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Phosphine ligand-free $RuCl_3$-catalyzed reductive N-alkylation of aryl nitro compounds

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ABSTRACT

Without using any additional ligands, $RuCl_3$ efficiently catalyses the reductive N-alkylation of aryl nitro compounds with alcohols using bio-based glycerol as the hydrogen source and without the need for any added solvents. The reaction can be easily manipulated to produce either imines or secondary amines in high yields. $RuCl_3$-catalyzed reductive N-alkylation of nitroarenes with alcohols affords the corresponding imine products in good to excellent yields. Under the same reaction conditions, the one-pot sequential reaction of nitroarenes with alcohols and glycerol also gives amines in higher yields.

1. Introduction

N-substituted amines are an important class of compounds in the pharmaceutical and agrochemical industries.[1–3] Reactions for their synthesis include alkylation of amines with alkyl halides,[4–6] direct reductive amination of ketones and aldehydes[7,8] and hydroamination of unsaturated hydrocarbons with amines.[9–13] These methods generally require environmentally harmful organic solvents, alkyl halides and/or stoichiometric quantities of reducing agents. In recent decades, much attention has focused on the use of inexpensive and low toxicity alcohols as the alkylation reagent.[14–27] The N-alkylation of anilines with alcohols using 'borrowing hydrogen (BH)' methodology,[20,28–33] in which water is the only byproduct, is an environmentally benign method for preparing N-functionalized anilines. Catalysts based on Ru, Ir, Rh, Au, Ag, Cu, Fe, Ni, Os and Pd have been developed for this coupling reaction.[34–37] However, aromatic amines are genotoxic and are therefore undesirable potential impurities in the product. Recently, the metal catalyzed synthesis of N-alkylated anilines using nitro compounds as the nitrogen source has attracted particular attention because nitrobenzenes are inexpensive, stable and readily available.[38–40] Some hydrogen transfer catalysts, particularly of Ru, have been screened for the synthesis of imines and secondary and tertiary amines from nitroarenes, using alcohols as the reducing and alkylation reagents. These methods involve toxic phosphine ligands and very excess alcohol. Deng and Li et al. reported the reaction of nitroarenes and primary alcohols could yield secondary and tertiary amines, which was catalyzed by $[Ru(acac)_3]$/dppe (dppe=1,2-bis(diphenylphosphino)ethane) or $Ru(CO)(H)_2(PPh_3)_3$/NHC (NHC=1,3-dimesitylimidazolium chloride).[41,42] Shi and co-workers demonstrated the controllable synthesis of mono- and di-substituted amines from nitrobenzenes with alcohols using $RuCl_3/PPh_3$ or $[\{Ru(p\text{-cymene})Cl_2\}_2]$/dppb (dppb=1,2-bis(diphenylphosphanyl)benzene).[43,44] Liu and co-workers prepared secondary amines from nitroarenes and alcohols in the presence of $(P{-}N)Ru(CO)_2Cl_2$ (P–N=*o*-(diphenylphosphino)aniline) or $(PNO)Ru(CO)_2Cl$ (PNO=2-(((2-(diphenylphosphanyl)phenyl)imino)methyl)phenol).[45,46] Viswanathamurthi and co-workers found ruthenium(II) carbonyl complexes with phosphine-functionalized type thiosemicarbazone ligands such as $[RuCl(CO)(PPh_3)(PNS\text{-}Me)]$ (PNS–Me=2-(2-(diphenylphosphino)benzylidene)-*N*-methylthiosemicarbazone) were efficient and versatile N-alkylation catalysts.[47] Zhang et al. reported the synthesis of quinolines from α-2-nitroaryl alcohols and alcohols using $Ru_3(CO)_{12}$/dppf as the catalyst or 2-nitroanilines and vicinal diols

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using $Ru_3(CO)_{12}$/dppp as the catalyst.[48,49] However, despite their versatility as ligands for stabilizing low valent metal transition states and intermediates, phosphines are often toxic, moisture and air sensitive and hard to separate from the organic products. Nano-Ru/Fe_3O_4[50] and $Ru(OH)_3$–Fe_3O_4[51] have been successfully employed as catalysts for the N-alkylation of amines, sulfonamides, sulfinamides, and nitroarenes using alcohols as the electrophile, which involve a large excess of alcohol. Very recently, Bera et al. have found that a hydroxy appendage substituted on the naphthyridine unit can promote the dehydrogenative coupling of alcohols with amines catalyzed by diruthenium complexes of naphthyridine-functionalized *N*-heterocyclic carbene (NHC) ligands.[52] Can, therefore, the alcohol substrates themselves work as labile ligands to accelerate Ru-catalyzed coupling of nitroarenes and alcohols?

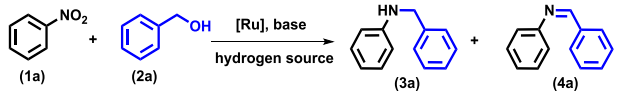
In general, excess alcohol is used in these reductive N-alkylations of aryl nitro compounds. The utilization of renewable biomass derivatives as the hydrogen source represents a more sustainable alternative.[53–55] Among various possible biomass derived alcohols, glycerol is now a readily available and cheap resource and has received much attention as a green solvent and reagent. Glycerol can be converted to various fuel units and is used as a starting substrate for 'bio'-hydrogen production via aqueous-phase reforming. Glycerol has been utilized as an environmentally benign hydrogen source for the reduction of various functional groups such as benzaldehyde, acetophenone, nitroarenes and several unfunctionalized olefins.[56–61] Herein, we present our findings of N-alkylation of nitro/imine compounds catalyzed by $RuCl_3$, using renewable glycerol as the hydrogen source in the absence of any additional organic ligands and solvents.

2. Results and discussion

Our initial investigations focused on the N-alkylation reaction of commercially available and inexpensive nitrobenzene (**1a**) and benzyl alcohol (**2a**) using the borrowing hydrogen strategy (Table 1). When **1a** (1.0 mmol) was reacted with excess **2a** (3.0 mmol) in the presence of 3.0 mol % $RuCl_2(PPh_3)_3$ as catalyst and stoichiometric K_2CO_3, none of the desired compound N-benzylaniline (**3a**) was formed, as determined by GC analysis. Instead, the compound 1-diphenylmethanimine (**4a**) was formed as the major product (98%) together with a large amount of benzaldehyde (Table 1, entry 1). This preliminary result implied that $RuCl_3$ could catalyse the formation of imine without extra organic ligands. Most importantly, it prompted us to suspect that the amine could also be obtained under suitably modified conditions. Subsequently, different ruthenium salts were investigated with this reaction under a nitrogen atmosphere (Table 1, entries 2–4). None of the desired product **3a** was observed when $Ru_3(CO)_{12}$, $[Ru(p\text{-cymene})Cl_2]_2$ or $RuCl_3\cdot 3H_2O$ was used as the catalyst, but **4a** was obtained in moderate to excellent yields (49%–99%). Bases such as carbonates, hydroxides alkoxides and phosphates worked approximately equally well (Table 1, entries 5–10). Reaction with triethylamine (Table 1, entry 11) also provided **4a**, but in a reduced yield under these conditions. Increasing the amount of benzyl alcohol did not increase reduction of imine to amine (Table 1, entry 12). However, less than three equivalents of benzyl alcohol decreased the yield of imine **4a**, approximately proportionately (entries 13–15).

Since excess benzyl alcohol could not further reduce imine to amine in our catalytic system, we wondered if an additional

Table 1
Optimizing the reaction conditions for the synthesis of amine and imine



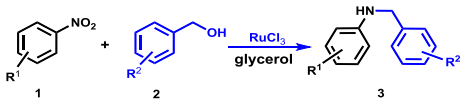
Entry[a]	Cat.	**1a**/**2a** (mol/mol)	Additive	Base	Yield of **3a** (%)[c]	Yield of **4a** (%)[c]
1	$RuCl_2(PPh_3)_3$	1/3		K_2CO_3	—	98
2	$Ru_3(CO)_{12}$	1/3		K_2CO_3	Trace	49
3	$[Ru(p\text{-cymene})Cl_2]_2$	1/3		K_2CO_3	Trace	71
4	$RuCl_3\cdot 3H_2O$	1/3		K_2CO_3	—	99
5	$RuCl_3\cdot 3H_2O$	1/3		NaOH	Trace	92
6	$RuCl_3\cdot 3H_2O$	1/3		KOH	Trace	90
7	$RuCl_3\cdot 3H_2O$	1/3		K_3PO_4	Trace	82
8	$RuCl_3\cdot 3H_2O$	1/3		Cs_2CO_3	—	98
9	$RuCl_3\cdot 3H_2O$	1/3		^tBuOK	—	98
10	$RuCl_3\cdot 3H_2O$	1/3		EtONa	Trace	87
11	$RuCl_3\cdot 3H_2O$	1/3		Et_3N	Trace	62
12	$RuCl_3\cdot 3H_2O$	1/10		K_2CO_3	—	99
13	$RuCl_3\cdot 3H_2O$	1/2		K_2CO_3	Trace	82
14	$RuCl_3\cdot 3H_2O$	1/1.5		K_2CO_3	Trace	63
15	$RuCl_3\cdot 3H_2O$	1/1		K_2CO_3	Trace	45
16	$RuCl_3\cdot 3H_2O$	1/3	Glycerol	K_2CO_3	84	Trace
17	$RuCl_3\cdot 3H_2O$	1/3	2-Propanol	K_2CO_3	Trace	Trace
18	$RuCl_3\cdot 3H_2O$	1/3	Pinacol	K_2CO_3	Trace	Trace
19	$RuCl_3\cdot 3H_2O$	1/3	Glycerol	NaOH	32	67
20	$RuCl_3\cdot 3H_2O$	1/3	Glycerol	KOH	30	69
21	$RuCl_3\cdot 3H_2O$	1/3	Glycerol	^tBuOK	81	Trace
22	$RuCl_3\cdot 3H_2O$	1/3	Glycerol	EtONa	53	38
23	$RuCl_3\cdot 3H_2O$	1/3	Glycerol	K_3PO_4	6	87
24	$RuCl_3\cdot 3H_2O$	1/3	Glycerol	Cs_2CO_3	69	Trace
25	$RuCl_3\cdot 3H_2O$	1/3	Glycerol	Et_3N	3	89
26[b]	$RuCl_3\cdot 3H_2O$	1/3	Glycerol	K_2CO_3	85	Trace
27	$RuCl_3\cdot 3H_2O$	1/2	Glycerol	K_2CO_3	83	Trace
28	$RuCl_3\cdot 3H_2O$	1/1.5	Glycerol	K_2CO_3	84	Trace
29	$RuCl_3\cdot 3H_2O$	1/1.2	Glycerol	K_2CO_3	61	Trace
30	$RuCl_3\cdot 3H_2O$	1/1	Glycerol	K_2CO_3	45	1

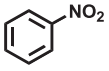
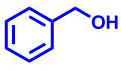
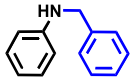
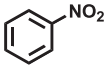
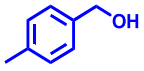
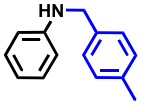
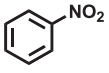
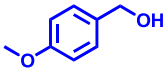
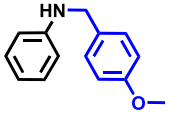
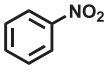
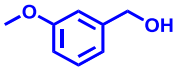
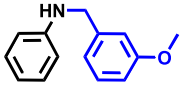
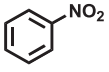
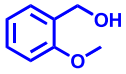
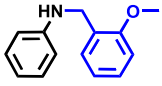
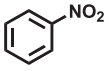
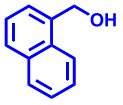
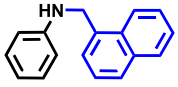
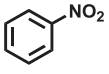
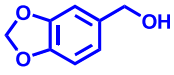
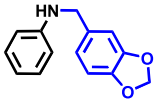
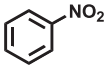
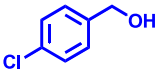
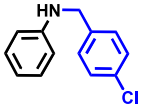
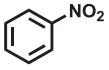
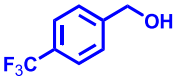
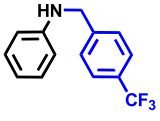
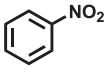
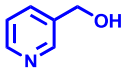
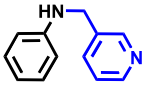
[a] Reaction conditions: 1.0 mmol nitrobenzene, benzyl alcohol, 3 mol % catalyst, 1.0 mmol base, 10 mmol additive, under nitrogen atmosphere, at 130 °C, for 24 h.
[b] At 150 °C.
[c] GC yield.

hydrogen source was needed. We investigated three alcohols in this respect, glycerol, 2-propanol and pinacol but glycerol was the only one that successfully reduced N-alkylation of nitrobenzene to amine under our conditions. When 10 mmol of glycerol was added into the system, 84% of **3a** was obtained (Table 1, entries 16–18). Encouraged by these results, we looked to optimize the reaction conditions. The influence of different bases was evaluated as before. Both K_3PO_4 and Et_3N were beneficial to the formation of imine (Table 1, entries 23 and 25) but not amine. However, when ^tBuOK, EtONa and Cs_2CO_3, were used, the yields of **3a** were 81%, 53% and 69%, respectively (Table 1, entries 21, 22 and 24). When the reaction temperature was raised to 150 °C, the yield of **3a** was not significantly improved (Table 1, entries 16 and 26). It is noted that the **2a**/**1a** ratio could be reduced from 3 to 1.5 without affecting the product yields (Table 1, entries 27 and 28). Upon decreasing the **2a**/**1a** ratio from 1.5 to 1, the yield of **3a** decreased (Table 1, entries 29 and 27–30). Thus, the optimal reaction conditions were nitrobenzene (1.0 mmol), benzyl alcohol (1.5 mmol), $RuCl_3 \cdot 3H_2O$ (3.0 mol %), K_2CO_3 (1.0 mmol), and glycerol (10 mmol) at 130 °C for 24 h, under a N_2 atmosphere.

In order to explore the scope and limitations of the $RuCl_3$ catalyst system, a variety of structurally diverse primary alcohols and nitrobenzenes were investigated. As shown in Table 2, the reductive N-alkylation of aryl nitro compounds were performed well for all

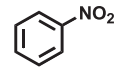
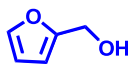
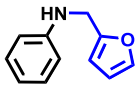
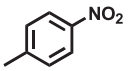
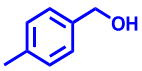
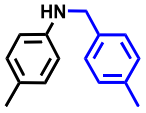
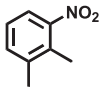
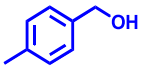
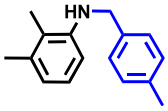
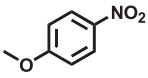
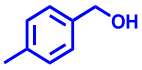
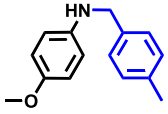
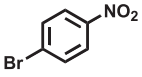
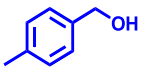
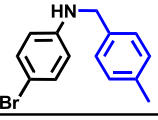
Table 2
$RuCl_3$-catalyzed reductive N-alkylation of nitroarenes



Entry[a]	Nitroarene		Alcohol		Product		Yield (%)[b]
1		**1a**		**2a**		**3a**	80
2		**1a**		**2b**		**3b**	84
3		**1a**		**2c**		**3c**	85
4		**1a**		**2d**		**3d**	76
5		**1a**		**2e**		**3e**	81
6		**1a**		**2f**		**3f**	83
7		**1a**		**2g**		**3g**	85
8		**1a**		**2h**		**3h**	62
9		**1a**		**2i**		**3i**	52
10		**1a**		**2j**		**3j**	48

(*continued on next page*)

Table 2 (*continued*)

Entry[a]	Nitroarene		Alcohol		Product		Yield (%)[b]
11		**1a**		**2k**		**3k**	63
12		**1b**		**2b**		**3l**	84
13		**1c**		**2b**		**3m**	87
14		**1d**		**2b**		**3n**	82
15		**1e**		**2b**		**3o**	46

[a] Reaction conditions: aryl alcohol (1.5 mmol), nitrobenzene (1.0 mmol), $RuCl_3 \cdot 3H_2O$ (3.0 mol %), K_2CO_3 (1.0 mmol) and glycerol (10 mmol) at 130 °C for 24 h, in the presence of N_2 atmosphere.
[b] GC yield.

the substrates examined, and the desired products were isolated in moderate to good yields. It seemed that the electronic nature of substituents on phenyl ring of alcohols had some effect on the catalytic activity towards the reductive N-alkylation of nitrobenzene. The electron-rich and -neutral benzyl alcohols reacted smoothly to give the corresponding secondary amine products in 76%–85% (**3a-g**) yields. While the benzyl alcohols with a *para* electron-withdrawing chloro or trifluoromethyl gave moderate yields (**3h** (62%) and **3i** (52%)). It appeared the *o*-, *m*-substituted groups on benzyl alcohols did not significantly hamper the reductive N-alkylation reactions (**3c-3e**). Notably, heteroatom-containing alcohols including nitrogen and oxygen atoms such as pyridin-3-ylmethanol, furan-2-ylmethanol were well tolerated under the catalytic conditions and moderate yields of the desired amines were obtained (**3j** and **3k**). The coordination by the N or O atom of these substrates to the Ru catalytic centre slowed the catalytic activity. To further examine the scope of N-alkylation reactions, we also investigated the catalytic reactivity towards nitroaromatic compounds. The transformation of aryl nitro compounds containing electron-donating substituents on the aryl ring proceeded in up to 87% yield (**3l**–**n**). However, the substrate with a *para* substituted electron-withdrawing bromide proceeded in lower yield (46%, **3o**).

We also investigated the efficiency of this catalytic reaction step by step and cascade synthesis (Table 3). In the first step of the condensation of nitroarenes with three equivalents of alcohols catalysed by 3.0 mol % $RuCl_3 \cdot 3H_2O$ at 130 °C to provide the corresponding imines, the reactions performed well to give good to excellent yields (72%–99%). Benzyl alcohols bearing electron-donating substituents on the phenyl ring proceeded smoothly to give the corresponding imines in high yields (Table 3, **4b-g**). Benzyl alcohols with *p*-Cl and *p*-CF_3 proceeded smoothly, but in lower yields (Table 3, **4h** and **4i**).

The heteroaromatic benzyl alcohols also reacted in moderate yields (Table 3, **4j**–**k**). Imines **4** were then reduced with glycerol as the hydrogen source in step 2. Similar to step 1, the electron-rich and -neutral benzyl alcohols yielded amine in relatively higher yields (Table 3, **4a**–**g**) compared with those bearing electron withdrawing groups or heteroaromatic rings (Table 3, **4h**–**i, j, k, o**). Generally, this two-step route, which needed more catalyst and aryl alcohol, was more efficient than the one-step syntheses of amines from nitroarenes.

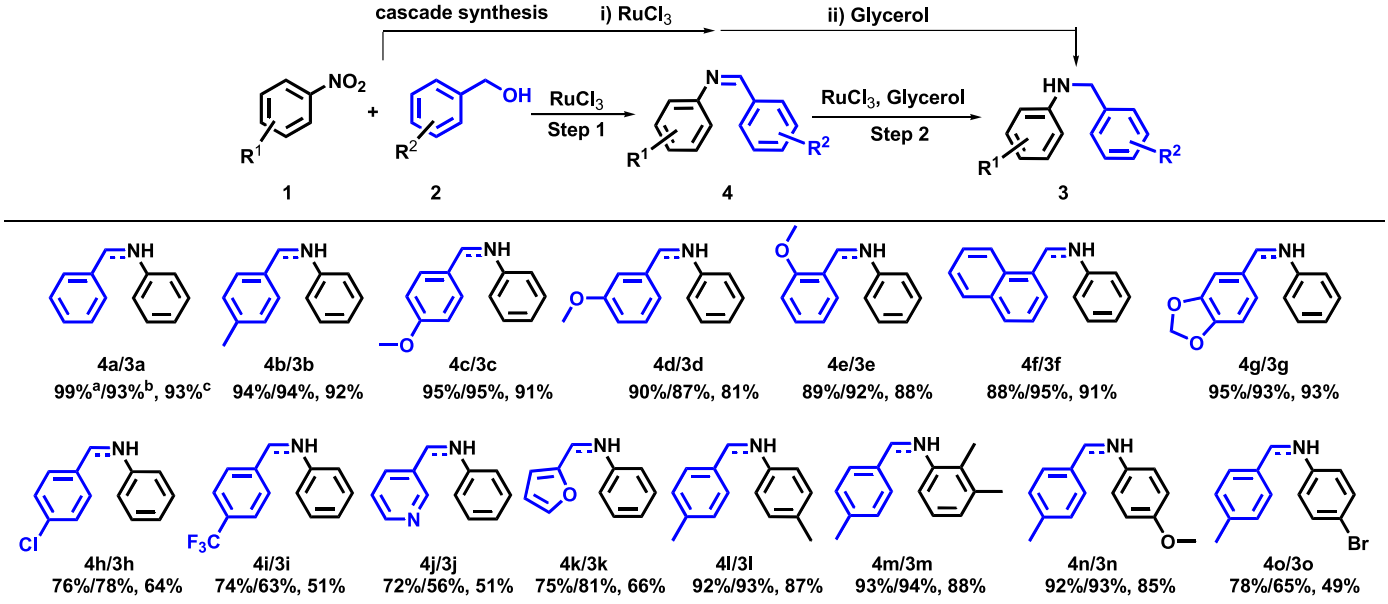
In addition, we investigated the one-pot sequential reaction of nitroarenes (**1**) with benzyl alcohols (**2**) in a 1: 3 M ratio at 130 °C in the presence of 3 mol % of $RuCl_3$. After completion of this reaction (24 h), 10 equiv of glycerol were added to the reaction mixture without the isolation of imines (**4**). To our delight, the desired product **3** was obtained in from 49% to 93% yield after 24 h. Comparative runs with [Ru(acac)$_3$]/dppe (87%),[41] $RuCl_3/PPh_3$ (86%),[43] and [{Ru(*p*-cymene)Cl_2}$_2$]/dppb (93%),[44] and (P-N)$Ru(CO)_2Cl_2$ (89%)[45] indicated that $RuCl_3$ exhibited almost equivalent catalytic performance for the synthesis of **3a**. In the presence of excess benzyl alcohol, some nanocatalysts such as Au/TiO_2 (99%; 8 equiv of benzyl alcohol),[38] and Pd_2/TiO_2 (96%; ca. 200 equivalents of benzyl alcohol)[62] displayed slightly higher activity than that of our catalytic system.

A proposed mechanism for the reductive N-alkylation of nitro aromatic compounds is given in Scheme 1. The first step is the oxidation of benzyl alcohol to benzaldehyde and a ruthenium-hydride intermediate. This ruthenium-hydride complex then reduces the nitrobenzene to aniline, which subsequently undergoes the condensation of aldehyde and aniline to provide the imine. Interestingly, in the absence of glycerol, the imine was not reduced to amine, even in a large excess of benzyl alcohol. Glycerol is necessary as the hydrogen source in this case, suggesting that this potentially chelating ligand might also play a role in stabilizing the ruthenium hydride intermediate or hydride transfer transition state.

3. Conclusions

An efficient and convenient $RuCl_3$-catalyzed system for the construction of aryl amines from nitroarenes and alcohols, or directly by reductions of imines without the necessity for hydrogen gas or reactive metal hydrides, has been developed. Most importantly, the reaction makes use of inexpensive and renewable

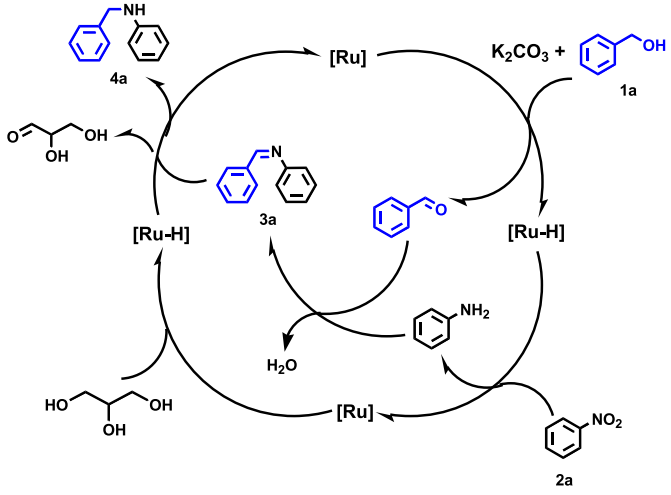
Table 3
$RuCl_3$-catalyzed reductive N-alkylation of aryl nitro compounds



[a] The yield of imine.

[b] The yield of amine from the corresponding imine.

[c] The yield of amine *via* the one-pot sequential reaction of nitroarene with alcohol and glycerol.



Scheme 1. Proposed mechanism for the reductive N-alkylation of nitro aromatics.

glycerol as the hydrogen source without extra organic ligands and solvents. The reaction can be easily manipulated to provide imine or amine cleanly and in high yield. The protocol provides a highly efficient synthesis of imine or amine.

4. Experimental

4.1. General

All commercial reagents were used without further purification. Column chromatography was performed on silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded on recorded at ambient temperature on a Varian UNITY plus-400 spectrometer. ^{1}H chemical shifts were referenced to Me_4Si (δ 0.0 ppm) and residual protons in DMSO-d_6 (δ 2.50 ppm). ^{13}C NMR spectra were reported relative to DMSO-d_6 (δ 39.5 ppm). High-resolution mass spectra were obtained by using a Micromа GCT-TOF instrument. The uncorrected melting points were measured on a Mel-Temo II apparatus.

4.2. General procedure for amine

A mixture of aryl alcohol (1.5 mmol), nitrobenzene (1.0 mmol), $RuCl_3 \cdot 3H_2O$ (3.0 mol %), K_2CO_3 (1.0 mmol) and glycerol (10 mmol) was stirred at 130 °C for 24 h in a sealed tube under a nitrogen atmosphere and then allowed to cool to room temperature. Water (10 mL) was added and the aqueous solution extracted with dichloromethane (3×10 mL). The combined extracts were dried with anhydrous Na_2SO_4, the solvent removed and the crude product purified on a short flash chromatography column.

*4.2.1. N-Phenylbenzylamine (**3a**).* White solid. Mp 39–40 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 4.26 (d, J=4.0 Hz, 2H), 6.22 (t, J=8.0 Hz, 1H), 6.50 (t, J=8.0 Hz, 1H), 6.57 (d, J=8.0 Hz, 2H), 7.03 (t, J=8.0 Hz, 2H), 7.22 (t, J=8.0 Hz, 1H), 7.31 (t, J=8.0 Hz, 2H), 7.36 (d, J=8.0 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 46.4, 112.2, 115.7, 126.6, 127.1, 128.2, 128.8, 140.3, 148.6. HRMS m/z calcd for $C_{13}H_{14}N$ $[M+H]^+$ 184.1048, found 184.1122.

*4.2.2. N-(4-Methylbenzyl)aniline (**3b**).* White solid. Mp 46–47 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 2.27 (s, 3H), 4.20 (d, J=8.0 Hz, 2H), 6.15 (t, J=8.0 Hz, 1H), 6.50 (t, J=8.0 Hz, 1H), 6.55 (d, J=8.0 Hz, 2H), 7.02 (t, J=8.0 Hz, 2H), 7.12 (d, J=8.0 Hz, 2H), 7.24 (d, J=8.0 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 21.1, 46.6, 112.7, 116.1, 127.6, 129.2, 129.3, 136.0, 137.6, 149.1. HRMS m/z calcd for $C_{14}H_{16}N$ $[M+H]^+$ 198.1205, found 198.1279.

*4.2.3. N-(4-Methoxybenzyl)aniline (**3c**).* White solid. Mp 65–67 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 3.71 (s, 3H), 4.17 (d, J=4.0 Hz, 2H), 6.12 (t, J=8.0 Hz, 1H), 6.49 (t, J=8.0 Hz, 1H), 6.55 (d, J=8.0 Hz, 2H), 6.87 (d, J=8.0 Hz, 2H), 7.02 (t, J=8.0 Hz, 2H), 7.27 (d, J=8.0 Hz,

2H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 45.9, 55.0, 112.3, 113.6, 115.7, 128.4, 128.7, 132.0, 148.7, 158.0. HRMS m/z calcd for $C_{14}H_{16}NO$ $[M+H]^+$ 214.1154, found 214.1236.

*4.2.4. N-(3-Methoxybenzyl)aniline (**3d**).* Yellow solid. Mp 62–63 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 3.73 (s, 3H), 4.26 (d, J=4.0 Hz, 2H), 6.23 (t, J=8.0 Hz, 1H), 6.53 (t, J=8.0 Hz, 1H), 6.23 (t, J=8.0 Hz, 1H), 6.80 (t, J=8.0 Hz, 2H), 6.96 (s, 2H), 7.05 (t, J=8.0 Hz, 2H), 7.24 (t, J=8.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 46.4, 54.9, 111.8, 112.3, 112.8, 115.8, 119.3, 128.8, 129.3, 142.1, 148.7, 159.4. HRMS m/z calcd for $C_{14}H_{16}NO$ $[M+H]^+$ 214.1154, found 214.1231.

*4.2.5. N-(2-Methoxybenzyl)aniline (**3e**).* White solid. Mp 72–73 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 3.38 (s, 3H), 4.22 (d, J=8.0 Hz, 2H), 6.03 (t, J=8.0 Hz, 1H), 6.52 (m, J=8.0 Hz, 3H), 6.87 (t, J=8.0 Hz, 1H), 6.99 (d, J=8.0 Hz, 1H), 7.03 (t, J=8.0 Hz, 2H), 7.21 (d, J=8.0 Hz, 1H), 7.25 (d, J=8.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 41.2, 55.3, 110.4, 112.1, 115.6, 120.1, 127.4, 127.7, 128.8, 148.8, 156.9. HRMS m/z calcd for $C_{14}H_{16}NO$ $[M+H]^+$ 214.1154, found 214.1237.

*4.2.6. N-(Naphthalen-1-ylmethyl)aniline (**3f**).* White solid. Mp 66–67 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 4.74 (d, J=8.0 Hz, 2H), 6.26 (t, J=8.0 Hz, 1H), 6.57 (t, J=8.0 Hz, 1H), 6.69 (d, J=8.0 Hz, 2H), 7.10 (t, J=8.0 Hz, 2H), 7.48 (t, J=8.0 Hz, 1H), 7.60 (m, J=8.0 Hz, 3H), 7.87 (d, J=8.0 Hz, 1H), 7.99 (d, J=8.0 Hz, 1H), 8.19 (d, J=8.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 44.6, 112.1, 115.7, 123.6, 125.0, 125.4, 125.7, 126.0, 127.3, 128.5, 128.9, 131.2, 133.4, 135.0, 148.9. HRMS m/z calcd for $C_{17}H_{16}N$ $[M+H]^+$ 234.1205, found 234.1279.

*4.2.7. N-(Benzo[1,3]dioxol-5-ylmethyl)aniline (**3g**).* White solid. Mp 77–79 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 4.16 (d, J=8.0 Hz, 2H), 5.96 (s, 2H), 6.15 (t, J=8.0 Hz, 1H), 6.50 (t, J=8.0 Hz, 1H), 6.56 (d, J=8.0 Hz, 2H), 6.83 (s, 2H), 6.91 (s, 1H), 7.03 (t, J=8.0 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 46.1, 100.7, 107.6, 108.0, 112.3, 115.7, 120.2, 128.8, 134.2, 145.9, 147.3, 148.5. HRMS m/z calcd for $C_{14}H_{14}NO_2$ $[M+H]^+$ 228.0946, found 228.1029.

*4.2.8. N-(4-Chlorobenzyl)aniline (**3h**).* White solid. Mp 78–80 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 4.30 (d, J=8.0 Hz, 2H), 6.31 (t, J=8.0 Hz, 1H), 6.55 (d, J=8.0 Hz, 1H), 6.59 (t, J=8.0 Hz, 2H), 7.08 (t, J=8.0 Hz, 2H), 7.41 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 45.7, 112.3, 115.9, 128.2, 128.8, 128.9, 131.1, 139.4, 148.4. HRMS m/z calcd for $C_{13}H_{13}ClN$ $[M+H]^+$ 218.0658, found 218.0734.

*4.2.9. N-(4-(Trifluoromethyl)benzyl)aniline (**3i**).* Yellow solid. Mp 79–80 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 4.38 (d, J=8.0 Hz, 2H), 6.39 (t, J=8.0 Hz, 1H), 6.53 (t, J=8.0 Hz, 1H), 6.57 (d, J=8.0 Hz, 2H), 7.05 (t, J=8.0 Hz, 2H), 7.57 (d, J=8.0 Hz, 2H), 7.67 (d, J=8.0 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 46.0, 112.3, 116.0, 123.0, 125.2, 125.7, 127.7, 128.9, 145.5, 148.3. HRMS m/z calcd for $C_{14}H_{13}F_3N$ $[M+H]^+$ 252.0922, found 252.0995.

*4.2.10. N-(Pyridin-3-ylmethyl)aniline (**3j**).* White solid. Mp 43–45 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 4.29 (d, J=8.0 Hz, 2H), 6.27 (t, J=8.0 Hz, 1H), 6.52 (t, J=8.0 Hz, 1H), 6.58 (d, J=8.0 Hz, 2H), 7.04 (t, J=8.0 Hz, 2H), 7.34 (m, J=8.0 Hz, 1H), 7.74 (d, J=8.0 Hz, 1H), 8.44 (d, J=8.0 Hz, 1H), 8.58 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 44.4, 112.8, 116.5, 123.9, 129.3, 135.5, 136.1, 148.4, 148.8, 149.3. HRMS calcd for $C_{12}H_{13}N_2$ $[M+H]^+$ 185.1001, found 185.1076.

*4.2.11. N-(Furan-2-ylmethyl)aniline (**3k**).* Light yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 4.24 (d, J=8.0 Hz, 2H), 6.06 (t, J=8.0 Hz, 1H), 6.29 (s, 1H), 6.38 (s, 1H), 6.56 (t, J=8.0 Hz, 1H), 6.66 (d, J=8.0 Hz, 2H), 7.08 (t, J=8.0 Hz, 2H), 7.57 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 39.9, 106.8, 110.3, 112.3, 116.0, 128.8, 141.8, 148.3, 153.4. HRMS m/z calcd for $C_{11}H_{12}NO$ $[M+H]^+$ 174.0841, found 174.0922.

*4.2.12. 4-Methyl-N-(4-methylbenzyl)aniline (**3l**).* White solid. Mp 55–56 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 2.14 (s, 3H), 2.29 (s, 3H), 4.20 (d, J=8.0 Hz, 2H), 5.97 (t, J=8.0 Hz, 1H), 6.50 (d, J=8.0 Hz, 2H), 6.86 (d, J=8.0 Hz, 2H), 7.13 (d, J=8.0 Hz, 2H), 7.25 (d, J=8.0 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 20.0, 20.6, 46.5, 112.4, 123.9, 127.1, 128.7, 129.2, 135.4, 137.3, 146.4. HRMS m/z calcd for $C_{15}H_{18}N$ $[M+H]^+$ 212.1361, found 212.1435.

*4.2.13. 2,3-Dimethyl-N-(4-methylbenzyl)aniline (**3m**).* White solid. Mp 57–58 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 2.11 (s, 3H), 2.23 (s, 3H), 2.30 (s, 3H), 4.34 (d, J=4.0 Hz, 2H), 5.52 (t, J=8.0 Hz, 1H), 6.30 (d, J=8.0 Hz, 1H), 6.44 (d, J=8.0 Hz, 1H), 6.81 (t, J=8.0 Hz, 1H), 7.14 (d, J=4.0 Hz, 2H), 7.28 (d, J=8.0 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 12.7, 20.4, 20.6, 46.5, 108.1, 118.0, 119.9, 125.6, 126.8, 128.8, 135.3, 135.5, 137.5, 146.1. HRMS m/z calcd for $C_{16}H_{20}N$ $[M+H]^+$ 226.1518, found 226.1597.

*4.2.14. 4-Methoxy-N-(4-methylbenzyl)aniline (**3n**).* White solid. Mp 76–78 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 2.29 (s, 3H), 3.63 (s, 3H), 4.18 (d, J=8.0 Hz, 1H), 5.77 (t, J=8.0 Hz, 1H), 6.54 (d, J=8.0 Hz, 2H), 6.69 (d, J=8.0 Hz, 2H), 7.14 (d, J=4.0 Hz, 2H), 7.26 (d, J=8.0 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 20.6, 47.0, 55.2, 113.3, 114.5, 127.2, 128.7, 135.4, 137.4, 142.9, 150.6. HRMS m/z calcd for $C_{15}H_{18}NO$ $[M+H]^+$ 228.1310, found 228.1387.

*4.2.15. 4-Bromo-N-(4-methylbenzyl)aniline (**3o**).* White solid. Mp 78–79 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 2.29 (s, 3H), 4.22 (d, J=8.0 Hz, 2H), 6.45 (t, J=8.0 Hz, 1H), 6.54 (d, J=8.0 Hz, 2H), 7.15 (d, J=8.0 Hz, 2H), 7.18 (d, J=8.0 Hz, 2H), 7.24 (d, J=8.0 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 20.6, 46.1, 106.2, 114.2, 127.1 128.9, 131.3, 135.7, 136.6, 147.9. HRMS m/z calcd for $C_{14}H_{15}BrN$ $[M+H]^+$ 276.0310, found 276.0384.

4.3. The procedure of two-step route

Step 1: A mixture of aryl alcohol (3.0 mmol), nitrobenzene (1.0 mmol), $RuCl_3\cdot 3H_2O$ (3.0 mol %) and K_2CO_3 (1.0 mmol) was stirred at 130 °C for 24 h in a sealed tube under a nitrogen atmosphere. After cooling to room temperature, water (10 mL) was added and the aqueous solution was extracted with dichloromethane (3×10 mL). The combined extracts were dried with anhydrous Na_2SO_4, the solvent was removed and the crude product was purified by a short flash chromatography column. Step 2: A mixture of imine (0.5 mmol), $RuCl_3\cdot 3H_2O$ (3.0 mol %), K_2CO_3 (0.5 mmol) and glycerol (5.0 mmol) was stirred at 130 °C for 24 h in a sealed tube under a nitrogen atmosphere. Workup and purification was as the same as Step 1.

*4.3.1. N-Benzylideneaniline (**4a**).* White solid. Mp 55–56 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 7.26 (t, J=8.0 Hz, 3H), 7.42 (t, J=8.0 Hz, 2H), 7.53 (s, 3H), 7.96 (d, J=4.0 Hz, 2H), 8.61 (s, 1H). ^{13}C NMR (150 MHz, DMSO-d_6, ppm): δ 121.4, 126.4, 129.1, 129.2, 129.6, 131.9, 136.5, 151.9, 161.1. HRMS m/z calcd for $C_{13}H_{12}N$ $[M+H]^+$ 182.0892, found 182.0968.

*4.3.2. N-Phenyl-1-(p-tolyl)methanimine (**4b**).* White solid. Mp 62–63 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 2.38 (s, 3H), 7.24(d, J=8.0 Hz, 3H), 7.33 (d, J=8.0 Hz, 2H), 7.41 (t, J=8.0 Hz, 2H), 7.81 (d, J=8.0 Hz, 2H), 8.56 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 21.2, 120.9, 125.8, 128.7, 129.2, 129.4, 133.5, 141.5, 151.6, 160.5. HRMS m/z calcd for $C_{14}H_{14}N$ $[M+H]^+$ 196.1048, found 196.1123.

*4.3.3. 1-(4-Methoxyphenyl)-N-phenylmethanimine (**4c**).* White solid. Mp 66–68 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 3.84 (s, 3H),

7.07(d, *J*=8.0 Hz, 2H), 7.22 (d, *J*=8.0 Hz, 3H), 7.41 (m, *J*=8.0 Hz, 2H), 7.89 (d, *J*=8.0 Hz, 2H), 8.52 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 55.4, 114.3, 120.9, 125.5, 128.9, 129.2, 130.5, 151.8, 159.9, 161.9. HRMS *m*/*z* calcd for $C_{14}H_{14}NO$ $[M+H]^+$ 212.0997, found 212.1077.

*4.3.4. 1-(3-Methoxyphenyl)-N-phenylmethanimine (**4d**).* White solid. Mp 65–67 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 3.81 (s, 3H), 7.10 (d, *J*=8.0 Hz, 1H), 7.26 (t, *J*=8.0 Hz, 3H), 7.42 (t, *J*=8.0 Hz, 3H), 7.53 (t, *J*=12.0 Hz, 2H), 8.57 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 55.6, 113.0, 118.2, 121.4, 122.1, 126.4, 129.6, 130.3, 137.9, 151.9, 160.0, 160.9. HRMS *m*/*z* calcd for $C_{14}H_{14}NO$ $[M+H]^+$ 212.0997, found 212.1077.

*4.3.5. 1-(2-Methoxyphenyl)-N-phenylmethanimine (**4e**).* White solid. Mp 43–44 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 3.88 (s, 3H), 7.06(t, *J*=8.0 Hz, 1H), 7.15 (d, *J*=8.0 Hz, 1H), 7.22 (m, *J*=8.0 Hz, 3H), 7.40 (t, *J*=8.0 Hz, 2H), 7.52 (t, *J*=8.0 Hz, 1H), 8.02 (d, *J*=8.0 Hz, 1H), 8.83 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 56.2, 112.4, 121.1, 121.3, 124.3, 126.3, 129.7, 133.6, 152.6, 156.0, 159.7. HRMS *m*/*z* calcd for $C_{14}H_{14}NO$ $[M+H]^+$ 212.0997, found 212.1078.

*4.3.6. 1-(Naphthalen-1-yl)-N-phenylmethanimine (**4f**).* White solid. Mp 68–70 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 7.29(t, *J*=8.0 Hz, 1H), 7.38 (d, *J*=8.0 Hz, 2H), 7.46(t, *J*=8.0 Hz, 2H), 7.64 (m, *J*=8.0 Hz, 3H), 8.04 (t, *J*=8.0 Hz, 1H), 8.12 (t, *J*=8.0 Hz, 1H), 8.18 (t, *J*=8.0 Hz, 1H), 9.23(t, *J*=8.0 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 113.8, 115.6, 121.1, 124.6, 125.4, 126.0, 126.3, 127.5, 128.7, 129.2, 133.5, 135.3, 136.8, 151.9, 160.0. HRMS *m*/*z* calcd for $C_{17}H_{14}N$ $[M+H]^+$ 232.1048, found 232.1127.

*4.3.7. 1-(Benzo[1,3]dioxol-5-yl)-N-phenylmethanimine (**4g**).* White solid. Mp 67–68 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 6.13 (s, 2H), 7.06(d, *J*=8.0 Hz, 1H), 7.22 (d, *J*=8.0 Hz, 3H), 7.40 (t, *J*=8.0 Hz, 3H), 7.48 (s, 1H), 8.50 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 101.7, 106.2, 108.4, 120.9, 125.7, 125.8, 129.2, 130.8, 148.0, 150.2, 151.5, 159.8. HRMS *m*/*z* calcd for $C_{14}H_{12}NO_2$ $[M+H]^+$ 226.0790, found 226.0865.

*4.3.8. 1-(4-Chlorophenyl)-N-phenylmethanimine (**4h**).* White solid. Mp 65–66 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 7.27(d, *J*=8.0 Hz, 3H), 7.43 (t, *J*=8.0 Hz, 2H), 7.60 (d, *J*=8.0 Hz, 2H), 7.96 (d, *J*=8.0 Hz, 2H), 8.64 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 121.0, 126.2, 129.0, 129.2, 130.3, 134.9, 136.0, 151.1, 159.5. HRMS *m*/*z* calcd for $C_{13}H_{11}ClN$ $[M+H]^+$ 216.0502, found 216.0575.

*4.3.9. 1-Phenyl-N-(4-(trifluoromethyl)phenyl)methanimine (**4i**).* Yellow solid. Mp 79–81 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 7.30 (m, *J*=8.0 Hz, 3H), 7.44 (t, *J*=8.0 Hz, 2H), 7.89 (d, *J*=8.0 Hz, 2H), 8.15 (d, *J*=8.0 Hz, 2H), 8.75 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 121.6, 123.1, 126.2, 127.1, 129.7, 131.3, 131.6, 140.0, 151.3, 159.9. HRMS *m*/*z* calcd for $C_{14}H_{11}F_3N$ $[M+H]^+$ 250.0765, found 250.0848.

*4.3.10. 1-Phenyl-N-(pyridin-3-yl)methanimine (**4j**).* White solid. Mp 45–46 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 7.29 (m, *J*=8.0 Hz, 3H), 7.44 (t, *J*=8.0 Hz, 2H), 7.56 (t, *J*=8.0 Hz, 1H), 8.32 (d, *J*=8.0 Hz, 1H), 8.71 (s, 2H), 9.07 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 121.1, 124.0, 126.4, 129.2, 131.5, 135.0, 150.3, 151.5, 151.9, 158.7. HRMS *m*/*z* calcd for $C_{12}H_{11}N_2$ $[M+H]^+$ 183.0844, found 183.0923.

*4.3.11. N-(Furan-2-yl)-1-phenylmethanimine (**4k**).* White solid. Mp 59–60 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 6.71(s, 1H), 7.16 (d, *J*=4.0 Hz, 1H), 7.24 (d, *J*=8.0 Hz, 3H), 7.40 (t, *J*=8.0 Hz, 2H), 7.95 (s, 1H), 8.43 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 112.5, 117.0, 120.9, 126.0, 129.2, 146.4, 148.4, 151.1, 151.9. HRMS *m*/*z* calcd for $C_{11}H_{10}NO$ $[M+H]^+$ 172.0684, found 172.0761.

*4.3.12. N,1-Di-p-tolylmethanimine (**4l**).* White solid. Mp 52–54 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 2.32 (s, 3H), 2.37 (s, 3H), 7.21(d, *J*=8.0 Hz, 4H), 7.32 (d, *J*=8.0 Hz, 2H), 7.81 (d, *J*=8.0 Hz, 2H), 8.65 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 21.0, 21.6, 121.4, 129.0, 129.8, 130.1, 134.1, 135.6, 141.7, 149.4, 159.9. HRMS *m*/*z* calcd for $C_{15}H_{16}N$ $[M+H]^+$ 210.1205, found 210.1284.

*4.3.13. 1-(2,3-Dimethylphenyl)-N-(p-tolyl)methanimine (**4m**).* White solid. Mp 53–55 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 2.22 (s, 3H), 2.26 (s, 3H), 2.38 (s, 3H), 6.85 (d, *J*=8.0 Hz, 1H), 7.02 (d, *J*=8.0 Hz, 1H), 7.10 (t, *J*=8.0 Hz, 1H), 7.33(d, *J*=8.0 Hz, 2H), 7.83(d, *J*=8.0 Hz, 2H), 8.41 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 13.5, 19.7, 21.1, 115.6, 126.0, 126.9, 128.5, 129.4, 129.7, 133.7, 136.9, 141.3, 150.5, 159.4. HRMS *m*/*z* calcd for $C_{16}H_{18}N$ $[M+H]^+$ 224.1361, found 224.1435.

*4.3.14. 1-(4-Methoxyphenyl)-N-(p-tolyl)methanimine (**4n**).* Yellow solid. Mp 81–83 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 2.37 (s, 3H), 3.77 (s, 3H), 6.97 (d, *J*=8.0 Hz, 2H), 7.30 (m, *J*=8.0 Hz, 4H), 7.80 (t, *J*=8.0 Hz, 2H), 8.58 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 21.1, 55.3, 114.4, 122.3, 128.4, 129.4, 133.8, 141.0, 144.2, 157.8, 158.2. HRMS *m*/*z* calcd for $C_{15}H_{16}NO$ $[M+H]^+$ 226.1154, found 226.1229.

*4.3.15. 1-(4-Bromophenyl)-N-(p-tolyl)methanimine (**4o**).* White solid. Mp 85–86 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 2.37 (s, 3H), 7.21 (d, *J*=8.0 Hz, 2H), 7.33 (d, *J*=8.0 Hz, 2H), 7.58 (d, *J*=12.0 Hz, 2H), 7.82 (d, *J*=8.0 Hz, 2H), 8.57 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 21.2, 118.3, 123.2, 128.8, 129.4, 132.0, 133.3, 141.8, 150.7, 161.2. HRMS *m*/*z* calcd for $C_{14}H_{13}BrN$ $[M+H]^+$ 274.0153, found 274.0232.

4.4. The procedure of one-pot sequential reaction

A mixture of aryl alcohol (3.0 mmol), nitrobenzene (1.0 mmol), $RuCl_3 \cdot 3H_2O$ (3.0 mol %) and K_2CO_3 (1.0 mmol) was stirred at 130 °C for 24 h in a sealed tube under a nitrogen atmosphere and then allowed to cool to room temperature. Then glycerol (10.0 mmol) was successively added at the same reaction temperature. The resulting reaction mixture was stirred at 130 °C for 24 h. Upon completion, water (10 mL) was added and the aqueous solution extracted with dichloromethane (3×10 mL). The combined extracts were dried with anhydrous Na_2SO_4, and the solvent was removed and the crude product was purified on a short flash chromatography column.

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Supplementary data

Supplementary data (The ^{1}H and ^{13}C NMR spectra for the isolated products) associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2016.05.036.

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