

Methylation of amines, nitrobenzenes and aromatic nitriles with carbon dioxide and molecular hydrogen†

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CO₂/H₂ was successfully employed in alkylation reactions by performing CO₂ reduction and amine *N*-methylation in one-pot. In the presence of a simple CuAlOx catalyst, *N*-methyl or *N,N*-dimethyl amines with different structures can be selectively synthesized with up to 96% yields by applying amine, nitrobenzene and nitrile as starting materials.

Introduction

The controllable activation and application of CO₂ as a building block in catalytic transformations is one of the goals of the scientific community. Since the 1970's, two directions for carbon dioxide utilization have been explored. One direction uses carbon dioxide as a carbonyl source in catalytic carbonylation reactions, such as the synthesis of carboxylic acid,¹ ester or lactone,² formamide,³ urea or carbamate⁴ and polymer⁵ *etc.* Another direction for CO₂ utilization is the incorporation of carbon dioxide into basic chemicals including methanol, light alkanes or olefins.⁶ Although great developments have been achieved on fundamental research of the CO₂ activation,⁷ few industrial processes which utilize CO₂ as a raw material were realized because CO₂ is the most oxidized state of carbon and its catalytic activation is difficult. Undoubtedly, the direct transformation of CO₂ into valuable chemicals is still a challenge, and the development of new reactions for the efficient utilization of CO₂, as a building block in chemical synthesis, is highly desirable.⁸

Methylation reactions, such as the *N*-methylation and *N,N*-dimethylation of amines, which use methanol as an alkylation reagent have a vital function in the chemical industry, and they represent a series of key intermediates for the synthesis of dyes, perfumes, pesticides and others.⁹ Currently, these compounds are obtained through the *N*-methylation of amines with methanol or formaldehyde¹⁰ while the amines are produced *via* nitrobenzene or nitrile hydrogenation.¹¹ Considering the importance of applying carbon dioxide as the carbon source for

the production of carbon-based chemicals, it should be an ideal route to synthesize *N*-methyl or *N,N*-dimethyl amines by the reductive methylation of amines, nitrobenzenes or nitriles with carbon dioxide and a reducing agent. This approach presents an economic and sustainable way for *N*-methyl or *N,N*-dimethyl amine syntheses however, efficient catalyst systems are still required. In order to develop such a catalyst, several crucial factors are required; *i.e.* the catalyst must be highly active for carbon dioxide hydrogenation and amine *N*-methylation but inactive for aromatic ring hydrogenation. Recently, it was reported that amine methylation with CO₂/PhSiH₃ was achieved using a homogeneous catalyst system,¹² which provided a new methodology for the utilization of CO₂. Subsequently, the use of CO₂/H₂, as an alkylation reagent for amine methylation using homogeneous catalysts was reported.¹³ However, the one-pot reductive methylation of nitrobenzenes and aromatic nitriles with CO₂ has not previously been reported.

It is well known that nitrobenzene^{11a-d} and carbon dioxide reductions^{6,14} are performed with hetero- or homogeneous catalysts, which involve the activation of hydrogen molecules through adsorption on the catalytic active site to form hydride, and the transfer of the hydride to the nitro group or carbon dioxide. These results, combined with the recent progress of amine alkylation with alcohols, provide inspiration for the direct use of CO₂ and H₂ for the alkylation of amines. It was shown that the reaction can take a hydride formation and transfer route, too.¹⁵ Thus, according to the known catalyst systems for nitrobenzene and carbon dioxide reduction, and aniline alkylation, it may be possible to design and prepare a catalyst capable of utilizing H₂ for the reductive *N*-methylation of nitrobenzene with CO₂. Moreover, in consideration of the catalytic conditions of the carbon dioxide reduction, a non-noble metal catalyst might be a suitable candidate, because aromatic ring reduction often happens in the presence of a noble metal catalyst.¹⁶ Based on the above discussions, copper should be a good choice to achieve the target because it is the common active species in nitrobenzene hydrogenation,¹¹

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carbon dioxide reduction^{6,14} and amine alkylation,¹⁵ but is less active in aromatic ring hydrogenation.

Results and discussion

The catalyst used here was prepared by a co-precipitation method by adding an aqueous solution of Na₂CO₃ into a Cu(NO₃)₂ and Al(NO₃)₃ solution. The CuAlOx catalyst was obtained after separation, washing, drying, calcination and reduction under hydrogen flow of the precipitate. XPS characterization of the catalyst suggested the formation of metallic copper and Cu₂O, Fig. S1.† This result was confirmed by XRD characterization, which showed the diffraction patterns of Cu(111), (200), (220), (311) and Cu₂O(111), Fig. S2.† Regarding the HR-TEM characterization, crystal lattices of Cu(111) and Cu(200) can be observed clearly. Line-scan EDS analysis of the catalyst sample suggested it was composed of nano-CuOx particles deposited on the plane of AlOx, Fig. 1. BET analysis showed the surface area of the catalyst to be 138 m² g⁻¹, Fig. S3.†

The catalyst screening was performed using mono-methylation of aniline as the model reaction. First, an 86% yield of *N*-methyl aniline with 95% aniline conversion was obtained using the prepared CuAlOx catalyst (Table 1, Entry 1). The methylation reaction did not occur in the absence of the catalysts and <2% *N*-methyl aniline was formed if using Al₂O₃, Cu, Cu₂O, CuO or the mixture of Al₂O₃/Cu, Al₂O₃/CuO, Al₂O₃/Cu₂O and Al₂O₃/Cu/Cu₂O as catalysts directly (Table S1†). Therefore, the synergy between copper and aluminium generated during the catalyst preparation should be the major reason for its high activity. Importantly, the conversion and yield of the reaction was maintained at 97% and 82% at the 3rd run, suggesting that the catalyst is stable during the reaction. XRD characterization of the used catalyst sample showed almost the same crystal structure while some CuCO₃ formed on the surface of the catalyst according to XPS analysis, Fig. S1 and 2.† TEM and

Table 1 Selective methylation of primary amine with CO₂/H₂^a

$\text{R-NH}_2 \xrightarrow{\text{CO}_2/\text{H}_2} \text{R-NH-CH}_3 \text{ or } \text{R-N(CH}_3)_2$			
Entry	Substrates	Products	Yields/%
1			86 (81 ^b)/82 ^c
2			79
3			80 (74 ^b)
4			65
5			80
6			70
7			43
8			83 (77 ^b)
9			80
10			85 (82 ^b)
11			64
12			81
13			71
14			75 (69 ^b)
15			83

^a Reaction conditions: Entries 1–7, 1.0 mmol amine, 50 mg catalyst, 2 mL hexane, 3.0 MPa CO₂, 6.0 MPa H₂, 160 °C, 24 h; Entries 8–15, 1.0 mmol amine, 50 mg catalyst, 2 mL hexane, 3.0 MPa CO₂, 7.0 MPa H₂, 160 °C, 48 h. The yields were obtained by GC-FID using biphenyl as the external standard material. ^b Isolated yield. ^c The yield at the 3rd run.

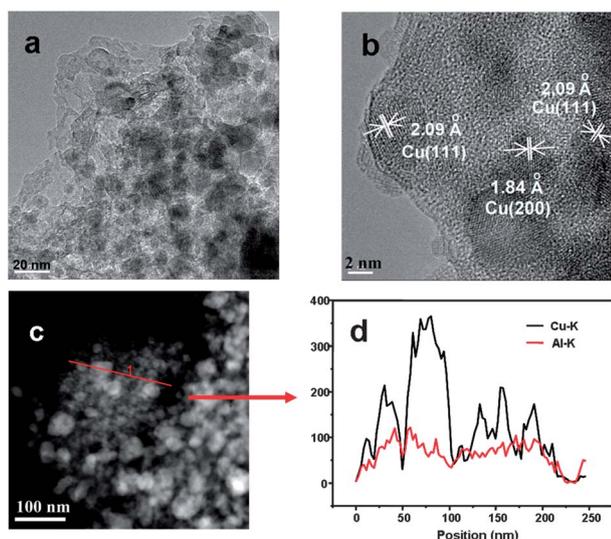


Fig. 1 TEM (a), HR-TEM (b) and line-scan EDS analysis (c) images of the CuAlOx catalyst sample (d).

line-scan EDS analysis of the used sample also showed a similar structure to the fresh catalyst, Fig. S4 and 5.† Furthermore, the reaction stopped if the catalyst was filtered off during the middle stage of the reaction and ICP-AES analysis showed that the metals which leached into the filtrate were below the detection limit. These findings suggest that the leached metals do not contribute significantly to the catalytic activity. In addition, if 10 mmol aniline was used as a starting material and 150 mg CuAlO_x was used as the catalyst, a 64% yield of *N*-methyl aniline was obtained with an 80% aniline conversion, Scheme S1.† This suggests that scaling up of the reaction is possible however, reducing the catalyst loading results in a low yield.

Following these initial studies, the *N*-methylation reactions of additional amines with CO₂/H₂ were explored. The transformation of anilines, which contain electron-donating as well as electron-withdrawing substituents at different positions, was carried out smoothly to obtain the corresponding products with 65–80% yields (Entries 2–4). During the methylation reaction, hydro-dechlorination of *p*-Cl-aniline was observed, which decreased the yield of the desired product. Biphenyl-2-amine and naphthalen-2-amine afforded the corresponding products with yields of 80% and 70% (Entries 5–6). However, dodecan-1-amine was converted into the corresponding product with a yield of only 43%, and the reason for its low activity is still currently unclear (Entry 7). The formation of tertiary amine products was observed to be the sole by-product of the mono-methylation reactions. We were encouraged by this result to further investigate the possibility of obtaining tertiary amines by tuning the reaction conditions. *N,N*-Dimethylaniline was produced with an 83% yield just by increasing the H₂ pressure from 6 MPa to 7 MPa and reacting for 48 h (Entry 8). Following this, we explored other *N,N*-dimethylation reactions to examine the scope and limitation of the current methodology. Anilines with either electron-donating or electron-withdrawing groups yielded the *N,N*-dimethyl amine products in moderate to good yields (Entries 9–11). The dechlorination also occurred and about 5% *N,N*-dimethylaniline was detectable if using *p*-Cl-aniline as a starting material. There are many pharmaceuticals containing the dimethylamino-methylene group, and we focused our attention on the synthesis of such compounds using CO₂/H₂ as the alkylating agent. First, we studied the methylation reaction of benzylamine and full conversion of benzylamine was observed with a yield of 81% (Entry 12). Benzylamines with different substituents such as methyl, methoxy and isopropyl groups were converted into the corresponding tertiary amines with yields of 71–83% (Entries 13–15).

Inspired by the results in Table 1, we investigated whether tertiary amines can be synthesized from secondary amines. Clearly, *N*-methyl aniline was converted into *N,N*-dimethylaniline successfully with a yield of 86% (Table 2, Entry 1). The reaction was also successful for the methylation of *N*-methyl-1-phenylmethanamine and dibenzylamine (Entries 2–3). Unfortunately, a dialkyl amine such as dioctylamine was difficult to be *N*-methylated. The yield of the desired product was only 45% (Entry 4). Notably, cyclic secondary amines including 1,2,3,4-tetrahydroisoquinoline, piperazine, and morpholine derivatives can be transformed into the corresponding tertiary amines with

Table 2 Selective methylation of secondary amine with CO₂/H₂^a

Entry	Substrates	Products	Yields/%
1			86
2			89
3			91
4			45
5			79
6			83
7			87
8			96 (87 ^b)
9			92
10			84
11			86
12			79 (75 ^b)

^a Reaction conditions: 1.0 mmol amine, 50 mg catalyst, 2 mL hexane, 3.0 MPa CO₂, 7.0 MPa H₂, 160 °C, 24 h. The yields were obtained by GC-FID using biphenyl as the external standard material. ^b Isolated yield.

yields of 79–96% and the heterocycles containing N and O atoms didn't retard the catalytic activity (Entries 5–12).

Since the amine methylation and dimethylation reactions can be achieved successfully, it was interesting to investigate the possibility of methylation reactions of nitrobenzenes and nitriles using CO₂/H₂ as the alkylation reagent. Under the same reaction conditions as in Table 2, *N,N*-dimethyl aniline can be synthesized with 50% yield using nitrobenzene as the starting material. When performing the reaction at 170 °C for 48 h, the yield of *N,N*-dimethyl aniline reached 86% (Table 3, Entry 1). The scope of nitrobenzenes bearing different groups was further investigated and good results were obtained (Entries 2–4). The yields of the corresponding *N,N*-dimethyl amines were 79–86%. Next, the dimethylation reactions of nitriles were investigated under the same reaction conditions. To our delight, the dimethylation of benzonitrile derivatives can also be carried out with moderate yields (Entries 5–7). The major

Table 3 Selective methylation of nitrobenzene and nitrile with CO₂/H₂^a

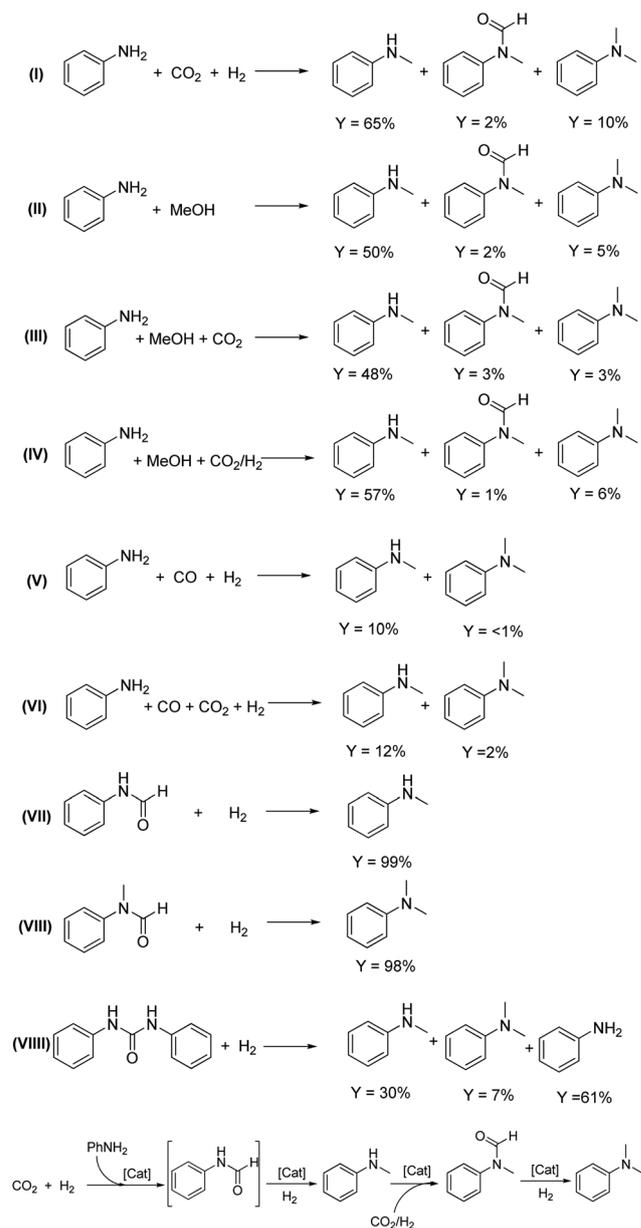
$\text{RNO}_2 \text{ or } \text{RCN} \xrightarrow{\text{CO}_2/\text{H}_2} \text{RN} \begin{matrix} \diagup \\ \diagdown \end{matrix} \text{ or } \text{R} \begin{matrix} \diagup \\ \diagdown \end{matrix} \text{N} \begin{matrix} \diagup \\ \diagdown \end{matrix}$			
Entry	Substrates	Products	Yields/%
1			86 (80 ^b)
2			79
3			86 (82 ^b)
4			83
5			55
6			45 (39 ^b)
7			51

^a Reaction conditions: 1.0 mmol nitrobenzene or nitrile, 50 mg catalyst, 2 mL hexane, 3.0 MPa CO₂, 7.0 MPa H₂, 170 °C, 48 h. The yields were obtained by GC-FID using biphenyl as the external standard material.

^b Isolated yield.

byproducts were an aldehyde intermediate and phenylmethanol, suggesting that the reductive hydrolysis of nitriles occurred. Meanwhile, nitrobenzene can be completely reduced to aniline however, 35% benzylamine and 65% dibenzylamine were obtained for benzonitrile hydrogenation without CO₂ (Scheme S2†).

Finally, the reaction mechanism with CO₂/H₂ as the alkylation reagent was explored for the synthesis of *N*-methyl or *N,N*-dimethyl aniline with nine parallel reactions, Scheme 1. All the reactions were progressed for 12 h and checked by GC-MS. In reaction (I), the products were 65% *N*-methyl aniline, 2% *N*-methyl-*N*-phenylformamide and 10% *N,N*-dimethyl aniline. In reaction (II), although 16 equivalents of methanol were applied, the conversion of aniline was 60% with the generation of 50% *N*-methyl aniline, 2% *N*-methyl-*N*-phenylformamide and 5% *N,N*-dimethyl aniline. Similar results were obtained if CO₂ or CO₂/H₂ was added, (III) and (IV), which means the presence of CO₂ or CO₂/H₂ does not promote the reaction of aniline and methanol. At the same time, the methanol concentration in the reaction mixture was <1% after the reaction of CO₂ and H₂ with or without the addition of aniline. Therefore the possibility of methanol as the reaction intermediate is much less. Interestingly, only 13% conversion of aniline was obtained in the reaction of



Scheme 1 Reaction mechanism exploration of the *N*-methylation reaction with CO₂/H₂. (I) 1 mmol aniline, 3.0 MPa CO₂, 6.0 MPa H₂, 50 mg CuAlOx catalyst, 160 °C, 12 h; (II) 1 mmol aniline, 16 mmol MeOH, 50 mg CuAlOx catalyst, 160 °C, 12 h; (III) 1 mmol aniline, 16 mmol MeOH, 3.0 MPa CO₂, 50 mg CuAlOx catalyst, 160 °C, 12 h; (IV) 1 mmol aniline, 3.0 MPa CO₂, 6.0 MPa H₂, 16 mmol methanol, 50 mg CuAlOx catalyst, 160 °C, 12 h; (V) 1 mmol aniline, 3.0 MPa CO, 6.0 MPa H₂, 50 mg CuAlOx catalyst, 160 °C, 12 h; (VI) 1 mmol aniline, 3.0 MPa CO₂, 1.0 MPa CO, 6.0 MPa H₂, 50 mg CuAlOx catalyst, 160 °C, 12 h; (VII) 1 mmol phenyl formamide, 6.0 MPa H₂, 50 mg CuAlOx catalyst, 160 °C, 12 h; (VIII) 1 mmol *N*-phenyl-*N*-methyl formamide, 6.0 MPa H₂, 50 mg CuAlOx catalyst, 160 °C, 12 h; (IX) 1 mmol diphenyl urea, 6.0 MPa H₂, 50 mg CuAlOx catalyst, 160 °C, 12 h. Y = yield and the numbers were obtained by the peak areas of GC-MS without correction.

aniline and CO/H₂, with a 10% yield of *N*-methyl aniline and a 2% yield of *N,N*-dimethyl aniline (V). Surprisingly, only 12% *N*-methyl aniline was produced even if aniline was reacted with CO/CO₂/H₂ (VI), suggesting that the presence of CO₂ did

not improve the reaction of aniline with CO/H₂ and that the presence of CO inhibited the reaction of aniline with CO₂/H₂. Based on this data, CO does not appear to be an important reaction intermediate. It is noteworthy that there was no detectable *N*-phenylformamide and *N*-methyl-*N*-phenylformamide. Therefore, the hydrogenation reactivities of *N*-phenylformamide and *N*-methyl-*N*-phenylformamide were then tested. Clearly, as the results show for reaction (VII) and (VIII), *N*-phenylformamide and *N*-methyl-*N*-phenylformamide were quantitatively converted into *N*-methyl aniline and *N,N*-dimethyl aniline. These results suggest that formamide was the possible intermediate for the *N*-methylation reaction. However, the formamide was not derived from carbon monoxide due to the poor results given in reaction (V). In addition, only 30% *N*-methyl aniline and 7% *N,N*-dimethyl aniline were produced if using *N,N*-diphenyl urea as the starting material (VIII), which suggests that di-substituted urea was not the reaction intermediate. According to the discussions above, a reaction mechanism is given in Scheme 1. First, aniline was carbonylated with CO₂/H₂ to generate *N*-phenylformamide and it was then quickly hydrogenated into *N*-methyl aniline. Following this, the *N*-methyl aniline was again reacted with CO₂/H₂ to form *N*-methyl-*N*-phenylformamide and following further hydrogenation, *N,N*-dimethyl aniline was produced.

Conclusion

In conclusion, the direct use of CO₂/H₂ in *N*-methylation reactions was achieved successfully. The results showed that by applying a simple CuAlOx catalyst, primary amines, secondary amines, nitrobenzene and aromatic nitrile derivatives can be efficiently and selectively transformed into the corresponding *N*-methyl or *N,N*-dimethyl products with excellent yields. It offers a clean and economic method for the synthesis of *N*-methyl and *N,N*-dimethyl amines. Furthermore, it also promotes the use and recycling of CO₂.

Experimental section

Generals

All solvents and chemicals were obtained commercially and were used as received. Mass spectra were in general recorded on an HP 6890/5973 GC-MS. High-resolution TEM analysis was carried out on a JEM 2010 operating at 200 keV. The catalyst samples after pretreatment were dispersed in methanol, and the solution was mixed ultrasonically at r.t. A part of the solution was dropped on the grid for the measurement of the TEM images. XRD measurements are conducted by a STADI P automated transmission diffractometer (STOE) equipped with an incident beam curved germanium monochromator selecting Cu K α 1 radiation and a 6° position sensitive detector (PSD). The XRD patterns are scanned in the 2 θ range of 20–90°. For the data interpretation WinXpov (STOE) software and the Powder Diffraction File (PDF) database of the International Centre of Diffraction Data (ICDD) were used. The XPS measurements were performed with a VG ESCALAB 210 instrument provided

with a dual Mg/Al anode X-ray source, a hemispherical capacitor analyser and a 5 keV Ar⁺ ion-gun. All spectra were recorded using non-monochromatic Mg Ka (1253.6 eV) radiation. Nitrogen adsorption–desorption isotherms were measured at 77 K using a Micromeritics 2010 instrument. The pore-size distribution was calculated by the Barrett, Joyner and Halenda (BJH) method from the desorption isotherm. The Cu and Al content of the catalyst was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES), using an Iris advantage Thermo Jarrel Ash device.

Typical procedure for catalyst preparation

1.45 g Cu(NO₃)₂·3H₂O (6.0 mmol), 2.25 g Al(NO₃)₃·9H₂O (6.0 mmol) were added into 100 mL deionized water and agitated until complete dissolution. Then, 20 mL Na₂CO₃ solution (0.94 M) was added in a dropwise manner and the mixture was further stirred for 4 h at room temperature. The reaction mixture was centrifuged and washed with water to remove the base until the pH value of the aqueous solution was ~7.0. Subsequently, the solid was dried at 120 °C for 4 h, calcined in static air at 350 °C for 12 h and reduced under hydrogen flow at 350 °C for 3 h. The catalyst was denoted as CuAlOx. According to the nitrogen absorption and desorption analysis, the BET surface area of the CuAlOx catalyst was 138 m² g⁻¹.

Typical reaction procedure for the *N*-methylation of amines

1.0 mmol amine, 50 mg CuAlOx catalyst and 2 mL hexane were added into an 80 mL autoclave. It was then exchanged with CO₂, and 3.0 MPa CO₂ and 6.0 MPa H₂ were introduced. The reaction was reacted at 160 °C for 24 h under magnetic stirring. Subsequently, the autoclave was cooled to room temperature, and 40 mg biphenyl and 10 mL ethanol were added for quantitative analysis by GC-FID (Agilent 6890A).

Typical reaction procedure for the *N,N*-dimethylation of amines

1.0 mmol amine, 50 mg CuAlOx catalyst and 2 mL hexane were added into an 80 mL autoclave. Then it was exchanged with CO₂, and 3.0 MPa CO₂ and 7.0 MPa H₂ were introduced. The reaction took place at 160 °C for 48 h under magnetic stirring. Subsequently, the autoclave was cooled to room temperature, and 40 mg biphenyl and 10 mL ethanol were added for quantitative analysis by GC-FID (Agilent 6890A).

Typical reaction procedure for the *N*-methylation of secondary amines

1.0 mmol amine, 50 mg CuAlOx catalyst and 2 mL hexane were added into an 80 mL autoclave. It was then exchanged with CO₂, and 3.0 MPa CO₂ and 7.0 MPa H₂ were introduced. The reaction took place at 160 °C for 24 h under magnetic stirring. Subsequently, the autoclave was cooled to room temperature, and 40 mg biphenyl and 10 mL ethanol were added for quantitative analysis by GC-FID (Agilent 6890A).

Typical reaction procedure for the *N,N*-dimethylation of nitrobenzenes and nitriles

1.0 mmol nitrobenzenes or nitriles, 50 mg CuAlO_x catalyst and 2 mL hexane were added into an 80 mL autoclave. It was then exchanged with CO₂, and 3.0 MPa CO₂ and 7.0 MPa H₂ were introduced. The reaction took place at 170 °C for 48 h under magnetic stirring. Subsequently, the autoclave was cooled to r.t., and 40 mg biphenyl and 10 mL ethanol were added for quantitative analysis by GC-FID (Agilent 6890A).

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