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Iridium-Catalyzed Transfer Hydrogenation of Nitroarenes to Anilines

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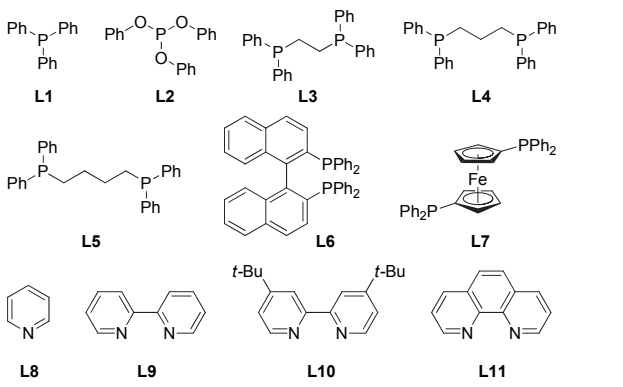
A simple and general homogeneous catalyst system composed of commercially available $[Ir(cod)Cl]_2$ and 1,10-phenanthroline has been developed for the selective transfer hydrogenation of nitroarenes to anilines. It utilized the readily accessible 2-propanol as a hydrogen donor and had a wide range of substrates scopes. A careful mechanistic investigation through a real-time detection and a series of controlled experiments with possible intermediates was also carried out, which showed the transformation proceed *via* both the phenylhydroxylamine and azobenzene intermediates and the reduction of hydrazobenzene leading to aniline might be the rate-determining step.

Introduction

Anilines are important building blocks in the synthesis of biologically active compounds, pharmaceuticals, agricultural chemicals, and other fine chemicals.[1] Among the available procedures for the preparation of anilines,[2] the selective reduction of nitroarenes represents a common and efficient methodology.[3] In the last decades, a variety of catalytic protocols applying stoichiometric reducing agents, such as silanes,[4] $NaBH_4$,[5] boranes,[6] or N_2H_4,[7] have been developed to complement the traditional reduction procedures (Béchamp reduction, sulfide reduction etc.).[8] However, most of these procedures suffer from drawbacks, such as toxicity and/or sensibility of the reducing agents, as well as the cost. In this respect, catalytic hydrogenation of nitroarenes provides an economical and environmentally friendly alternative for the synthesis of anilines.[9] Typically, these routes employ explosive H_2 at high pressures which therefore require special pressure vessels and may cause potential safety issues. Furthermore, in many cases of halonitroarenes, the reduction of nitro group was accompanied by the reductive dehalogenation processes which caused a mixture of haloaniline and dehalogenated aniline.[10]

Transfer hydrogenations employing alcohols as hydrogen source provided an attractive complement to traditional catalytic hydrogenations without the need for high-pressure apparatus.[11] In the last decades, a range of transfer hydrogenation protocols derived from Ir,[12] Au,[13] Ru,[14] etc., has been developed for the reduction of nitroarenes. Among them, most of the catalysts require tedious preparation steps as well as the characterization which limit their application especially in laboratory hydrogenations. Only a few reports concern on the commercially available[15] or *in situ* generated catalyst[14], and most of them also suffer from drawbacks such as low yields and/or high temperature.

As part of our continuing interest in homogeneous iridium catalysts for organic transformations,[16] we herein reported a readily accessible iridium catalyst system consisting of commercially available $[Ir(cod)Cl]_2$ and 1,10-phenanthroline for the reduction of nitroarenes to anilines with 2-PrOH.



Scheme 1. Ligands investigated in the iridium-catalyzed transfer hydrogenation of nitrobenzene.

Results and discussion

In the preliminary study, nitrobenzene was chosen as the model substrate under various conditions (Table 1). Without an additional ligand, the reaction proceeded sluggishly in the presence of $[Ir(cod)Cl]_2$ and KOH, and only 12% yield of aniline was obtained with large amount of recovered nitrobenzene (Table 1, entry 1). Then a series of ligands were investigated (Scheme 1). Clearly, the ligands have a strong influence on the catalytic efficiency (entries 2-12). The monodentate phosphine

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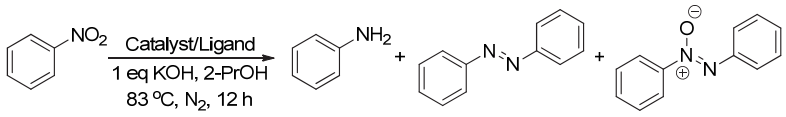
† Electronic Supplementary Information (ESI) available: Copies of the ^{1}H NMR and ^{13}C NMR spectra for all isolated products. See DOI: 10.1039/x0xx00000x

Table 1. Iridium-catalyzed transfer hydrogenation of nitrobenzene in the presence of different ligands[a]



Entry	Catalyst	Ligand	Nitrobenzene[b](recovered)	Aniline[b]	Azobenzene[b]	Azoxybenzene[b]
1	$[Ir(cod)Cl]_2$	-	75	12	3	8
2	$[Ir(cod)Cl]_2$	L1	82	9	2	5
3	$[Ir(cod)Cl]_2$	L2	100	0	0	0
4	$[Ir(cod)Cl]_2$	L3	0	35	60	2
5	$[Ir(cod)Cl]_2$	L4	0	41	53	0
6	$[Ir(cod)Cl]_2$	L5	0	38	58	1
7	$[Ir(cod)Cl]_2$	L6	0	40	56	0
8	$[Ir(cod)Cl]_2$	L7	0	36	61	1
9	$[Ir(cod)Cl]_2$	L8	0	83	15	0
10	$[Ir(cod)Cl]_2$	L9	0	87	12	0
11	$[Ir(cod)Cl]_2$	L10	0	94	3	0
12	$[Ir(cod)Cl]_2$	L11	0	96	2	0
13[c]	$[Ir(cod)Cl]_2$	L11	0	98	0	0
14	$IrCl_3 \cdot 3H_2O$	L11	94	0	0	6
15	$[Ru(p\text{-cymene})_2Cl_2]_2$	L11	93	4	0	3
16	$[Rh(cod)Cl]_2$	L11	91	9	0	0
17	$[IrCp^*Cl_2]_2$	L11	0	45	55	0
18	-	L11	100	0	0	0
19[d]	$[Ir(cod)Cl]_2$	L11	100	0	0	0

[a] Reaction conditions: Nitrobenzene (0.2 mmol), Catalyst (1 mmol%), Ligand (2 mmol%), KOH (0.2 mmol), 2-PrOH (1 mL), 83 °C, N_2, 12 h. [b] Yields were determined by GC analysis and GCMS. [c] 15 h. [d] Without KOH.

ligands (L1-2) displayed low catalytic efficiency (entries 2-3), while the bidentate phosphine ligands (L3-7) gave a full conversion of nitrobenzene and 35%-41% yields of aniline (entries 4-8). To our delight, when nitrogen ligands (L8-11) were added, the catalytic efficiency was remarkably improved (entries 9-12). Among them, 1,10-phenanthroline displayed the best performance, yielding aniline in 96% with 2% azobenzene (entry 12). Prolonging the reaction time to 15 h, the azobenzene was fully converted to the aniline (entry 13). Nevertheless, the combination of L11 with other metal complexes such as $IrCl_3 \bullet 3H_2O$, $[Ru(p\text{-cymene})Cl_2]_2$,[17] and $[Rh(cod)Cl]_2$, resulted in low conversion of nitrobenzene (< 10%; entries 14-16), while the $[IrCp^*Cl_2]_2$ afforded aniline in 45% yield (entry 17).[18] In addition, without catalyst or base, no conversion of nitrobenzene was observed (entries 18-19).[19]

It has been generally accepted that transfer hydrogenation of nitroarenes to anilines proceed *via* the similar routes as the catalytic hydrogenation protocol. To further probe the mechanism, a time-dependence of the product formation and a series of controlled experiments were carried out. Figure 1 showed the time-dependent change of substrate and products during transfer hydrogenation of nitrobenzene monitored by GC-MS. It should be noted that the 1,2-diphenylhydrazine and phenylhydroxylamine intermediates were unstable during the GC analyses, so the quantity of the phenylhydroxylamine could not be detected, while the 1,2-diphenylhydrazine was determined as azobenzene after oxidation in the air. Under the optimal conditions (Table 1, entry 13), a full conversion of nitrobenzene was achieved within 5 min, and a mixture consisting of aniline and intermediates was obtained.[20] This result showed that the induction period for generating the

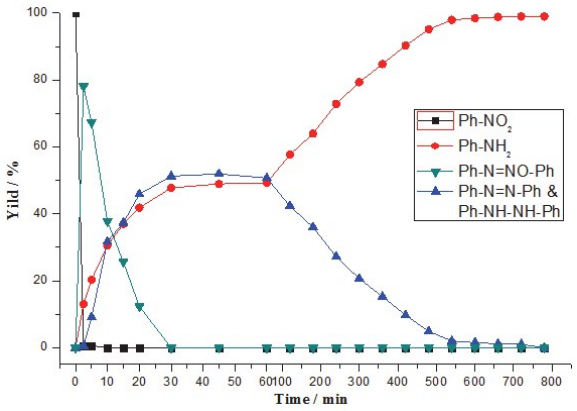
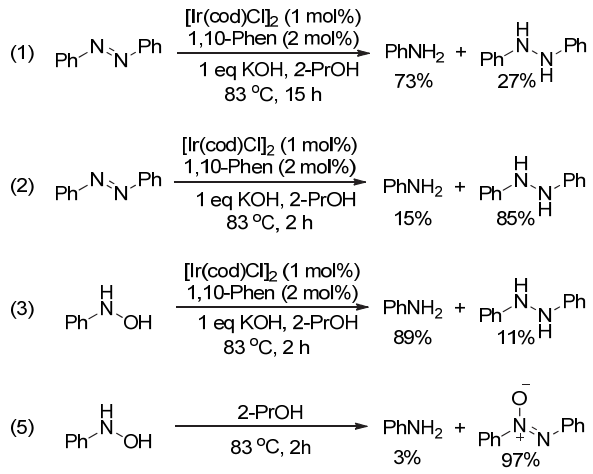


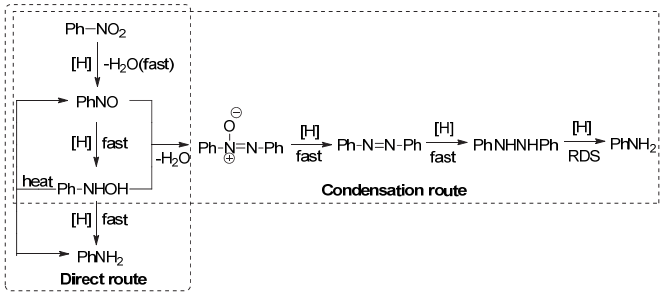
Figure 1. Products distribution during transfer hydrogenation of nitrobenzene.



iridium-hydride catalyst was very short.[19] From 5 min to 30 min, both the azobenzene and aniline increased immediately as soon as the azoxybenzene was consumed. Then the azobenzene was converted to the aniline over a long period of time.

On starting with azobenzene, 73% aniline and 27% hydrazobenzene was obtained as products under the present conditions [Eq. (1)]. In fact, the azobenzene could be totally converted to hydrazobenzene and aniline within 2 h, with hydrazobenzene as the major product [Eq. (2)]. On using phenylhydroxylamine as a substrate, the catalytic system delivered a full conversion with 89% aniline and 11% hydrazobenzene in 2 h [Eq. (3)]. These experimental results clearly indicated that both the phenylhydroxylamine and hydrazobenzene intermediates could be reduced to aniline under the present conditions, and the reduction of the phenylhydroxylamine was faster than the hydrazobenzene. In the absence of catalyst and base, heating the phenylhydroxylamine in 2-PrOH at 83 ^{o}C under nitrogen for 2 h, the phenylhydroxylamine was fully converted to the aniline and azoxybenzene *via* a disproportionation and a condensation [Eq. (4)].[21]

On the basis of the above results and the literature data, a catalytic mechanism shown in Scheme 2 can be formulated.[21] Under the present condition, the reduction of nitrobenzene aniline occurs *via* both the direct route and the condensation route, and the reduction of hydrazobenzene leading to aniline may be the rate-determining step (RDS). There is a competition between the reduction of phenylhydroxylamine and the comdensation with nitrosobenzene. From 0 to 30 min, the increase of aniline mainly derives from the direct route, while from 30 min to the end, the condensation route should be the dominated route. In addition, the role of base in this system is not only accelerating the generation of iridium-hydride species, but also promoting the conversion of the intermediates.[22]



Scheme 2. Postulated reaction pathway for the transfer hydrogenation of nitrobenzene.

With the optimal conditions in hand (Table 1, entry 13), the scope of the reaction was examined (Table 2). The reaction of alkyl substituted nitrobenzenes proceeded smoothly, delivering corresponding anilines in 96-98% yields (Table 2, entries 2-5). Halogenated nitrobenzenes were compatible with the reaction conditions, yielding corresponding anilines in good yields without the reductive dehalogenation (entries 6-9). For nitrobenzenes bearing strong electron-withdrawing group CF_3- or electron-donating group MeO-, the corresponding anilines were also obtained in 98 and 96% yields, respectively (entries 10-11). Several multifunctional anilines were also produced in 85-99% yields from the corresponding nitrobenzenes (entries 12-15). In the cases of nitroanilines, diaminoarenes were obtained in moderated to good yields, (entries16-18). 1-(2-Nitrophenyl)pyrrole and 4-nitro-benzenesulfonamid also gave the desired products in 97 and 98% yields, respectively (entries19-20). Additionally, the reduction of heterocyclic nitroarenes 6-nitroquinoline and 5-nitroindole gave the desired heterocyclic amines in 95 and 57% yields, respectively (entries 21-22). It should be noted that in the case of 6-nitroquinoline, the additive ligand was not necessary because the 6-nitroquinoline could act as a ligand. When the nitrogen atom of 5-nitroindole was blocked by a methyl group, the yield was remarkably improved (entry 23). An attempt to reduce the *meta*-dinitrobenzene resulted in 91% yield of *m*-phenylenediamine (entry 24).

Conclusion

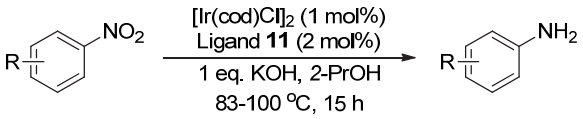
We have demonstrated that $[Ir(cod)Cl]_2$/1,10-phenanthroline was a highly effective and versatile catalyst system for the transfer hydrogenation of nitroarenes to anilines. The simplicity of this protocol employing commercially available $[Ir(cod)Cl]_2$ and 1,10-phenanthroline makes it attractive for laboratory hydrogenations without the need for hazardous H_2, especially as it is applicable to a wide range of nitroarenes substrates. The reduction steps containing both the hydroxylamine and azobenzene intermediates were also determined by a monitoring experiment and a series of controlled experiments.

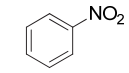
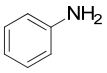
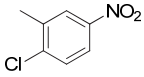
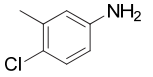
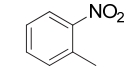
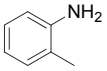
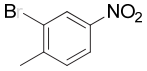
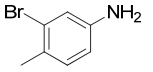
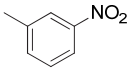
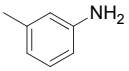
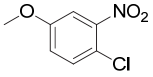
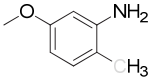
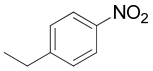
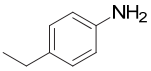
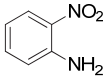
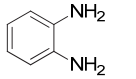
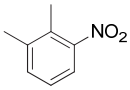
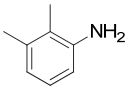
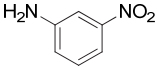
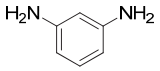
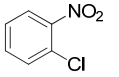
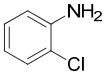
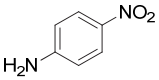
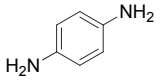
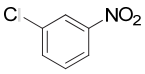
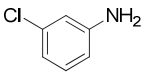
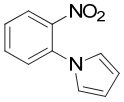
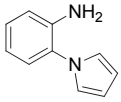
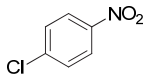
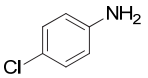
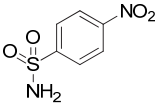
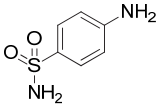
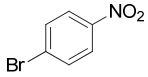
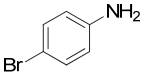
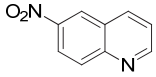
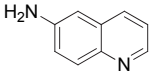
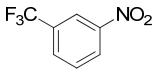
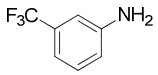
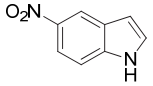
Experimental

General experimental details

All air-sensitive manipulations were carried out under the inert gas atmosphere using standard Schlenk techniques. Glassware was oven or flame dried immediately prior to use. All solvents and commercial reagents were used as supplied without further purification unless stated otherwise. ^{1}H NMR, and ^{13}C NMR spectra were recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz, and 125 MHz in $CDCl_3$, respectively, and chemical shifts were reported in ppm relative to the center of the singlet at 7.27 ppm for $CDCl_3$ or downfield from internal tetramethylsilane). GC-MS were performed on an ISQ Trace 1300 (electrospray ionization: EI). GC analysis were performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: 30 m × 320 μm × 0.25 μm, carrier gas: N_2, FID detector. Phenylhydroxylamine was prepared according to previously reported procedure, recrystallized from CH_2Cl_2-petroleum ether, and kept under 0 ^{o}C in the dark.[23]

Table 2. Iridium-catalyzed transfer hydrogenation of nitroarenes[a]



Entry	Nitroarene	Aniline	GC yield[b] (%)	Entry	Nitroarene	Aniline	GC yield[b] (%)
1			98	13[c]			94(90)
2			97	14[c]			98(94)
3			98	15[c]			99(96)
4			96	16[c]			70
5			96	17[c]			95
6[c]			85	18[c]			84
7[c]			91	19[c]			97(92)
8[c]			97(93)	20[c]			98
9[c]			92(87)	21[c]			95(90)
10[c]			98	22[c,d]			57
11			96(91)	23			98(95)
12[c]			85(81)	24[c,d]			91

[a] Reaction conditions: Nitroarene (0.5 mmol), $[Ir(cod)Cl]_2$ (1 mmol%), Ligand 11 (2 mmol%), KOH (0.5 mmol), 2-PrOH (5 mL, containing 50 µL *n*-hexadecane as internal standard), 83 °C, N_2, 15 h. [b] Yields in parentheses were the isolated yields. [c] At 100 °C. [d] 8 h. [e] $[Ir(cod)Cl]_2$ (2 mmol%), Ligand 11 (4 mmol%), 24 h.

General procedure for the reduction of nitroarenes with 2-PrOH catalyzed by $[Ir(cod)Cl]_2$/1,10-phenanthroline system. An Ar purged flame-dried Schlenk tube (50 mL) containing nitroarene (0.50 mmol, 1 equiv), $[Ir(cod)Cl]_2$ (3.5 mg, 0.005 mmol, 1 mol%), 1,10-phenanthroline (1.8 mg, 0.01 mmol, 2 mol%), and KOH (28 mg, 0.50 mmol, 1 equiv) was added 2-PrOH (5 mL, containing 50 µL *n*-hexadecane as internal standard). The reaction mixture was stirred at 83 °C in an oil bath for 15 h unless stated otherwise. The reaction mixture was cooled to ambient temperature. A sample of the mixture was filtered with 0.22µ organic filter head and then directly subjected to GC analysis. The isolated yield was obtained after removing the solvent under reduced pressure and purification by flash column chromatography on silica gel (PE/EtOAc).

General procedure for the time-dependence transfer hydrogenation experiments. An Ar purged flame-dried Schlenk tube (50 mL) containing nitroarene (0.50 mmol, 1 equiv), $[Ir(cod)Cl]_2$ (3.5 mg, 0.005 mmol, 1 mol%), 1,10-phenanthroline (1.8 mg, 0.01 mmol, 2 mol%), and KOH (28 mg, 0.50 mmol, 1 equiv) was added 2-PrOH (5 mL, containing 50 µL *n*-hexadecane as internal standard). The reaction mixture was stirred at 83 °C in an oil bath. After certain times small aliquots

were taken out of the reaction mixture, the sample was exposed to air in a 1.5 mL centrifuge tube for a period until all the hydrazobenzene was converted to the azobenzene (determined by TLC), followed by GC-MS analysis.

General procedure for the reduction of azobenzene with 2-PrOH catalyzed by $[Ir(cod)Cl]_2$/1,10-phenanthroline system. An Ar purged flame-dried Schlenk tube (50 mL) containing azobenzene (0.50 mmol, 1 equiv), $[Ir(cod)Cl]_2$ (3.5 mg, 0.005 mmol, 1 mol%), 1,10-phenanthroline (1.8 mg, 0.01 mmol, 2 mol%), and KOH (28 mg, 0.50 mmol, 1 equiv) was added 2-PrOH (5 mL, containing 50 μL *n*-hexadecane as internal standard). The reaction mixture was stirred at 83 °C in an oil bath for 15 h or 2 h. The reaction mixture was cooled to ambient temperature. TLC analysis showed that all azobenzene had been consumed. Then the reaction mixture was exposed to air for a period until all the hydrazobenzene was converted to the azobenzene (determined by TLC), followed by GC-MS analysis.

General procedure for the reduction of phenylhydroxylamine with 2-PrOH catalyzed by $[Ir(cod)Cl]_2$/1,10-phenanthroline system. An Ar purged flame-dried Schlenk tube (50 mL) containing phenylhydroxylamine (0.50 mmol, 1 equiv), $[Ir(cod)Cl]_2$ (3.5 mg, 0.005 mmol, 1 mol%), 1,10-phenanthroline (1.8 mg, 0.01 mmol, 2 mol%), and KOH (28 mg, 0.50 mmol, 1 equiv) was added 2-PrOH (5 mL, containing 50 μL *n*-hexadecane as internal standard). The reaction mixture was stirred at 83 °C in an oil bath for 2 h. The reaction mixture was cooled to ambient temperature. TLC analysis showed that all phenylhydroxylamine had been consumed and no azobenzene was observed. Then the reaction mixture was exposed to air for a period until all the hydrazobenzene was converted to the azobenzene (determined by TLC), followed by GC-MS analysis.

General procedure for the transformation of phenylhydroxylamine with 2-PrOH under the catalyst- and base-free condition. An Ar purged flame-dried Schlenk tube (50 mL) containing phenylhydroxylamine (0.50 mmol, 1 equiv), was added 2-PrOH (5 mL, containing 50 μL *n*-hexadecane as internal standard). The reaction mixture was stirred at 83 °C in an oil bath for 2 h. The reaction mixture was cooled to ambient temperature. TLC analysis showed that all phenylhydroxylamine had been consumed. Then the reaction mixture was analyzed by GC-MS.

4-Chloroaniline *(Table 2, entry 8).*[24] 1-Chloro-4-nitrobenzene（78 mg, 0.5 mmol）were reacted following the general procedure at 100 °C, and isolated by flash column chromatography on silica gel (initially eluted with 1% Et_3N in PE) eluted by 20% EtOAc in PE, and then 50% EtOAc in PE, yielding the product as tan crystals (59 mg, 93%). GCMS (EI) m/z: 127 (M^+); ^1H NMR (500 MHz, $CDCl_3$) δ 7.16-7.05 (m, 2H), 6.66-6.57 (m, 2H), 3.67 (s, 2H).

4-Bromoaniline *(Table 2, entry 9).*[24] 1-Bromo-4-nitrobenzene（100 mg, 0.5 mmol）were reacted following the general procedure at 100 °C, and isolated by flash column chromatography on silica gel (initially eluted with 1% Et_3N in PE) eluted by 20% EtOAc in PE, and then 50% EtOAc in PE, yielding the product as a white solid (74 mg, 87%). GCMS (EI) m/z: 170 (M^+); ^1H NMR (500 MHz, $CDCl_3$) δ 7.27-7.22 (m, 2H), 6.63-6.50 (m, 2H), 3.67 (s, 2H).

4-Methoxyaniline *(Table 2, entry 11).*[25] 1-Methoxy-4-nitrobenzene（77 mg, 0.5 mmol）were reacted following the general procedure, and isolated by flash column chromatography on silica gel (initially eluted with 1% Et_3N in PE) eluted by 20% EtOAc in PE, and then 80% EtOAc in PE, yielding the product as tan crystals (56 mg, 91%). GCMS (EI) m/z: 123 (M^+); ^1H NMR (500 MHz, $CDCl_3$) δ 6.82-6.70 (m, 2H), 6.70-6.62 (m, 2H), 3.76 (s, 3H), 3.36 (s, 2H).

3,5-Dichloroaniline *(Table 2, entry 12).*[26] 1,3-Dichloro-5-nitrobenzene（95 mg, 0.5 mmol）were reacted following the general procedure at 100 °C, and isolated by flash column chromatography on silica gel (initially eluted with 1% Et_3N in PE) eluted by 20% EtOAc in PE, yielding the product as tan crystals (65 mg, 81%). GCMS (EI) m/z: 160 (M^+); ^1H NMR (500 MHz, $CDCl_3$) δ 6.72 (t, *J* = 1.7 Hz, 1H), 6.54 (d, *J* = 1.7 Hz, 2H), 3.80 (s, 2H).

4-Chloro-3-methylaniline *(Table 2, entry 13).*[27] 1-Chloro-2-methyl-4-nitrobenzene（86 mg, 0.5 mmol）were reacted following the general procedure at 100 °C, and isolated by flash column chromatography on silica gel (initially eluted with 1% Et_3N in PE) eluted by 20% EtOAc in PE, and then 30% EtOAc in PE, yielding the product as a white solid (63 mg, 90%). GCMS (EI) m/z: 141 (M^+); ^1H NMR (500 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.4 Hz, 1H), 6.53 (d, *J* = 2.6 Hz, 1H), 6.44 (dd, *J* = 8.4, 2.7 Hz, 1H), 3.57 (s, 2H), 2.26 (s, 3H).

3-Bromo-4-methylaniline *(Table 2, entry 14).*[25] 2-Bromo-1-methyl-4-nitrobenzene（107 mg, 0.5 mmol）were reacted following the general procedure at 100 °C, and isolated by flash column chromatography on silica gel (initially eluted with 1% Et_3N in PE) eluted by 20% EtOAc in PE, yielding the product as a yellow oil (86 mg, 94%). GCMS (EI) m/z: 184 (M^+); ^1H NMR (500 MHz, $CDCl_3$) δ 6.98 (d, *J* = 8.1 Hz, 1H), 6.88 (d, *J* = 2.4 Hz, 1H), 6.52 (dd, *J* = 8.1, 2.4 Hz, 1H), 3.56 (s, 2H), 2.27 (s, 3H).

2-Chloro-5-methoxyaniline *(Table 2, entry 15).*[25] 1-Chloro-4-methoxy-2-nitrobenzene（94 mg, 0.5 mmol）were reacted following the general procedure at 100 °C, and isolated by flash column chromatography on silica gel (initially eluted with 1% Et_3N in PE) eluted by 20% EtOAc in PE, yielding the product as pale yellow solid (75 mg, 96%). GCMS (EI) m/z: 157 (M^+); ^1H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.7 Hz, 1H), 6.32 (d, *J* = 2.8 Hz, 1H), 6.27 (dd, *J* = 8.7, 2.8 Hz, 1H), 4.03 (s, 2H), 3.75 (s, 3H).

2-(1H-Pyrrol-1-yl)aniline *(Table 2, entry 19).*[28] 1-(2-Nitrophenyl)-1H-pyrrole（94 mg, 0.5 mmol）were reacted following the general procedure at 100 °C, and isolated by flash column chromatography on silica gel (initially eluted with 1% Et_3N in PE) eluted by 20% EtOAc in PE, yielding the product as a white solid (73 mg, 92%). GCMS (EI) m/z: 158 (M^+); ^1H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.13 (m, 2H), 6.85 (t, *J* = 2.0 Hz, 2H), 6.83-6.77 (m, 2H), 6.36 (t, *J* = 2.0 Hz, 2H), 3.72 (s, 2H).

Quinolin-6-amine *(Table 2, entry 21).*[24] 6-Nitroquinoline (87 mg, 0.5 mmol) was reacted following the general procedure at 100 °C, and isolated by flash column chromatography on silica gel (initially eluted with 1% Et_3N in PE) eluted by 20% EtOAc in PE, and then 100% EtOAc, yielding the product as a brown solid (65 mg, 90%). GCMS (EI) m/z: 144 (M^+); ^1H NMR (500

MHz, $CDCl_3$) δ 8.67 (d, *J* = 2.6 Hz, 1H), 7.92 (dd, *J* = 8.4, 4.0 Hz, 2H), 7.31-7.28 (m, 1H), 7.18 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.92 (d, *J* = 2.5 Hz, 1H), 3.97 (s, 2H).

1-Methyl-1H-indol-5-amine *(Table 2, entry 23).*[29] 1-Methyl-5-nitro-1H-indole（88 mg, 0.5 mmol）was reacted following the general procedure, and isolated by flash column chromatography on silica gel (initially eluted with 1% Et_3N in PE) eluted by 20% EtOAc/PE, and then 100% EtOAc, yielding the product as a brown solid (69 mg, 95%). GCMS (EI) m/z: 146 (M^+); ^1H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.6 Hz, 1H), 6.94 (dd, *J* = 17.0, 2.5 Hz, 2H), 6.69 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.29 (d, *J* = 2.9 Hz, 1H), 3.71 (s, 3H), 3.48 (s, 2H).

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