# RSC Sustainability

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ROYAL SOCIETY
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## Sustainability Spotlight

The two-step method of the utilization of carbon disulfide ($CS_2$) to *N*-methylanilines or *N,N*-dimethylanilines *via* thioureas intermediate is a promising way to use $CS_2$ as feedstock, lowering its emission from rubber, viscose-fiber and agrochemical industries. We report herein a convenient and highly efficient method of the hydrogenation of thioureas with $PhSiH_3$, using earth-abundant metal catalysis, leading to the formation of *N*-methylamines and *N,N*-dimethylamines based on the well-studied first step, and proceeding under atmospheric pressure with high carbon utilization. Notable functional group tolerance and environmental-friendly chemoselective reduction highlight the potential of this reaction on chemical transformations of renewable feedstocks. **This work aligns with industry, innovation, and infrastructure (UN SDG 9), and Responsible Consumption and Production (UN SDG 12).**

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# Chemoselective Reduction of Thioureas to *N*-Methylamines and *N,N*-Dimethylamines Using Cu-based Catalyst

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We report a general copper-catalyzed hydrogenative reduction of thioureas to *N*-methylamine and *N,N*-dimethylamine (10 examples, 42-99% carbon utilization rate) using $PhSiH_3$ as the hydrogenation reagent, which realize the highly efficient indirect utilization of carbon in carbon disulfide ($CS_2$). This strategy provides a mild and environmental-friendly platform for $CS_2$ pollutant valorization, holding a potential for sustainable chemical manufacturing.

## Introduction

Realizing the high-value-added directional conversion of industrial waste gases is an important research direction that urgently needs in-depth exploration in the current field of sustainable development. Carbon disulfide ($CS_2$) is primarily found in natural gas, petroleum gas, water gas, and industrial exhaust gases from typical automotive and chemical industries.[1-4] In environment it readily transforms into acid rain, thereby causing serious ecological threats and environmental damage.[2, 3] Therefore, it is essential to control its emission into the atmospheric environment.[3, 5] Various techniques have been developed to remove $CS_2$, such as physical and chemical adsorption,[6, 7, 8] hydrolysis,[9, 10] and hydrolysis-oxidation coupling.[11] The production of thiourea from $CS_2$ and amines is an effective method for fixing it, and it has been extensively studied.[1, 12, 13-18] Furthermore, reducing thiourea into high-value-added products is an indirect way to utilize $CS_2$ waste.

Currently, the important progresses have been made in the conversion of thioamides into amines or/and thiols by Milstein and other groups;[19-26] (**Fig. 1, a, b**) however, the study for hydrogenation reduction of thioureas remains scarce.[27] *N*-methylamine and *N,N*-dimethylamine are widely used as solvents and significant in the synthesis of fine chemicals such as dyes, surfactants, pesticides, petrochemicals, rubber, and pharmaceuticals.[28-33] Catalytic reduction of thioureas to produce them is thus an effective method for recycling the useful carbon resources in $CS_2$ to high-value-added products (**Fig. 1**). To achieve this goal, there are challenges including a) the sulfur compounds generated during the reaction are prone to poisoning the catalyst; b) site-selectivity on cleavage of the C=S and/or C–N bond of thioureas.[25] Moreover, because of $n_N \rightarrow \pi^*$ C=S resonance from thioureas C–N bonds and C=S bond, and the large radius of sulfur atom, the thiourea C–N bond has a high rotational barrier, hampering its chemical transformation and application.[34] Khurana pioneered the catalytic reduction of 1,3-diphenylthiourea into *N*-methylanilines with $NaBH_4$ as reduction reagent using $NiCl_2$ as the catalyst.[27]

Hydrosilanes, served as the mild and cheaply available hydrogenation reducing reagents, are commonly-used reducing agents in catalytic transfer hydrogenation reactions for a variety of organic functionalities including esters, amides, ureas, and thioamides.[35-40] Despite this significant advantage with respect both to environmental friendliness and cost as compared to borohydrides, a widely applied, operationally simple, mild, and cheap method for catalytic reduction of thioureas using silanes has yet to be developed. Moreover, it is noteworthy that the use of the noble metals is limited for its low content, high price, and high toxicity.[41, 42] Regarding to green and sustainable chemistry, earth-abundant transition metals can be excellent alternatives to the rare precious metals[43, 44]. Among them, copper is abundant on the earth with low cost and toxicity, forming a wide variety of coordination modes with ligands.[41, 45-48] Effort to explore more sustainable and environmental-friendly copper catalysis for the hydrogenation reduction of thioureas and their derivatives is therefore quite valuable.

Herein, we disclose the reduction of thioureas with hydrosilanes as the reduction reagent into *N*-methylamines and *N,N*-dimethylamines using the earth-abundant metal copper-based catalyst, which can indirectly realize the high carbon utilization of $CS_2$ waste.

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†Electronic supplementary information (ESI) available: Additional data on experimental procedure, optimization, GC-MS, $^1H$ NMR and $^{13}C$ NMR data (Fig. S1 to S39, Tables S1 to S10).

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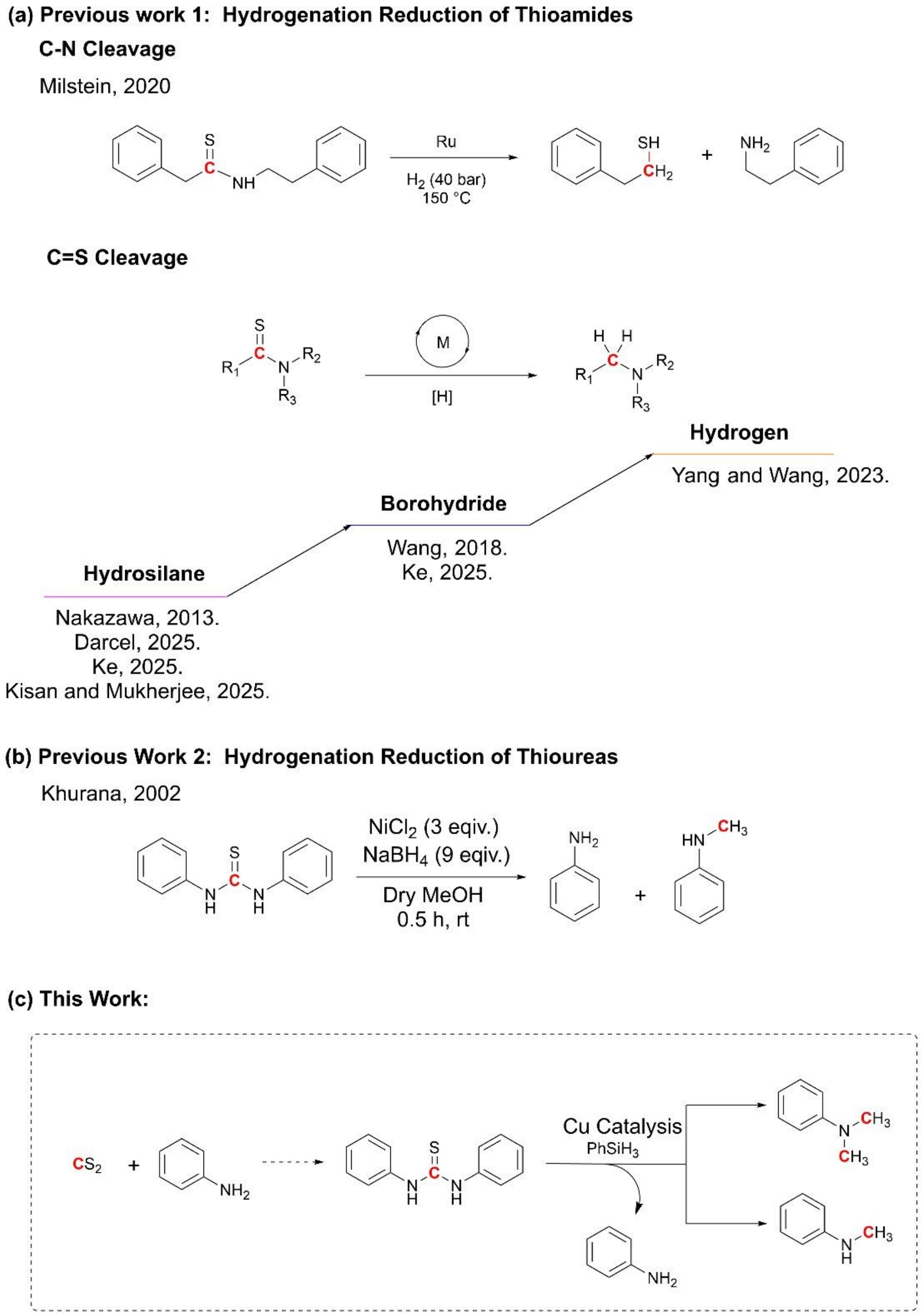

**Fig. 1** Previous work on hydrogenation reduction of thioamides and thioureas, and this work on reduction of thioureas with $PhSiH_3$ by Cu catalyst

## Results and Discussion

We initially screened the metals and found that Cu metal exhibited good catalytic performance in hydrosilylation of 1,3-diphenylthiourea (**1a**) during the experimental exploration stage (Table S1). Among various Cu metal precursors,[49-51] $CuCl_2$ showed the most prominent catalytic effect (Table S2). Having identified $CuCl_2$ as the metal precursor, we investigated the influence of ligands on the catalytic performance of Cu-based catalyst systems (Table 1, entries 1-6). We started our investigation by studying the hydrosilylation reaction with $PhSiH_3$ (5 equivalents) using $CuCl_2$ (20 mol%) and the bidentate phosphine ligand (40 mol%) at 130 °C for 24 h in THF (3 mL). By

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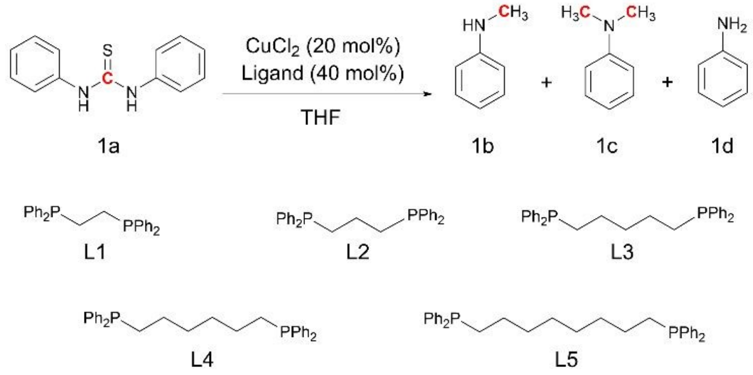
evaluating from ligands **L1-L5**, we found that ligands were crucial for the product distribution of the reaction (entries 1-5). As the carbon chain structure in ligands **L1-L5** became more complex, the proportion of dimethylaniline in the reaction product gradually increased from 20% to 60%, while the proportion of methylaniline also gradually decreased from 62% to 30%. Among them, the catalyst system composed of $CuCl_2$ and ligand **L3** achieved a high carbon utilization rate of 92%, with the yields of monomethylaniline (**1b**) and dimethylaniline (**1c**) being 42% and 50% respectively. Note that $CuCl_2$ has a relatively low catalytic performance without additional ligand (entry 6). In addition, appropriately increasing the reaction temperature and time can effectively enhance the reaction rate (entries 3 and 8-14), and the carbon utilization rate reaches 96% at 140 °C for 24 h (entry 8). Overreacting, however, will lead to a decline in carbon utilization.

**Table 1** Optimization of desulfurization reduction of thiourea with silanes[a]



| Entry | Ligand | T (h) | Temp. (°C) | $PhSiH_3$ (equiv.) | Yield of 1b (%) | Yield of 1c (%) | Carbon Utilization[b] (%) | Conv. (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | L1 | 24 | 130 | 5.0 | 62 | 20 | 82 | 95 |
| 2 | L2 | 24 | 130 | 5.0 | 57 | 27 | 84 | 96 |
| 3 | L3 | 24 | 130 | 5.0 | 42 | 50 | 92 | 98 |
| 4 | L4 | 24 | 130 | 5.0 | 34 | 52 | 86 | 97 |
| 5 | L5 | 24 | 130 | 5.0 | 30 | 60 | 90 | 97 |
| 6[c] | - | 24 | 130 | 5.0 | 5 | 11 | 16 | 16 |
| 7 | L3 | 24 | 120 | 5.0 | 28 | 45 | 71 | 86 |
| 8 | L3 | 24 | 140 | 5.0 | 46 | 50 | 96 | >99 |
| 9 | L3 | 24 | 150 | 5.0 | 39 | 49 | 88 | >99 |
| 10 | L3 | 6 | 140 | 5.0 | 27 | 27 | 54 | 70 |
| 11 | L3 | 12 | 140 | 5.0 | 40 | 47 | 87 | 93 |
| 12 | L3 | 18 | 140 | 5.0 | 44 | 47 | 91 | >99 |
| 13 | L3 | 30 | 140 | 5.0 | 39 | 52 | 91 | >99 |
| 14 | L3 | 36 | 140 | 5.0 | 33 | 50 | 83 | >99 |
| 15[d] | L3 | 24 | 140 | 5.0 | 0 | 7 | 7 | 33 |
| 16[e] | L3 | 24 | 140 | 5.0 | - | - | - | NR |
| 17 | L3 | 24 | 140 | 3.0 | 44(41) | 49(48) | 93(89) | >99 |
| 18 | L3 | 24 | 140 | 1.0 | 21 | 20 | 41 | 58 |
| 19 | L3 | 24 | 140 | 7.0 | 45 | 45 | 90 | >99 |

[a] Reaction conditions: substrate (0.8 mmol), $CuCl_2$ (20 mol%), ligand (40 mol%), hydrosilanes (1.0-7.0 equiv.), THF (3.0 mL), 120-150 °C (bath temperature). Determined by GC using biphenyl as an internal standard unless otherwise noted. Isolated yield in parentheses. Identification of the products were also confirmed by GC-MS. [b] Carbon Utilization was calculated by adding yield of **1b** and yield of **1c**. [c] No ligands were used. [d] $Ph_2SiH_2$ were used instead of $PhSiH_3$. [e] $Ph_3SiH$ were used instead of $PhSiH_3$.

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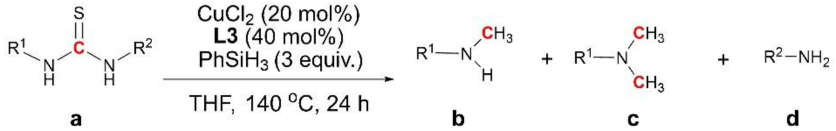
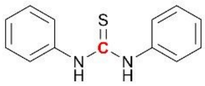
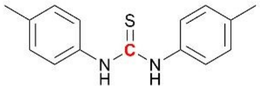
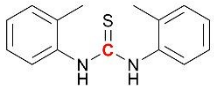
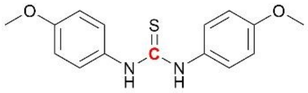
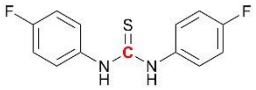
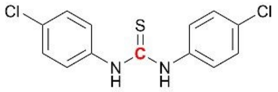
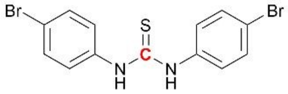
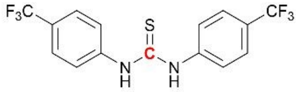
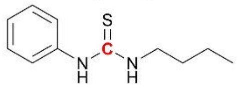
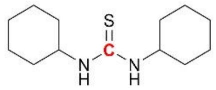
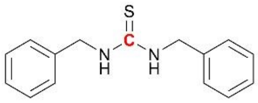
**Table 2** Catalytic hydrogenation of organic thiourea derivatives to *N*-methylanilines and *N,N*-dimethylanilines by copper catalyst[a]



| Entry | Substrate | Yield of **b** (%) | Yield of **c** (%) | Carbon Utilization[b] (%) | Conv. (%) |
|---|---|---|---|---|---|
| 1 |  | 44(41) | 49(48) | 93(89) | >99 |
| 2 |  | 34 | 56 | 90 | >99 |
| 3 |  | 73 (69) | 0 | 73 (69) | 93 |
| 4 |  | 26 (23) | 73 (69) | 99 (92) | >99 |
| 5[c] |  | 29 | 47 | 73 | >99 |
| 6 |  | 44 | 43 | 87 | >99 |
| 7[c, d] |  | 41 | 49 | 90 | 95 |
| 8 |  | 60 | 22 | 82 | 96 |
| 9 |  | 29 | 14 | 43 | 91 |
| 10 |  | 37 | 26 | 63 | 85 |
| 11[e] |  | 19 | 13 | 32 | 71 |

[a] Reaction conditions: substrate (0.8 mmol), $CuCl_2$ (20 mol %), **L3** (40 mol %), $PhSiH_3$ (3.0 equiv.), THF (3.0 mL), 140 °C (bath temperature), 24h. Determined by GC using biphenyl as an internal standard unless otherwise noted. Identification of the products were also confirmed by GC-MS and $^1H$ NMR. Isolated yield in parentheses. [b] Carbon Utilization was calculated by adding yield of 1b and yield of 1c. [c] Reaction condition: substrate (0.4 mmol), $CuCl_2$ (20 mol%), **L3** (40 mol%), $PhSiH_3$ (3.0 equiv.), THF (3.0 mL), 140 °C (bath temperature), 24h. [d] Determined by GC using 1,3,5-trimethylbenzene as an internal standard. [e] Reaction condition: $PhSiH_3$ (5.0 equiv.).

Subsequently, $Ph_2SiH_2$ and $Ph_3SiH$ were used as reducing reagents.[52] (entries 15 and 16) With the decrease of Si-H, the reduction efficiency gradually declined (entries 8, 15 and 16). Finally, we attempted to carry out the catalytic reaction under the condition of a lower addition amount of $PhSiH_3$ (entries 17 and 18). When $PhSiH_3$ is reduced to 3 equivalents, it has a reduction efficiency similar to that of 5 equivalents.[53] (entry 17) However, further reduction of $PhSiH_3$ will lead to a significant decrease in reduction efficiency (entry 18).

Having in hand the optimal reaction conditions for the reduction of substrate 1a, we explored the substrate scope for the catalytic hydrosilylation of thiourea derivative to N-methylaniline (b) and N,N-dimethylaniline (c) using CuCl2 and L3 ligand as the in-situ catalyst system (Table 2). Initially, we selected substrates with electron-donating functional groups at the para position of the benzene rings (Table 2, entries 2 and 4), which exhibited carbon utilization rates exceeding 90%, and the yield of *N,N*-dimethylamine was higher than that of *N*-

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methylamine. On the other hand, we checked electron-withdrawing functional groups at the para position of the benzene rings, such as halides or trifluoromethyl, the carbon utilization rate ranged between 73% and 90%. (Table 2, entries 5-8) and the yield of *N*-methylamine was higher than that of *N,N*-dimethylamine in the product (Table 2, entry 8). Additionally, we investigated the cases where the benzene ring was substituted with ortho-positions. Surprisingly, the carbon utilization rate reached 73%. All products in this reaction were the substituted *N*-methylamine, and no substituted *N,N*-dimethylamine (**c**) was formed, possibly because of the steric hindrance effect brought by ortho-position functional groups (Table 2, entry 3). As expected, compared with the symmetric thioureas above, the asymmetric thiourea 1-phenyl-3-butyl-2-thiourea exhibited a 43% carbon utilization rate, lower than carbon utilization rates of the symmetric thioureas, with a 29% yield of *N*-methylaniline and a 14% yield of *N,N*-dimethylaniline in the products (Table 2, entry 9). Finally, we found that when the two benzene rings on *N,N*-diphenylthiourea were completely replaced with aliphatic substituents like 1,3-dicyclohexyl and 1,3-dibenzyl groups, carbon utilization rate decreased significantly, with carbon utilization rates of 63% and 32%, respectively (Table 2, entries 10-11). In summary, the exploration on the substrate scope of the catalyst system implied that the catalyst system demonstrated good tolerance toward para-substituents on the benzene ring, such as methyl, methoxy, trifluoromethyl, and halogens, as well as moderate tolerance toward benzyl and cyclohexyl groups, and that the nature of substituents on the thiourea benzene ring were able to significantly influence the reaction outcomes.

After exploring the substrate suitability of the Cu-based catalyst, the reaction mechanism for catalysing hydrosilylation of thiourea derivatives to prepare *N*-methylaniline (**1b**) and *N,N*-dimethylaniline (**1c**) was explored.[54, 55] This reaction may go through the following two paths: (1) thiourea first forms amine and thioformamide *via* a single C–N bond cleavage, and then the latter continues to be hydrogenated to form monomethylamine via the C–S bond cleavage; (2) thiourea form formamidine *via* first the C=S double bond cleavage, which then hydrogenates to generate monomethylamine via single C–N bond cleavage. Based on this, we carried out the hydrosilylation reactions of thioformamide (intermediate **A**) and formamidine (intermediate **B**), respectively (**Fig. 2a and 2b**). Thioformamide was successfully reduced to *N*-methylamine and *N,N*-dimethylamine products (**Fig. 3a**), while formamidine was difficult to undergo hydrosilylation reactions (**Fig. 2b**). Therefore, this reaction may generate a N-methylamine product from the thioformamide intermediate A rather than the formamidine intermediate B.

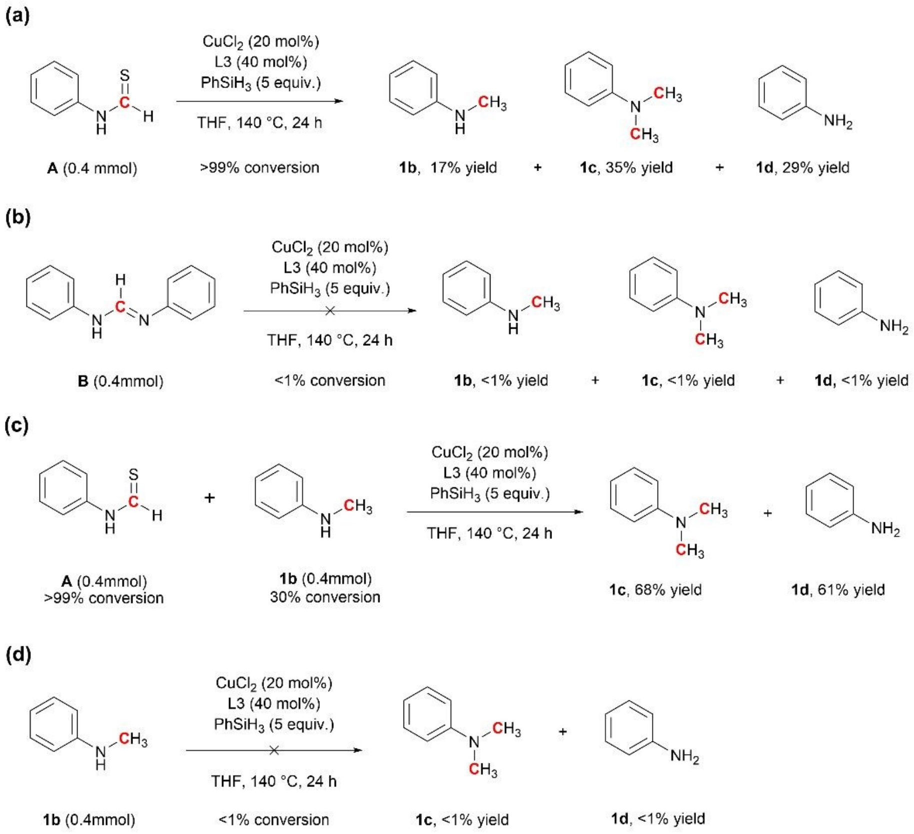

**Fig. 2** Control catalytic experiments

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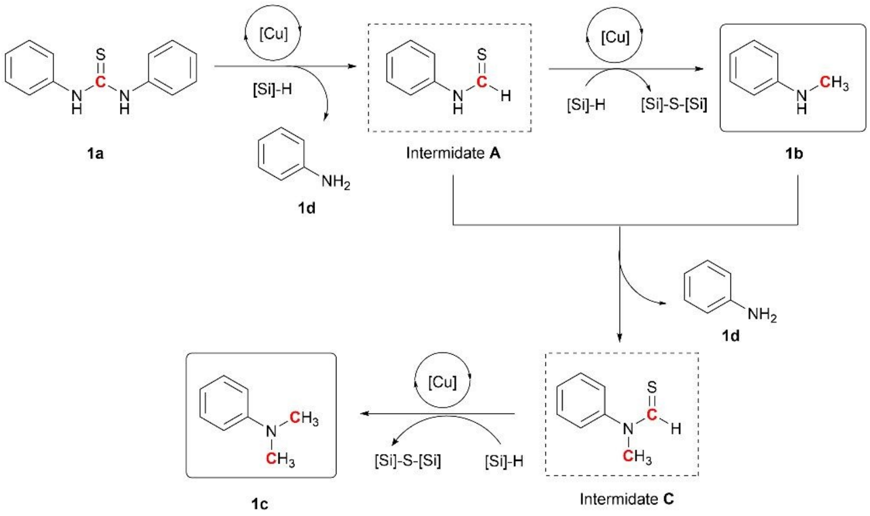

**Fig. 3** Proposed mechanism

Encouraged by this, we also investigated the source of *N,N*-dimethylamine. When *N*-methylamine and thioformamide were used as substrates simultaneously, in addition to the complete conversion of thioformamide, 30% of *N*-methylamine was also converted, and similar yields of *N,N*-dimethylamine (68%) and amine (61%) were produced (**Fig. 2c**). Moreover, only *N*-methylamine as a substrate cannot yield *N,N*-dimethylamine under the same reaction conditions (**Fig. 2d**). These results suggest that *N,N*-dimethylamine is formed by the further reaction of the *N*-methylamine product and the thioformamide intermediate **A**. Based on the control experiments and our and other group previous reports on the ureas hydrogenation reaction,[56-62] along with reports on the C-N cleavage reaction of thioamide,[63, 64] we propose a possible reaction mechanism for the reduction of thiourea by $PhSiH_3$ to N-methylamine and N,N-dimethylamine (**Fig. 3**). Thiourea is first hydrogenated to generate the intermediate **A** and amine *via* C–N bond cleavage. The intermediate **A** is then reduced by $PhSiH_3$ to form *N*-methylamine. Meanwhile, the Si–H bond of $PhSiH_3$ dissociates to form a Si–S bond, which is eliminated in the form of $PhH_2Si–S–SiH_2Ph$ ([Si]–S–[Si]). Furthermore, the generated methylamine and intermediate **A** react to form intermediate **C**, which subsequently desulfurizes to produce *N,N*-dimethylamine.

## Conclusions

In summary, we have developed a general copper-catalyzed system on the reductive desulfurization of thioureas to *N*-methylamine and *N,N*-dimethylamine using $PhSiH_3$ as the reduction reagent. This new catalytic system not only prepared the extra *N,N*-dimethylamines products, but also got a higher utility of carbon. This system is applicable to various aliphatic and aromatic thiourea derivatives. Especially, good utility of carbon is obtained for various aromatic thioureas, including those with halogen, trifluoromethyl, hydroxyl, methyl, methoxy or other groups on the benzene ring. This catalytic system may offer a new perspective and accelerate the further development and on the reduction of unsaturated organic sulfides and the chemical recovery of sulfur-containing resins, also broaden the application on the chemo-selective hydrogenation reaction and transfer hydrogenation reaction of unsaturated organic sulfides.

## Author contribution

Yuanchen Jie: investigation, formal analysis, visualization and writing -original draft. Jun Zhu: methodology and writing- review & editing. Yongtao Wang: visualization. Jia Yao: methodology and resources. Haoran Li: conception, funding acquisition, project administration, supervision and writing-review & editing.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the Supplementary Information.†

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## Sustainability Spotlight Statement

The two-step method of the utilization of carbon disulfide ($CS_2$) to *N*-methylanilines or *N,N*-dimethylanilines *via* thioureas intermediate is a promising way to use $CS_2$ as feedstock, lowering its emission from rubber, viscose-fiber and agrochemical industries. We report herein a convenient and highly efficient method of the hydrogenation of thioureas with $PhSiH_3$, using earth-abundant metal catalysis, leading to the formation of *N*-methylamines and *N,N*-dimethylamines based on the well-studied first step, and proceeding under atmospheric pressure with high carbon utilization. Notable functional group tolerance and environmental-friendly chemoselective reduction highlight the potential of this reaction on chemical transformations of renewable feedstocks. This work aligns with industry, innovation, and infrastructure (UN SDG 9), and Responsible Consumption and Production (UN SDG 12).

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## Data availability

The data supporting this article have been included as part of the Supplementary Information.†

† Electronic supplementary information available: Additional data on experimental procedure, optimization, GC-MS, $^{1}H$ NMR and $^{13}C$ NMR data (Fig. S1 to S39, Tables S1 to S10).