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Nano Cu-catalyzed efficient and selective reduction of nitroarenes under combined microwave and ultrasound irradiation

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Abstract

In situ preparation of copper nanoparticles from a copper acetate precursor and its application as an efficient catalyst for the selective reduction of aromatic nitro compounds with hydrazine hydrate under combined microwave and ultrasound irradiation were described in detail. The results reveal the synergetic effect of microwave and ultrasound on the synthesis of copper nanoparticles, and formation of various amino derivatives.

Keywords: Microwave, Ultrasound, Nanoparticle, Reduction, Nitroarene

Introduction

From the viewpoint of environmentally benign and sustainable chemistry, there has been an increasing interest in the search for more sustainable chemical processes during the last decade [1,2]. Based on this context, the use of efficient synthetic method, nontoxic chemicals, and benign solvents, is the most valuable feature for the design of a "ideal" chemical protocol. Recently, microwave (MW) and ultrasound (US) technologies have been widely adopted as important synthetic methods in modern organic chemistry, owing to the fact that these technologies can usually reduce the reaction time, minimize energy consumption and in certain cases, increase the yield and selectivity of product [3-6].

Catalytic reduction of aromatic nitro compounds remains appealing because it is widely employed in numerous syntheses of intermediates and final products throughout the dyes, agricultural chemicals, pharmaceuticals and materials both in the laboratory and in industry [7-9]. Although many synthetic routes have been reported for the preparation of anilines from the corresponding aromatic nitro compounds [10-14], there is still necessary for the development of cost-effective catalysts with high activity in particular Fe- [15] and Cu-catalyzed [16] protocol. Recently, much attention has been attracted

to the metal nanoparticles catalysts which have revealed high catalytic activities that far exceed those of conventional homogeneous catalysts, owing to their extremely small dimensions and huge special surface [17,18]. A few procedures involving hydrogenation of nitrobenzene into aniline catalyzed by metal Pt [19-22], Ru [23], Au [24-26] and Rh [27] nanoparticles have been demonstrated. Pal et al. obtained amino derivatives by the reduction of aromatic nitro compounds with $NaBH_4$ catalyzed by coinage of metal nanoparticles (Cu/Ag/Au) [28]. Wen et al. studied the catalytic transfer hydrogenation of aromatic nitro compounds in presence of polymer-supported nano-amorphous Ni-B catalyst [29]. Among the pioneering works of Cu nanoparticles [30-34] emerged as a promising catalyst for organic synthesis, Saha and Ranu [35] reported the reduction of nitro-compounds catalyzed by nano copper particles, however, synthesis required high stoichiometric ratio of copper nanoparticles (3 equiv.) and excess reductant (5 equiv.) to nitro-compounds, long reaction time (8–12 hours) and argon protection.

As our continuing efforts on microwave and ultrasound-assisted reaction [36-40], we found that combined microwave and ultrasound irradiation (CMUI) could strongly promote the nano Cu-catalyzed reduction of aromatic nitro compounds due to its simultaneous enhancement on heat and mass transfer. High reaction rate, low dosage of catalyst and excellent yields were achieved via a chemoselective reduction of aromatic nitro compounds with hydrazine hydrate under CMUI.
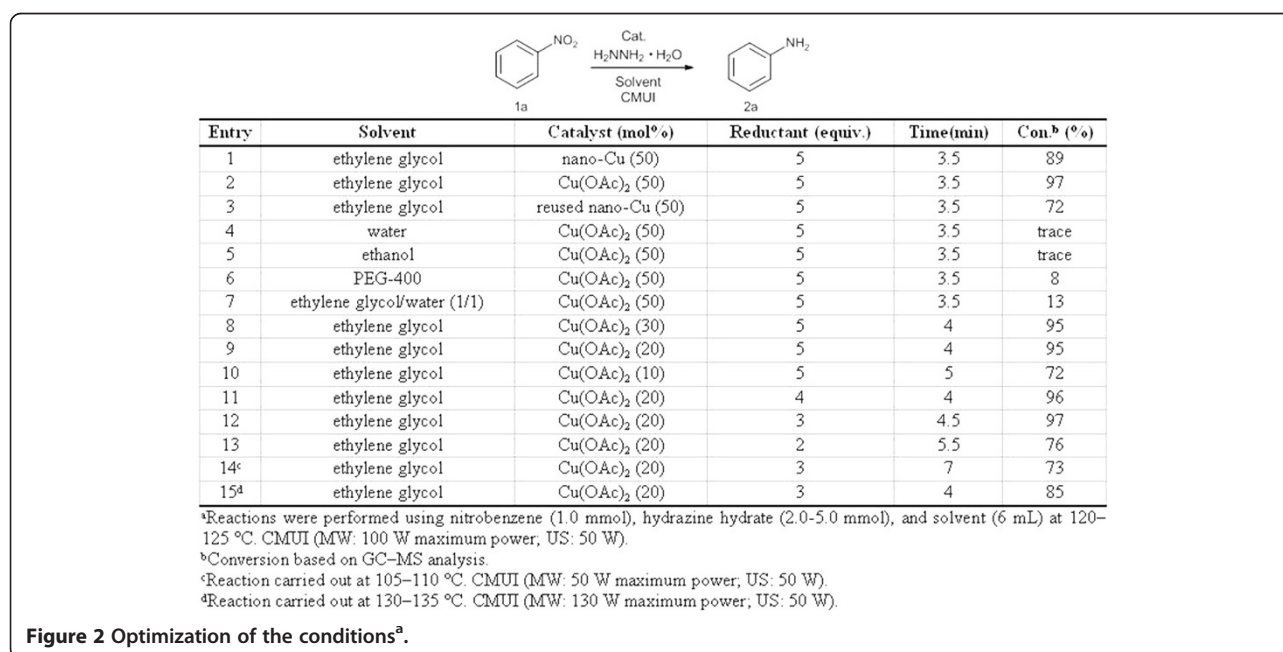
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Figure 1 XRD pattern (a) and TEM images (b) of Cu nanoparticles.
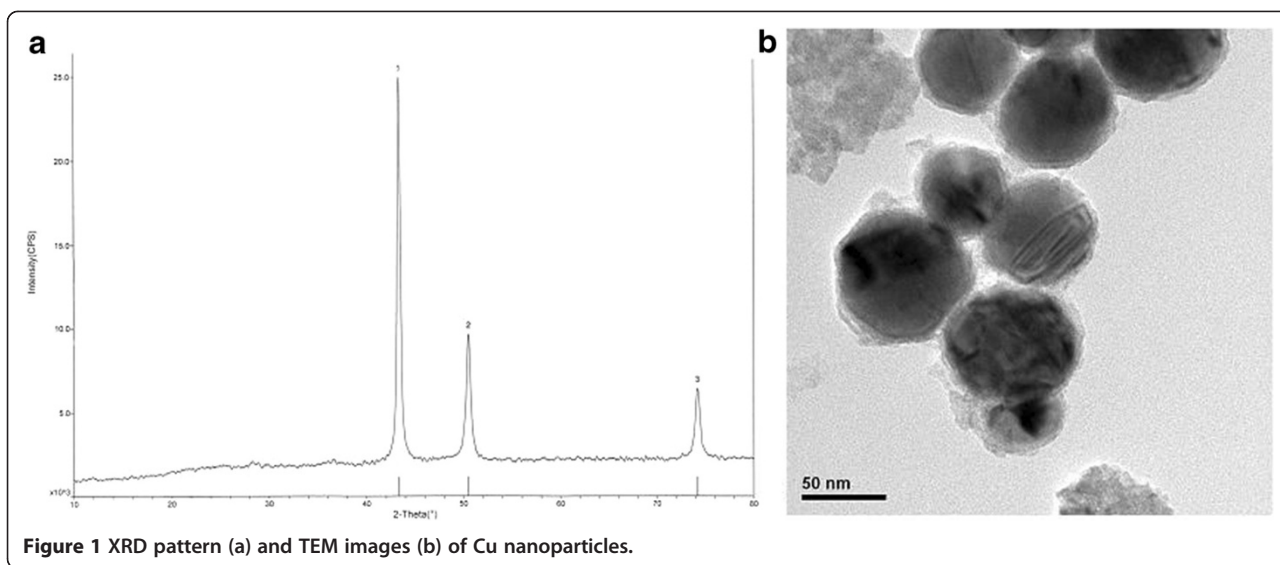
Results and discussion

As stated in the literature [41,42], the initial copper nanoparticles were generated via a reduction of copper acetate (1 mmol) with hydrazine hydrate (2 equiv) in ethylene glycol (8 mL) under combined irradiation of MW: 100 W maximum power and US: 50 W at 120–125°C for 5 min. Characterization of the copper nanoparticles were investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM). All the peaks on the XRD pattern can be readily indexed to pure copper (JCPDS file No. 04–0836) as shown in Figure 1(a). TEM image of the catalyst exhibited that the spherical nanoparticles dispersed very well (Figure 1(b)). The Cu

nanoparticles were then employed to catalyze the reduction of **1a** with hydrazine hydrate. The desired product aniline **2a** was obtained in 89% yield in 3.5 minutes under CMUI (Figure 2, entry 1). Encouraged by this result, we then investigated the possibility of reducing nitrobenzene with hydrazine hydrate using $Cu(OAc)_2$ as a catalyst precursor under CMUI. 97% yield of **2a** was formed (Figure 2, entry 2), and Cu nanoparticles were obtained by centrifuging and washing with ethanol. Nevertheless, the yield of **2a** greatly reduced to 72% applying this reused Cu nanoparticle catalyst (Figure 2, entry 3). The activity decrease of catalyst was owing to the agglomeration and increase of particle size after reuse (Figure 3). This two-step
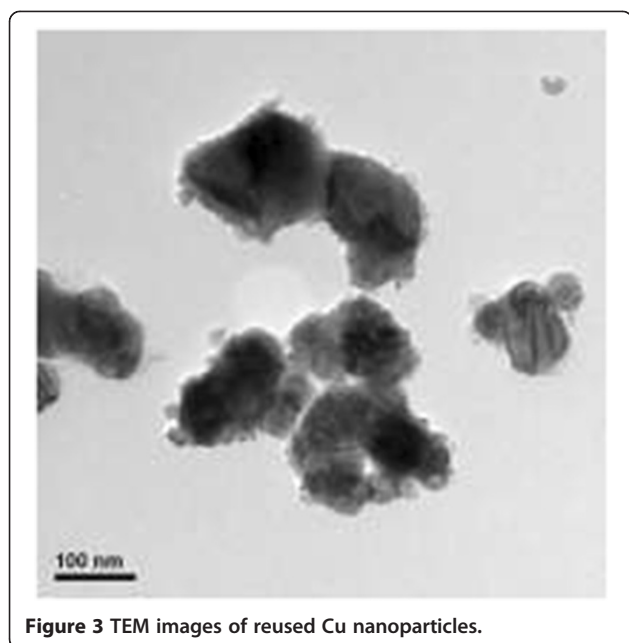
Entry	Solvent	Catalyst (mol%)	Reductant (equiv.)	Time(min)	Con.[b] (%)
1	ethylene glycol	nano-Cu (50)	5	3.5	89
2	ethylene glycol	$Cu(OAc)_2$ (50)	5	3.5	97
3	ethylene glycol	reused nano-Cu (50)	5	3.5	72
4	water	$Cu(OAc)_2$ (50)	5	3.5	trace
5	ethanol	$Cu(OAc)_2$ (50)	5	3.5	trace
6	PEG-400	$Cu(OAc)_2$ (50)	5	3.5	8
7	ethylene glycol/water (1/1)	$Cu(OAc)_2$ (50)	5	3.5	13
8	ethylene glycol	$Cu(OAc)_2$ (30)	5	4	95
9	ethylene glycol	$Cu(OAc)_2$ (20)	5	4	95
10	ethylene glycol	$Cu(OAc)_2$ (10)	5	5	72
11	ethylene glycol	$Cu(OAc)_2$ (20)	4	4	96
12	ethylene glycol	$Cu(OAc)_2$ (20)	3	4.5	97
13	ethylene glycol	$Cu(OAc)_2$ (20)	2	5.5	76
14[c]	ethylene glycol	$Cu(OAc)_2$ (20)	3	7	73
15[d]	ethylene glycol	$Cu(OAc)_2$ (20)	3	4	85

[a]Reactions were performed using nitrobenzene (1.0 mmol), hydrazine hydrate (2.0-5.0 mmol), and solvent (6 mL) at 120–125 °C. CMUI (MW: 100 W maximum power; US: 50 W).
[b]Conversion based on GC–MS analysis.
[c]Reaction carried out at 105–110 °C. CMUI (MW: 50 W maximum power; US: 50 W).
[d]Reaction carried out at 130–135 °C. CMUI (MW: 130 W maximum power; US: 50 W).

Figure 2 Optimization of the conditions[a].

Figure 3 TEM images of reused Cu nanoparticles.

domino reaction would involve an *in situ* preparation of nano Cu catalyst followed by reduction of nitrobenzene. We subsequently examined various solvents under CMUI in the presence of 50 mol% Cu(OAc)$_2$ (Figure 2, entries 4–7). None of the solvents other than ethylene glycol could give a satisfactory. This is mainly due to the fact that the reduction of simple copper salts usually tend to stop at the Cu$_2$O stage in the presence of a number of oxygenous water without protective agents, the di-OH group of ethylene glycol is probable a stabilizer of Cu^{2+} in aqueous and prevents the agglomeration and growth

of nanoparticles [43]. Among the concentration of Cu (OAc)$_2$ (Figure 2, entries 8–10) and hydrazine hydrate (Figure 2, entries 11–13) tested, 20 mol% Cu(OAc)$_2$ and 3 equiv. hydrazine hydrate seemed to be the most efficient condition for this reaction. A lower reaction temperature of 105–110°C with relatively longer reaction time reduced the yield of the amine **2a** to 73% (Figure 2, entries 14), while increasing the temperature to 130–135°C also resulted in a decreased yield of 85% (Figure 2, entry 15).

Having optimized the conditions in hand (Figure 2, entry 12), we next evaluated the scope of the procedure by varying aromatic nitro compounds. The results shown in Figure 4 indicated that all reactions proceeded very smoothly (yields: 89–99%) and quickly (shorter than 6.5 min) under CMUI. Both electron-rich and electron-deficient aromatic nitro compounds **1** provided the desired product **2** in good yields. Substantial steric hindrance to the reduction was tolerated (Figure 4, entries 2, 5 and 10). Moreover, it is noteworthy that the dehalogenation was successfully avoided during the progress of the catalytic reduction of aromatic nitro compounds to the corresponding anilines under reaction conditions (Figure 4, entries 6–10) [44]. The chemoselective reduction was also observed in the case of *m*-dinitrobenzene (Figure 4, entry 11), where one nitro group remained intact. The extremely efficient dielectric heating along with intensive mass transfer in heterogeneous systems resulted in dramatic reaction rate enhancement, and the highly catalytic activity of in situ preparation of nano Cu made the reduction reaction more efficient with lower amount of catalyst (20 mol%) and hydrogen source (3 equiv.).

To investigate the action of CMUI, we evaluated the reduction of nitrobenzene **1a** with hydrazine hydrate in
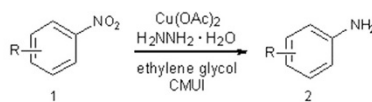
Entry	R =	Time (min)	Product 2	Yield[b] (%)
1	H	4.5	2a	94
2	2-CH$_3$	6.5	2b	90
3	3-CH$_3$	4	2c	96
4	4-CH$_3$	4.5	2d	94
5	2-OH	5.5	2e	89
6	3-Cl	4.5	2f	93
7	4-Cl	4	2g	95
8	3-Br	4	2h	96
9	4-F	5	2i	93
10	2,5-diCl	6	2j	90
11	3-NO$_2$	4.5	2k	95[c]

[a]Reactions were performed using aromatic nitro compounds (1 mmol), copper acetate (0.2 mmol) and hydrazine hydrate (3 mmol) in ethylene glycol (6 mL) at 120–125 °C for the indicated time (monitored by TLC). CMUI (MW: 100 W maximum power; US: 50 W).
[b]Isolated yields
[c]30 mol% Cu(OAc)$_2$ was used.

Figure 4 CMUI-assisted nano Cu-catalysed aromatic nitro reduction[a].

Table 1 Reduction of nitrobenzene using different methods[a]

Entry	Catalyst (mol%)	Method	Time	Con.[b] (%)
1	Cu(OAc)$_2$ (20)	MW + US	4.5 min	97
2	Cu(OAc)$_2$ (20)	convention heating	12 h	52
3	Cu(OAc)$_2$ (20)	MW	30 min	83
4	Cu(OAc)$_2$ (20)	US	3 h	48
5	metallic Cu (20)	MW + US	5 min	35

[a]Reactions were performed using nitrobenzene (1.0 mmol), hydrazine hydrate (3 mmol) and ethylene glycol (6 mL) at 120–125°C, CMUI (MW: 100 W maximum power; US: 50 W).
[b]Conversion based on GC–MS analysis.

the present of pre-catalyst Cu(OAc)$_2$ under conventional conditions. Only 52% yield of aniline was obtained after 12 hours at 120°C (Table 1, entry 2). Moreover, a lower yield was obtained when using either MW or US irradiation (Table 1, entries 3, 4). The viability of commercial metallic Cu powder as a catalyst in the reduction of nitrobenzene under CMUI (Table 1, entry 5) was also examined. Previous described enhancement of CMUI on heterogeneous system, as well as the activation of nano-size catalysts were clearly demonstrated herein.

The proposed reaction mechanism of this reduction process is shown in Scheme 1. Firstly, Cu(OAc)$_2$ is reduced by hydrazine hydrate to provide activated copper nanoparticles which would react with another hydrazine hydrate resulting in the formation of CuH. This further proceeds to generate Cu and hydrogen by the thermal decomposition under the CMUI. Then the nitro compound is reduced to a nitroso compound which follows to provide the hydroxylamine and finally gives rise to amine via a hydrogenation process [45].

Conclusions

In conclusion, we have presented an efficient and convenient method for the chemoselective reduction of aromatic nitro compounds catalyzed by *in situ* prepared Cu nanoparticles under combined microwave and ultrasound irradiation. It allowed us to achieve wide range of anilines bearing both electron-donating and electron-withdrawing substituents in excellent yields. The intriguing results presented herein might open a promising new approach for the efficient preparation and application of nanoparticles.

Experimental

All solvents and reagents were purchased from commercial sources and were used without prior purification. All combined microwave and ultrasound irradiation experiments were carried out in a apparatus (a professional TCMC–102 microwave apparatus (Nanjing Lingjiang Technological Development Company, China), operating at a frequency of 2.45 GHz with continuous irradiation power from 0 to 500 W, and a FS–250 professional ultrasound apparatus (Shanghai S. X. Ultrasonics, China), operating at a frequency of 20 KHz with controllable irradiation power from 10 to 100 W. The reactions were carried out in 15 mL two-necked Pyrex flask, placed in the microwave cavity and the tip of detachable horn should be immersed just under the liquid surface. TLC analysis was performed on aluminum backed plates SIL G/UV254. The products were purified by column chromatography and were identified by ^{1}H NMR, ^{13}C NMR spectra recorded on 400 MHz Bruker NMR instrument and GC–MS.

General experimental procedure for the peduction of nitroarenes

A mixture of nitro compounds (1 mmol), copper acetate (0.2 mmol), hydrazine hydrate (3 mmol) and ethylene glycol (4 mL) was subjected to microwave-ultrasound activation condition. Then hydrazine hydrate (3 mmol) in ethylene glycol (2 mL) was added and the ultrasound and microwave source are switched on successively (power level: US 50 W, MW 100 W maximum power). The mixture was irradiated simultaneously by microwaves and ultrasound until nearly complete conversion of aromatic nitro compounds. The progress of the reactions was monitored by TLC and GC–MS. The reaction mixture was then subjected to centrifugation. After decanting the liquid, the Cu nanoparticles were washed with ethanol (5 mL, three times), which was combined with the decantate. Water (10 mL) was added to the centrifugal liquid, and the product was extracted into ethyl acetate. Evaporation of solvent and the crude product was purified by column chromatography over silica gel
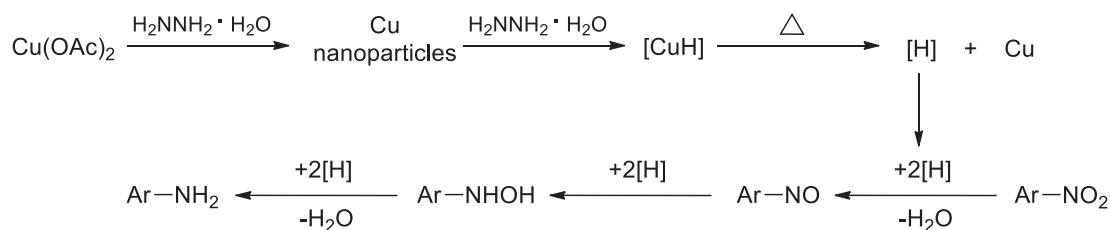
Scheme 1 Proposed reaction mechanism.

(ethyl acetate/petroleum ether = 1:9–1:6) to afford the products.

Aniline (2a)
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.34 (t, *J* = 7.5 Hz, 2H), 6.95 (d, *J* = 7.4 Hz, 1H), 6.80 (dd, *J* = 8.4, 0.8 Hz, 2H), 3.69 (s, 2H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 146.78, 129.49, 118.60, 115.33. MS (GC-MS): 93 (M$^+$)

o-toluidine (2b)
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.25 (t, *J* = 7.0 Hz, 2H), 7.25 (t, *J* = 7.0 Hz, 2H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.87–6.77 (m, 1H), 6.86–6.78 (m, 1H), 3.67 (s, 2H), 3.67 (s, 2H), 2.33 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 144.89, 130.64, 127.16, 122.48, 118.73, 115.13, 17.50. MS (GC-MS): 107 (M$^+$)

m-toluidine (2c)
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.36–7.18 (m, 1H), 6.78 (dd, *J* = 16.7, 7.8 Hz, 1H), 6.64 (ddd, *J* = 21.0, 11.0, 10.1 Hz, 2H), 3.73 (s, 2H), 2.43 (d, *J* = 34.7 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ146.77, 139.21, 129.36, 119.52, 116.16, 112.50, 21.64. MS (GC-MS): 107 (M$^+$)

p-toluidine (2d)
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.01 (d, *J* = 8.0 Hz, 2H), 6.69–6.62 (m, 2H), 3.49 (s, 1H), 2.29 (s, 2H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 143.82, 129.77, 127.80, 115.29, 20.47. MS (GC-MS): 107 (M$^+$)

2-aminophenol (2e)
^{1}H NMR (400 MHz, DMSO-d$_6$): δ 8.93 (s, 1H), 6.63 (dd, *J* = 7.7, 1.3 Hz, 1H), 6.55 (dtd, *J* = 9.1, 7.7, 1.6 Hz, 2H), 6.45–6.32 (m, 1H), 4.46 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d$_6$): δ 143.93, 136.49, 119.46, 116.38, 114.39, 114.31. MS (GC-MS): 109 (M$^+$)

3-chlorobenzenamine (2f)
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.11 (t, *J* = 8.0 Hz, 1H), 6.86–6.74 (m, 1H), 6.69 (t, *J* = 2.1 Hz, 1H), 6.56 (ddd, *J* = 8.1, 2.2, 0.8 Hz, 1H), 3.71 (s, 2H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 147.86, 134.79, 130.46, 118.41, 114.98, 113.39. MS (GC-MS): 127 (M$^+$)

4-chlorobenzenamine (2g)
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.17–7.08 (m, 2H), 6.68–6.57 (m, 2H), 3.57 (s, 2H).
^{13}C NMR (101 MHz, CDCl$_3$): δ 145.00, 129.12, 123.11, 116.26. MS (GC-MS): 127 (M$^+$)

3-bromobenzenamine (2h)
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.05 (t, *J* = 8.0 Hz, 1H), 6.93 (ddd, *J* = 7.9, 1.7, 0.9 Hz, 1H), 6.85 (t, *J* = 2.0 Hz, 1H), 6.60 (ddd, *J* = 8.0, 2.2, 0.9 Hz, 1H), 3.73 (s, 2H). ^{13}C NMR

(101 MHz, CDCl$_3$): δ 148.06, 130.80, 123.08, 121.31, 117.86, 113.84. MS (GC-MS): 170 (M$^+$)

4-fluorobenzenamine (2i)
^{1}H NMR (400MHz, CDCl$_3$): δ 6.99–6.80 (m, 2H), 6.69–6.55 (m, 2H), 3.56 (s, 2H). ^{13}C NMR (101MHz, CDCl$_3$): δ 157.54, 155.21, 142.70, 142.68, 116.15, 116.08, 115.77, 115.55. MS (GC-MS): 111(M$^+$)

2,5-dichlorobenzenamine (2j)
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.17 (d, *J* = 8.5Hz, 1H), 6.77 (d, *J* = 2.3 Hz, 1H), 6.68 (dd, *J* = 8.5, 2.4 Hz, 1H), 4.08 (s, 2H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 143.82, 133.12, 130.19, 118.84, 117.44, 115.37. MS (GC-MS): 162(M$^+$)

3-nitrobenzenamine (2k)
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.64–7.53 (m, 1H), 7.53–7.46 (m, 1H), 7.36–7.20 (m, 1H), 6.96 (ddd, *J* = 8.0, 2.3, 0.8 Hz, 1H), 4.03 (s, 2H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 149.24, 147.48, 129.91, 120.64, 113.11, 109.01. MS (GC-MS): 138(M$^+$)

Authors' contributions
HDF and GHS designed the research with HDF and YL performing the experiments; HDF and SJL analyzed the data; HDF, EVDE and GHS wrote the paper, and all authors read and approved the final manuscript.

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