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# Electrocatalytic, Sm-Promoted Synthesis of Aminoarenes from Nitroaromatic Derivatives in MeOH

Yu-Feng Zhang,<sup>§[a]</sup> Emmanuelle Schulz<sup>[a]</sup> and Mohamed Mellah\*<sup>[a]</sup>

[a] Dr Y.-F. Zhang, Dr E. Schulz, Dr M. Mellah  
 Université Paris-Saclay, CNRS  
 Institut de Chimie Moléculaire et des Matériaux d'Orsay  
 91400 Orsay, France  
 E-mail: mohamed.mellah@universite-paris-saclay.fr

§ current address: Shenzhen Grubbs Institute and Department of Chemistry  
 Southern University of Science and Technology  
 Shenzhen 518055, China

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**Abstract:** A new mild and chemoselective method for the preparation of various aminoarenes is described, based on the electrochemical catalytic reduction of nitroaryl derivatives promoted by samarium salts in methanol. The reactions are carried out in air, in an undivided electrochemical cell, at room temperature and tolerate a wide range of functional groups, including some reducible ones, without leading to by-products. This procedure is also effective for the complete reduction of challenging substrates, namely those capable of coordinating metals, traditionally leading to the need for drastic conditions in terms of pressure, reaction time or temperature. 47 examples are described, including one nitroalkane, and all lead to the targeted reduced product in yields that are almost always over 90%.

## Introduction

Aromatic amines such as aniline and amino-pyridine derivatives are fundamental building blocks in many applications including pharmaceuticals, biochemicals, agrochemicals, but also dyes and pigments or materials precursors.<sup>[1]</sup> Their straightforward preparation mainly involves catalytic reduction of nitro compounds,<sup>[2]</sup> often via heterogeneous catalysis using noble metals dispersed on various supports such as FeO<sub>x</sub>-supported Pt,<sup>[3]</sup> organosilica physically doped with nanostructured Pt,<sup>[4]</sup> Ru-nanoparticles stabilized on Montmorillonite clay,<sup>[5]</sup> Rh-Fe<sub>3</sub>O<sub>4</sub> heterodimer nanocrystals,<sup>[6]</sup> Pd nanoparticles in SiO<sub>2</sub> supported ionic liquid brushes<sup>[7]</sup> or Pd/C,<sup>[8]</sup> to name but a few examples. Base metals have also proved effective in this transformation, particularly iron, by the Beller group, in the presence of organosilanes,<sup>[9]</sup> hydrazine<sup>[10]</sup> and formic acid.<sup>[11,12]</sup> Lipshutz proposed later a mild procedure for nitro group reductions under aqueous micellar catalysis conditions in the presence of inexpensive carbonyl iron powder<sup>[13]</sup> or zinc dust in water.<sup>[14]</sup> Wang reported the preparation through self-assembly of cobalt and N-doped carbon nanotubes hybrids for the efficient hydrogenation of various nitroarenes.<sup>[15]</sup> Reduction of nitroarenes was also performed using a dispersed Ni/SiO<sub>2</sub> catalyst prepared by atomic layer deposition and hydrazine hydrate as a hydrogen donor.<sup>[16]</sup> This important transformation could also be achieved efficiently under reducing conditions without the need to introduce

metals. For example, efficient reduction has been promoted with super-stoichiometric diboron reagents,<sup>[17]</sup> and in the presence of 4,4'-bipyridine as organocatalyst.<sup>[18,19]</sup> Other systems have also led to the chemoselective reduction of nitroarenes, involving boronic acids and phosphine catalysis with phenyl silane as terminal reducing agent,<sup>[20]</sup> a mixture of trichlorosilane and a tertiary amine,<sup>[21]</sup> or a combination of sodium iodide and triphenylphosphine.<sup>[22]</sup> The reduction of nitroarenes in the presence of divalent samarium was published by Kagan's group in 1983, where they described the need for eight equivalents of SmI<sub>2</sub> in a THF/MeOH mixture leading however to incomplete conversion and poor selectivity towards aniline.<sup>[23]</sup> A few years later, Kende et Mendoza used this method to reduce nitroalkane derivatives in high yields,<sup>[24]</sup> and more recently Brady and Keogh proposed a detailed mechanistic study of this transformation by isolating intermediate species and characterizing them by NMR spectroscopy and X-ray analysis.<sup>[25]</sup> Samarium(0) was also implied in an electron-transfer method involving the presence of a catalytic amount of a 4,4'-bipyridinium dibromide salt for the chemoselective reduction of aromatic nitro groups, in aromatic amines.<sup>[26]</sup>

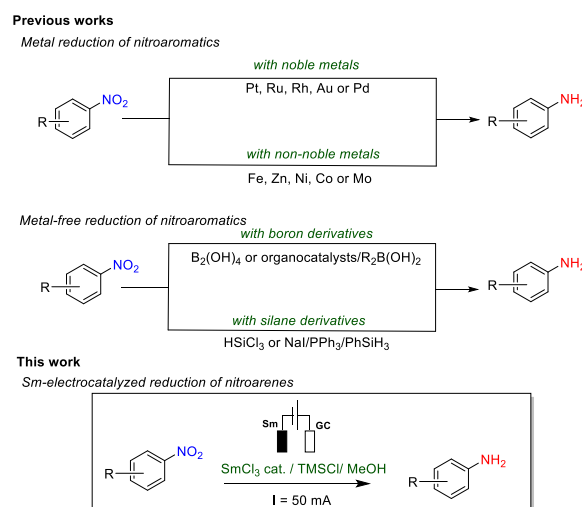


Figure 1. State of the art and present work.

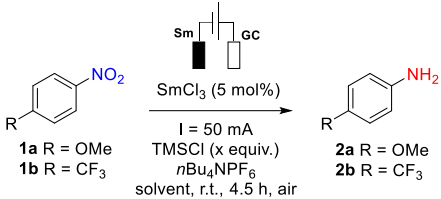
## RESEARCH ARTICLE

As part of the development of samarium catalytic procedures,<sup>[27-30]</sup> we have previously reported the successful catalytic use of electrogenerated samarium diiodide<sup>[31-33]</sup> to afford the reduction of nitroarenes in corresponding azobenzene derivatives in high yields under mild conditions.<sup>[34]</sup> In the course of our optimization studies, we noticed that presence of MeOH impacted dramatically the chemoselectivity, with formation of aniline derivatives as by-products. Here we describe our efforts to set up an analogous electrochemically-driven method to selectively and smoothly lead to functionalized aniline derivatives.<sup>[35]</sup>

## Results and Discussion

The study of this reactivity has been conducted starting from the conditions that were set up previously for the reduction of nitroarenes into azobenzenes but in the presence of MeOH as proton donor. Therefore, the electrochemical process was conducted using a glassy carbon anode and a samarium cathode, in the presence of SmCl<sub>3</sub> (5 mol%) as catalyst. The reaction was performed in THF at a 1.0 mmol scale, in the presence of *n*Bu<sub>4</sub>NPF<sub>6</sub> as electrolyte and 2 equivalents of TMSCl as strong oxophile to release the Sm salts and allow their regeneration.<sup>[36]</sup> In the presence of 10 equiv. MeOH, 1-methoxy-4-nitrobenzene **1a** as test substrate was fully converted but yielded only traces of the targeted 4-methoxyaniline **2a** together with the corresponding azobenzene derivative as main product. Increasing the amount of MeOH reversed the selectivity, allowing the formation of **2a** in 81% yield using 100 equiv. MeOH (see Table 1, entries 1-3). **1a** could fortunately be fully converted to **2a** when 8 equiv. of TMSCl were added in the electrochemical cell (entry 4). 1-Nitro-4-(trifluoromethyl)benzene **1b** was taken up under these reactions conditions to test the electronic effect of substituents on this reactivity and **2b** was isolated in 81% yield (entry 5). Increasing the amount of MeOH to 300 equiv provided only minor yield optimization, but its use as a solvent led to complete conversion of **1b** to **2b** (entries 6 and 7). Proton donors are important additives of many reactions mediated by Sm(II). Among them, water and MeOH have proven to be unique proton sources in Sm(II) chemistry resulting generally in increased reactivity, specifically for the reduction of challenging substrates.<sup>[37,38]</sup> This result represents, to our knowledge, the very first use of MeOH as a solvent in Sm(II) chemistry, used without further precaution in air, as a commercially available anhydrous source. This solvent is moreover a good solvation agent for the electrolyte, enabling a higher current density to be obtained than in THF. The quantity of TMSCl introduced was then studied, but could not be reduced (entries 8-11) and it was verified that the use of MeOH as a solvent was also compatible with the reduction of substrates containing electron-donating groups (entry 12). Finally, no reaction occurred in the absence of current density (entry 13) or in absence of catalyst (entry 14).

**Table 1.** Optimization of the conditions: effect of the solvent<sup>[a]</sup>

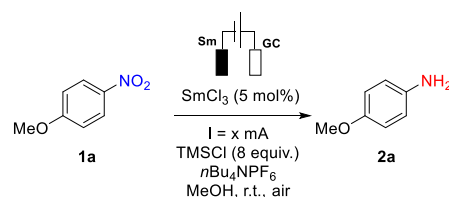


Entry	Substrate	Solvent	MeOH (equiv.) <sup>[d]</sup>	TMSCl (equiv.)	Conv. (%)	Yield <b>2a</b> or <b>2b</b> (%) <sup>[b]</sup>
1	<b>1a</b>	THF	10	2	>99	traces
2	<b>1a</b>	THF	50	2	>99	27
3	<b>1a</b>	THF	100	2	>99	81
4	<b>1a</b>	THF	100	8	>99	98
5	<b>1b</b>	THF	100	8	>99	81
6	<b>1b</b>	THF	300	8	>99	83
7	<b>1b</b>	MeOH		8	>99	98
8	<b>1b</b>	MeOH		0	27	traces
9	<b>1b</b>	MeOH		2	77	56
10	<b>1b</b>	MeOH		4	91	80
11	<b>1b</b>	MeOH		6	>99	88
12	<b>1a</b>	MeOH		8	>99	98
13 <sup>[c]</sup>	<b>1a</b>	MeOH		8	<5	-
14 <sup>[d]</sup>	<b>1a</b>	MeOH		8	<5	-

[a] Reaction conditions: **1a** or **1b** (1.0 mmol), SmCl<sub>3</sub> (0.05 equiv.), MeOH (10-300 equiv.), TMSCl (0 to 8 equiv.), *n*Bu<sub>4</sub>NPF<sub>6</sub> (0.01 mol/L) in THF or MeOH (50 ml), Sm cathode, carbon anode, I = 50 mA, r.t. in air. [b] Isolated yield. [c] Without current. [d] Without SmCl<sub>3</sub>.

Further research was carried out to try and optimize other reactions parameters, such as the current intensity and the concentration of the reaction mixture (Table 2). This survey was performed with **1a** as the test substrate, but increasing the current density from 50 to 400 mA, although leading to faster transformation, also led to a drop in selectivity (entries 1-4). In addition, increasing the concentration affected both the conversion and selectivity of the reaction (entries 5-7), which could be restored somewhat by working with a current density of 100 mA. The use of a doubled electrode surface area at 100 mA enabled **2b** to be synthesized on a gram scale in a reasonable time and with a high yield (entry 9).

**Table 2.** optimization of the conditions: effect of the current density and the concentration<sup>[a]</sup>



Entry <sup>[b]</sup>	<b>1a</b> (mmol)	I (mA)	t (h)	Conv. (%)	Yield (%) <sup>[b]</sup>
1	1	50	4.5	>99	98
2	1	100	3.5	>99	94
3	1	200	2.5	>99	92
4	1	400	2.0	>99	87
5	2	50	10	>99	96
6	5	50	28	87	77
7	10	50	50	61	49
8	10	100	30	87	64
9 <sup>[c]</sup>	10	100	30	91	76

[a] Reaction conditions: **1a** (1.0 to 10 mmol), SmCl<sub>3</sub> (0.05 equiv.), TMSCl (8 equiv.), *n*Bu<sub>4</sub>NPF<sub>6</sub> (0.01 mol/L) in MeOH (50 ml), Sm cathode, carbon anode, I = 50 to 400 mA, r.t. in air. [b] Isolated yield. [c] Doubled electrode surface.

The scope of the reaction was carried out on a mmol scale, varying many of the substituents on the nitroarenes under the optimized conditions (see Table 2, entry 1), in MeOH. The results obtained are summarized in Figure 2. Methoxy and methyl donating groups were introduced at different positions on the aromatic (**1c** to **1i**), resulting in almost quantitative yields in all cases, including the synthesis of the hindered 2,6-dimethylaniline **2h**. This applies to the preparation of amino naphthalenes (**2j**, **2k**) and many halogenated anilines compounds (**2l** to **2u**). The absence of a dehalogenation process in all cases is noteworthy, leading to the formation of the corresponding functional anilines in excellent yields. The particular chemoselectivity of this electrocatalysed reduction is also tangible for the reduction of nitroarenes carrying sensitive functional groups. This reaction is tolerant for cyano-, ester-, benzyloxy- and keto- groups affording compounds **2v** to **2a'** in very high yields. Although ketones are usually prompt to undergo pinacol coupling or reduction in the presence of Sm(II) salts, reduction of the nitro group is interestingly favored under these electrochemical catalysis conditions. In addition, the reduction of 1,4-dinitrobenzene can be carried out sequentially to obtain **2b'** in high yield, which can then be reduced to dianiline **2c'** very efficiently.

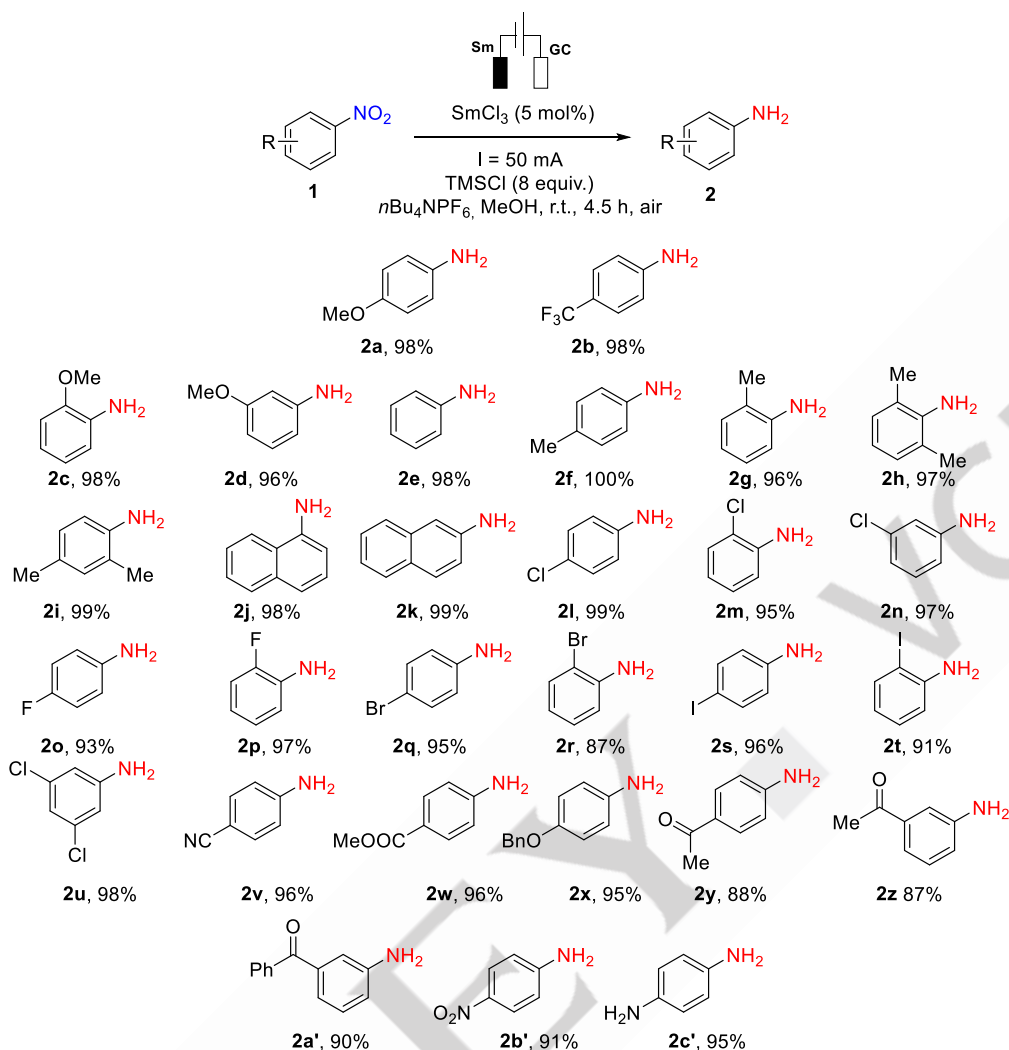


Figure 2. Sm electrocatalytic reduction of nitroarenes.

Some challenging substrates have proved difficult to reduce in the literature due to the presence of a labile, acidic hydrogen atom in their structure, which hinders efficient metal-catalyzed reduction by potential strong coordination and subsequent poisoning. This is for instance the case of hydroxyl or carboxylic acid groups. Such substrates were investigated in the electrocatalytic catalysis promoted by samarium salts (Figure 3). The optimized conditions used for the scope study only led to a very low yield of product **3a** after 4.5 h of electrolysis. While extending the reaction time favored the formation of by-products, doubling the amount of catalyst to 10 mol% gave **3a** in 96% yield, all other things being equal. This procedure enabled to isolate aminophenol (**3a**, **3b**) and (aminophenyl)methanol derivatives (**3c**, **3d**) in excellent yields, as well as aminobenzoic acids (**3e**, **3f**), the latter being particularly well known as poisons for metal catalysts.

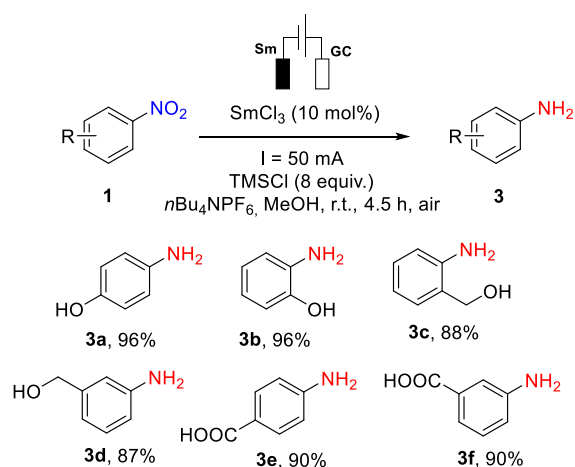
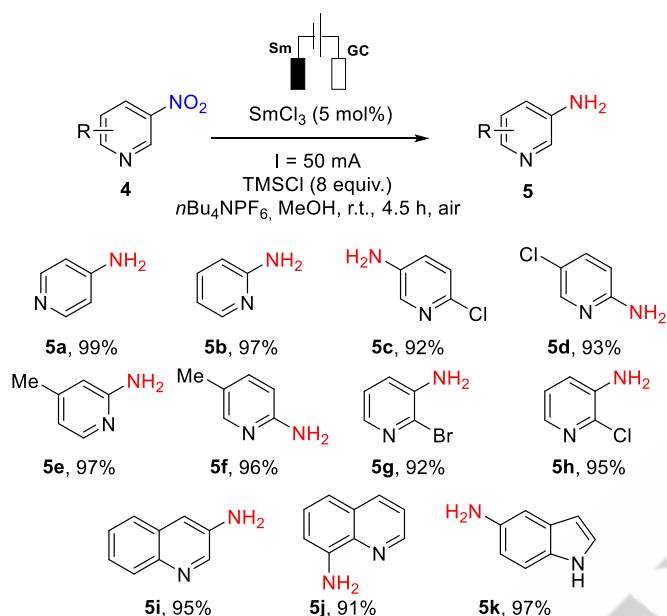


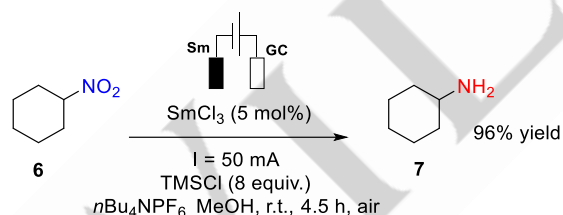
Figure 3. Sm-electrocatalysed formation of aminophenol, (aminophenyl)methanol and aminobenzoic acid derivatives.

Other challenging substrates, which often lead to the use of high catalytic ratios and high temperatures and pressures, are nitrogen-based aromatic heterocycles, which nevertheless lead by reduction to useful synthons for the pharmaceutical industry. Functionalized nitropyridines, nitroquinolines, but also 5-nitro-1*H*-indole (Figure 4) delightfully were converted in the corresponding anilines in very high yield in the presence of only 5 mol%  $\text{SmCl}_3$ .



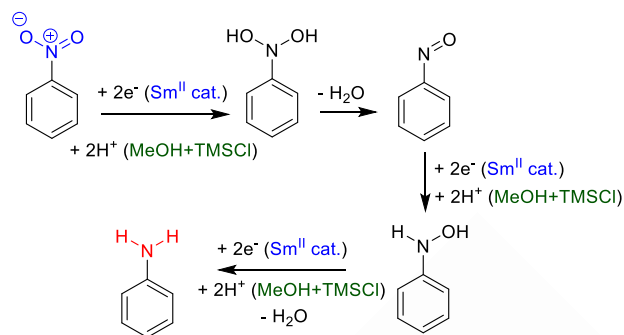
**Figure 4.** Sm electrocatalytic reduction of nitro-pyridines, indoles and arenes.

An extension to the reduction of nitroalkanes has been initiated, since nitrocyclohexane has been selectively reduced to the amine **7** (Figure 5), once again in almost quantitative yield.



**Figure 5.** Sm electrocatalytic reduction of nitrocyclohexane.

Following the mechanism we have proposed for the electrocatalytic synthesis of azobenzenes,<sup>[35]</sup> we suggest that the use of  $\text{Sm(II)}$  in MeOH as a solvent together with TMSCl provides a catalytic system that enables the chemoselective reduction of nitro derivatives by proton-coupled electron transfer (PCET), as shown in Figure 6. In this case, we propose that TMSCl acts both as a better oxophile than Sm to facilitate its release and reacts with MeOH producing TMSOMe and HCl, the latter being involved in the rapid protonation of intermediates leading to efficient chemoselective reduction.



**Figure 6.** Proposed mechanism.

## Conclusion

In summary, the electrocatalytic reduction of nitroaromatics, promoted by Sm, has been carried out efficiently under mild conditions. The reaction selectively leads to the formation of various aniline derivatives in excellent yields and is applicable to the reduction of nitrogen-containing nitroheterocycles and nitroalkanes, with equal success. This procedure tolerates a large number of different functional groups, including metal-coordinating moieties or groups that may also suffer from potential reduction, while maintaining perfect chemoselectivity. It therefore offers a relevant alternative to other more drastic and less selective processes for the preparation of all these valuable building blocks for the pharmaceutical industry. The reduction takes place in pure methanol at room temperature and does not require an inert atmosphere. The use of methanol as a solvent in the presence of TMSCl as an additive proved here to be fully compatible with samarium chemistry, even under catalytic conditions.

## Experimental Part

### General

THF was distilled from sodium metal/benzophenone before use. All commercially available chemicals were used without purification.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on either a Bruker AM 360 (360 MHz), AM 300 (300 MHz), or AM 250 (250 MHz) instrument with samples dissolved in  $\text{CDCl}_3$ .  $^1\text{H}$  NMR chemical shifts were referenced to the residual solvent signal;  $^{13}\text{C}$  NMR chemical shifts were referenced to the deuterated solvent signal. Data are represented as follows: chemical shift  $\delta$  (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant ( $J$ ) in Hz and integration. Mass spectra were recorded on a micrOTOF-q Bruker Daltonics spectrometer. Flash chromatography (FC) was performed on 40–63  $\mu\text{m}$  silica gel with mixtures of ethyl acetate (EA) and pentane. TLC plates were visualized by exposure to UV (254 nm) and/or  $\text{KMnO}_4$  stain. Electrolysis were performed with a AUTOLAB potentiostat/galvanostat (model: PGSTAT302N), in an undivided three-electrodes cell containing a samarium rod working electrode, a standard glassy carbon counter electrode and a

saturated calomel electrode (SCE) as reference. The samarium electrode used is a samarium rod of 12.7 mm (0.5 in) diameter and 5 cm length (purchased from Alfa Aesar, 99.9 % metals basis excluding Ta), directly connected to a copper wire to ensure current conductivity. This self-made electrode is stored under inert atmosphere when not used.

### General procedure for the electrocatalytic reduction

The reactions were carried out in a single-compartment cell containing a magnetic stirring bar, a samarium cathode (20 cm<sup>2</sup> surface area), a glassy carbon anode (20 cm<sup>2</sup> surface area) and an SCE as reference electrode. The cell is then charged with 50 mL of an electrolyte solution containing 0.01 M *n*Bu<sub>4</sub>NPF<sub>6</sub> in MeOH. The nitroarene derivative (1.0 mmol), SmCl<sub>3</sub> (0.05 mmol or 0.1 mmol) and trimethylsilyl chloride (8.0 mmol) are then added to the mixture. Electrolysis was carried out at *i* = 50 mA for 5 hours in air. The mixture was then diluted by EtOAc (50 mL), quenched with NaHCO<sub>3</sub> (20 mL) and extracted with EtOAc (3x20 mL). The combined extracts were washed with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and brine. The organic layer was dried over MgSO<sub>4</sub> and the solvent removed under reduced pressure. The crude product was purified by flash chromatography on silica gel. The compounds obtained were identified by comparing their physical and spectral data with those in the literature.

### Characterization data of amino compounds

**4-methoxyaniline 2a**;<sup>[39]</sup> column (Ethyl acetate: Pentane = 1: 1), colorless crystal (120 mg, 0.97 mmol, 98%); m.p. = 57 °C; <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 6.75 (d, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 8.9 Hz, 2H), 3.75 (s, 3H), 3.11 (brs, 2H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>) δ 152.8, 139.94, 116.4, 114.8, 55.7; HRMS (ESI) Calcd for C<sub>7</sub>H<sub>10</sub>NO (M+H<sup>+</sup>): 124.0757. Found: 124.0762.

**4-(trifluoromethyl)aniline 2b**;<sup>[40]</sup> Column (Ethyl acetate: Pentane = 1: 5), colorless oil (158 mg, 0.98 mmol, 98%); <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 7.44 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 3.94 (brs, 2H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>) δ 149.5, 129.4, 126.7 (d, *J* = 4.0 Hz), 123.0 (q, *J* = 268.7 Hz), 119.9 (q, *J* = 32.4 Hz), 114.2; HRMS (ESI) Calcd for C<sub>7</sub>H<sub>7</sub>F<sub>3</sub>N (M+H<sup>+</sup>): 162.0525. Found: 162.0526.

**2-methoxyaniline 2c**;<sup>[41]</sup> Column (Ethyl acetate: Pentane = 1: 3), yellow oil (121 mg, 0.98 mmol, 98%); <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 6.99-6.79 (m, 4H), 3.94 (s, 3H), 3.88 (brs, 2H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>) δ 147.4, 136.4, 121.2, 118.5, 115.1, 110.6, 55.5; HRMS (ESI) Calcd for C<sub>7</sub>H<sub>10</sub>NO (M+H<sup>+</sup>): 124.0757. Found: 124.0761.

**3-methoxyaniline 2d**;<sup>[42]</sup> Column (Ethyl acetate: Pentane = 1: 3), brown oil (118 mg, 0.96 mmol, 96%); <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 7.14 (t, *J* = 8.0 Hz, 1H), 6.45-6.25 (m, 3H), 3.82 (s, 3H), 3.75 (brs, 2H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>) δ 160.8, 148.0, 130.2, 108.0, 103.9, 101.0, 55.1; HRMS (ESI) Calcd for C<sub>7</sub>H<sub>10</sub>NO (M+H<sup>+</sup>): 124.0757. Found: 124.0763.

**aniline 2e**;<sup>[41]</sup> Column (Ethyl acetate: Pentane = 1: 5), yellow oil (91 mg, 0.98 mmol, 98%); <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 7.31 (t, *J* = 7.7 Hz, 2H), 6.98-6.86 (m, 1H), 6.79 (d, *J* = 7.6 Hz, 2H), 3.64 (brs, 2H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>) δ 146.6, 129.4, 118.6, 115.3; HRMS (ESI) Calcd for C<sub>6</sub>H<sub>8</sub>N (M+H<sup>+</sup>): 94.0651. Found: 94.0648.

***p*-toluidine 2f**;<sup>[39]</sup> Column (Ethyl acetate: Pentane = 1: 2), colorless crystal (107 mg, 1 mmol, 100%); m.p. = 44 °C; <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 7.02 (d, *J* = 7.9 Hz, 2H), 6.66 (d, *J* = 7.9 Hz, 2H), 3.41 (brs, 2H), 2.30 (s, 3H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>) δ 143.8, 129.8, 127.8, 115.3, 20.5; HRMS (ESI) Calcd for C<sub>7</sub>H<sub>10</sub>N (M+H<sup>+</sup>): 108.0808. Found: 108.0810.

***o*-toluidine 2g**;<sup>[39]</sup> Column (Ethyl acetate: Pentane = 1: 2), yellow oil (103 mg, 0.96 mmol, 96%); <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 7.21-7.11 (m, 2H), 6.90-6.80 (m, 1H), 6.79-6.73 (m, 1H), 3.61 (brs, 2H), 2.28 (s, 3H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>) δ 144.7, 130.5, 127.0, 122.4, 118.7, 115.0, 17.4; HRMS (ESI) Calcd for C<sub>7</sub>H<sub>10</sub>N (M+H<sup>+</sup>): 108.0808. Found: 108.0810.

**2,6-dimethylaniline 2h**;<sup>[39]</sup> Column (Ethyl acetate: Pentane = 1: 5), brown oil (117 mg, 0.97 mmol, 97%); <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 6.53 (s, 1H), 6.42 (s, 2H), 3.56 (brs, 2H), 2.34 (s, 6H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>) δ 146.5, 139.1, 120.5, 113.2, 21.4; HRMS (ESI) Calcd for C<sub>8</sub>H<sub>12</sub>N (M+H<sup>+</sup>): 122.0964. Found: 122.0967.

**2,4-dimethylaniline 2i**;<sup>[43]</sup> Column (Ethyl acetate: Pentane = 1: 2), yellow oil (120 mg, 0.99 mmol, 99%); <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 7.22 (d, *J* = 7.5 Hz, 2H), 6.93 (t, *J* = 7.5 Hz, 1H), 3.73 (brs, 2H), 2.42 (s, 6H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>) δ 143.0, 128.5, 121.8, 118.2, 17.8; HRMS (ESI) Calcd for C<sub>8</sub>H<sub>12</sub>N (M+H<sup>+</sup>): 122.0964. Found: 122.0967.

**naphthalen-1-amine 2j**;<sup>[41]</sup> Column (Ethyl acetate: Pentane = 1: 2), brown solid (140 mg, 0.98 mmol 98%); m.p. = 48 °C; <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 7.89-7.80 (m, 2H), 7.55-7.47 (m, 2H), 7.41-7.30 (m, 2H), 6.84-6.78 (m, 1H), 3.96 (brs, 2H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>) δ 142.1, 134.4, 128.6, 126.4, 125.9, 124.9, 123.6, 120.8, 119.0, 109.7; HRMS (ESI) Calcd for C<sub>10</sub>H<sub>10</sub>N (M+H<sup>+</sup>): 144.0808. Found: 144.0807.

**naphthalen-2-amine 2k**;<sup>[44]</sup> Column (Ethyl acetate: Pentane = 1: 2), yellow solid (141 mg, 0.99 mmol, 99%); m.p. = 111 °C; <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 7.80-7.60 (m, 3H), 7.48-7.37 (m, 1H), 7.31-7.23 (m, 1H), 7.05-6.94 (m, 2H), 3.79 (brs, 2H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>) δ 144.1, 134.9, 129.2, 12.1, 127.7, 126.3, 125.8, 122.5, 118.2, 108.6; HRMS (ESI) Calcd for C<sub>10</sub>H<sub>10</sub>N (M+H<sup>+</sup>): 144.0808. Found: 144.0810.

**4-chloroaniline 2l**;<sup>[41]</sup> Column (Ethyl acetate: Pentane = 1: 2), yellow oil (126 mg, 0.99 mmol, 99%); <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 7.14 (d, *J* = 8.2 Hz, 2H), 6.63 (d, *J* = 8.2 Hz, 2H), 3.62 (brs, 2H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>) δ 145.1, 129.1, 123.0, 116.3; HRMS (ESI) Calcd for C<sub>6</sub>H<sub>7</sub>ClN (M+H<sup>+</sup>): 128.0262. Found: 128.0266.

**2-chloroaniline 2m**;<sup>[45]</sup> Column (Ethyl acetate: Pentane = 1: 2), brown oil (121 mg, 0.95 mmol, 95%); <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 7.38-7.30 (m, 1H), 7.20-7.10 (m, 1H), 6.82-6.72 (m, 2H), 4.02 (brs, 2H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>) δ 143.0, 129.5, 127.7, 119.3, 119.1, 116.0; HRMS (ESI) Calcd for C<sub>6</sub>H<sub>7</sub>ClN (M+H<sup>+</sup>): 128.0262. Found: 128.0265.

**3-chloroaniline 2n**;<sup>[43]</sup> Column (Ethyl acetate: Pentane = 1: 2), yellow oil (123 mg, 0.97 mmol, 97%); <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 7.10-7.00 (m, 1H), 6.78-6.69 (m, 1H), 6.65 (s, 1H), 6.56-6.47 (m, 1H), 3.68 (brs, 2H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>) δ 147.7, 134.8, 130.4, 118.4, 114.9, 113.3; HRMS (ESI) Calcd for C<sub>6</sub>H<sub>7</sub>ClN (M+H<sup>+</sup>): 128.0262. Found: 128.0265.

**4-fluoroaniline 2o**;<sup>[39]</sup> Column (Ethyl acetate: Pentane = 1: 3), yellow oil (103 mg, 0.93 mmol, 93%); <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>)

$\delta$  6.96-6.85 (m, 2H), 6.70-6.60 (m, 2H), 3.48 (brs, 2H);  $^{13}\text{C}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  156.5 (d,  $J = 235.0$  Hz), 142.5, 116.1 (d,  $J = 7.8$  Hz), 115.6 (d,  $J = 22.3$  Hz); HRMS (ESI) Calcd for  $\text{C}_6\text{H}_7\text{FN}$  ( $\text{M}+\text{H}^+$ ): 112.0557. Found: 112.0562.

**2-fluoroaniline 2p**;<sup>[39]</sup> Column (Ethyl acetate: Pentane = 1: 2), yellow oil (108 mg, 0.97 mmol, 97%);  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  7.15-6.985 (m, 2H), 6.90-6.74 (m, 2H), 3.73 (brs, 2H);  $^{13}\text{C}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  151.8 ( $J = 236.3$  Hz), 134.6 ( $J = 13.1$  Hz), 124.5 ( $J = 2.6$  Hz), 118.6 ( $J = 7.8$  Hz), 117.0 ( $J = 2.7$  Hz), 115.3 ( $J = 18.4$  Hz); HRMS (ESI) Calcd for  $\text{C}_6\text{H}_7\text{FN}$  ( $\text{M}+\text{H}^+$ ): 112.0557. Found: 112.0559.

**4-bromoaniline 2q**;<sup>[42]</sup> Column (Ethyl acetate: Pentane = 1: 3), yellow crystal (163 mg, 0.95 mmol, 95%); m.p. = 61 °C;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 (d,  $J = 8.3$  Hz, 2H), 6.58 (d,  $J = 8.3$  Hz, 2H), 3.66 (brs, 2H);  $^{13}\text{C}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  145.5, 132.0, 116.8, 110.1; HRMS (ESI) Calcd for  $\text{C}_6\text{H}_7\text{BrN}$  ( $\text{M}+\text{H}^+$ ): 171.9756 and 173.9736. Found: 171.9762 and 173.9742.

**2-bromoaniline 2r**;<sup>[44]</sup> Column (Ethyl acetate: Pentane = 1: 3), red oil (149 mg, 0.87 mmol, 87%);  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62-7.28 (m, 1H), 7.26-6.98 (m, 1H), 6.88-6.75 (m, 1H), 6.73-6.59 (m, 1H), 3.99 (brs, 2H);  $^{13}\text{C}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  144.1, 132.6, 128.3, 119.4, 115.8, 109.3; HRMS (ESI) Calcd for  $\text{C}_6\text{H}_7\text{BrN}$  ( $\text{M}+\text{H}^+$ ): 171.9756 and 173.9736. Found: 171.9756 and 173.9740.

**4-iodoaniline 2s**;<sup>[41]</sup> Column (Ethyl acetate: Pentane = 1: 2), colorless crystal (211 mg, 0.96 mmol, 96%); m.p. = 63 °C;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (d,  $J = 8.8$  Hz, 2H), 6.50 (d,  $J = 8.5$  Hz, 2H), 3.55 (brs, 2H);  $^{13}\text{C}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  146.1, 137.9, 117.3, 79.4; HRMS (ESI) Calcd for  $\text{C}_6\text{H}_7\text{IN}$  ( $\text{M}+\text{H}^+$ ): 219.09618. Found: 219.9618.

**2-iodoaniline 2t**;<sup>[46]</sup> Column (Ethyl acetate: Pentane = 1: 3), brown solid (200 mg, 0.91 mmol, 91%); m.p. = 56 °C;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81-7.53 (m, 1H), 7.30-6.97 (m, 1H), 6.90-6.74 (m, 1H), 6.60-6.40 (m, 1H), 4.03 (brs, 2H);  $^{13}\text{C}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  146.8, 139.0, 129.4, 120.0, 114.8, 84.3; HRMS (ESI) Calcd for  $\text{C}_6\text{H}_7\text{IN}$  ( $\text{M}+\text{H}^+$ ): 219.09618. Found: 219.9617.

**3,5-dichloroaniline 2u**;<sup>[47]</sup> Column (Ethyl acetate: Pentane = 1: 5), grey solid (158 mg, 0.98 mmol, 98%); m.p. = 50 °C;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  6.76 (s, 1H), 6.57 (s, 2H), 3.84 (brs, 2H);  $^{13}\text{C}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  148.2, 135.4, 118.3, 113.2; HRMS (ESI) Calcd for  $\text{C}_6\text{H}_6\text{Cl}_2\text{N}$  ( $\text{M}+\text{H}^+$ ): 161.9872. Found: 161.9877.

**4-aminobenzonitrile 2v**;<sup>[40]</sup> Column (Ethyl acetate: Pentane = 1: 2), yellow solid (113 mg, 0.96 mmol, 96%); m.p. = 85 °C;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (d,  $J = 8.7$  Hz, 2H), 6.67 (d,  $J = 8.7$  Hz, 2H), 4.29 (brs, 2H);  $^{13}\text{C}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  150.7, 133.8, 120.3, 114.4, 99.7; HRMS (ESI) Calcd for  $\text{C}_7\text{H}_6\text{N}_2\text{Na}$  ( $\text{M}+\text{Na}^+$ ): 141.0423. Found: 141.0421.

**methyl 4-aminobenzoate 2w**;<sup>[39]</sup> Column (Ethyl acetate: Pentane = 1: 3), yellow solid (143 mg, 0.95 mmol, 95%); m.p. = 110 °C;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (d,  $J = 8.6$  Hz, 2H), 6.66 (d,  $J = 8.6$  Hz, 2H), 4.16 (brs, 2H), 3.87 (s, 3H);  $^{13}\text{C}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  167.2, 150.9, 131.6, 113.8, 51.6; HRMS (ESI) Calcd for  $\text{C}_8\text{H}_{10}\text{NO}_2$  ( $\text{M}+\text{H}^+$ ): 152.0706. Found: 152.0711.

**4-(benzyloxy)aniline 2x**;<sup>[48]</sup> Column (Ethyl acetate: Pentane = 1: 1), red solid (189 mg, 0.95 mmol, 95%); m.p. = 46 °C;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58-7.35 (m, 5H), 6.88 (d,  $J = 8.8$  Hz, 2H), 6.68 (d,  $J = 8.8$  Hz, 2H), 5.05 (s, 2H), 3.41 (brs, 2H);  $^{13}\text{C}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  152.0, 140.3, 137.5, 128.5, 127.8, 127.6, 116.4,

116.1, 70.8; HRMS (ESI) Calcd for  $\text{C}_{13}\text{H}_{14}\text{NO}$  ( $\text{M}+\text{H}^+$ ): 200.1070. Found: 200.1077.

**1-(4-aminophenyl)ethanone 2y**;<sup>[39]</sup> Column (Ethyl acetate: Pentane = 1: 3), yellow solid (119 mg, 0.88 mmol, 88%); m.p. = 106 °C;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  8.18-7.60 (m, 2H), 6.65 (dd,  $J = 8.7, 2.4$  Hz, 1H), 4.25 (brs, 2H), 2.47 (s, 3H);  $^{13}\text{C}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  196.7, 151.4, 130.8, 127.5, 113.6, 26.1; HRMS (ESI) Calcd for  $\text{C}_8\text{H}_9\text{NNaO}$  ( $\text{M}+\text{Na}^+$ ): 158.0576. Found: 158.0576.

**1-(3-aminophenyl)ethanone 2z**;<sup>[39]</sup> Column (Ethyl acetate: Pentane = 1: 1), red solid (118 mg, 0.87 mmol, 87%); m.p. = 64 °C;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35-7.15 (m, 3H), 6.88-6.80 (m, 1H), 3.96 (brs, 2H), 2.50 (s, 3H);  $^{13}\text{C}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  198.7, 147.0, 138.1, 129.4, 119.7, 118.5, 113.9, 26.7; HRMS (ESI) Calcd for  $\text{C}_8\text{H}_9\text{NO}$  ( $\text{M}+\text{H}^+$ ): 136.0757. Found: 136.0764.

**(2-aminophenyl)(phenyl)methanone 2a**;<sup>[49]</sup> Column (Ethyl acetate: Pentane = 1: 3), grey solid (177 mg, 0.90 mmol, 90%); m.p. = 105 °C;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72-7.63 (m, 2H), 7.58-7.44 (m, 4H), 7.36-7.66 (m, 1H), 6.79-6.70 (m, 1H), 6.66-6.59 (m, 1H), 6.16 (brs, 2H);  $^{13}\text{C}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  199.1, 151.0, 140.1, 134.6, 134.3, 131.0, 129.1, 128.1, 118.1, 117.0, 115.5; HRMS (ESI) Calcd for  $\text{C}_{13}\text{H}_{11}\text{NNaO}$  ( $\text{M}+\text{Na}^+$ ): 220.0733. Found: 220.0734.

**4-nitroaniline 2b**;<sup>[39]</sup> Column (Ethyl acetate: Pentane = 1: 3), colorless crystal (125 mg, 0.91 mmol, 91%); m.p. = 147 °C;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 (d,  $J = 9.0$  Hz, 2H), 6.66 (d,  $J = 9.0$  Hz, 2H), 4.44 (brs, 2H);  $^{13}\text{C}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  152.5, 139.1, 126.4, 113.4; HRMS (ESI) Calcd for  $\text{C}_6\text{H}_7\text{N}_2\text{O}_2$  ( $\text{M}+\text{H}^+$ ): 139.0502. Found: 139.0506.

**benzene-1,4-diamine 2c**;<sup>[39]</sup> Column (Ethyl acetate: Methanol = 5: 1), red crystal (106 mg, 0.98 mmol, 98%); m.p. = 141 °C;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  6.61 (s, 4H), 3.19 (brs, 4H);  $^{13}\text{C}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  138.6, 116.7; HRMS (ESI) Calcd for  $\text{C}_6\text{H}_9\text{N}_2$  ( $\text{M}+\text{H}^+$ ): 109.0760. Found: 109.0763.

**4-aminophenol 3a**;<sup>[45]</sup> Column (Ethyl acetate: Methanol = 10: 1), colorless crystal (101 mg, 0.93 mmol, 93%); m.p. = 187 °C;  $^1\text{H}$  NMR (250 MHz,  $\text{DMSO}-d_6$ )  $\delta$  8.38 (brs, 1H), 6.53-6.35 (m, 4H), 4.40 (brs, 2H);  $^{13}\text{C}$  NMR (62.5 MHz,  $\text{DMSO}-d_6$ )  $\delta$  148.6, 141.1, 116.0, 115.7; HRMS (ESI) Calcd for  $\text{C}_6\text{H}_8\text{NO}$  ( $\text{M}+\text{H}^+$ ): 110.0600. Found: 110.0604.

**2-aminophenol 3b**;<sup>[46]</sup> Column (Ethyl acetate: Pentane = 1: 2), colorless crystal (105 mg, 0.96 mmol, 96%); m.p. = 174 °C;  $^1\text{H}$  NMR (250 MHz,  $\text{DMSO}-d_6$ )  $\delta$  8.96 (brs, 1H), 6.70-6.32 (m, 4H), 4.48 (brs, 2H);  $^{13}\text{C}$  NMR (62.5 MHz,  $\text{DMSO}-d_6$ )  $\delta$  144.4, 136.9, 120.0, 119.9, 114.8; HRMS (ESI) Calcd for  $\text{C}_6\text{H}_8\text{NO}$  ( $\text{M}+\text{H}^+$ ): 110.0600. Found: 110.0603.

**(2-aminophenyl)methanol 3c**;<sup>[50]</sup> Column (Ethyl acetate: Pentane = 4: 1), white solid (113 mg, 0.92 mmol, 92%); m.p. = 84 °C;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  7.15-7.08 (m, 1H), 7.05-6.096 (m, 1H), 6.74-6.62 (m, 2H), 4.63 (s, 2H), 3.49 (brs, 3H);  $^{13}\text{C}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  145.9, 129.3, 129.2, 124.9, 118.2, 116.1, 64.2; HRMS (ESI) Calcd for  $\text{C}_7\text{H}_9\text{NNaO}$  ( $\text{M}+\text{Na}^+$ ): 146.0576. Found: 146.0591.

**(3-aminophenyl)methanol 3d**;<sup>[51]</sup> Column (Ethyl acetate: Pentane = 4: 1), white solid (115 mg, 0.93 mmol, 93%); m.p. = 95 °C;  $^1\text{H}$  NMR (360 MHz,  $\text{DMSO}-d_6$ )  $\delta$  6.97 (t,  $J = 7.7$  Hz, 1H), 6.58 (s, 1H), 6.50-6.41 (m, 2H), 5.05 (t,  $J = 5.8$  Hz, 1H), 4.98 (s, 2H), 4.38 (d,  $J = 5.8$  Hz, 2H);  $^{13}\text{C}$  NMR (90 MHz,  $\text{DMSO}-d_6$ )  $\delta$



148.8, 143.5, 128.9, 114.5, 112.8, 112.6, 63.7; HRMS (ESI) Calcd for  $C_7H_{10}NO$  ( $M+H^+$ ): 124.0757. Found: 124.0760.

**4-aminobenzoic acid 3e**;<sup>[41]</sup> Column (Ethyl acetate: Pentane = 9: 1), brown solid (131 mg, 0.96 mmol, 96%); m.p. = 190 °C; <sup>1</sup>H NMR (360 MHz, DMSO- $d_6$ )  $\delta$  11.99 (brs, 1H), 7.63 (d,  $J$  = 7.9 Hz, 2H), 6.55 (d,  $J$  = 7.9 Hz, 2H), 5.88 (brs, 2H); <sup>13</sup>C NMR (90 MHz, DMSO- $d_6$ )  $\delta$  168.0, 153.6, 131.7, 117.3, 113.0; HRMS (ESI) Calcd for  $C_7H_8NO_2$  ( $M+H^+$ ): 138.0550. Found: 138.0552.

**3-aminobenzoic acid 3f**;<sup>[41]</sup> Column (Ethyl acetate: Pentane = 8: 1), yellow solid (121 mg, 0.88 mmol, 88%); m.p. = 174 °C; <sup>1</sup>H NMR (360 MHz, DMSO- $d_6$ )  $\delta$  12.5 (brs, 1H), 7.21-7.12 (m, 1H), 7.10-7.02 (m, 2H), 6.81-6.73 (m, 1H), 5.38 (brs, 2H); <sup>13</sup>C NMR (90 MHz, DMSO- $d_6$ )  $\delta$  168.3, 149.2, 131.7, 129.3, 118.4, 117.0, 114.8; HRMS (ESI) Calcd for  $C_7H_8NO_2$  ( $M+H^+$ ): 138.0550. Found: 138.0552.

**pyridin-4-amine 5a**;<sup>[46]</sup> Column (Ethyl acetate: Pentane = 1: 1), colorless crystal (93 mg, 0.99 mmol, 99%); m.p. = 158 °C; <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>)  $\delta$  8.20-8.16 (m, 2H), 6.50-6.45 (m, 2H), 4.16 (brs, 2H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>)  $\delta$  152.6, 150.2, 109.6; HRMS (ESI) Calcd for  $C_5H_7N_2$  ( $M+H^+$ ): 95.0604. Found: 95.0604.

**pyridin-2-amine 5b**;<sup>[46]</sup> Column (Ethyl acetate: Pentane = 1: 1), yellow solid (91 mg, 0.97 mmol, 97%); m.p. = 56 °C; <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>)  $\delta$  8.04-8.00 (m, 1H), 7.40-7.33 (m, 1H), 6.62-6.56 (m, 1H), 6.47-6.42 (m, 1H), 4.48 (brs, 2H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>)  $\delta$  158.5, 148.0, 137.7, 113.9, 108.6; HRMS (ESI) Calcd for  $C_5H_7N_2$  ( $M+H^+$ ): 95.0604. Found: 95.0604.

**6-chloropyridin-3-amine 5c**;<sup>[51]</sup> Column (Ethyl acetate: Pentane = 1: 1), yellow solid (118 mg, 0.92 mmol, 92%); m.p. = 78 °C; <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>)  $\delta$  7.81-7.77 (m, 1H), 7.07-6.90 (m, 2H), 3.56 (brs, 2H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>)  $\delta$  141.8, 140.1, 136.3, 124.8, 124.1; HRMS (ESI) Calcd for  $C_5H_6ClN_2$  ( $M+H^+$ ): 129.0214. Found: 129.0213.

**5-chloropyridin-2-amine 5d**;<sup>[52]</sup> Column (Ethyl acetate: Pentane = 1: 1), grey crystal (119 mg, 0.93 mmol, 93%); m.p. = 136 °C; <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>)  $\delta$  8.0"-8.00 (m, 1H), 7.42-7.37 (m, 1H), 6.49-6.45 (m, 1H), 4.4" (brs, 2H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>)  $\delta$  156.8, 146.4, 137.5, 120.9, 109.4; HRMS (ESI) Calcd for  $C_5H_6ClN_2$  ( $M+H^+$ ): 129.0214. Found: 129.0212.

**4-methylpyridin-2-amine 5e**;<sup>[52]</sup> Column (Ethyl acetate: Pentane = 1: 1), yellow solid (105 mg, 0.97 mmol, 97%); m.p. = 96 °C; <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>)  $\delta$  7.89-7.85 (s, 1H), 6.44-6.40 (m, 1H), 6.27-6.25 (m, 1H), 4.42 (brs, 2H), 2.18 (s, 3H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>)  $\delta$  158.7, 148.7, 147.7, 155.4, 108.9, 21.0; HRMS (ESI) Calcd for  $C_6H_9N_2$  ( $M+H^+$ ): 109.0760. Found: 109.0763.

**5-methylpyridin-2-amine 5f**;<sup>[53]</sup> Column (Ethyl acetate: Pentane = 1: 1), yellow solid (104 mg, 0.96 mmol, 96%); m.p. = 76 °C; <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>)  $\delta$  7.83 (s, 1H), 7.2-7.13 (m, 1H), 6.4-6.32 (m, 1H), 4.43 (brs, 2H), 2.12 (s, 3H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>)  $\delta$  156.5, 147.5, 138.7, 122.6, 108.4, 17.4; HRMS (ESI) Calcd for  $C_6H_9N_2$  ( $M+H^+$ ): 109.0760. Found: 109.0762.

**2-bromopyridin-3-amine 5g**;<sup>[54]</sup> Column (Ethyl acetate: Pentane = 1: 1), orange crystal (159 mg, 0.92 mmol, 92%); m.p. = 77 °C; <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>)  $\delta$  7.70-7.67 (m, 1H), 6.99-6.92 (m, 2H), 4.15 (brs, 2H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>)  $\delta$  141.5, 139.0, 129.5, 123.7 122.0; HRMS (ESI) Calcd for  $C_5H_6BrN_2$  ( $M+H^+$ ): 172.9709. Found: 172.9707.

**2-chloropyridin-3-amine 5h**;<sup>[55]</sup> Column (Ethyl acetate: Pentane = 1: 1), yellow crystal (121 mg, 0.95 mmol, 95%); m.p. = 76 °C; <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>)  $\delta$  7.70-7.67 (m, 1H), 7.00-6.92 (m, 2H), 4.18 (brs, 2H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>)  $\delta$  139.9, 138.3, 136.7, 123.4, 122.5; HRMS (ESI) Calcd for  $C_5H_6ClN_2$  ( $M+H^+$ ): 129.0214. Found: 129.0213.

**quinolin-3-amine 5i**;<sup>[56]</sup> Column (Ethyl acetate: Pentane = 1: 1), red solid (137 mg, 0.95 mmol, 95%); m.p. = 92 °C; <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>)  $\delta$  8.57-8.40 (m, 1H), 8.05-7.90 (m, 1H), 7.61-7.50 (m, 1H), 7.49-7.32 (m, 2H), 7.22-7.10 (m, 1H), 3.99 (brs, 2H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>)  $\delta$  143.1, 142.6, 139.9, 129.2, 128.9, 126.9, 125.9, 125.5, 114.8; HRMS (ESI) Calcd for  $C_9H_9N_2$  ( $M+H^+$ ): 145.0760. Found: 145.0764.

**quinolin-8-amine 5j**;<sup>[57]</sup> Column (Ethyl acetate: Pentane = 1: 1), red solid (131 mg, 0.91 mmol, 91%); m.p. = 62 °C; <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>)  $\delta$  8.85-8.72 (m, 1H), 8.11-7.97 (m, 1H), 7.42-7.28 (m, 2H), 7.13-7.08 (m, 1H), 7.00-6.86 (m, 1H), 5.06 (brs, 2H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>)  $\delta$  147.4, 144.0, 138.4, 136.0, 128.8, 127.4, 121.3, 116.0, 110.0; HRMS (ESI) Calcd for  $C_9H_9N_2$  ( $M+H^+$ ): 145.0760. Found: 145.0768.

**1H-indol-5-amine 5k**;<sup>[45]</sup> Column (Ethyl acetate: Pentane = 1: 1), grey solid (128 mg, 0.97 mmol, 97%); m.p. = 132 °C; <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>)  $\delta$  8.05 (brs, 1H), 7.20-7.08 (m, 2H), 6.95-6.92 (m, 1H), 6.68-6.61 (m, 2H), 6.37-6.34 (m, 1H), 3.34 (brs, 2H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>)  $\delta$  139.4, 130.7, 128.7, 124.7, 112.9, 111.5, 105.5, 101.5; HRMS (ESI) Calcd for  $C_8H_9N_2$  ( $M+H^+$ ): 133.0760. Found: 133.0764.

**cyclohexanamine 7**;<sup>[51]</sup> Column (Ethyl acetate: Pentane = 2: 1), brown oil (95 mg, 0.96 mmol, 96%); <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>)  $\delta$  2.56-2.41 (m, 1H), 1.70-1.761 (m, 2H), 1.60-1.51 (m, 2H), 1.50-1.40 (m, 1H), 1.20-0.81 (m, 7H); <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>)  $\delta$  50.3, 36.8, 25.6, 25.0; HRMS (ESI) Calcd for  $C_6H_{14}N$  ( $M+H^+$ ): 100.1121. Found: 100.1117.

## Supporting Information

Supporting information for this article is available on the WWW under <https://doi.org/.....>

## Acknowledgements

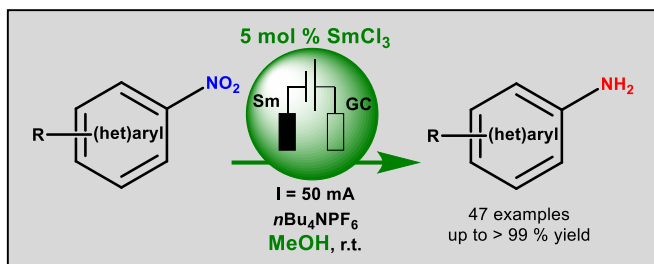
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## Entry for the Table of Contents



The preparation of various aminoarenes is described based on the Sm-promoted catalytic electrochemical reduction of corresponding nitroarenes. This mild procedure tolerates a wide range of functional groups and yields the targeted products in almost all cases in excess of 90%.

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