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Gold-Catalyzed Reductive Transformation of Nitro Compounds Using Formic Acid: Mild, Efficient, and Versatile

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Developing new efficient catalytic systems to convert abundant and renewable feedstocks into valuable products in a compact, flexible, and target-specific manner is of high importance in modern synthetic chemistry. Here, we describe a versatile set of mild catalytic conditions utilizing a single gold-based solid catalyst that enables the direct and additive-free preparation of four distinct and important amine derivatives (amines, formamides, benzimidazoles, and dimethlyated amines) from readily available formic acid (FA) and nitro starting materials with high level of chemoselectivity. By controlling the stoichiometry of the employed FA, which has attracted considerable interest in the area of sustainable chemistry because of its potential as an entirely renewable hydrogen carrier and as a versatile C_1 source, a facile atom- and step-efficient transformation of nitro compounds can be realized in a modular fashion.

Chemical reduction of unsaturated bonds of readily available chemical feedstocks is one of the most fundamental transformations in organic chemistry.[1] In particular, the reductive transformation of molecules containing nitro functional groups is of special interest since the reduced products (amines and related derivatives) are key intermediates or targets in the synthesis of pharmaceuticals, dyes, agrochemicals, pigments, and polymers.[2,3] Despite many known methods, there are unceasing efforts to develop new clean, facile, cost-effective, green, and chemoselective procedures that eliminate the use of large excess of expensive and perilous stoichiometric reducing agents.[4] In this respect, H_2 gas is arguably one of the most popular and attractive means to effect reduction, thereby leading to a number of catalytic hydrogenation procedures amenable to reduce nitro compounds.[5] However, application of these processes is constrained by the need for specialized equipment, limited functional group tolerance, and potential safety issues regarding H_2 handling. Even more importantly, it is pertinent to point out that the use of H_2 is not perfectly atom-economical as it might seem owing to current industrial production of H_2 relying overwhelmingly on fossil fuels and the fact that the associated emissions have led to a net increase in global CO_2 levels.[6]

There is considerable current interest in exploiting formic acid (FA) as a promising molecule for hydrogen storage and delivery, which has been advocated as a carbon-neutral energy source to meet the ever-increasing demand for a sustainable and affordable energy supply.[7] Of the most attractive features of FA, apart from its accessibility as a major product from biomass processing, is the possibility to establish an integrated energy storage scheme for a dispatchable solar- and wind-powered energy system based on a reversible FA–CO_2 interconversion.[8] Given the fact that FA easily undergoes selective dehydrogenation to yield H_2, FA can be envisioned as an appealing terminal reductant.[9] With regard to green organic synthesis, this approach is particularly attractive in light of the apparent and compelling advantage of using FA as a biorenewable C_1 source for attaching CO, CHO, or methyl groups.[10] In this regard, reductive transformation using FA may bring about new opportunities for the construction of molecular complexity.[10b,c] Despite the prospects for contributions to both flexibility and step economy of such types of transformations, progress in this area, especially expanding the scope of the FA–nitro reaction, has been largely limited to nitro-to-amine transformations.[11] Moreover, the reported reactions generally necessitate the use of FA in large excess,[11a–d] which adversely affects the overall atom efficiency.

Heterogeneous Au catalysis has recently emerged as an important and powerful tool for clean and resource-efficient chemical synthesis.[12] In particular, various supported Au catalysts have been reported to show distinct reactivity, activity, and selectivity in a number of industrially important processes,[13] complementing and expanding the existing areas of traditional platinum-group metal (PGM) catalysis. As part of our continuing exploration into new reaction chemistry by supported Au nanoparticles (NPs),[14] we recently discovered the outstanding catalytic ability of Au NPs for FA activation, wherein we found that subnanomeric gold NPs (ca. 0.8 nm) finely dispersed on ZrO_2 can promote efficient and selective H_2 generation from FA dehydrogenation under ambient conditions.[14a] Realizing the advantages of adopting the Au-based reduction protocols and also utilizing the excellent catalytic activity of supported Au toward FA activation,[12–14] we became intrigued by the catalytic utility of the Au–FA protocol to develop innovative catalytic processes that enable direct and ad-

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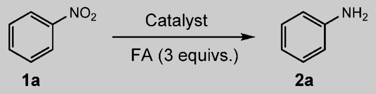
ditive-free transformation of nitro compounds under mild and clean conditions. Herein, we report an efficient, versatile, and scalable approach to the target-specific transformation of nitro compounds employing FA as the hydrogen source using a single supported Au catalyst system under mild and atom-efficient conditions.

Initial experiments were aimed at evaluating the feasibility of Au-catalyzed nitro-to-amine reduction using only a stoichiometric amount of FA under base-free conditions. As a preliminary test, the reductive conversion of nitrobenzene (**1a**) was carried out, where 3.0 equivalents of FA were used as a hydrogen source, with the Au/ZrO_2–NCs (NC = nanoclusters; 1 mol%) catalyst in toluene at 60 °C. Unfortunately, this experiment afforded only modest yield (ca. 10%) of aniline (**2a**), with appreciable amounts of formanilide (**3a**) as a sole by-product resulting from the direct reductive formylation of **1a** (Table 1, entry 1). It was hypothesized that the extremely high activity of the subnanometric Au/ZrO_2–NCs catalyst toward FA activation favors rapid H_2 gas release as a result of unproductive FA decomposition, thus preventing the desired conversion of **1a** into **2a**. In agreement with this reasoning, the use of Au/ZrO_2, which is less reactive toward FA decomposition as a catalyst and which possesses a larger average Au particle size (ca. 1.8 nm) compared to the Au/ZrO_2–NCs material (0.8 nm), resulted in dramatic improvements, thus providing a boosted conversion of **1a** and a moderate yield (30%) of **2a** (entry 2). While an attempt to further optmize the process parameters failed to give higher yields of **2a** (Table S1, entries 1 and 2), even by prolonging the reaction time or elevating the reaction temperature, careful analysis of the gas phase reaction mixtures at the end of a typical reaction employing the Au/ZrO_2 catalyst showed a CO_2-to-H_2ratio of ca. 1.8, demonstrating that about 51% of the consumed FA was decomposed to H_2 (see Section 2.1 in the Supporting Information).

Table 1. Reduction of nitrobenzene to aniline under various conditions.[a]



Entry	Catalyst	T [°C]	Solvent	Conversion [%]	Selectivity [%]
1	Au/ZrO_2–NCs	60	toluene	15	71
2	Au/ZrO_2	60	toluene	43	72
3	Au/TiO_2	60	toluene	68	>99
4	Au/rutile	60	toluene	>99	>99
5	Au/anatase	60	toluene	16	>99
6	Au/Al_2O_3	60	toluene	47	78
7	Au/CeO_2	60	toluene	40	76
8	Au/SiO_2	60	toluene	6	85
9[b]	Au/rutile	25	toluene	>99	>99
10[b]	Pd/rutile	25	toluene	n.r.	–
11[b]	Ru/rutile	25	toluene	n.r.	–
12[b]	Pt/rutile	25	toluene	n.r.	–
13[b]	Ir/rutile	25	toluene	n.r.	–
14[c]	Au/rutile	90	toluene	>99	>99
15[d]	Au/rutile	120	toluene	97	>99
16	Au/rutile	60	ethanol	78	91
17	Au/rutile	60	cyclohexane	73	99
18	Au/rutile	60	THF	69	86
19	Au/rutile	60	1,4-dioxane	23	87
20[e]	Au/rutile	60	water	>99	>99
21[f]	Au/rutile	60	water	>99	>99
22[g]	Au/rutile	70	toluene	>99	>99
23[h]	Au/rutile	40	toluene	>99	>99

[a] **1a** (1 mmol), FA (3 mmol), catalyst (1 mol% metal), solvent (5 mL), N_2 (1 bar), 40 min; GC analysis using *n*-decane as an internal standard; n.r. = no reaction. [b] 12 h. [c] **1a** (2 mmol), FA (6 mmol), Au (0.01 mol%), 4 h. [d] **1a** (10 mmol), FA (30 mmol), Au (0.001 mol%), 25 h. [e] 30 min. [f] 30 min, under air. [g] 15 min. [h] 3.5 h.

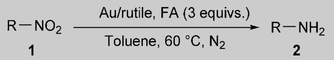
Given the recognized critical role of the support for rendering the catalytic properties of supported Au, we turned our attention to Au deposited on various other support materials for converting **1a** to **2a**. It turns out that the integration of Au and TiO_2 was essential for this particular transformation. Gratifyingly, the use of high surface area rutile TiO_2 as the support yielded the highest activity to give a quantitative formation of the desired **2a** in 40 min at 60 °C (Table 1, entry 4). Note that Au/rutile successfully promoted the reduction reaction even at room temperature (Table 1, entry 9), conditions under which other supported metals, such as Pd, Pt, Ir and Ru, are completely inefficient (Table 1, entries 10–13). Remarkably, the reaction was equally efficacious even upon decreasing the Au loading to 0.01 mol% (Table 1, entry 14). Thus, in a gram-scale reaction of **1a** (tenfold scale up) for 5 h, 99% yield of **2a** was obtained (Figure S1). In this case, no traces of hydroxylamine (<1%), an unwanted potentially explosive by-product that usually formed in appreciable levels with traditional protocols under mild conditions,[4,5] are observed during the reaction. Furthermore, the recovered Au/rutile can also be reused at least five times while still maintaining the high conversion value on this scale (Figure S1). At an even a lower loading of 0.001 mol% of Au, a high conversion of 97% was still achievable, although a longer reaction time at elevated temperature is required (Table 1, entry 15). This correponds to a turnover number (TON) close to 9.7×10^4, which is, to the best of our knowledge, the highest value ever recorded in FA-mediated catalytic reduction of nitroaromatics.

By filtering off the Au/rutile catalyst after conducting the nitro-to-amine reduction for 10 min, we observed no further conversion during the next 30 min under the same conditions (Scheme S1), indicating that the heterogeneous reaction involves minimal catalyst leaching and that mechanisms entailing homogeneous reactions are not likely operating. Additional investigation under FA-limited conditions revealed that lower amounts of FA (1 or 2 equivalents) lead to incomplete reduction (Table S2), albeit **2a** was still the sole product during the whole reaction process. Furthermore, it was found that the choice of solvent has a profound influence on the reaction outcome (Table 1, entries 16–20). In contrast to previously reported activities using Fe-based complexes,[11b] less polar organic solvents appear to be more suitable and the highest efficiency is obtained in toluene. Interestingly, the use of neat water as a solvent can lead to an even higher reduction efficiency (Table 1, entry 20). Of yet further interest is that this catalytic system can also afford quantitative formation of **2a** in air

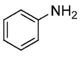
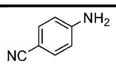
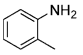
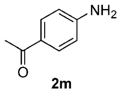
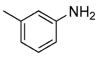
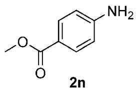
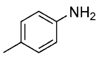
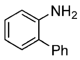
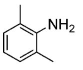
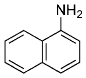
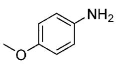
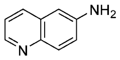
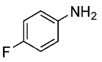
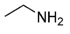
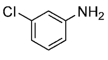
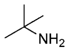
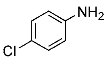
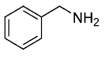
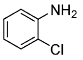
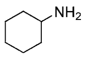
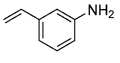
(Table 1, entry 21), thus offering distinct practical advantages over existing methods to establish a more convenient and industrially viable amine production process. To the best of our knowledge, a simple heterogeneous catalytic system that does not have ligands and additives and is highly efficient for reduction of nitro compounds by chemically equivalent amounts of FA in neat water has not been reported to date.

To investigate the scope and limits of this FA-mediated nitro reduction process, we next tested various structurally diverse functionalized nitro compounds. Remarkable amine selectivities were observed by applying a variety of nitro aromatics with both electron-withdrawing and electron-donating groups (Table 2, entries **2b**–**2p**). Note that reduction of halogen-substituted nitroaromatics, such as fluoro- or chlorobenzenes, proceeded smoothly and selectively, affording the corresponding anilines in excellent yields with no observable dehalogenation (Table 2, entries **2g**–**2j**). In the transformation of chloronitroaromatics as well as methylnitrobenzene, the higher reaction rate found for *p*-substituted nitrobenzene compared to the corresponding *o*- or *m*-substituted counterparts can be attributed to the steric effects. Moreover, a number of other reducible functional groups are also tolerated, including ester, ketone, alkene, nitrile (Table 2, entries **2k**–**2n**), and phenyl (Table 2, entry **2p**) functionality. In these transformations, the significant chemoselectivity for the specific reduction of the nitro group in the reactant is most likely due to the higher reactivity of the nitro group than that of the other reducible groups over the Au/rutile–FA system. This assumption is strongly supported by the intermolecular competitive reduction of nitrobenzene and other unsaturated substrates, such as acetophenone, benzonitrile, and styrene (Table S3). Especially noteworthy is that 6-aminoquinoline, possessing value as important intermediate for dyes, could be also successfully obtained from 6-nitroquinoline with excellent yield, indicating the heterocyclic ring was compatible in this reaction (entry **2q**). As more challenging examples, reduction proceeded almost quantitatively with non-activated aliphatic nitro compounds by employing this Au/rutile–FA system, resulting in complete consumption of the reactants accompanied by excellent selectivity (Table 2, entries **2r**–**2u**).

Table 2. Reduction of nitro compounds to corresponding amines with FA.[a,b]



$$R{-}NO_2 \xrightarrow[\text{Toluene, 60 °C, } N_2]{\text{Au/rutile, FA (3 equivs.)}} R{-}NH_2$$

Product	Yield [%]	Time [h]	Product	Yield [%]	Time [h]
 **2a**	> 99	0.67	 **2l**	> 99	2.0
 **2b**	> 99	2	 **2m**	> 99	1.5
 **2c**	> 99	1.5	 **2n**	> 99	1.5
 **2d**	> 99	1.0	 **2o**	> 99	2.5
 **2e**	> 99	2.5	 **2p**	> 99	2.5
 **2f**	98	2.0	 **2q**	> 99	2.5
 **2g**	> 99	1.0	 **2r**	> 99	4.0
 **2h**	> 99	1.5	 **2s**	> 99	4.0
 **2i**	> 99	1.0	 **2t**	> 99	4.0
 **2j**	> 99	2.0	 **2u**	> 99	4.0
 **2k**	97	2.0			

[a] Substrate (1 mmol), FA (3 mmol), Au (1 mol%), toluene (5 mL), N_2 (1 bar), 60 °C. [b] Yields determined using *n*-decane as an internal standard.

The outstanding catalytic activity for FA-mediated nitro reduction at above-mentioned conditions over Au/rutile clearly reflects the fast surface kinetics towards the desired transformation, presumably due to an unusual and extraordinary metal–support synergy enabling a facile surface-mediated highly specific reduction of **1a** to **2a**. By investigating the physicochemical properties of the Au/rutile catalyst, the following information was obtained. From the X-ray absorption near edge structure (XANES) results, it can be seen that there is only the metallic Au species present in the Au/rutile catalyst (Figure S2).[15] Inductively coupled plasma–atomic emission spectroscopy (ICP–AES) data revealed that there were no Au species in the solution after the reaction, demonstrating the absence of Au leaching during the whole reaction.[16] The X-ray diffraction (XRD) analysis showed that both the fresh and used Au/rutile catalysts had the similar crystal phase and there were no clear diffraction features for the Au species in these two samples, suggesting that the Au particle sizes were quite small (Figure S3). Transmission electron microscopy (TEM) was further used to confirm that the average diameters of Au particles were about 2.2 nm in the fresh and used Au/rutile catalysts, demonstrating that no Au NP aggregation occurred during the reaction (Figure S4). These results account for the remarkable durability of the Au/rutile catalyst in the recycling tests.

To better understand the superior activity and selectivity, we conducted several experiments to gain mechanistic insight into the present Au/rutile-FA nitro reduction system. We confirmed in separate experiments that sole FA decomposition did not occur to any practical degree in the absence of nitrobenzene and only traces of aniline (4%) were detected when the reaction was carried out with H_2 under otherwise identical conditions (Table S4). These results indicate that the present Au/rutile-mediated nitro reduction catalysis is entirely a transfer hydrogenation process, excluding the possibility of direct hydrogenation by H_2 generated from FA decomposition. In addition, variation of the hydrogen source revealed that FA is most effective (Table S5, entries 1–3). Compared to all other tested formates, FA is unique in terms of functioning as a stoichiometric reductant without the formation of any by-products under the present conditions. Hence, the addition of a base, for example, NEt_3, which is usually required for transfer hydrogenation,[11c] is not necessary.

To gain more insight into the Au/rutile-catalyzed nitro reduction, the dependency of reaction rates in the FA-mediated reduction of **1a** was investigated. The initial rates (R_0) were linearly proportional to the amount of Au/rutile and independent of the concentration of **1a** (Figure S7). From deuterium-labeling studies using DCOOD, we observed a relatively large kinetic isotope effect (KIE) of 5.25. A KIE of 4.67 was observed using DCOOH, and a KIE of 1.13 was observed using HCOOD (Table 3). These results suggest that the C–H bond breaking of chemisorbed FA is the rate-limiting step of the present reduction, which is in agreement with previous reports clarifying the dehydrogenative activation of FA over supported Au catalysts.[14a] Relevant mechanistic information is further obtained upon studying the reaction of hydroxylamine and nitroso-, azoxy-, and azobenzenes (Table S6), respectively, which indicates that the formation of **2a** in the presence of the Au/rutile catalyst preferentially takes place through the direct "nitro-nitroso-hydroxylamine" route (Scheme S2). An interesting observation that can be made upon inspection of Table S6 is that the product distribution turns out to be very complex when the reduction of intermediate hydroxylamine and nitroso was carried out under otherwise identical conditi ons described in Table 2, although the reduction of these two intermediates occurred with much higher rates than that for **1a**. This observation, together with the fact that only unreacted **1a** and the product amine were identified as transient species in solution during the entire course of the reaction, underscores the inherent surface-driven nature of the present FA-mediated nitro reduction. To elucidate the role of the support in the catalytic process, Fourier transform infrared (FTIR) studies of the adsorption ability of various supports for **1a** and FA were carried out. The adsorption abilities of supports exhibited good correlation with the catalytic activities of supported Au NPs (Figure S8). These results indicated that the high adsorption affinity of the rutile support may play an important role in favoring a higher concentration of **1a** and FA on the surface of Au/rutile, which appears to be the key factor for achieving high activity in the FA-induced nitro reduction. To shed more light on the mechanism behind this surface-mediated reaction, a further study of the reactions under 1 bar of H_2 with DCOOD or D_2 with HCOOH (Table S7) was carried out. It is revealed that the protons of the resulting amines come solely from FA. All these re-

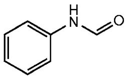
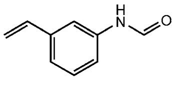
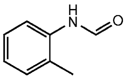
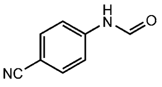
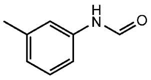
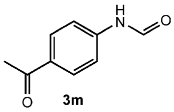
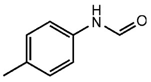
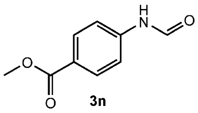
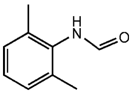
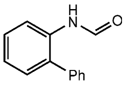
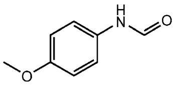
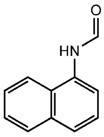
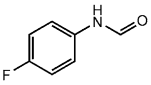
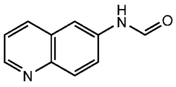
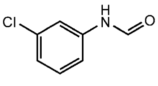
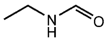
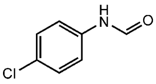
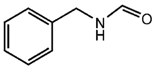
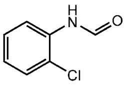
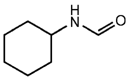
Table 3. Reduction of nitrobenzene to aniline with D-substituted FA over the Au/rutile catalyst.[a]

Entry	FA	Reaction rate [mmol min^{-1} $g_{Au}{}^{-1}$]	KIE[b]
1	HCOOH	42	–
2	HCOOD	37	1.13
3	DCOOH	9	4.67
4	DCOOD	8	5.25

[a] Nitrobenzene (1 mmol), FA (3 mmol), Au (1 mol %), toluene (5 mL), N_2 (1 bar), 60 °C; GC analysis using *n*-decane as an internal standard. [b] KIE = rate(entry 1)/rate(entry *n*); *n* = 2–4.

Table 4. Reductive *N*-formylation of nitro compounds to the corresponding formamides with FA.[a]

$$\underset{\mathbf{1}}{R{-}NO_2} \xrightarrow[\text{Toluene, 70 °C, } N_2]{\text{Au/rutile, FA (4 equivs.)}} \underset{\mathbf{3}}{R{-}NHCHO}$$

Product	Yield[b] [%]	Time [h]	Product	Yield[b] [%]	Time [h]
 **3a**	> 99 (96)	2.0	 **3k**	97 (92)	3.0
 **3b**	> 99 (95)	3.5	 **3l**	> 99 (94)	3.0
 **3c**	> 99 (95)	3.0	 **3m**	> 99 (95)	3.0
 **3d**	> 99 (96)	2.0	 **3n**	> 99 (95)	3.0
 **3e**	> 99 (94)	4.0	 **3o**	> 99 (96)	4.0
 **3f**	97 (93)	3.0	 **3p**	> 99 (95)	4.0
 **3g**	> 99 (96)	2.0	 **3q**	> 99 (94)	4.0
 **3h**	> 99 (94)	3.0	 **3r**	> 99 (94)	8.0
 **3i**	> 99 (96)	2.0	 **3s**	> 99 (95)	8.0
 **3j**	> 99 (95)	4.0	 **3t**	> 99 (95)	8.0

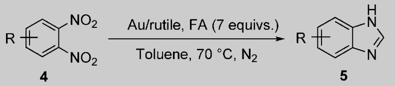
[a] Substrate (1 mmol), FA (4 mmol), Au (1 mol %), toluene (5 mL), N_2 (1 bar), 70 °C. [b] Yields determined using *n*-decane as an internal standard; data in parentheses indicate isolated yields.

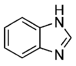
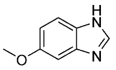
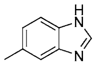
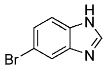
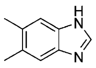
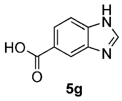
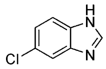
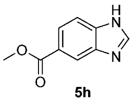
sults further confirm that the reaction proceeds via a Langmuir–Hinshelwood kinetic model in which chemisorption of both reactants (i.e., FA and nitrobenzene) occurred prior to their interconversion.

Having demonstrated the synthetic utility of the Au–FA-mediated nitro-to-amine process, we sought to evaluate the feasibility of establishing a tandem direct transformation of nitro compounds to formamides, an important class of intermediates widely used in the construction of pharmaceutically valuable compounds.[10c,17] This envisioned transformation of nitro compounds to formamides requires the presence of at least 4 equivs. of FA. It should be emphasized that there have been no reports of this particular transformation, despite the anticipated advantages of such a clean renewable process. We were pleased to find that a wide diversity of formamides can be achieved by performing a direct reductive nitro formylation using Au/rutile with only 4 equivs. of FA (Table 4, entries **3b**–**3t**). As with the case with nitro-to-amine conversion, this unprecedented one-pot protocol is tolerant to significant functional group variations on the aromatic ring. Moreover, excellent levels of direct reductive *N*-formylation are accomplished using various structurally diverse non-activated aliphatic nitro compounds. The utility and effectiveness of this one-pot reductive formylation procedure is further exemplified in the straightforward and efficient tandem synthesis of a diversity of benzimidazoles, which are prevalent in natural products and pharmaceutical agents and are important synthetic targets for drug discovery and development,[18] using various substituted *o*-dinitroarenes and again only 7 equivs. of FA as the starting materials (Table 5). Compared to previous known procedures, the Au-catalyzed one-pot reductive *N*-formylation process established here is notable for its expediency, the atom-efficient utilization of renewable feedstocks, mild reaction conditions, structural delivery of products, and excellent functional-group tolerance.

The high versatility of the Au-FA system for selective nitro transformation encouraged us to explore the feasibility of direct one-pot *N*-methylation of nitroaromatics to produce methylated amines, an important class of bioactive compounds widely found in many pharmaceuticals,[19] using FA as a convenient and straightforward C_1 source. Traditional methods for *N*-methylation make use of toxic formaldehyde or aggressive reagents such as methyl iodide and dimethyl sulfate as the C_1 source.[20] Several recent reports describe the use of abundantly available CO_2 as the benign C_1 feedstock for *N*-methylation.[21] However, due to the inherent thermodynamic stability of CO_2, strong reducing agent such as organosilanes[21a] or drastic reaction conditions (commonly $>150\,^{\circ}C$ and overall pressure higher than 80 bar)[21b,c] are generally required. There was, therefore, a strong incentive for the development of new efficient *N*-methylation methods relying on the use of more sustainable reagents. Preliminary attempts to carry out the direct nitro *N*-methylation with **1a** in the presence of excess FA (20–40 equivs.), however, resulted in a complex mixture of mono- and dimethyl anilines, formamides, and other intermediate products, with selectivity to methylated aniline products generally lower than 52% (Table S8, entry 3). The larger production of oxygenated products such as formamides, in the range 36–48%, over methylated anilines pointed to a lack of hydrogen in the reaction system. Thus, aiming to facilitate the *N*-methylation reaction, we turned to introducing additional H_2 gas. Our expectation was realized by applying a required amount of 40 bar H_2 (Table S8, entry 6), and we were able to acess several synthetically interesting functionalized dimethylanilines in excellent yields (Table 6) using this newly established reductive methylation procedure.[22] These results are, to the

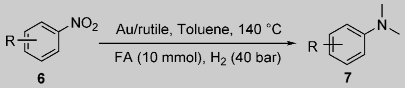
Table 5. Synthesis of benzimidazoles with *o*-dinitrobenzenes and FA.[a]

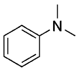
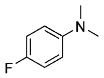
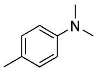
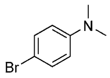
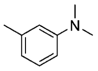
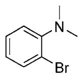
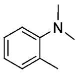
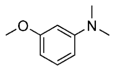


Product	Yield[b] [%]	Product	Yield[b] [%]
 **5a**	> 99 (97)	 **5e**	> 99 (94)
 **5b**	> 99 (96)	 **5f**	> 99 (96)
 **5c**	> 99 (95)	 **5g**	97 (93)
 **5d**	> 99 (95)	 **5h**	> 99 (95)

[a] Substrate (1 mmol), FA (7 mmol), Au (1 mol%), toluene (5 mL), N_2 (1 bar), 70 °C, 6 h. [b] Yields determined using *n*-decane as an internal standard; data in parentheses indicate isolated yields.

Table 6. Synthesis of dimethlyated amines from nitroarenes with FA/H_2.[a]



Product	Yield[b] [%]	Product	Yield[b] [%]
 **7a**	> 99 (95)	 **7e**	> 99 (96)
 **7b**	> 99 (95)	 **7f**	> 99 (94)
 **7c**	> 99 (95)	 **7g**	> 99 (95)
 **7d**	> 99 (94)	 **7h**	> 99 (94)

[a] Substrate (0.25 mmol), FA (10 mmol), Au (4 mol%), toluene (5 mL), H_2 (40 bar), 140 °C, 3 h. [b] Yields determined using *n*-decane as an internal standard; data in parentheses indicate isolated yields.

best of our knowledge, unprecedented examples of the construction of the methyl group using clean and renewable FA as the key starting material.

In summary, distinct examples of the use of the Au–formic acid (FA) combination as a versatile means for simple, mild, flexible, and scalable transformation of industrially important nitro compounds have been described. The present work illustrates the potential of this approach in terms of highly direct and controlled entries to amines, formamides, benzimidazoles, and dimethlyated amines. The synthesis of the latter relies upon the versatile use of FA as both a terminal reductant and renewable C_1 source. The chemistry described here, which exploits abundant and readily available bio-derived feedstocks, is expected to become an essential part of what could be termed the "new catalytic chemistry",[23] which exploits and utilizes the renewable natural resources for the synthesis of virtually any important organic compound.

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Keywords: formic acid · gold · heterogeneous catalysis · nitro compounds · selective transformation

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[22] Preliminary mechanistic studies by subjecting possible intermediates to the *N*-methylation reaction under otherwise identical conditions described in Table 6 have verified that this *N*-methylation reaction would proceed through a series of consecutive steps in a cascade mode (Scheme S3 in the Supporting Information), in which the reduction of **3a** and **8a** appeared to be the kinetically relevant steps of the overall reaction (Table S9).

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