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Internal 2D networking of silver bromide with a bidentate N-heterocyclic carbene ligand enables the formation of an inherently heterogeneous reusable catalyst for multicomponent A^3 coupling†

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We report the synthesis of a heterogenous silver catalyst stabilized by bidentate N-heterocyclic carbene ligands. The heterogeneous nature of the catalyst is inherently derived from the unprecedented internal structural features observed for the catalyst. X-ray studies show that the silver complex forms a two-dimensional cross-linked system, where one dimension of the network is formed by inorganic polymer strings and the second direction is formed by the interconnection of these inorganic strings with NHC bidentate ligands. This organized internal arrangement renders the complex insoluble in many common organic solvents and enables its utilization as a reusable heterogeneous catalyst in multicomponent A^3 coupling reactions. Notably, propargylic amines were obtained with yields of up to 97%, and the catalyst demonstrated reusability for six cycles. These results can facilitate the further development of heterogeneous NHC catalysts.

Introduction

Silver catalysis has gained considerable attention in the past decade due to the low toxicity and cost-effectiveness of silver compared to other transition metals. Furthermore, it offers an attractive alternative in various catalytic applications, notably also in industrial processes such as the production of ethylene oxide[1] or formaldehyde.[2] In academic research, silver catalysts have been employed for fundamental construction of C–C bond,[3–5] as well as for forming C–N,[6–8] C–P,[9] C–F,[10,11] and C–B bonds.[12] Silver functions as a redox-neutral Lewis acid catalyst, activating diverse moieties such as alkynes,[13,14] allenes,[15,16] or isocyanates.[17] Additionally, it can activate substrates like alkenes, phosphonates,[9] benzylic,[10] or other reactive C–H bonds through radical-forming processes, involving one-electron redox cycles (Ag^0/Ag^I, Ag^I/Ag^{II} were proposed).

N-heterocyclic carbenes have demonstrated efficacy as ligands for silver ions, resulting in a diverse array of structural motifs. Silver(I) can be stabilized by a single NHC while simultaneously coordinating with an anionic ligand (typically halide), forming neutral complexes. Conversely, silver(I) can coordinate with two NHC ligands, generating a cationic species, usually stabilized by non-coordinating species (Fig. 1A).[18–20] The structural diversity is further expanded with the use of bidentate ligands. In most instances, each NHC moiety coordinates to a different silver(I) atom, potentially leading to dimeric neutral or cationic monomeric species (Fig. 1B).[19–22] However, our recent findings,[23] as well as other studies, have revealed the possibility of silver(I) atom chelation by bidentate ligands (Fig. 1C).[24–27]

Also, polymeric complexes of silver with NHC carbenes were described as well. The polymeric chain can be of an inorganic origin, resulting from silver–halogen bridging (Fig. 1D),[21,28,29] or can result from linking bidentate ligands with silver atoms (or silver halide bridges, Fig. 1E).[28]

Heterogeneous silver catalysis presents an opportunity for catalyst recycling, typically achieved through the use of silver nanoparticles or by anchoring silver onto the surface of a heterogeneous solid support. However, employing nanoparticles often demands meticulous control during preparation, posing challenges in regulating parameters such as size and shape. Furthermore, the small size of nanoparticles may impede their reusability. Alternatively, utilizing a solid support

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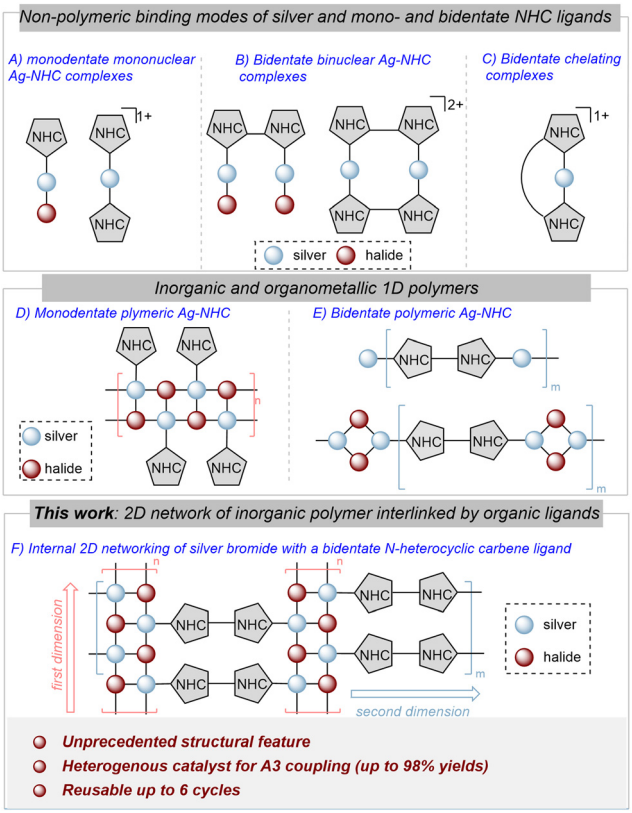


Fig. 1 Current work in the context of previous research.

necessitates the laborious anchoring or encapsulation of the catalytic species onto the support material.[30]

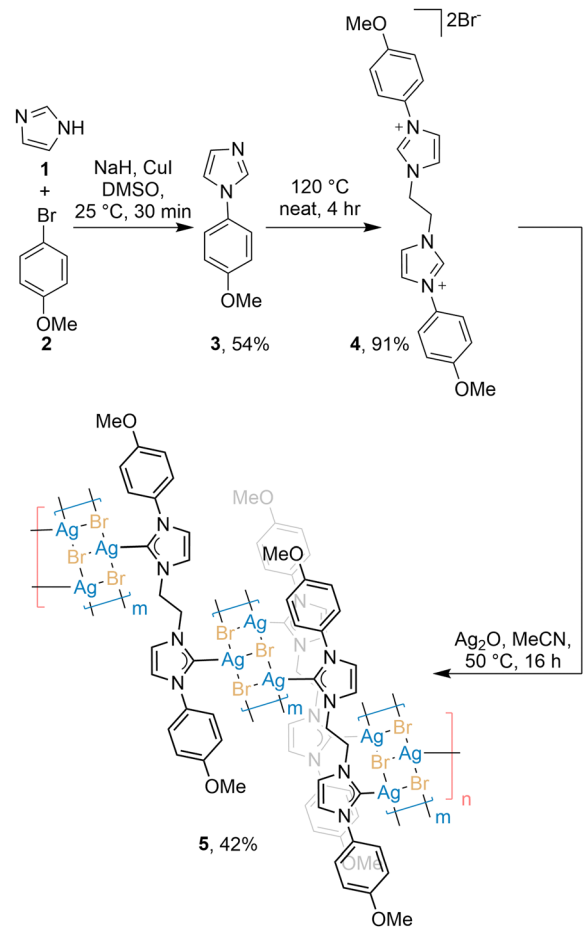
In our ongoing exploration of silver–NHC complexes, we developed a bidentate NHC ligand which upon complexation to silver facilitated the formation of a two-dimensional cross-linked internal network, an unprecedented feature within the silver–NHC ligand system. This resulting 2D structure, integrating polymeric features, leads to the insolubility of the complex in many common organic solvents, presenting it as a promising candidate for heterogeneous catalysis.

Our primary objective is to showcase the efficiency of this newly synthesized heterogeneous catalyst through a multicomponent A^3 coupling reaction involving aldehydes, secondary amines, and alkynes, ultimately yielding propargylic amines.[23,31–36] While prior studies have relied on silver and other metal catalysts supported on solid materials for this reaction,[37–43] our research stands out as the first instance of executing the reaction in a heterogeneous manner without the need for any solid support. The central focus of our research is to assess the catalyst performance, emphasizing high yields and showcasing its recoverability and reusability, ensuring no loss of catalytic activity across multiple reaction cycles.

Results and discussion

The synthesis of the silver–NHC complex began with the preparation of a ligand. First, 4-iodoanisole **1**, was subjected to a copper-catalyzed C–N cross-coupling reaction with imidazole **2**, resulting in the formation of substituted imidazole **3** in 54% yield. Subsequent reaction of compound **3** with dibromomethane under neat conditions yielded the bisimidazolium ligand precursor **4**, obtained in 91% yield. The ligand precursor was then treated with 1.1 equivalent of silver oxide in acetonitrile at 50 °C for 16 hours, leading to the formation of the desired complex **5** in 42% yield (Scheme 1). The structural features of complex **5** were analysed with various spectroscopic techniques, such as NMR and X-ray crystallography. ^{1}H NMR spectroscopy revealed the symmetrical nature of the complex, indicating two distinct sets of aromatic protons: one from the anisole ring with chemical shifts of 7.33 and 6.92 ppm, and another one from the imidazole ring with shifts of 7.72 and 7.62 ppm. Additionally, signals corresponding to the ethylene bridge and the anisole moiety were observed at 4.67 and 3.78 ppm, respectively. In the ^{13}C NMR spectrum, except for the signals corresponding to the aromatic and aliphatic parts of the ligand, we also identified a signal at 178.9 ppm characteristic of the silver carbene carbon.

Furthermore, a single crystal suitable for X-ray diffraction was successfully grown from a DMF/Et_2O solvent system. The compound crystallized in a monoclinic system with space group $P21/c$. The X-ray analysis revealed the 2D networking of the newly formed complex. One dimension of the network was formed by a staircase-like motif of silver–halogen bridging



Scheme 1 Synthesis of the catalyst.

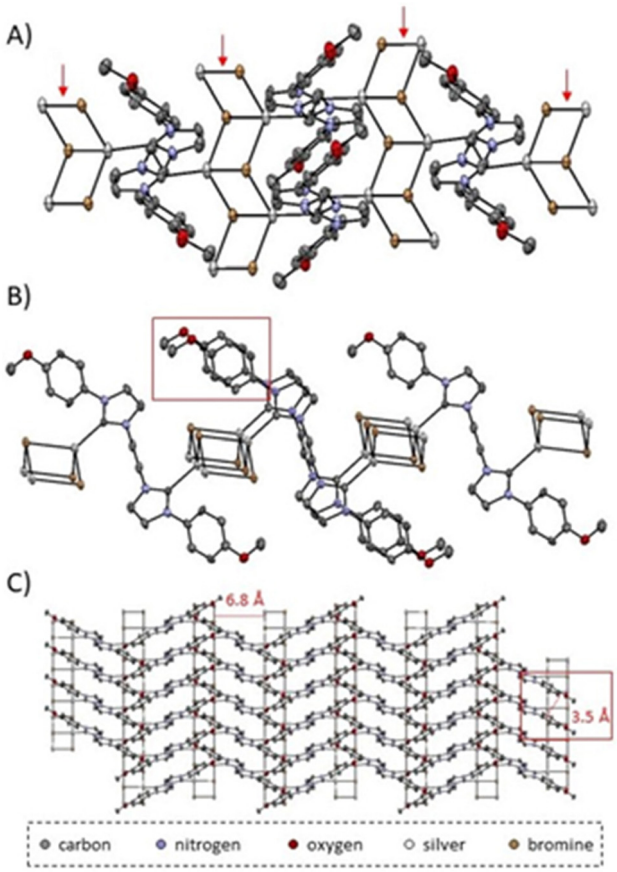


Fig. 2 View on the molecule with 50% ellipsoid probability emphasizing: (A) inorganic silver halide staircase-like strings, (B) cross-linking of the inorganic strings with bidentate NHC-carbene based ligand, and (C) the overall 2D cross-linked network.

atoms, thus purely of an inorganic nature (Fig. 2A, highlighted by red arrows). The second dimension of the network arose from the crosslinking of the inorganic staircase-like strings with bidentate ligands. In this arrangement, the silver atoms of one string are connected to one NHC moiety of the ligand, while the second NHC moiety of the same ligand is connected to a silver atom from a separate staircase-like silver–halide string (Fig. 2B). Overall, such cross-linking results in 2D networking, with the separation distance between the inorganic string equal to 6.8 Å. Their interconnection is mediated by the bidentate ligands, oriented in a zig-zag arrangement (Fig. 2C).

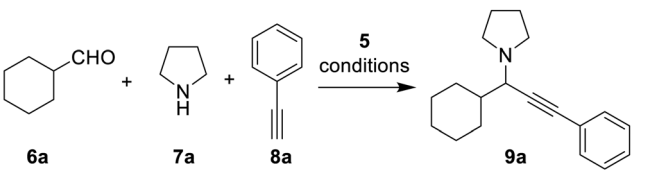
Interestingly, previous studies have shown that the presence of simple methyl groups at the terminal positions of the imidazole moieties of the ligand does not lead to 2D cross-linking, but rather to one-dimensional string formation, lacking the inorganic polymeric motif (as depicted in Fig. 1E).[21] We hypothesize that the presence of an aromatic anisole scaffold at the terminal position of the imidazole moieties of the ligand enables the intermolecular π–π interactions between the neighbouring NHC-ligand. These π–π interactions bring silver and bromide atoms into proximity and allow the formation of the inorganic staircase motif. The proximity and the parallel-displaced character of the π–π interaction of the aromatic rings are visible in Fig. 2B and C (red box). The distance between the planes defined by the anisole aromatic rings is 3.5 Å, falling into the range of π–π interaction distances.

Furthermore, the silver–NHC complex **5** was subjected to anionic exchange with various counter anions, such as NH_4PF_6 and KI in order to evaluate the internal structural integrity. In the presence of PF_6, the ligand decomplexation from the silver metal is observed even at room temperature. In contrast, when exposed to KI at room temperature, the complex remains largely unchanged. However, upon increasing the temperature to 100 °C, decomposition is observed, resulting in a complex reaction mixture.

The complex was further used as a heterogeneous catalyst in A^3 multicomponent coupling. The optimization of the reaction began with evaluating the possibility of performing the reaction under neat conditions. Encouragingly, the reaction provided 83% of the desired product after 5 hours at 80 °C with 0.5 mol% catalytic loading (Table 1, entry 1). Bearing in mind the possibility of reusability of the catalyst, we attempted to reuse the catalyst for the second run. However, the reaction yield dropped below 10% (Table 1, entry 2). To gain an insight into the possible cause of the yield drop, the catalyst alone was kept for 5 hours at 80 °C and afterwards cooled to room temperature. Subsequently, we found that the catalyst pretreated in such a way completely lost its catalytic activity, suggesting that elevated temperatures compromise the integrity of the catalyst (Table 1, entry 3). Therefore, the reaction was attempted at room temperature. However, under neat conditions, the reaction yielded only 48% of the product (Table 1, entry 4). Therefore, we decided to perform the reaction in a solvent. When ethanol was used, the reaction yielded the product in 68% yield, while diethyl ether resulted in a drop to 44% (Table 1, entries 5 and 6).

Similar drops in product yield were observed with acetonitrile or toluene, yielding 53% and 34%, respectively (Table 1,

Table 1 Optimization of A^3 coupling



Entry	Catalyst load (mol%)	Solvent	Temp. (°C)	Isolated yield (%)
1	**5** (0.5)	Neat	80	83
2[a]	**5** (0.5)	Neat	80	10
3[b]	**5** (0.5)	Neat	80	0
4	**5** (0.5)	Neat	rt	48
5	**5** (0.5)	EtOH	rt	68
6	**5** (0.5)	Et_2O	rt	44
7	**5** (0.5)	CH_3CN	rt	53
8	**5** (0.5)	Toluene	rt	34
9	**5** (0.5)	$CHCl_3$	rt	97
10[a]	**5** (0.5)	$CHCl_3$	rt	97
11	—	$CHCl_3$	rt	—
12	AgBr (0.5)	$CHCl_3$	rt	73

[a] Reaction carried out with recovered catalyst. [b] Catalyst pre-treated at 80 °C for 5 hours, cooled to room temperature and then used for the reaction.

entries 7 and 8). The best result was obtained with chloroform as the solvent, yielding the desired propargylic amine **9a** in an excellent 97% yield and no yield drop was observed when reused catalyst was applied for the transformation (Table 1, entries 9 and 10). We also carried out a blank experiment, but under the given conditions, no conversion of the starting material was observed (Table 1, entry 11). Additionally, to compare the catalytic activity of the newly prepared silver complex with that of commercially available silver catalysts, we conducted the reaction using AgBr under the optimized conditions. The desired product was isolated with a 73% yield (Table 1, entry 12), demonstrating that the 2D silver complex exhibits superior catalytic activity compared to commercially available silver salts. Moreover, the homogeneous nature of the system does not allow for any reusability of the catalyst. To verify, if the reaction is catalyzed heterogeneously by the complex **5** or by silver species dissolved in the solution, we carried out a leaching experiment. The catalyst (0.5 mol%) was taken in two different oven-dried reaction flasks and treated with the solvent for 2 hours at two different temperatures, one at room temperature and the other one at 80 °C. Subsequently, the solids were filtered and the reaction was performed in the remaining liquid phase. There was no conversion of the starting material towards the product in both cases, excluding the option of the catalyst leaching, and strongly suggesting that the reaction is catalyzed heterogeneously.

Having the best-optimized conditions in hand, subsequently, we explored the scope of the transformation (Fig. 3). Reactions were conducted in chloroform at room temperature, with representative examples also evaluated under neat conditions at 80 °C for comparison. Initially, we investigated the substitution of the aryl alkyne. When electron-neutral phenylacetylene was replaced with *p*-methoxyphenylacetylene, the reaction yielded 97% of the desired product **9b**.

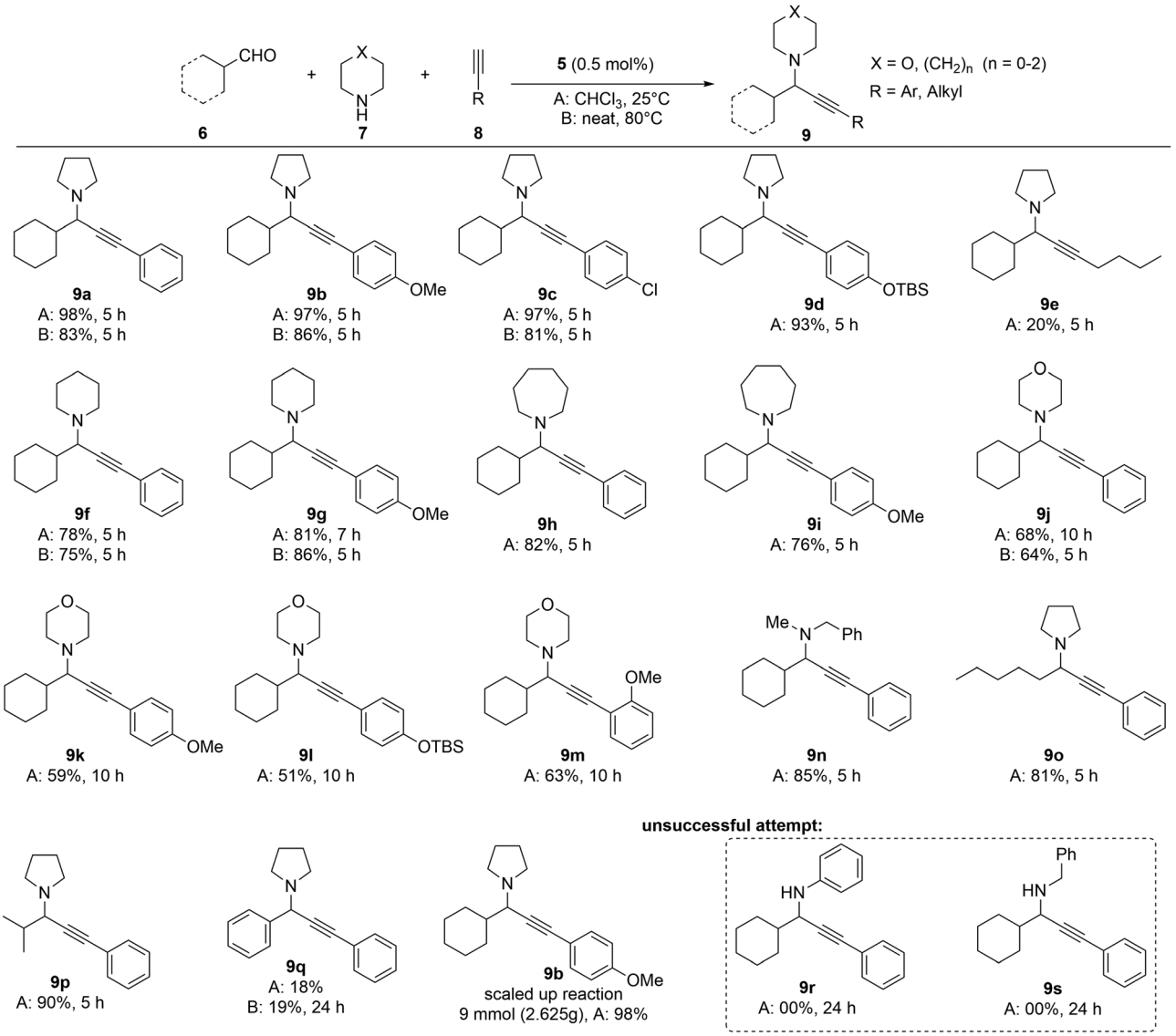


Fig. 3 Scope study for A^3 coupling catalysed by complex **5**.

Similarly, using 4-chlorophenylacetylene led to the formation of the corresponding propargylic amine **9c** in an identical 97% yield. Additionally, the reaction with TBS-protected *p*-hydroxyphenylacetylene resulted in an excellent 93% yield of the amine **9d**. Apart from aromatic alkynes, we have also tested aliphatic alkynes, such as 1-heptyne **9e**, under the optimized conditions. However, we observed a significant reduction in yield to 20%. Furthermore, we explored various secondary amines. When the reaction was conducted with cyclohexanecarbaldehyde, piperidine, and phenylacetylene or 4-methoxyphenylacetylene, the products **9f** and **9g** were formed in respective yields of 78% and 81%. Similarly, the reaction of cyclohexanecarbaldehyde, azepine, and phenylacetylene yielded the desired amine **9h** in a very good yield of 82%. The reaction between the same aldehyde and amine with 4-methoxyphenylacetylene resulted in the formation of product **9i** in 76% yield. A slight decrease in yield was observed when morpholine was used. Specifically, the reaction between cyclohexanecarbaldehyde, morpholine, and phenylacetylene yielded 68% of the desired amine **9j**, while the reaction with 4-methoxyphenyl acetylene resulted in the formation of the corresponding propargylic amine **9k** in a yield of 59%. The challenging nature of the morpholine prompted us to investigate this substrate further. The reaction was further carried out with TBS-protected 4-hydroxyphenyl acetylene and yielded 51% of the tertiary amine **9l**. Also, the reaction with 2-methoxyphenylacetylene yielded **9m** in 63% yield. Furthermore, replacing the cyclic amine with a linear secondary amine, such as *N*-methyl-1-phenylmethanamine, resulted in the desired product **9n** with good yields. Finally, the cyclic aldehyde was replaced with aliphatic hexanal, which in reaction with pyrrolidine and phenylacetylene provided 81% of amine **9o** and reaction with isobutyraldehyde with pyrrolidine and phenylacetylene led to the formation of the desired product **9p** in an excellent 90% yield. Aromatic aldehydes proved to be the limitation of the reaction. We tested benzaldehyde in the reaction with pyrrolidine and phenylacetylene; however, the product **9q** was obtained with only an 18% yield. However, when we attempted to use primary amines **9r** and **9s** in the A^3 coupling reaction, the reaction did not yield the desired product formation.

In addition, we have selected a few examples and carried out the reaction under neat conditions. In general, the reaction provided slightly lower yields. For instance, tertiary amine **9a** was obtained in 83%, compared to 98% yield for the reaction carried out in chloroform. The yield of the propargyl amine **9b** dropped from 97% to 83%, and compound **9c** was obtained in 81%, compared to 97% yield. The yields decreased less dramatically for other employed secondary amines. The reaction between cyclohexanecarbaldehyde, phenylacetylene and piperidine provided the desired product **9e** in 75% yield, which compared to 78% for the reaction in the solvent, and the yield of amine **9i**, with morpholine as the secondary amine decreased from 68% to 64%. Additionally, to assess the catalyst's efficiency in an industrial-scale reaction, we conducted a gram-scale reaction using the optimized conditions. The desired product **9b** was then isolated with a yield of 98%, resulting in 2.625 grams of the product. After exploring the reaction scope, and encouraged by preliminary data on catalyst recyclability, we focused on pushing the limits of the silver catalyst's reusability (Fig. 4). Reactions were conducted at the 0.5 mmol scale in 2 ml of chloroform. Following each cycle, the catalyst was centrifuged, the liquids were decanted, and the catalyst was washed with chloroform before being reused in the next cycle. Overall, the catalyst was utilized for six cycles, and we observed only an insignificant decrease in the yields, for instance, amine **9a** was formed in 98% yield in the first two reaction runs, then in 95%, 93% and 90%, and the last run provided the compound in 87% yield. Similarly, amine **9b** was obtained in 97% yields for runs one and two, then in 95%, 93%, 91%, and finally in 86% in the last run. Reaction with electron-deficient alkyne yielded the product **9c** in 97% yield in the first run, 96% and 97% for runs two and three, further 95% and 92% for the following two runs and finally 92% for run number six. Furthermore, we have demonstrated the reusability test with a 6-membered cyclic amine to access the desired *tert*-amine **9e** for up to 6 cycles.

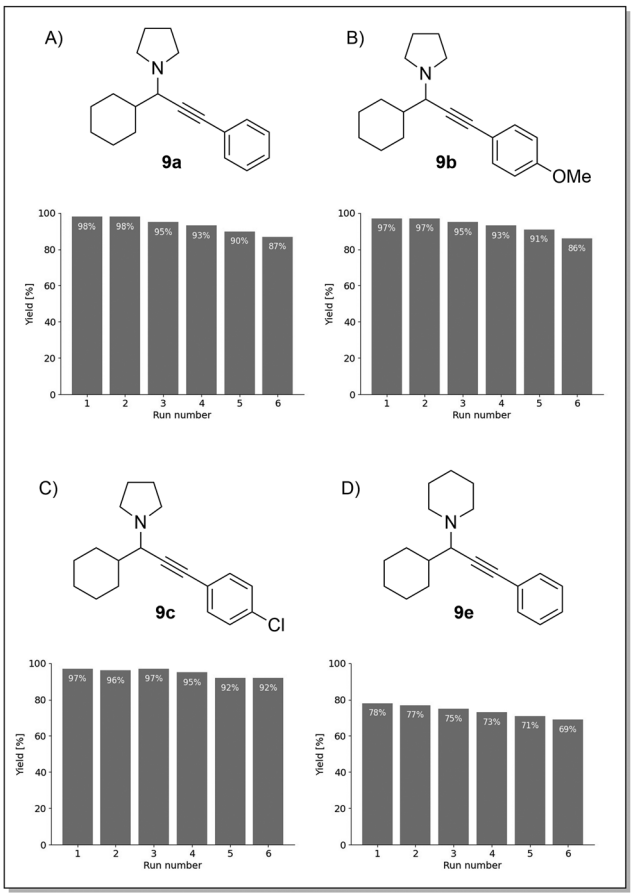


Fig. 4 Reusability of the catalyst.

Conclusions

We synthesized a heterogeneous silver catalyst based on a linear bidentate NHC-based ligand, with each NHC moiety

bearing a terminal aromatic substituent. We observed an unprecedented 2D crosslinking of the silver halide and the bidentate ligand units. The first dimension of the 2D network is formed purely by an inorganic staircase-like Ag–Br string containing silver and halide atoms, while the second dimension is formed by crosslinking these inorganic strings with the bidentate NHC ligands, where one NHC moiety connects *via* a silver atom of one string and the second NHC moiety connects to the neighbouring Ag–Br string. The aromatic moiety attached at the terminal positions of the NHC units plays a critical role in the formation of the 2D network. The π–π interactions between two aromatic substituents allow the inorganic atoms to come into proximity, facilitating the formation of the inorganic string.

This 2D cross-linking contributes to the very low solubility of the complex. Therefore, we explored the possibility of using it as a heterogeneous catalyst in multicomponent A^3 coupling reactions. The reaction provided the desired propargylic amines in yields up to 98%, with a high tolerance towards various cyclic secondary amines and aryl acetylenes. Aliphatic aldehydes, both cyclic and linear, were also well tolerated. However, aromatic aldehydes posed a limitation due to moderate yield.

Moreover, we investigated the reusability of the catalyst for selected reactions and revealed that the catalyst is active for up to six cycles of reuse, with minimal loss of activity.

Author contributions

SN: investigation, methodology, validation, visualization, writing – original draft and writing – review & editing; OK: investigation, methodology and writing – review & editing; AK: investigation and writing – review & editing; RP: conceptualization, and writing – review & editing; IC: investigation; LR: conceptualization, data curation, funding acquisition, project administration, resources, supervision, visualization, writing – original draft, and writing – review & editing.

Data availability

Crystallographic data for complex **5** has been deposited at the CCDC under CCDC No. 2348298 and the other data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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