceed through the condensation/reduction pathway.

CONCLUSIONS

In summary, an efficient and selective protocol for the reduction of nitroarenes with various alcohols was efficiently developed using the Knölker iron catalyst *via* a transfer

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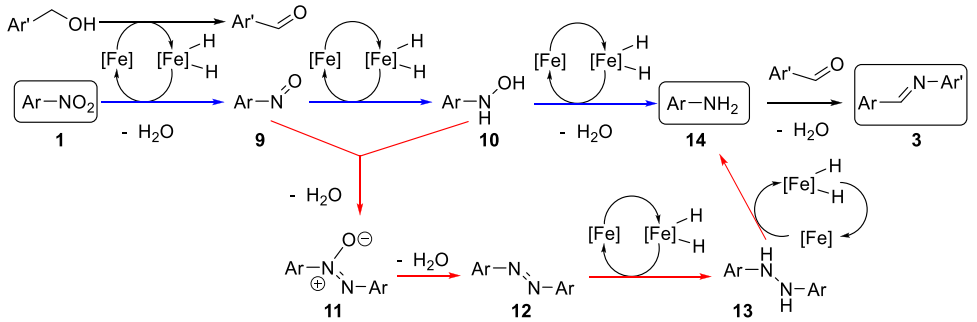
Scheme 6. Proposed Pathways for the Iron-Catalyzed Hydrogen Transfer Reaction of Nitroarenes with Alcohols



hydrogen methodology. This protocol led specifically to imines in 30−91% yields, exhibiting a good functional group tolerance. This represents one of the rare examples of reduction of nitroarenes, leading to exclusively imines derivatives. Starting from *o*-nitroaniline derivatives, in the presence of alcohols, benzimidazoles were selectively obtained if the reaction was performed with DDQ as a final oxidant, whereas in the presence of 1,2-diols, quinoxalines were synthetized in 28−96% yields. This hydrogen transfer methodology, unprecedented at iron for imine synthesis from nitroarenes, also provides a sustainable alternative for the preparation of quinoxalines and benzimidazoles.

EXPERIMENTAL SECTION

Materials and General Methods. All reagents were obtained from commercial sources and used as received. All reactions were carried out with dried glassware using standard Schlenk techniques under an inert atmosphere of dry argon. Technical grade heptane and ethyl acetate were used for column chromatography. Analytical TLC was performed on Merck 60F254 silica gel plates (0.25 mm thickness) and 60F254 aluminum oxide neutral plates. Column chromatography was performed on Acros Organics Ultrapure silica gel (mesh size 40−60 μm, 60 Å) and aluminum oxide (40−300 μm, 60 Å).

^{1}H NMR spectra were recorded in $CDCl_3$, CD_2Cl_2, or DMSO-d_6 at ambient temperature on Bruker AVANCE 400 spectrometers at 400.1 MHz using the solvent as the internal standard ($CDCl_3$ 7.26 ppm, CD_2Cl_2 5.32 ppm, DMSO-d_6 2.5 ppm). ^{13}C NMR spectra were obtained at 100 MHz and referenced to the internal solvent signals ($CDCl_3$, central peak 77.16 ppm, CD_2Cl_2 53.84 ppm, and DMSO-d_6 39.52 ppm). ^{19}F NMR spectra were obtained at 376 MHz in $CDCl_3$. Chemical shift (δ) and coupling constants (J) are given in ppm and in Hz, respectively. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and br for broad.

Melting points of the new solid compounds were measured using Kofler hot-stage apparatus and are uncorrected.

GC analyses were performed with GC-2014 (Shimadzu) 2010 equipped with a 30-m capillary column (Supelco, SPBTM-20, fused silica capillary column, 30 M × 0.25 mm × 0.25 mm film thickness), which was used with N_2/air as vector gas. The following GC conditions were used: initial temperature of 80 °C for 2 min, then rate was 10 °C/min until 220 and 220 °C for 15 min. The sample was prepared by GC−MS and measured by GCMS-QP2010S (Shimadzu) with GC-2010 equipped with a 30 m capillary column (Supelco, SLBTM-5ms, fused silica capillary column, 30 M × 0.25 mm × 0.25 mm film thickness), which was used with helium as vector gas. The following GC−MS conditions were used: initial temperature of 100 °C for 2 min, then rate was 10 °C/min until 250 and 250 °C for 10 min. At the end of the reaction, after cooling, dodecane as an internal standard was introduced in the mixture which was then diluted with 5 mL of ethyl acetate. 1 mL of solution was then filtrate through Celite in a vial for GC−MS analysis.

HR−MS spectra were performed using a time flight Agilent 6510 [Agilent Technologies Santa Clara (CA), USA] in an electrospray positive ionization mode at the Centre Régional de Mesures Physiques de l'Ouest, (CRMPO, ScanMAT, UMS 2001 CNRS—University Rennes 1). The Knölker complex [**Fe**] was prepared, according to a published procedure.[10a]

General Procedures for the Synthesis of Imine Derivatives. A typical procedure for the Fe-catalyzed reductive coupling of nitro derivatives with alcohols is as follows: in a dried Schlenk tube containing a magnetic bar, Knölker complex [Fe] (10.2 mg, 0.025 mmol, 5 mol %), Me_3NO (3.8 mg, 0.05 mmol, 10 mol %), nitroarene derivative **1** (0.5 mmol, 1 equiv), $K_3PO_4{\cdot}H_2O$ (345.4 mg, 1.5 mmol, 3 equiv), alcohol **2** (2 mmol, 4 equiv), and 5 mL of toluene were added successively under an argon atmosphere. Then, the tube was sealed and the mixture was stirred at 140 °C using an oil bath for 20 h. After cooling to room temperature, the resulting solution was filtrated through a pad of neutral alumina and washed with dichloromethane or ethyl acetate. The filtrate was collected and concentrated in vacuo. The residue was purified by neutral alumina column chromatography using dichloromethane/heptane or ethyl acetate/heptane as the eluent to afford the desired product **3**.

N-(4-Methoxyphenyl)-1-phenylmethanimine ***3a***.[23d] Following the general procedure, **3a** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:20) as the eluent. White solid (78 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (s, 1H), 7.95−7.88 (m, 2H), 7.52−7.45 (m, 3H), 7.27 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 158.6, 158.4, 145.1, 136.6, 131.2, 128.9, 128.7, 122.3, 114.5, 55.6. GC−MS: m/z (%): 211 (M^+, 90), 196 (100), 167 (20), 141 (10), 92 (10), 77 (10).

Procedure for the Gram-Scale Synthesis of ***3a***. In a dried Schlenk tube containing a magnetic bar, Knölker complex [Fe] (102.0 mg, 0.25 mmol, 5 mol %), Me_3NO (37.5 mg, 0.5 mmol, 10 mol %), 4-nitroanisole **1a** (765.8 mg, 5 mmol, 1 equiv), $K_3PO_4{\cdot}H_2O$ (3.4 g, 15 mmol, 3 equiv), benzylalcohol **2a** (2.1 g, 20 mmol, 4 equiv), and 50 mL of toluene were added successively under an argon atmosphere. Then, the tube was sealed and the mixture was stirred at 140 °C using an oil bath for 48 h. After completion and cooling to room temperature, the resulting solution was filtrated through a pad of neutral alumina and washed with ethyl acetate. The filtrate was collected and concentrated in vacuo. The residue was purified by neutral alumina column chromatography using ethyl acetate/heptane (1:20) as the eluent to afford the desired product **3a** as a white solid (859 mg, 81% yield).

1-Phenyl-N-(p-tolyl)methanimine ***3b***.[35] Following the general procedure, **3b** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:20) as the eluent. Yellow oil (74 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (s, 1H), 8.02−7.94 (m, 2H), 7.56−7.49 (m, 3H), 7.27 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.3 Hz, 2H), 2.44 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 159.6, 149.5, 136.4, 135.8, 131.2, 129.8, 128.8, 128.8, 120.9, 21.1. GC−MS: m/z (%): 195 (M^+, 100), 118 (20), 91 (55), 77 (10), 65 (30), 51 (10).

1-Phenyl-N-(m-tolyl)methanimine ***3c***.[36a] Following the general procedure, **3c** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:20) as the eluent. Yellow oil (66 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47

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(s, 1H), 7.96−7.90 (m, 2H), 7.52−7.46 (m, 3H), 7.30 (t, J = 7.7 Hz, 1H), 7.12−7.00 (m, 3H), 2.42 (s, 3H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$): δ 160.2, 152.2, 139.1, 136.4, 131.4, 129.1, 128.9, 128.8, 126.8, 121.7, 118.0, 21.5. GC−MS: m/z (%): 195 (M^+, 100), 118 (15), 91 (60), 77 (10), 65 (30), 51 (10).

1-Phenyl-N-(o-tolyl)methanimine ***3d***.[23d] Following the general procedure, **3d** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:20) as the eluent. Yellow oil (73 mg, 75%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 8.01−7.95 (m, 2H), 7.58−7.49 (m, 3H), 7.28 (t, J = 8.1 Hz, 2H), 7.19 (t, J = 6.8 Hz, 1H), 6.99 (d, J = 7.8 Hz, 1H), 2.44 (s, 3H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$): δ 159.5, 151.3, 136.6, 132.0, 131.3, 130.4, 128.9, 126.8, 125.8, 117.8, 18.0. GC−MS: m/z (%): 195 (M^+, 60), 118 (100), 91 (45), 65 (40), 51 (10).

N,1-Diphenylmethanimine ***3e***.[23d] Following the general procedure, **3e** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:20) as the eluent. Yellow solid (60 mg, 66%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.50 (s, 1H), 7.99−7.91 (m, 2H), 7.55−7.38 (m, 5H), 7.31−7.23 (m, 3H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$): δ 160.5, 152.2, 136.4, 131.5, 129.3, 128.9, 128.9, 126.1, 121.0. GC−MS: m/z (%): 181 (M^+,75), 152 (5), 104 (20), 77 (100), 51 (40).

N-([1,1′-Biphenyl]-3-yl)-1-phenylmethanimine ***3f***. Following the general procedure, **3f** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:30) as the eluent. Colorless oil (90 mg, 70%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.53 (s, 1H), 7.93 (dd, J = 6.5, 3.0 Hz, 2H), 7.65 (d, J = 7.2 Hz, 2H), 7.53−7.41 (m, 8H), 7.37 (t, J = 7.2 Hz, 1H), 7.24−7.17 (m, 1H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$): δ 160.8, 152.7, 142.5, 141.0, 136.3, 131.6, 129.9, 129.1, 129.0, 129.0, 128.8, 127.6, 124.9, 119.9, 119.7. HR-MS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{16}N^+$, 258.1277; found, 258.1278.

N-(2,6-Dimethylphenyl)-1-phenylmethanimine ***3g***.[36b] Following the general procedure, **3g** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:20) as the eluent. Colorless oil (29 mg, 28%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 1H), 7.98−7.89 (m, 2H), 7.57−7.45 (m, 3H), 7.10−6.93 (m, 3H), 2.16 (s, 6H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$): δ 162.7, 151.3, 136.2, 131.6, 128.9, 128.6, 128.2, 127.3, 123.8, 18.4. GC−MS: m/z (%): 209 (M^+, 50), 193 (15), 132 (100), 117 (20), 89 (10), 77 (40), 51 (15).

4-(Benzylideneamino)-N,N-dimethylaniline ***3h***.[36c] Following the general procedure, **3h** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:20) as the eluent. Brown solid (89 mg, 80%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.53 (s, 1H), 7.89 (dd, J = 7.4, 2.1 Hz, 2H), 7.50−7.40 (m, 3H), 7.28 (d, J = 9.0 Hz, 2H), 6.77 (d, J = 9.0 Hz, 2H), 2.99 (s, 6H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$): δ 156.1, 149.7, 141.0, 137.0, 130.6, 128.8, 128.5, 122.4, 113.0, 40.9. GC−MS: m/z (%): 224 (M^+, 100), 209 (20), 180 (5), 111 (15), 104 (15), 77 (20), 51 (5).

N-(4-Fluorophenyl)-1-phenylmethanimine ***3i***.[23d] Following the general procedure, **3i** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:20) as the eluent. White solid (59 mg, 59%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.94−7.86 (m, 2H), 7.52−7.44 (m, 3H), 7.24−7.17 (m, 2H), 7.09 (t, J = 8.7 Hz, 2H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$): δ 161.4 (d, J = 234 Hz), 160.3, 148.2 (d, J = 2.9 Hz), 136.2, 131.6, 128.93, 128.91, 122.3 (d, J = 8.2 Hz), 116.0 (d, J = 22 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −117.3. GC−MS: m/z (%): 199 (M^+, 100), 151 (5), 122 (20), 95 (60), 75 (35), 51 (15).

N-(4-Chlorophenyl)-1-phenylmethanimine ***3j***.[23d] Following the general procedure, **3j** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:20) as the eluent. White solid (52 mg, 48%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, 1H), 7.93−7.88 (m, 2H), 7.51−7.47 (m, 3H), 7.36 (d, J = 8.7 Hz, 2H), 7.15 (d, J = 8.7 Hz, 2H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$): δ 160.9, 150.7, 136.1, 131.8, 131.6, 129.4, 129.0, 129.0, 122.3. GC−MS: m/z (%): 217 (M^+, 33), 215 (M^+, 100), 180(5), 138 (20), 111 (45), 89 (20), 75 (30), 51 (15).

N-(4-Bromophenyl)-1-phenylmethanimine ***3k***.[36c] Following the general procedure, **3k** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:20) as the eluent. White solid (85 mg, 65%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 1H), 7.90 (m, 2H), 7.55−7.42 (m, 5H), 7.09 (d, J = 8.6 Hz, 2H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$): δ 160.9, 151.2, 136.1, 132.3, 131.8, 129.0, 129.0, 122.7, 119.5. GC−MS: m/z(%) = 261 (M^+, 25), 259 (M^+, 30), 179 (10), 155 (20), 90 (45), 76 (100), 63 (30), 50 (60).

N-(3-Bromophenyl)-1-phenylmethanimine ***3m***.[23d] Following the general procedure, **3m** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:20) as the eluent. White solid (51 mg, 39%). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.44 (s, 1H), 7.90 (dd, J = 7.6, 1.8 Hz, 2H), 7.54−7.47 (m, 3H), 7.37 (m, 2H), 7.29 (t, J = 8.2 Hz, 1H), 7.18−7.14 (m, 1H). $^{13}C\{1H\}$ NMR (101 MHz, CD_2Cl_2): δ 161.8, 154.0, 136.4, 132.1, 130.9, 129.3, 129.2, 129.0, 124.1, 123.0, 120.3. GC−MS: m/z (%): 261 (M^+, 95), 259 (M^+,100), 179 (20), 155 (35), 90 (50), 76 (60), 51 (25).

N-(4-Iodophenyl)-1-phenylmethanimine ***3n***.[37] Following the general procedure, **3n** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:30) as the eluent. Yellow solid (46 mg, 30%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 7.90 (m, 2H), 7.70 (d, J = 8.6 Hz, 2H), 7.54−7.44 (m, 3H), 6.97 (d, J = 8.6 Hz, 2H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$): δ 160.9, 151.8, 138.3, 136.0, 131.8, 129.0, 128.9, 123.1, 90.4. GC−MS: m/z (%): 307 (M^+, 100), 230 (10), 203 (10), 179 (20), 152 (10), 90 (20), 76 (65), 50 (20).

N-(4-(Benzyloxy)phenyl)-1-phenylmethanimine ***3o***. Following the general procedure, **3o** was purified by neutral alumina column chromatography using a mixture of dichloromethane and heptane (1:1) as the eluent. White solid (102 mg, 71%). mp 122 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.50 (s, 1H), 7.96−7.89 (m, 2H), 7.53−7.46 (m, 5H), 7.42 (t, J = 7.2 Hz, 2H), 7.37 (d, J = 7.2 Hz, 1H), 7.27 (d, J = 8.9 Hz, 2H), 7.04 (d, J = 8.9 Hz, 2H), 5.11 (s, 2H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$): δ 158.6, 157.6, 145.3, 137.1, 136.6, 131.1, 128.8, 128.7, 128.1, 127.6, 122.3, 115.5, 70.4. HR-MS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{18}NO^+$, 288.1383; found, 288.1384.

N,N′-(1,4-Phenylene)bis(1-phenylmethanimine) ***3p***.[38] Following the general procedure, **3p** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:10) as the eluent. Gray solid (81 mg, 57%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.52 (s, 2H), 7.96−7.90 (m, 4H), 7.52−7.46 (m, 6H), 7.29 (s, 4H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$): δ 159.9, 150.1, 136.4, 131.5, 128.9, 128.9, 122.0. GC−MS: m/z (%): 284 (M^+, 100), 207 (5), 180 (10), 152 (20), 128 (10), 89 (5), 77 (20), 51 (10).

N,1-Bis(4-Methoxyphenyl)methanimine ***3q***.[29] Following the general procedure, **3q** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:10) as the eluent. White solid (109 mg, 91%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 1H), 7.84 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 8.9 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H), 3.83 (s, 3H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$): δ 162.2, 158.1, 158.0, 145.4, 130.4, 129.6, 122.2, 114.5, 114.3, 55.6, 55.6. GC−MS: m/z (%): 241 (M^+, 90), 226 (100), 154 (20), 121 (15), 92 (10), 77 (15), 64 (10), 51 (5).

Procedure for the Gram-Scale Synthesis of ***3q***. In a dried Schlenk tube containing a magnetic bar, Knölker complex [Fe] (102.0 mg, 0.25 mmol, 5 mol %), Me_3NO (37.5 mg, 0.5 mmol, 10 mol %), 4-nitroanisole **1a** (765.8 mg, 5 mmol, 1 equiv), $K_3PO_4·H_2O$ (3.4 g, 15 mmol, 3 equiv), 4-methoxybenzylalcohol (2.76 g, 20 mmol, 4 equiv), and 50 mL of toluene were added successively under an argon atmosphere. Then, the tube was sealed and the mixture was stirred at 140 °C using an oil bath for 48 h. After completion and cooling to room temperature, the resulting solution was filtrated through a pad of neutral alumina and washed with ethyl acetate. The filtrate was collected and concentrated in vacuo. The residue was purified by neutral alumina column chromatography using ethyl acetate/heptane (1:10) as the eluent to afford the desired product **3q** as a white solid (1.00 g, 83% yield).

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N-(4-Methoxyphenyl)-1-(p-tolyl)methanimine **3r**.[39] Following the general procedure, **3r** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:15) as the eluent. Gray solid (92 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.80 (d, J = 8.1 Hz, 2H), 7.29−7.23 (m, 4H), 6.94 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H), 2.43 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 158.5, 158.2, 145.2, 141.6, 134.0, 129.6, 128.7, 122.3, 114.5, 55.6, 21.7. GC−MS: m/z (%): 225 (M^+, 85), 210 (100), 181 (10), 167 (10), 155 (10), 91 (10), 77 (15), 64 (10), 51 (5).

1-(4-Isopropylphenyl)-N-(4-methoxyphenyl)methanimine **3s**.[40] Following the general procedure, **3s** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:30) as the eluent. White solid (86 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.82 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H), 3.04−2.90 (m, 1H), 1.29 (d, J = 6.9 Hz, 6H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 158.7, 158.3, 152.6, 145.3, 134.3, 128.9, 127.0, 122.3, 114.5, 55.7, 34.4, 24.0. GC−MS: m/z (%): 253 (M^+, 100), 238 (65), 222 (15), 196 (15), 119 (10), 77 (15), 64 (5).

N-(4-Methoxyphenyl)-1-(o-tolyl)methanimine **3t**.[41] Following the general procedure, **3t** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:20) as the eluent. White solid (80 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (s, 1H), 8.07 (dd, J = 7.6, 1.3 Hz, 1H), 7.37−7.27 (m, 2H), 7.23 (d, J = 8.9 Hz, 3H), 6.95 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H), 2.59 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 158.3, 157.3, 145.7, 138.4, 134.5, 131.1, 130.8, 127.8, 126.5, 122.3, 114.5, 55.7, 19.5. GC−MS: m/z (%): 225 (M^+, 50), 208 (100), 194 (20), 180 (15), 165 (35), 116(65), 77 (55), 64 (30), 51 (15).

1-(4-Fluorophenyl)-N-(4-methoxyphenyl)methanimine **3u**.[39] Following the general procedure, **3u** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:20) as the eluent. Gray solid (90 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, 1H), 7.91−7.87 (m, 2H), 7.23 (d, J = 8.9 Hz, 2H), 7.17−7.13 (m, 2H), 6.94 (d, J = 8.9 Hz, 2H), 3.83 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 164.6 (d, J = 251.6 Hz), 158.5, 156.9, 144.8, 133.0 (d, J = 3.1 Hz), 130.6 (d, J = 8.7 Hz), 122.3, 116.0 (d, J = 22.0 Hz), 114.5, 55.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ −108.7. GC−MS: m/z (%): 229 (M^+, 90), 214 (100), 185 (25), 159 (10), 133 (5), 107 (10), 92 (5), 77 (10), 64 (10), 51 (5).

1-(2-Fluorophenyl)-N-(4-methoxyphenyl)methanimine **3v**.[42] Following the general procedure, **3v** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:20) as the eluent. Brown oil (39 mg, 34%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (s, 1H), 8.18 (td, J = 7.6, 1.7 Hz, 1H), 7.43 (td, J = 7.3, 1.8 Hz, 1H), 7.29−7.21 (m, 3H), 7.12 (m, 1H), 6.94 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 162.9 (d, J = 253.0 Hz), 158.7, 151.4 (d, J = 4.9 Hz), 144.9, 132.6 (d, J = 5.8 Hz), 127.8 (d, J = 2.7 Hz), 124.6 (d, J = 3.5 Hz), 124.4 (d, J = 9.0 Hz), 122.5, 115.9 (d, J = 21.1 Hz), 114.5, 55.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ −121.5. GC−MS: m/z (%): 229 (M^+, 85), 214 (100), 185 (25), 159 (5), 133 (10), 92 (10), 77 (15), 64 (15), 50 (5).

1-(4-Chlorophenyl)-N-(4-methoxyphenyl)methanimine **3w**.[39] Following the general procedure, **3w** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:20) as the eluent. White solid (106 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, 1H), 7.83 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.9 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 158.6, 156.8, 144.6, 137.1, 135.1, 129.9, 129.2, 122.4, 114.6, 55.7. GC−MS: m/z (%): 247 (M^+, 35), 245 (M^+, 100), 230 (100), 201 (10), 167 (20), 77 (15), 64 (15).

1-(2-Chlorophenyl)-N-(4-methoxyphenyl)methanimine **3x**.[43] Following the general procedure, **3x** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:20) as the eluent. Yellow oil (109 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.95 (s, 1H), 8.24 (dd, J = 7.1, 2.4 Hz, 1H), 7.44−7.33 (m, 3H), 7.29 (d, J = 8.9 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 158.8, 154.8, 144.8, 135.9, 133.6, 131.9, 130.0, 128.5, 127.2, 122.7, 114.7, 55.6. GC−MS: m/z (%): 247 (M^+, 35), 245 (M^+, 90), 230 (100), 167 (20), 92 (10), 77 (15), 64 (10), 51 (5).

1-(2-Bromophenyl)-N-(4-methoxyphenyl)methanimine **3y**.[44] Following the general procedure, **3y** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:20) as the eluent. Brown solid (125 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (s, 1H), 8.25 (dd, J = 7.8, 1.7 Hz, 1H), 7.63 (dd, J = 8.0, 1.0 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 7.35−7.29 (m, 3H), 6.98 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 158.8, 157.2, 144.6, 134.9, 133.3, 132.1, 128.9, 127.8, 126.0, 122.7, 114.6, 55.6. GC−MS: m/z (%): 291 (M^+, 95), 289 (M^+, 100) 275 (80), 167 (50), 139 (20), 77 (20), 63 (20), 51 (10).

N-(4-Methoxyphenyl)-1-(4-(trifluoromethyl)phenyl)methanimine **3z**.[42] Following the general procedure, **3z** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:15) as the eluent. White solid (113 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (s, 1H), 8.00 (d, J = 8.2 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.9 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 159.0, 156.4, 144.2, 139.7, 132.5 (q, J = 32.3 Hz), 128.8, 125.8 (q, J = 3.8 Hz), 124.1 (q, J = 273.0 Hz), 122.5, 114.6, 55.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.8. GC−MS: m/z (%): 279 (M^+, 85), 264 (100), 235 (10), 209, (5), 167 (10), 134 (10), 92 (10), 77 (15), 64 (15), 50 (5).

4-(((4-Methoxyphenyl)imino)methyl)benzonitrile **3aa**.[43] Following the general procedure, **3aa** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:10) as the eluent. Gray solid (57 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (s, 1H), 7.99 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.9 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 3.85 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 159.2, 155.5, 143.8, 140.4, 132.6, 129.0, 122.7, 118.7, 114.7, 114.1, 55.7. GC−MS: m/z (%): 236 (M^+, 85), 221 (100), 192 (20), 140 (10), 92 (10), 77 (15), 64 (15), 50 (5).

N-(4-Methoxyphenyl)-3-phenylprop-2-en-1-imine **3ab**.[45] Following the general procedure, **3ab** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:10) as the eluent. Gray solid (69 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (m, 1H), 7.53 (dd, J = 7.7, 0.7 Hz, 2H), 7.42−7.30 (m, 3H), 7.25−7.07 (m, 4H), 6.92 (d, J = 8.9 Hz, 2H), 3.82 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 159.6, 158.5, 144.7, 143.1, 135.9, 129.5, 129.0, 128.9, 127.5, 122.3, 114.5, 55.6. GC−MS: m/z (%): 237 (M^+, 100), 193 (10), 115 (55), 77 (20), 64 (10).

N-(4-Methoxyphenyl)-1-(pyridin-2-yl)methanimine **3ac**.[46] Following the general procedure, **3ac** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:10) as the eluent. Brown oil (75 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (m, 1H), 8.62 (s, 1H), 8.18 (d, J = 7.9 Hz, 1H), 7.78 (m, 1H), 7.35−7.28 (m, 3H), 6.94 (d, J = 8.9 Hz, 2H), 3.83 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 159.1, 158.3, 155.0, 149.7, 143.8, 136.7, 124.9, 122.8, 121.7, 114.6, 55.6. GC−MS: m/z (%): 212 (M^+, 100), 197 (30), 170 (25), 142 (20), 92 (25), 79 (45), 64 (25), 52 (15).

1-(Furan-2-yl)-N-(4-methoxyphenyl)methanimine **3ad**.[43] Following the general procedure, **3ad** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:10) as the eluent. Brown solid (69 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (s, 1H), 7.60 (d, J = 1.5 Hz, 1H), 7.27 (d, J = 9.0 Hz, 2H), 6.97−6.88 (m, 3H), 6.55 (dd, J = 3.4, 1.8 Hz, 1H), 3.83 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 158.5, 152.4, 145.8, 145.4, 144.3, 122.4, 115.6, 114.5, 112.2, 55.5. GC−MS: m/z (%): 201 (M^+, 90), 186 (100), 157 (10), 130 (10), 103 (10), 92 (10), 77 (20), 64 (10), 51 (10).

N-(4-Methoxyphenyl)-1-(thiophen-2-yl)methanimine **3ae**.[47] Following the general procedure, **3ae** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:20) as the eluent. Brown solid (73 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (s, 1H), 7.47 (m, 2H), 7.23 (d, J = 8.9 Hz, 2H), 7.12 (dd, J = 5.0, 3.7 Hz, 1H), 6.92 (d, J = 8.9 Hz, 2H), 3.83 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 158.4, 151.2, 144.5, 143.3,

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131.7, 129.9, 127.8, 122.4, 114.5, 55.6. GC−MS: m/z (%): 217 (M^+, 85), 202 (100), 173 (25), 147 (10), 77 (10), 64 (15), 51 (10).

1-(Furan-2-yl)-N-phenylmethanimine ***3af***.[27b] Following the general procedure, **3af** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:10) as the eluent. Yellow oil (50 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (s, 1H), 7.62 (d, J = 1.5 Hz, 1H), 7.43−7.34 (m, 2H), 7.26−7.20 (m, 3H), 6.96 (d, J = 3.4 Hz, 1H), 6.56 (dd, J = 3.4, 1.8 Hz, 1H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 152.2, 151.5, 147.9, 145.8, 129.3, 126.4, 121.1, 116.4, 112.3. GC−MS: m/z (%): 171 (M^+, 100), 142 (40), 115 (35), 77 (90), 51 (50).

N-Phenyl-1-(thiophen-2-yl)methanimine ***3ag***.[23c] Following the general procedure, **3ag** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:10) as the eluent. Yellow oil (69 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 1H), 7.55−7.46 (m, 2H), 7.42−7.36 (m, 2H), 7.26−7.20 (m, 3H), 7.14 (dd, J = 5.0, 3.7 Hz, 1H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 153.1, 151.5, 143.0, 132.3, 130.4, 129.2, 127.8, 126.1, 121.1. GC−MS: m/z (%): 187 (M^+, 100), 115 (10), 93 (10), 77 (65), 51 (30).

N-(4-(Benzyloxy)phenyl)-1-(furan-2-yl)methanimine ***3ah***. Following the general procedure, **3ah** was purified by neutral alumina column chromatography using a mixture of ethyl acetate and heptane (1:20) as the eluent. White solid (94 mg, 68%). mp 93 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (s, 1H), 7.60 (d, J = 1.1 Hz, 1H), 7.47−7.32 (m, 5H), 7.28−7.23 (m, 2H), 7.00 (d, J = 8.9 Hz, 2H), 6.91 (d, J = 3.4 Hz, 1H), 6.54 (dd, J = 3.4, 1.7 Hz, 1H), 5.08 (s, 2H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 157.8, 152.4, 146.0, 145.5, 144.6, 137.0, 128.7, 128.1, 127.6, 122.4, 115.7, 115.5, 112.2, 70.4. HR-MS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{16}NO_2^+$, 278.1176; found, 278.1172.

N-(4-(Benzyloxy)phenyl)-1-(thiophen-2-yl)methanimine ***3ai***. Following the general procedure, **3ai** was purified by neutral alumina column chromatography using a mixture of dichloromethane and heptane (1:1) as the eluent. White solid (71 mg, 48%). mp 117 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (s, 1H), 7.55−7.27 (m, 7H), 7.22 (d, J = 8.9 Hz, 2H), 7.12 (dd, J = 5.0, 3.7 Hz, 1H), 6.99 (d, J = 8.9 Hz, 2H), 5.08 (s, 2H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 157.6, 151.3, 144.7, 143.3, 137.1, 131.7, 129.9, 128.7, 128.1, 127.8, 127.6, 122.4, 115.5, 70.4. HR-MS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{16}NOS^+$, 294.0947; found, 294.0949.

General Procedure for the Synthesis of Benzimidazole Derivatives 6. A typical procedure for the Fe-catalyzed reductive coupling of *ortho*-nitroaniline derivatives with alcohols is as follows: in a dried Schlenk tube containing a magnetic bar, Knölker complex [Fe] (10.2 mg, 0.025 mmol, 5 mol %), Me_3NO (3.8 mg, 0.05 mmol, 10 mol %), *ortho*-nitroaniline derivatives **5** (0.5 mmol, 1 equiv), $K_3PO_4{\cdot}H_2O$ (115.1 mg, 0.5 mmol, 1 equiv), alcohols **2** (2 mmol, 4 equiv), and 3 mL of mesitylene were added successively under an argon atmosphere. Then, the tube was sealed and the mixture was stirred at 160 °C using an oil bath for 15 h. After addition of DDQ (56.8 mg, 0.25 mmol, 0.5 equiv) to the mixture under the flow of argon at room temperature, the tube was sealed again and heated at 160 °C for 24 h. After cooling, the mixture was filtrated through a pad of Celite and washed with dichloromethane or ethyl acetate. The filtrate was collected and concentrated in vacuo. The residue was purified by silica gel column chromatography using ethyl acetate/heptane as the eluent to afford the desired product **6**.

2-Phenyl-1H-benzo[d]imidazole ***6a***.[33b] Following the general procedure, **6a** was purified by silica gel column chromatography using a mixture of ethyl acetate and heptane (1:5) as the eluent. White solid (62 mg, 64%). ^{1}H NMR (400 MHz, DMSO): δ 12.93 (s, 1H), 8.20 (d, J = 7.1 Hz, 2H), 7.79−7.43 (m, 5H), 7.21 (m, 2H). ^{13}C{1H} NMR (101 MHz, DMSO): δ 151.3, 144.1, 135.4, 130.2, 129.9, 129.0, 126.5, 122.2, 122.1, 119.0, 111.4. GC−MS: m/z (%): 194 (M^+, 100), 166 (5), 97 (10), 77 (10), 63 (15).

5,6-Dimethyl-2-phenyl-1H-benzo[d]imidazole ***6b***.[33b] Following the general procedure, **6b** was purified by silica gel column chromatography using a mixture of ethyl acetate and heptane (1:5) as the eluent. White solid (72 mg, 65%). ^{1}H NMR (400 MHz, DMSO): δ 12.64 (s, 1H), 8.14 (d, J = 7.3 Hz, 2H), 7.52 (t, J = 7.3 Hz, 2H), 7.48−7.26 (m, 3H), 2.33 (s, 3H), 2.31 (s, 3H). ^{13}C{1H} NMR (101 MHz, DMSO): δ 150.3, 142.5, 133.5, 131.1, 130.5, 129.9, 129.4, 128.8, 126.1, 118.9, 111.3, 20.0. GC−MS: m/z (%): 222 (M^+, 100), 207 (50), 111 (10), 103 (10), 91 (25), 77 (15), 65 (10), 51 (10).

2-(4-Methoxyphenyl)-5,6-dimethyl-1H-benzo[d]imidazole ***6c***.[48] Following the general procedure, **6c** was purified by silica gel column chromatography using a mixture of ethyl acetate and heptane (1:5) as the eluent. White solid (91 mg, 72%). ^{1}H NMR (400 MHz, DMSO): δ 12.46 (s, 1H), 8.08 (d, J = 8.9 Hz, 2H), 7.32 (m, 2H), 7.08 (d, J = 8.9 Hz, 2H), 3.83 (s, 3H), 2.31 (s, 6H). ^{13}C{1H} NMR (101 MHz, DMSO): δ 160.3, 150.5, 130.3, 127.8, 123.0, 114.3, 55.3, 20.0. GC−MS: m/z (%): 252 (M^+, 100), 237 (50), 209 (20), 126 (15), 91 (10), 65 (5).

General Procedure for the Synthesis of Quinoxaline Derivatives 8. A typical procedure for the Fe-catalyzed reductive coupling of *ortho*-nitroaniline derivatives with diols is as follows: in a dried Schlenk tube containing a magnetic bar, Knölker complex [Fe] (10.2 mg, 0.025 mmol, 5 mol %), Me_3NO (3.8 mg, 0.05 mmol, 10 mol %), *ortho*-nitroaniline derivatives **5** (0.5 mmol, 1 equiv), $K_3PO_4{\cdot}H_2O$ (345.4 mg, 1.5 mmol, 3 equiv), diols **7** (1.5 mmol, 3 equiv), and 2.5 mL of toluene were added successively under an argon atmosphere. Then, the tube was sealed and the reaction mixture was heated at 150 °C using an oil bath for 48 h. After that, the resulting solution was filtrated through a pad of neutral alumina and washed with dichloromethane or ethyl acetate. The filtrate was collected and concentrated in vacuo. The residue was purified by silica gel column chromatography using ethyl acetate/heptane as the eluent to afford the desired product **8**.

2-Phenylquinoxaline ***8a***.[33b] Following the general procedure, **8a** was purified by silica gel column chromatography using a mixture of ethyl acetate and heptane (1:10) as the eluent. White solid (83 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.33 (s, 1H), 8.24−8.09 (m, 4H), 7.81−7.71 (m, 2H), 7.60−7.49 (m, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 151.9, 143.4, 142.4, 141.7, 136.9, 130.4, 130.3, 129.7, 129.6, 129.2, 127.6. GC−MS: m/z (%): 206 (M^+, 100), 179 (35), 152 (5), 103 (25), 76 (45), 50 (25).

6,7-Dimethyl-2-phenylquinoxaline ***8b***.[33b] Following the general procedure, **8b** was purified by silica gel column chromatography using a mixture of ethyl acetate and heptane (1:10) as the eluent. White solid (97 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.21 (s, 1H), 8.16 (d, J = 7.0 Hz, 2H), 7.90 (s, 1H), 7.84 (s, 1H), 7.60−7.46 (m, 3H), 2.50 (s, 6H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 151.1, 142.5, 141.4, 140.9, 140.7, 140.2, 137.3, 129.9, 129.2, 128.8, 128.3, 127.5, 20.5, 20.5. GC−MS: m/z (%): 234 (M^+, 100), 219 (15), 207 (15), 192 (10), 117 (15), 103 (30), 77 (25), 63 (10), 51 (10).

2,3-Diphenylquinoxaline ***8c***.[33b] Following the general procedure, **8c** was purified by silica gel column chromatography using a mixture of ethyl acetate and heptane (1:20) as the eluent. White solid (134 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (dd, J = 6.4, 3.4 Hz, 2H), 7.77 (dd, J = 6.4, 3.4 Hz, 2H), 7.54 (dd, J = 7.6, 1.7 Hz, 4H), 7.38−7.30 (m, 6H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 153.5, 141.3, 139.2, 130.0, 129.9, 129.3, 128.9, 128.4. GC−MS: m/z (%): 282 (M^+, 100), 205 (5), 179 (35), 140 (20), 76 (45), 50 (30).

6,7-Dimethyl-2,3-diphenylquinoxaline ***8d***.[23d] Following the general procedure, **8d** was purified by silica gel column chromatography using a mixture of ethyl acetate and heptane (1:20) as the eluent. White solid (149 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 2H), 7.55−7.47 (m, 4H), 7.36−7.29 (m, 6H), 2.52 (s, 6H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 152.6, 140.6, 140.3, 139.5, 130.0, 128.6, 128.3, 128.3, 20.5. GC−MS: m/z (%): 310 (M^+, 100), 295 (5), 207 (5), 192 (5), 155 (15), 103 (30), 77 (15), 51 (5).

6-Fluoro-2,3-diphenylquinoxaline ***8e***.[49] Following the general procedure, **8e** was purified by silica gel column chromatography using a mixture of dichloromethane and heptane (1:1) as the eluent. White solid (107 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (dd, J = 9.2, 5.8 Hz, 1H), 7.81 (dd, J = 9.2, 2.7 Hz, 1H), 7.58−7.48 (m, 5H), 7.39−7.31 (m, 6H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 164.2, 161.7, 154.3, 152.9 (d, J = 3.2 Hz), 142.1 (d, J = 13.3 Hz), 138.9, 138.8, 138.5 (d, J = 0.6 Hz), 131.4 (d, J = 10.1 Hz), 129.9, 129.9, 129.1, 129.0, 128.4, 120.4 (d, J = 26.0 Hz), 112.7 (d, J = 21.5 Hz). ^{19}F

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NMR (376 MHz, $CDCl_3$): δ −108.1. GC−MS: m/z (%): 300 (M^+, 100), 197 (35), 170 (10), 150 (20), 103 (10), 94 (30), 77 (15), 51 (10).

1,2,3,4-Tetrahydrophenazine ***8f***.[50] Following the general procedure, **8f** was purified by silica gel column chromatography using a mixture of ethyl acetate and heptane (1:5) as the eluent. Brown solid (55 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01−7.91 (m, 2H), 7.69−7.60 (m, 2H), 3.20−3.11 (m, 4H), 2.05−2.00 (m, 4H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 154.3, 141.3, 129.0, 128.5, 33.3, 22.9. GC−MS: m/z (%): 184 (M^+, 100), 169 (30), 156 (10), 129 (10), 102 (15), 77 (15), 50 (15).

7,8-Dimethyl-1,2,3,4-tetrahydrophenazine ***8g***.[50] Following the general procedure, **8g** was purified by silica gel column chromatography using a mixture of ethyl acetate and heptane (1:5) as the eluent. White solid (72 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (s, 2H), 3.13−3.05 (m, 4H), 2.42 (s, 6H), 2.02−1.95 (m, 4H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 153.0, 140.2, 139.3, 127.5, 33.2, 23.0, 20.4. GC−MS: m/z (%): 212 (M^+, 100), 197 (25), 103 (15), 77 (20), 51 (10).

Procedure for the Gram-Scale Synthesis of ***8g***. In a dried Schlenk tube containing a magnetic bar, Knölker complex [Fe] (102.0 mg, 0.25 mmol, 5 mol %), Me_3NO (37.5 mg, 0.5 mmol, 10 mol %), 3,4-dimethyl-6-nitroaniline (830.9 mg, 5 mmol, 1 equiv), $K_3PO_4{\cdot}H_2O$ (3.4 mg, 15 mmol, 3 equiv), cyclohexane-1,2-diol (1.74 g, 15 mmol, 3 equiv), and 25 mL of toluene were added successively under an argon atmosphere. Then, the tube was sealed and the reaction mixture was heated at 150 °C using an oil bath for 48 h. After that, the resulting solution was filtrated through a pad of neutral alumina and washed with ethyl acetate. The filtrate was collected and concentrated in vacuo. The residue was purified by silica gel column chromatography using ethyl acetate/heptane (1:5) as the eluent to afford the desired product **8g** as a white solid (696 mg, 66% yield).

6-Methyl-1,2,3,4-tetrahydrophenazine ***8h***.[50] Following the general procedure, **8h** was purified by silica gel column chromatography using a mixture of ethyl acetate and heptane (1:10) as the eluent. White solid (60 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.2 Hz, 1H), 7.54−7.48 (m, 1H), 7.45 (d, J = 6.9 Hz, 1H), 3.19−3.09 (m, 4H), 2.74 (s, 3H), 2.04−1.96 (m, 4H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 153.5, 153.0, 141.3, 140.6, 136.7, 128.9, 128.6, 126.3, 33.5, 33.2, 23.0, 17.3. GC−MS: m/z (%): 198 (M^+, 100), 183 (15), 169 (10), 116 (10), 89 (30), 77 (10), 63 (15), 51 (10).

7-Methyl-1,2,3,4-tetrahydrophenazine ***8i***.[50] Following the general procedure, **8i** was purified by silica gel column chromatography using a mixture of ethyl acetate and heptane (1:5) as the eluent. Brown solid (69 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 8.5 Hz, 1H), 7.68 (s, 1H), 7.43 (dd, J = 8.5, 1.7 Hz, 1H), 3.09 (s, 4H), 2.50 (s, 3H), 2.01−1.94 (m, 4H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 153.9, 153.1, 141.3, 139.7, 139.2, 131.2, 127.9, 127.3, 33.2, 33.1, 22.9, 21.8. GC−MS: m/z (%): 198 (M^+, 100), 183 (25), 170 (10), 116 (10), 89 (35), 77 (15), 63 (15), 51 (10).

7,8-Dichloro-1,2,3,4-tetrahydrophenazine ***8j***. Following the general procedure, **8j** was purified by silica gel column chromatography using a mixture of ethyl acetate and heptane (1:5) as the eluent. White solid (61 mg, 48%). mp 180 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 2H), 3.15−3.10 (m, 4H), 2.05−2.00 (m, 4H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 155.8, 140.2, 133.5, 129.3, 33.4, 22.8. HR-MS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{11}N_2Cl_2^+$, 253.0294; found, 253.0293.

7-Bromo-1,2,3,4-tetrahydrophenazine ***8k***.[51] Following the general procedure, **8k** was purified by silica gel column chromatography using a mixture of ethyl acetate and heptane (1:10) as the eluent. Brown solid (37 mg, 28%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 2.1 Hz, 1H), 7.82 (d, J = 8.9 Hz, 1H), 7.72 (dd, J = 8.9, 2.1 Hz, 1H), 3.18−3.11 (m, 4H), 2.08−2.01 (m, 4H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 155.4, 154.8, 142.0, 140.1, 132.6, 130.9, 129.8, 122.8, 33.3, 22.8. GC−MS m/z (%): 264 (M^+, 95), 262 (M^+, 100), 247 (20), 236 (5), 182 (20), 168 (10), 155(20), 75 (50), 50 (20).

6,7-Dimethylquinoxaline ***8l***.[52] Following the general procedure with *t*-BuOK (0.5 mmol, 56 mg, 1 equiv) as the substituent, **8l** was purified by silica gel column chromatography using a mixture of ethyl acetate and heptane (1:5) as the eluent. White solid (33 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (s, 2H), 7.83 (s, 2H), 2.48 (s, 6H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 144.2, 142.1, 140.8, 128.6, 20.5. GC−MS m/z (%): 158 (M^+, 100), 143 (60), 104 (25), 77 (15), 63 (10), 51 (10).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02505.

Optimization procedures, NMR spectra, and HR-MS spectra (PDF)

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Notes

The authors declare no competing financial interest.

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