


Article

A Reusable $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /Cationic 2,2'-Bipyridyl Catalytic System for Reduction of Nitroarenes in Water

Tsai-Yu Hung [†], Wen-Sheng Peng [†], Jing-Wen Tang and Fu-Yu Tsai ^{*} 

Institute of Organic and Polymeric Materials, National Taipei University of Technology, 1, Sec. 3, Chung-Hsiao E. Rd., Taipei 10608, Taiwan

^{*} Correspondence: fuyutsai@ntut.edu.tw; Tel.: +886-2-2771-2171 (ext. 2437)

[†] These authors contributed equally to this work.

Abstract: The association of a commercially-available iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) with cationic 2,2'-bipyridyl in water was proven to be an operationally simple and reusable catalytic system for the highly-selective reduction of nitroarenes to anilines. This procedure was conducted under air using 1–2 mol% of catalyst in the presence of nitroarenes and 4 equiv of hydrazine monohydrate ($\text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O}$) in neat water at 100 °C for 12 h, and provided high to excellent yields of aniline derivatives. After separation of the aqueous catalytic system from the organic product, the residual aqueous solution could be applied for subsequent reuse, without any catalyst retreatment or regeneration, for several runs with only a slight decrease in activity, proving this process eco-friendly.

Keywords: iron (III) chloride hexahydrate; nitroarene reduction; water; reusable catalyst; green chemistry



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1. Introduction

Aniline and its derivatives are important key intermediates in the chemical industry, widely-used for the preparation of dyes, drugs, agrochemicals, and polymers [1–3]. The common process for the preparation of anilines is the reduction of nitroarenes utilizing transition metals as catalysts, with various hydrogen sources [4]. Catalyzation of nitroarene reduction by precious metal complexes, such as Re [5], Ru [6–19], Rh [20,21], Pd [20,22–25], Ir [20], Pt [20,26,27], Au [28,29], and Ir-Au bimetallic [30], and first series metal complexes, such as Cr [31], Mn [32], Co [33–35], Ni [36,37], Cu [35,38], and Zn [39], has been well-documented. Alternatively, transition metal nanoparticles have also been widely applied to catalyze the reduction of nitroarenes recently [4,40–52].

Iron, as the most abundant, cheapest, and nontoxic transition metal, is an ideal catalyst candidate instead of other transition metals for nitroarene reduction. Its single atom [53–57], powder [58–64], salts [65–71], and complexes [6,22,72–81] are widely applied to mediate or catalyze the reduction of nitroarenes to anilines in organic or organic/ H_2O mixed solvents. Recently, iron-based heterogeneous catalysts have also been applied for the reduction of nitroarenes [40–51]. However, such nanocatalysts are usually obtained through precursor hydrothermal treatment, complex pyrolysis, or treatment with moisture-sensitive reagents, which may limit their widespread application. On the other hand, water is an idea solvent to reduce the environmental impact and costs due to its environmental compatibility, nontoxicity, abundance, and low cost. When neat water has been used as the reaction medium, however, an excess amount of iron was usually required for nitroarene reduction [82,83]. Only rare examples, including Fe(II)-citrate in situ forming nanoscale zero-valent iron (nZVI) with sodium borohydride (NaBH_4), catalyzing the reduction of *p*-nitrophenol [84], and iron carbonyl clusters ($\text{Fe}_3\text{E}_2(\text{CO})_9$, E = S, Se, Te) with hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) catalyzing the reduction of nitroarenes in neat water [85], have been reported.

Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) is one of the most readily available iron sources; however, its reduction of nitroarenes usually requires stoichiometric or excess amounts to accomplish the transformation, leading to wastage of the metal [66,71]. An example of successful catalysis employed largely excess amounts of *N,N*-dimethylhydrazine against nitroarenes under refluxed methanol [65]. Therefore, the development of an eco-friendly protocol using this commonly-available iron source, without the requirement for high temperature or moisture-sensitive reagent pretreatment, in neat water to reduce wastage of metal and eliminate the use of an organic solvent as the reaction medium, is highly desirable (See Table 1 for the comparison of the Fe catalysts). As part of our interest in $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ catalysis under an aqueous phase [86–88], in this report, the association of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ with a water-soluble cationic bipyridyl ligand acted as a green catalytic system to accomplish nitroarene reduction for the formation of anilines in neat water. In order to avoid the manipulation of hazardous H_2 under high pressure at high temperature, the safe-to-handle and low-cost dihydrogen precursor hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) was employed as the reducing agent, because H_2 and N_2 are generated in situ in the presence of a catalytic amount of transition metal, leaving no residual waste [89]. Moreover, after separation of the catalytic system from the organic products by simple extraction, the residual aqueous phase could be reused for the next run immediately without any retreatment or regeneration (Scheme 1).

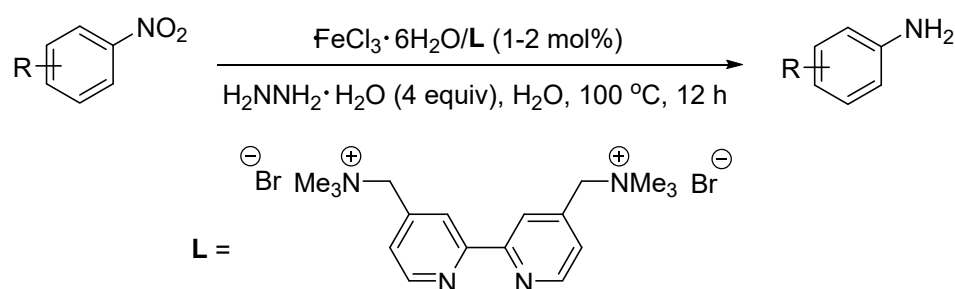
Table 1. Comparison of the reaction conditions of iron catalysts for the reduction of nitroarenes.

Type of Iron Catalyst	H_2 Source	Solvent	Temp. (°C)	Ref.
Iron single atom site				
FeSA@NC-20A (0.42 mol%)	$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (3 equiv)	EtOH	rt	[53]
$\text{Fe}_1/\text{N-C}$	H_2 (5 bar)	$i\text{PrOH}$	160	[54]
$\text{FeSAs}/\text{Fe}_2\text{O}_3\text{ACs}/\text{NPC}$	$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (40 equiv)	EtOH	rt	[55]
Fe-P900-PCC	H_2 (4 Mpa)	Heptane	150	[56]
$\text{Fe}_1/\text{N-C}$	$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (5 equiv)	EtOH	60	[57]
Iron powder (stoichiometric or excess)				
$\text{Fe}/\text{NH}_4\text{Cl}$		$\text{MeOH}/\text{H}_2\text{O}$	Reflux	[58]
Fe/CaCl_2		$\text{EtOH}/\text{H}_2\text{O}$	60	[59]
Fe/HCl		EtOH	70	[60]
$\text{Fe}/\text{NH}_4\text{Cl}$		$\text{H}_2\text{O}/\text{Acetone}$	Reflux	[61]
Fe/AcOH		$\text{EtOH}/\text{H}_2\text{O}$	Sonication	[62]
Activated Fe		H_2O	210	[63]
Fe/HCl		$\text{EtOH}/\text{H}_2\text{O}$	65	[64]
Iron salts				
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.33 mol%)	H_2NNMe_2 (10.5 equiv)	MeOH	Reflux	[65]
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (3 equiv)/Zn		$\text{DMF}/\text{H}_2\text{O}$	100	[66]
$\text{Fe}(\text{acac})_3$ (10 mol%)	TMDS (4 equiv)	THF	60	[67]
FeS_2 (0.83 equiv)	H_2 (50 bar)	$\text{THF}/\text{H}_2\text{O}$	120	[68]
$\text{Fe}(\text{OTf})_3$ (10 mol%)	NaBH_4 (20 equiv)	EtOH	rt	[69]
FeS (5 equiv)/ NH_4Cl		$\text{MeOH}/\text{H}_2\text{O}$	Reflux	[70]
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1 equiv)/In		$\text{MeOH}/\text{H}_2\text{O}$	Sonication	[71]
Iron complex				
$\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ (0.5 mol%) or $\text{Fe}(\text{CO})_3(\text{AsPh}_3)_2$ (0.5 mol%)	H_2 (80 atm)	$\text{C}_6\text{H}_6/\text{EtOH}$	125	[6]
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{Na}_2\text{EDTA}$ (0.075 mol%)	H_2 (400 psi)	$\text{CH}_3\text{C}_6\text{H}_5/\text{H}_2\text{O}$	150	[72]
$\text{FeBr}_2/\text{PPh}_3$ (10 mol%)	PhSiH_3 (2.5 equiv)	$\text{CH}_3\text{C}_6\text{H}_5$	110	[73]
$\text{FePc}/\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.5 mol%)	$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (2 equiv)	$\text{H}_2\text{O}/\text{EtOH}$	120	[74]
$\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}/\text{PP}_3$ (4 mol%)	HCO_2H (4.5 equiv)	EtOH	40	[75]
$[\text{FeF}(\text{PP}_3)][\text{BF}_4]$ (2 mol%)	H_2 (20 bar)	<i>t</i> -AmOH	120	[76]
$\text{Fe}(\text{III})(\text{Furf})$ (2 mol%)	$\text{HSi}(\text{OEt})_3$ (4 equiv)	CH_3CN	80	[77]
$\text{Fe}(\text{CO})_4(\text{IMes})$ (5 mol%)	PhSiH_3 (3 equiv)	$\text{CH}_3\text{C}_6\text{H}_5$	90, <i>hν</i>	[78]
ImmFe-IL (3 mol%)	$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (3 equiv)	Ethylene glycol	110	[79]

Table 1. Cont.

Type of Iron Catalyst	H ₂ Source	Solvent	Temp. (°C)	Ref.
(TPP)Fe(III)Cl (0.06 mol%)	NaBH ₄ (1.6 equiv)	Diglyme	30	[80]
PcFe(II) (2 mol%)	NaBH ₄ (2 equiv)	Diglyme	rt	[81]
Carbonyl iron powder (5 equiv)	NH ₄ Cl (3 equiv)	H ₂ O	45	[83]
FeSO ₄ /Citrate (1 mol%)	NaBH ₄ (400 equiv)	H ₂ O	rt	[84]
Fe ₃ Se ₂ (CO) ₉ (3 mol%)	N ₂ H ₄ ·H ₂ O (2 equiv)	H ₂ O	110	[85]
This work FeCl ₃ ·6H ₂ O/Cationic 2,2'-bipyridyl (1–2 mol%)	N ₂ H ₄ ·H ₂ O (4 equiv)	H ₂ O	100	

Abbreviations are as follows: TMDS = 1,1,3,3-tetramethyldisiloxane; Pc = phthalocyanine; PP₃ = tetraphosphine; Furf = tetrahydro-2-furanyl; IMes = 1,3-bis(2,4,6-trimethyl-phenyl)imidazol-2-ylidene; ImmFe-IL = immobilized iron metal-containing ionic liquid; TPP = tetraphenylporphyrin.



Scheme 1. Iron-catalyzed reduction of nitroarenes in water.

2. Results and Discussion

First, various readily-available iron salts were associated with the water-soluble bipyridyl ligand, **L**, in water in order to evaluate the efficiency for reduction of 1-nitronaphthalene **1a**. The reaction was conducted using **1a** (1.0 mmol) and N₂H₄·H₂O (4.0 mmol) as the reducing agent in water (2 mL) at 100 °C for 6 h (Table 2, Entries 1–7). Among the iron salts, FeCl₃·6H₂O (≥99% purity) was found to be the best catalyst, which rendered 1-naphthylamine **2a** in a 69% yield (Entry 7). As expected, the reduction did not take place in the absence of the iron salt (Entry 8). Therefore, the FeCl₃·6H₂O/**L** system (1 mol%) was then selected for further optimization. A reaction duration of 12 h was found to be sufficient to obtain a near-quantitative yield of **2a** (Entries 9 and 10). Reducing the amount of N₂H₄·H₂O or lowering the reaction temperature led to decreasing product yields (Entries 11 and 12). Ligand **L** plays a decisive role in obtaining a high yield of **2a** in the reaction and, hence, an inferior yield of **2a** resulted when the reaction was conducted in the absence of **L** (Entry 13). This result was consistent with a published paper stating that the combination of FeCl₃·6H₂O and N₂H₄·H₂O for nitroarene reduction is ineffective [65]. In addition, only 43% of **2a** was furnished when **L** was replaced with neutral 2,2'-bipyridine (Entry 14). Lipshutz et al. reported that Fe/ppm Pd nanoparticles prepared from commercially-available FeCl₃ (≥97% purity, contains 300 to 350 ppm Pd) or doped with 350 ppm Pd(OAc)₂ were able to catalyze Suzuki–Miyaura coupling [90]. Alternatively, Fe/80 ppm Pd nanoparticles can be applied to reduce nitroarenes to anilines in the presence of NaBH₄ as the reducing agent [91,92]. In order to exclude catalysis resulting from contaminated metals in commercially-available sources, the palladium impurity was analyzed by inductively coupled plasma mass (ICP-MASS) spectrometry, which showed that FeCl₃·6H₂O (≥99% purity) contained only 0.8 ppm of Pd [87]. A further reaction performed with a 99.99% purity of FeCl₃ as the catalyst provided **2a** in a 98% yield, which indicated that this reduction is indeed catalyzed by iron (Entry 15). Other common reducing agents, such as NH₄Cl and HCOONH₄, failed to reduce **1a** and, hence, **1a** remained intact (Entries 16 and 17). It is worth mentioning that a large-scale reaction

employing 10 mmol of **1a** and 40 mmol of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ under the conditions of Entry 9 was achieved, giving rise to **2a** in a 97% isolated yield (Entry 18).

Table 2. Iron-catalyzed hydrogenation of 1-nitronaphthalene in water ^a.

Reaction scheme: 1-nitronaphthalene (**1a**) $\xrightarrow[\text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O}, \text{H}_2\text{O}, 100\text{ }^\circ\text{C}]{\text{Fe salt/L}}$ 1-aminonaphthalene (**2a**)

Entry	Iron Salt	Duration (h)	Yield (%) ^b
1	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	6	34
2	FeBr_2	6	35
3	$\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	6	33
4	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	6	11
5	FeBr_3	6	32
6	$\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	6	0
7	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	6	69
8	none	6	0
9	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	12	98
10	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	24	98
11 ^c	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	24	73
12 ^d	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	12	41
13 ^e	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	12	18
14 ^f	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	12	43
15 ^g	FeCl_3	12	98
16 ^h	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	12	0
17 ⁱ	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	12	0
18 ^j	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	12	97

^a Reaction conditions are as follows: 1-nitronaphthalene **1a** (1.0 mmol), Fe/L (1 mol%), $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (4.0 mmol), H_2O (2 mL) at 100 °C for 12 h. ^b Isolated yields. ^c 3 equiv of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ were employed. ^d At 80 °C. ^e In the absence of L. ^f Neutral 2,2'-bipyridine was employed instead of L. ^g 99.99% purity of FeCl_3 was used. ^h HCOONH_4 was used as the reducing agent. ⁱ NH_4Cl was used as the reducing agent. ^j 1-Nitronaphthalene **1a** (10 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /L (1 mol%), $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (40 mmol), H_2O (20 mL) at 100 °C for 12 h.

Following identification of the optimal conditions, a variety of nitroarenes were applied to the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /L system to assess the scope and limitations of this process (Table 3). It was found that this catalytic system reduced 4-halonitrobenzenes **1b–1d** efficiently, producing corresponding 4-haloanilines **2b–2d** in excellent yields with no side products of hydrodehalogenation compounds (Entries 1–3), which has been observed in several hydrogenation processes [93–95]. When applying activating groups at the 4-position, the reduction took place smoothly under 1–2 mol% catalyst loading, and high yields of corresponding aniline derivatives **2e–2l** were obtained (Entries 4–11). This catalytic system also worked efficiently with nitroarenes bearing cyano, ester, and amide groups (**1m–1o**), giving **2m–2o** in excellent yields (Entries 12–14). Procainamide **2p**, a drug for the treatment of cardiac arrhythmias, could be synthesized using this protocol in an excellent yield (Entry 15). These results indicated that the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /L system possessed excellent tolerance to a wide variety of reducible functional groups. Multi-substituted nitroarenes **1q–1v**, except for sterically-hindered **1v**, were reduced to the corresponding products smoothly (Entries 16–21). In general, this reduction was clean. For instance, no intermediates or by-products were detected after 12 h in the reduction of **1v**, which gave only **2v** and unreacted **1v** (Entry 21). This may indicate that the intermediates were more reactive than the nitroarene in our system [64]. This protocol was applicable to the reduction of heterocyclic substrates, which are important intermediates for pharmaceuticals [96]. Hence, **1w–1z** were reduced smoothly, giving **2w–2z** in high yields (Entries 22–25). Nitroarenes bearing formyl (**3a**) and keto (**3b**) groups can react with hydrazine to give hydrazone compounds [19,35,65]; **4a** and **4b** were, therefore, obtained in 83% and 90% yields, respectively (Entries 26 and

27). The reduction of a nitroarene with a terminal C=C bond showed no selectivity, and both nitro group and π -bonds were reduced (Entry 28). With internal alkene **3d**, the double bond was partially protected, which gave **4d/4d'** in a 7.9/1 ratio (Entry 29). Similar results have also been observed in a FePc/FeSO₄·7H₂O system using N₂H₄·H₂O as the reducing agent [74]. Dinitro compounds, such as **5a** and **5b**, were reduced efficiently and, hence, furnished 4,4'-oxydianiline **6a** and diaminodiphenyl sulfone (Dapsone) **6b** in high yields (Entries 30 and 31).

Table 3. Iron-catalyzed hydrogenation of substituted nitroarenes in water ^a.

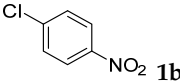
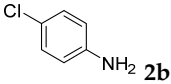
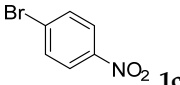
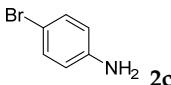
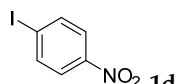
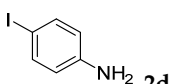
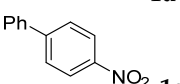
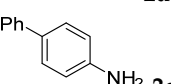
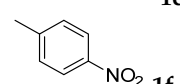
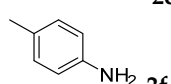
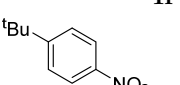
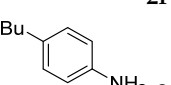
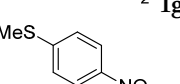
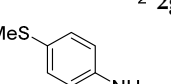
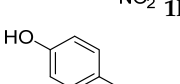
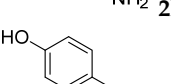
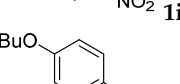
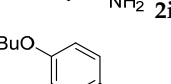
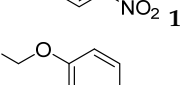
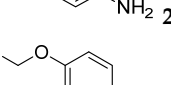
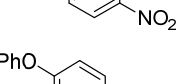
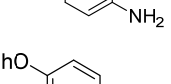
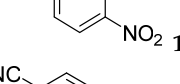
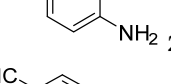
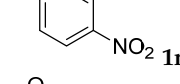
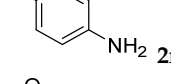
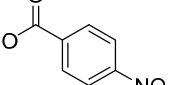
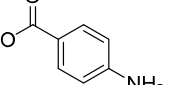
Entry	Nitroarene	Product	Yield (%) ^b
1	 1b	 2b	99
2	 1c	 2c	97
3	 1d	 2d	97
4	 1e	 2e	83
5	 1f	 2f	92
6 ^c	 1g	 2g	99
7 ^c	 1h	 2h	88
8 ^c	 1i	 2i	72
9 ^c	 1j	 2j	78
10 ^c	 1k	 2k	70
11 ^c	 1l	 2l	89
12	 1m	 2m	90
13	 1n	 2n	86
14	 1o	 2o	92

Table 3. Cont.

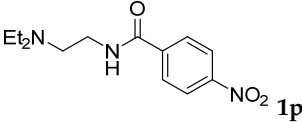
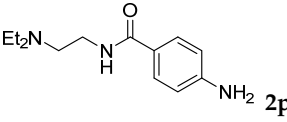
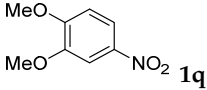
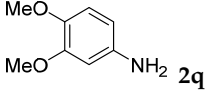
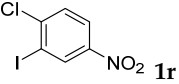
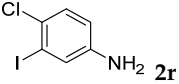
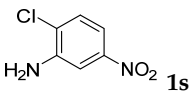
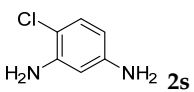
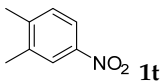
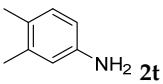
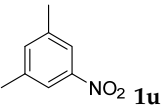
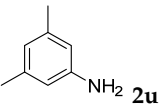
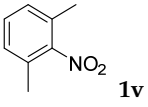
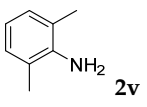
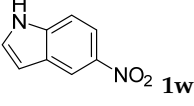
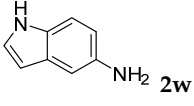
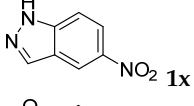
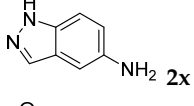
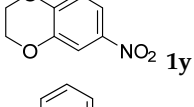
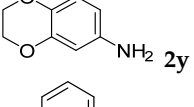
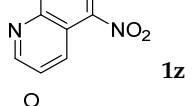
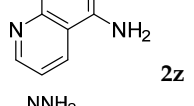
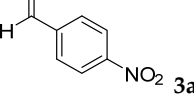
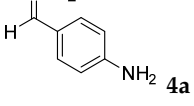
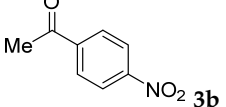
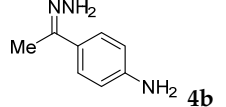
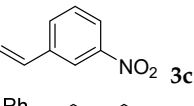
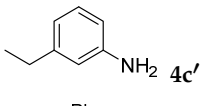
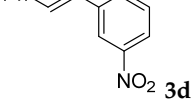
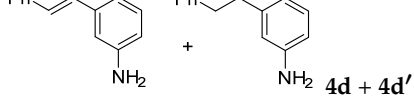
Entry	Nitroarene	Product	Yield (%) ^b
15			98
16 ^c			95
17			95
18			95
19			86
20			96
21 ^c			49
22			82
23			93
24			95
25			92
26			83
27			90
28			79
29			77 ^d

Table 3. Cont.

Entry	Nitroarene	Product	Yield (%) ^b
30 ^e			80
31 ^e			87

^a Reaction conditions are as follows: nitroarene (1.0 mmol), FeCl₃·6H₂O/L (1 mol%), N₂H₄·H₂O (4.0 mmol), H₂O (2 mL) at 100 °C for 12 h. ^b Isolated yield. ^c 2 mol% FeCl₃·6H₂O/L was used. ^d 4d/4d' = 7.9/1. ^e 2 mol% FeCl₃·6H₂O/L and 8.0 mmol N₂H₄·H₂O were used.

It is recognized that the reusability of a catalytic aqueous solution is one of the major advantages of performing the reaction in neat water, thus, reducing the environmental impact and cost of the procedure. The reusability of this green catalytic system was, therefore, examined, and **1a** and **1h** were selected as the representative reactants. As shown in Table 4, the reduction of **1a** with 1 mol% catalyst loading resulted in the formation of **2a** in a 98% yield in the initial run. After extracting the reaction mixture with EtOAc (3 × 5 mL), the residual aqueous phase was applied for subsequent reuse studies without any retreatment or regeneration. It was observed that, at the third reuse run, an 80% isolated yield of **2a** could still be achieved (Entry 1). In addition, the catalyst reuse studies for **1h** were performed with a 2 mol% catalyst loading, and a 78% yield of **2h** was obtained in the third reuse run (Entry 2). The gradual decrease in catalytic activity in reuse studies might be due to the deactivation of the catalyst or a gradual decrease in the catalyst concentration upon successive extraction of the aqueous solution.

Table 4. Reuse studies of the Fe-catalyzed reduction of nitroarenes.

Entry	Product	Isolated Yield (%)			
		Initial Run	1st Reuse Run	2nd Reuse Run	3rd Reuse Run
1 ^a	2a	98	94	87	80
2 ^b	2h	99	93	86	78

^a FeCl₃·6H₂O/L (1 mol%). ^b FeCl₃·6H₂O/L (2 mol%).

3. Materials and Methods

3.1. Instruments and Reagents

Iron salts and most nitroarenes were acquired from commercial suppliers and were used without further purification. Here, **1j** [97], **1k** [98], **1n** [99], **1p** [100], and **3d** [101] were synthesized according to published procedures. The water-soluble bipyridyl ligand **L** was obtained by our published method [102]. The ¹H- and ¹³C-NMR spectra were obtained at 25 °C in CDCl₃, DMSO-*d*₆ or acetone-*d*₆ solution on a Bruker Biospin AG 300 NMR spectrometer (Bruker Co., Faellanden, Switzerland), in which the chemical shifts (δ in ppm) were established with respect to CHCl₃, non-deuterated DMSO, and acetone, which were employed as the reference (¹H-NMR as follows: CHCl₃ at 7.24, non-deuterated DMSO at 2.49, and non-deuterated acetone at 2.05 ppm; ¹³C-NMR as follows: CDCl₃ at 77.0, DMSO-*d*₆ at 39.5, and acetone-*d*₆ at 29.9 ppm). The spectral data of all nitroarene reduction products and copies of their ¹H and ¹³C NMR spectra can be found in the Supplementary Materials.

3.2. Experimental Method

3.2.1. General Procedure for Reduction of Nitroarenes

A 20 mL sealable glass tube equipped with a magnetic stirrer bar was charged with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2.7 mg for 1 mol% or 5.4 mg for 2 mol% reactions), **L** (4.6 mg for 1 mol% or 9.2 mg for 2 mol% reactions), and H_2O (2 mL). This mixture was stirred at room temperature for 30 min to give a wine-red solution. After the addition of nitroarene (1 mmol) and $\text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O}$ (0.2 mL, 4 mmol), the tube was sealed under air and stirred at 100 °C for 12 h. After cooling the reaction to room temperature, the aqueous solution was extracted with EtOAc (3×5 mL), the combined organic phase was dried over MgSO_4 , and the solvent was removed under vacuum. Column chromatography on silica gel eluted with *n*-hexane/EtOAc (2/1) provided the desired products.

3.2.2. General Procedure for Catalyst Reuse Studies

After finishing the initial run and separating the product from the aqueous phase as mentioned above, the residual aqueous solution was recharged with nitroarene (1 mmol) and $\text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O}$ (0.2 mL, 4 mmol). The tube was then sealed and stirred at 100 °C for 12 h for the reuse run.

4. Conclusions

In conclusion, we have successfully developed an operationally simple and reusable protocol for the reduction of nitroarenes to anilines catalyzed by a green catalytic system in water. This procedure features (i) inexpensive, nontoxic, and commonly-available iron salt as the catalyst, and the greenest solvent, water, as the sole reaction medium; (ii) compatibility with a broad spectrum of functional groups; and (iii) potential for reuse of the catalytic aqueous solution several times without any retreatment or regeneration, proving it an eco-sustainable process.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/catal12080924/s1>: spectral data and copies of ^1H - and ^{13}C -NMR spectra for all products.

Author Contributions: Experimental design and performance, T.-Y.H. and W.-S.P.; spectral analysis, T.-Y.H., W.-S.P. and J.-W.T.; writing and editing, F.-Y.T. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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