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SiO_2–NHC–Cu(I): an efficient and reusable catalyst for [3+2] cycloaddition of organic azides and terminal alkynes under solvent-free reaction conditions at room temperature

Pinhua Li [a], Lei Wang [a,b,*], Yicheng Zhang [a]

[a] Department of Chemistry, Huaibei Coal Teachers College, Huaibei, Anhui 235000, PR China
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, PR China

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ABSTRACT

A novel SiO_2–NHC–Cu(I) **3b** was developed and used as a highly efficient catalyst for [3+2] cycloaddition of organic azides and terminal alkynes. In the presence of SiO_2–NHC–Cu(I) **3b** (1 mol %), the reactions of terminal alkynes with organic azides underwent smoothly to generate the corresponding regiospecific 1,4-disubstituted 1,2,3-triazoles in excellent yields under solvent-free reaction conditions at room temperature. Furthermore, catalyst **3b** was quantitatively recovered from the reaction mixture by a simple filtration and reused for 10 cycles without loss of its activity.

1. Introduction

1,2,3-Triazoles have been widely used in synthetic intermediates and industrial applications, such as dyes, anticorrosive agents, photostabilizers, photographic materials, and agrochemicals.[1] Although the 1,2,3-triazole structural moiety does not occur in nature, it may display biological activities and there are numerous examples in the literature including anti-HIV activity,[2] anti-microbial activity against Gram positive bacteria,[3] anti-allergic,[4] anticonvulsant,[5] β-lactamase inhibitory,[6] selective β3 adrenergic receptor agonism,[7] et al.[8]

Numerous synthetic methods for the preparation of 1,2,3-triazole derivatives have been developed. Among them, Huisgen 1,3-dipolar cycloaddition between an alkyne and an azide is the classical and extensively used method.[9] However, the regioselectivity of this cycloaddition reaction is generally low and the reaction usually leads to a mixture of 1,4- and 1,5-regioisomer.[10] Cu(I)-catalyzed ligation (click chemistry) of organic azides and terminal alkynes has enjoyed much use since its discovery independently by the groups of Sharpless and Meldal in 2002.[11] Exclusive regioselectivity, wide substrate scope, mild reaction conditions, effective catalysis system and high yields have made it the method of choice for making permanent connections by means of 1,4-disubstituted 1,2,3-triazoles in the presence of copper catalyst. The catalyst can be introduced as a Cu(I) salt generated in situ by reduction of Cu(II) salts,[12] comproportionation of Cu(0) and Cu(II),[13] Cu(0) nanosize cluster,[14] and Cu(II) salt.[15] However, little attention has been paid to cuprous salts due to their inherent thermodynamic instability and the formation of undesired alkyne–alkyne homo-coupling products observed in their presence.[11b] On the other hand, a Ru(II) complex was used for the reaction only to give the corresponding 1,5-disubstituted 1,2,3-triazoles with complete conversion.[16] It should be noted that the high cost of transition metal catalysts coupled with the toxic effects associated with many transition metals has led to an increasing interest in immobilizing catalysts onto a support. This class of supported reagent can facilitate both the isolation and recycling of the catalyst by filtration, thus providing environmentally cleaner processes.[17]

N-Heterocyclic carbenes (NHCs) are widely used as ligands in inorganic and organometallic chemistry since Arduengo and coworkers isolated the first stable *N*-heterocyclic carbene.[18] NHCs were first considered as simple phosphine mimics in organometallic chemistry.[19] However, increasing experimental data clearly show that NHC–metal catalysts can surpass their phosphine-based

* Corresponding author. Tel.: +86 561 380 2069; fax: +86 561 309 0518.
E-mail address: leiwang@hbcnc.edu.cn (L. Wang).

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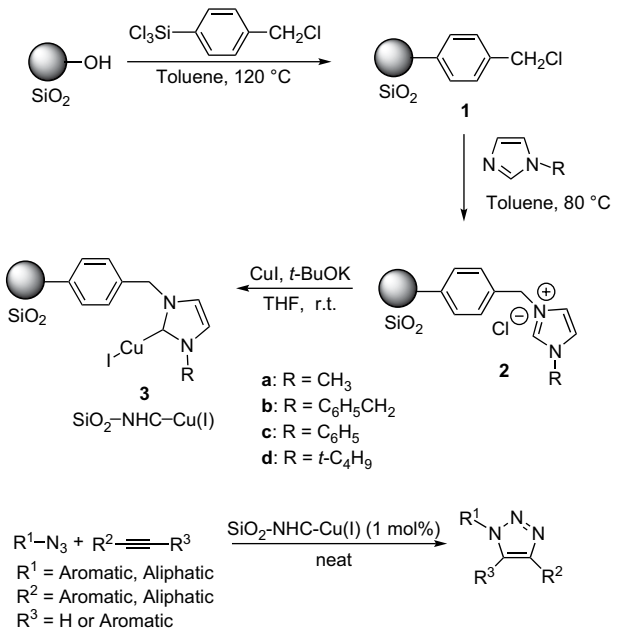
counterparts in both activity and scope.[20] NHCs are stronger σ-donors and weaker π-acceptors, making the properties of NHC–metal complexes notably different from a corresponding phosphine complex. Because of their specific coordination chemistry, NHCs both stabilize and activate metal centres in quite different key catalytic steps of organic syntheses, such as, C–C, C–H, C–O, C–N bond formations and cycloaddition.[21] To avoid catalyst leaching, polymer-, PEG- or silica-supported NHC–metal complexes were synthesized and applied successfully to organic reactions.[22]

We herein report an efficient SiO_2–NHC–Cu(I) **3b** heterogeneous catalyst for [3+2] cycloaddition of organic azides and terminal alkynes. In the presence of **3b** (1 mol %), the reactions of terminal alkynes with organic azides underwent smoothly to generate the corresponding regiospecific 1,4-disubstituted 1,2,3-triazoles in excellent yields under solvent-free reaction conditions at room temperature. Furthermore, **3b** catalyst was quantitatively recovered from the reaction mixture by a simple filtration and reused for 10 cycles without loss of its activity (Scheme 1).



Scheme 1.

2. Results and discussion

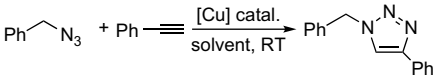
The synthesis of a number of SiO_2–NHC–Cu(I) catalysts was shown in Scheme 1. They were readily prepared in good yields through a straightforward three-step procedure from commercially available starting materials and reagents. The activated silica reacted with trichloro[4-(chloromethyl)phenyl]silane in dry toluene at 120 °C under an inert atmosphere for 24 h to afford the benzyl chloride functionalized silica **1**. The obtained **1** was then reacted with *N*-substituted imidazoles in toluene at 80 °C for 24 h to generate the corresponding silica supported ionic liquids **2a**–**2d**, respectively. Then, the ionic liquids **2a**–**2d** reacted with freshly prepared CuI in the presence of *t*-BuOK in dry THF at room temperature for 6 h under an inert atmosphere and the corresponding SiO_2–NHC–Cu(I) catalysts **3a**–**3d**, as a grey-green powders, were obtained. The copper metal amounts of **3a**–**3d** were found to be 0.86, 0.87, 0.85 and 0.82 mmol g^{-1}, respectively, based on inductively coupled plasma (ICP) analysis.

Our initial investigation was focused on the catalytic activity of SiO_2–NHC–Cu(I) catalysts **3a**–**3d**. The above catalysts were used in a model [3+2] cycloaddition reaction of benzyl azide and phenylacetylene at room temperature in C_2H_5OH. The results are listed in Table 1. The influence of a substituted group of imidazolium salts in **3a**–**3d** on their catalytic activity for [3+2] cycloaddition is $C_6H_5CH_2$>C_6H_5>*t*-C_4H_9>CH_3. It is obvious that when **3a**–**3d** were used in the Huisgen [3+2] cycloaddition, however, several catalysts gave quite similar yields (65, 81, 77, 72%) according to the results from Table 1, entries 1–4.

The effect of solvent on [3+2] cycloaddition of benzyl azide and phenylacetylene using **3b** as catalyst was investigated (Table 1, entries 5–14). Among the solvents tested in Table 1, acetone, DMSO, DMF, CH_3OH, C_2H_5OH and CH_2Cl_2 were the most suitable reaction media for [3+2] cycloaddition (Table 1, entries 5–9). CH_3CN, $C_2H_5OC_2H_5$ and H_2O were inferior and generated the corresponding products in 71–79% yields (Table 1, entries 10–12), whereas toluene and THF afforded moderate yields of desired products (Table 1, entries 13 and 14). Surprisingly, 93% yield of the desired product was isolated when the reaction was carried out under neat reaction conditions (Table 1, entry 15). To avoid the use of volatile solvents and reduce the environmental pollution, all [3+2] cycloaddition reactions were performed under solvent-free reaction conditions. The optimized reaction conditions for this [3+2] cycloaddition reaction are SiO_2–NHC–Cu(I) catalyst **3b** (1 mol %) under neat reaction conditions at room temperature for 0.5 h.

To examine the scope of the Huisgen [3+2] cycloaddition of organic azides and alkynes, a variety of organic azides reacted with terminal alkynes smoothly and generated the corresponding 1,4-disubstituted 1,2,3-triazoles in good yields in a short reaction time under optimized reaction conditions. The results are listed in Table 2. At the beginning of the search for the organic azides substrate scope, different azides with phenylacetylene used as a model substrate were examined (Table 2, entries 1–11). The results indicated that the reactions of benzyl azide and its analogues (Table 2, entries 1–3), as well as phenyl azides and its derivatives (Table 2, entries 4–6), with phenylacetylene proceeded smoothly to complete within 0.5 h, and the corresponding 1,4-disubstituted 1,2,3-triazoles were isolated in excellent yields and high purity after simple filtration or extraction.

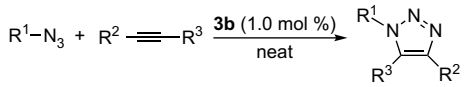
Table 1
Effect of catalyst and solvent on Huisgen [3+2] cycloaddition[a]

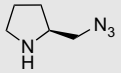
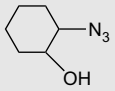


Entry	Catalyst	Solvent	Yield[b](%)
1	**3a**	C_2H_5OH	65
2	**3b**	C_2H_5OH	81
3	**3c**	C_2H_5OH	77
4	**3d**	C_2H_5OH	72
5	**3b**	CH_3COCH_3	89
6	**3b**	DMSO	88
7	**3b**	DMF	85
8	**3b**	CH_3OH	84
9	**3b**	CH_2Cl_2	83
10	**3b**	CH_3CN	79
11	**3b**	$C_2H_5OC_2H_5$	78
12	**3b**	H_2O	71
13	**3b**	Toluene	68
14	**3b**	THF	63
15	**3b**	Neat	93
16	**3a**	Neat	76
17	**3c**	Neat	88
18	**3d**	Neat	81
19	**3b**	Neat	61[c]

[a] Reaction conditions: benzyl azide (1.0 mmol), phenylacetylene (1.0 mmol), SiO_2–NHC–Cu(I) (1 mol %), solvent (0.5 mL), nitrogen atmosphere at room temperature for 0.5 h.
[b] Isolated yields.
[c] Using 0.5 mol % of **3b**.

Table 2
[3+2] Cycloaddition of azides and alkynes catalyzed by **3b**[a]



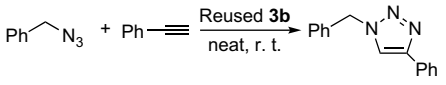
Entry	Organic azide	Alkyne	T (h)	Yield[b] (%)
1	$C_6H_5CH_2N_3$	$C_6H_5C{\equiv}CH$	0.5	93
2	p-$CH_3C_6H_4CH_2N_3$	$C_6H_5C{\equiv}CH$	0.5	95
3	p-$NO_2C_6H_4CH_2N_3$	$C_6H_5C{\equiv}CH$	0.5	97
4	$C_6H_5N_3$	$C_6H_5C{\equiv}CH$	0.5	90
5	p-$CH_3C_6H_4N_3$	$C_6H_5C{\equiv}CH$	0.5	88
6	p-$ClC_6H_4N_3$	$C_6H_5C{\equiv}CH$	0.5	89
7	n-$C_6H_{13}N_3$	$C_6H_5C{\equiv}CH$	3	87
8	n-$C_8H_{17}N_3$	$C_6H_5C{\equiv}CH$	3	90
9	n-$C_{10}H_{21}N_3$	$C_6H_5C{\equiv}CH$	3	86
10		$C_6H_5C{\equiv}CH$	3	91
11		$C_6H_5C{\equiv}CH$	3	90
12	$C_6H_5CH_2N_3$	p-$CH_3C_6H_4C{\equiv}CH$	0.5	96
13	$C_6H_5CH_2N_3$	p-$ClC_6H_4C{\equiv}CH$	0.5	98
14	$C_6H_5CH_2N_3$	p-$BrC_6H_4C{\equiv}CH$	0.5	95
15	$C_6H_5CH_2N_3$	n-$C_6H_{13}C{\equiv}CH$	3	82
16	$C_6H_5CH_2N_3$	$C_2H_5O_2CC{\equiv}CH$	3	97
17	$C_6H_5CH_2N_3$	$HOCH_2C{\equiv}CH$	3	91
18	$C_6H_5CH_2N_3$	$C_6H_5C{\equiv}CC_6H_5$	24	54[c]

[a] Reaction conditions: organic azide (1.0 mmol), alkyne (1.0 mmol), SiO_2–NHC–Cu(I) **3b** (1 mol %), nitrogen atmosphere under neat reaction conditions at room temperature for 0.5–3 h.
[b] Isolated yields.
[c] At 80 °C for 24 h.

As is evident from the above results, electron-donating group (such as CH_3) or electron-withdrawing groups (such as NO_2 and Cl) and their locations on the aromatic ring had little effect on the reaction. It is interesting to note that the reactions of alkyl azides, except benzylic ones, with phenylacetylene led to slower reactions and generated the products in high yields within 3 h (Table 2, entries 7–11). Subsequently, a variety of alkynes were also examined for the Huisgen [3+2] cycloaddition by using benzyl azide-terminal alkynes combination (Table 2, entries 12–17). As can be seen from the Table 2, both of the reactivity of aliphatic and aromatic alkynes was observed, in which aromatic alkynes were often much more reactive than aliphatic alkynes. Aromatic alkynes, such as phenylacetylene, *p*-methylphenylacetylene, *p*-chlorophenylacetylene and *p*-bromophenylacetylene were able to undergo 'click reaction' smoothly and generated the corresponding products in excellent yields within 0.5 h (Table 2, entries 1 and 12–14). On the other hand, the reactions involving aliphatic alkynes also gave both higher conversions and isolated yields, leading to the corresponding 1,4-disubstituted 1,2,3-triazoles in greater yields after 3 h (Table 2, entries 15–17). However, disubstituted acetylene, such as diphenylacetylene could not react with benzyl azide under the optimized reaction conditions at room temperature, and 54% yield of the desired product was isolated after 24 h at 80 °C (Table 2, entry 18).

The recyclability of SiO_2–NHC–Cu(I) catalyst **3b** was also investigated. After the reaction, the catalyst **3b** was separated by simple filtration and washed with acetone. After being dried, it could be reused directly without further purification. The recovered catalyst was used in the next run and almost consistent activity was observed for 10 consecutive cycles (Table 3, entries 1–10). Meanwhile, copper leaching in **3b** was determined. Inductively coupled plasma (ICP) analyses of the clear filtrates obtained by filtration after the reaction indicated that Cu content is <0.1 ppm. However, only trace amount of the desired product was isolated for the model reaction by adding substrates to a filtrate obtained from the filtration of the supported catalyst after the reaction.

Table 3
Successive trials using recoverable **3b** as catalyst[a]



Cycle	Yield[b] (%)	Cycle	Yield[b] (%)
1	93	6	92
2	93	7	90
3	91	8	90
4	92	9	88
5	89	10	87

[a] Reaction conditions: benzyl azide (1.0 mmol), phenylacetylene (1.0 mmol), reused SiO_2–NHC–Cu(I) **3b** (1 mol %), nitrogen atmosphere under neat reaction conditions at room temperature for 0.5 h.
[b] Isolated yields.

3. Conclusion

In conclusion, we have successfully developed a versatile, highly efficient and environmentally friendly catalytic system for the Huisgen [3+2] cycloaddition of organic azides and alkynes by using SiO_2–NHC–Cu(I) **3b** as catalyst (1 mol %) at room temperature under solventless reaction conditions. The reactions generated the corresponding 1,4-disubstituted 1,2,3-triazoles in high yields and were applicable to aromatic and aliphatic organic azides and alkynes. In addition, this methodology offers the competitive of recyclability of the catalyst without significant loss of its activity, and the catalyst could be readily recovered and reused for 10 cycles, thus making this procedure more environmentally acceptable whilst no catalyst leaching was observed. Further investigation on the application of this kind of supported catalysts in organic synthesis, as well as in asymmetric organic reaction is still underway in our laboratory.

4. Experimental

4.1. Physical measurements and materials

All ^1H NMR spectra were recorded at 300 MHz MHz by Bruker FT-NMR spectrometers. Chemical shift are given as δ value with reference to tetramethylsilane (TMS) as internal standard. IR spectra were obtained by using a Nicolet NEXUS 470 spectrophotometer. The CHN analysis was performed on a Vario El III elementar. The Cu content was determined by a Jarrell-Ash 1100 ICP analysis. Specific surface areas and pore volumes of the samples were determined in a Micromeritics ASAP-2000 automated nitrogen physisorption apparatus and calculated according to the BET method. Products were purified by flash chromatography on 230–400 mesh silica gel, SiO_2.

The chemicals were purchased from commercial suppliers (Aldrich, USA and Shanghai Chemical Company, China) and were used without purification prior to use.

4.2. Preparation of benzyl chloride functionalized silica 1

Into a 100 mL of round-bottomed flask, were introduced successively 30 mL of anhydrous toluene, 5.0 g of activated silica, and 2.0 g of trichloro[4-(chloromethyl)phenyl]silane. The solution was refluxed for 24 h at 120 °C under an inert atmosphere. The solution was filtered and the solid was washed subsequently with toluene, dichloromethane and methanol, and dried under reduced pressure

at 80 °C for 10 h. The benzyl chloride functionalized silica **1** was obtained (5.81 g).[17i] The loading of the modified silica was readily quantified via CHN microanalysis and found to be 1.12 mmol g^{-1} based on C percentage. The surface area and pore volume of the modified silica were found to be 433 $m^2 g^{-1}$ and 0.53 $cm^3 g^{-1}$, respectively.

4.3. Preparation of silica supported ionic liquid 2a

Under nitrogen atmosphere, *N*-methylimidazole (0.41 g, 5.0 mmol) and benzyl chloride functionalized silica **1** (2.0 g, loading 1.12 mmol g^{-1}) were mixed in toluene (15 mL) in a round-bottomed flask. The reaction was carried out at 80 °C for 24 h. Then the solution was filtered and the solid was washed with chloroform, methanol and ethyl acetate, respectively, and dried under vacuum at 60 °C; 2.08 g of a pale powder **2a** was obtained.[17e] The loading of **2a** was quantified via CHN microanalysis and found to be 0.96 mmol g^{-1} based on N percentage. The surface area and pore volume of **2a** were found to be 319 $m^2 g^{-1}$ and 0.43 $cm^3 g^{-1}$, respectively. ^{29}Si NMR (solid): δ=−79.4 (br, SiC), −111.5 (br, SiO_2) ppm. IR (KBr): ν=1643, 1513, 1438, 1089 cm^{-1}.

4.4. Preparation of silica supported ionic liquid 2b

Under nitrogen atmosphere, *N*-benzylimidazole (0.790 g, 5.0 mmol) and benzyl chloride functionalized silica **1** (2.0 g, loading 1.12 mmol g^{-1}) were mixed in toluene (15 mL) in a round-bottomed flask. The reaction was carried out at 80 °C for 24 h. Then the solution was filtered, and the solid was washed with toluene, methanol and ethyl acetate, and dried under vacuum at 60 °C to yield 2.20 g of silica supported ionic liquid **2b** as a pale powder, and its loading was quantified by CHN microanalysis and found to be 0.97 mmol g^{-1} based on the N content. The surface area and pore volume of **2b** were found to be 321 $m^2 g^{-1}$ and 0.45 $cm^3 g^{-1}$, respectively. ^{29}Si NMR (solid): δ=−79.2 (br, SiC), −111.5 (br, SiO_2) ppm. IR (KBr): ν=1640, 1453, 1147 cm^{-1}.

4.5. Preparation of silica supported ionic liquid 2c

Under nitrogen atmosphere, *N*-phenylimidazole (0.720 g, 5.0 mmol) and benzyl chloride functionalized silica **1** (2.0 g, loading 1.12 mmol g^{-1}) were mixed in toluene (15 mL) in a round-bottomed flask. The reaction was carried out at 80 °C for 24 h. Then the solution was filtered, and the solid was washed with toluene, methanol and ethyl acetate, and dried under vacuum at 60 °C to yield 2.18 g of silica supported ionic liquid **2c** as a pale powder, and its loading was quantified by CHN microanalysis and found to be 0.95 mmol g^{-1} based on the N content. The surface area and pore volume of **2c** were found to be 316 $m^2 g^{-1}$ and 0.44 $cm^3 g^{-1}$, respectively. ^{29}Si NMR (solid): δ=−79.0 (br, SiC), −111.5 (br, SiO_2) ppm. IR (KBr): ν=1636, 1555, 1497, 1098 cm^{-1}.

4.6. Preparation of silica supported ionic liquid 2d

Under nitrogen atmosphere, *N-tert*-butylimidazole (0.620 g, 5.0 mmol) and benzyl chloride functionalized silica **1** (2.0 g, loading 1.12 mmol g^{-1}) were mixed in toluene (15 mL) in a round-bottomed flask. The reaction was carried out at 80 °C for 24 h. Then the solution was filtered, and the solid was washed with toluene, methanol and ethyl acetate, and dried under vacuum at 60 °C to yield 2.17 g of silica supported ionic liquid **2d** as a pale powder, and its loading was quantified by CHN microanalysis and found to be 0.92 mmol g^{-1} based on the N content. The surface area and pore volume of **2d** were found to be 317 $m^2 g^{-1}$ and 0.43 $cm^3 g^{-1}$, respectively. ^{29}Si NMR (solid): δ=−79.1 (br, SiC), −111.5 (br, SiO_2) ppm. IR (KBr): ν=1633, 1553, 1383, 1083 cm^{-1}.

4.7. Preparation of SiO_2–NHC–Cu(I) catalyst 3a

In an oven-dried Schlenk flask, freshly prepared CuI (0.190 g, 1.0 mmol), NaO-*t*-Bu (0.096 g, 1.0 mmol), **2a** (1.1 g) and THF (5 mL) were added. The resulting suspension was stirred at room temperature for 6 h under an inert atmosphere. Then the solution was filtered and the solid was washed with water, methanol, acetone, respectively, and dried under vacuum at 60 °C for 12 h. The SiO_2–NHC–Cu(I) catalyst **3a** was obtained as a grey-green powder (1.14 g).[23] The copper metal amount of **3a** was found to be 0.86 mmol g^{-1} based on ICP analysis. The surface area and pore volume of **3a** were found to be 235 $m^2 g^{-1}$ and 0.32 $cm^3 g^{-1}$, respectively. ^{29}Si NMR (solid): δ=−78.7 (br, SiC), −111.5 (br, SiO_2) ppm. IR (KBr): ν=1668, 1553, 1457, 1097 cm^{-1}.

4.8. Preparation of SiO_2–NHC–Cu(I) catalyst 3b

In an oven-dried Schlenk flask, freshly prepared CuI (0.190 g, 1.0 mmol), *t*-BuONa (0.096 g, 1.0 mmol), **2b** (1.1 g) and THF (5 mL) were added. The resulting suspension was stirred at room temperature under an inert atmosphere for 6 h. Then the solution was filtered, and the solid was washed with water, methanol, acetone and dried under vacuum at 60 °C for 12 h. The SiO_2–NHC–Cu(I) catalyst **3b** was obtained as a grey-green powder (1.15 g). The copper content of **3b** was found to be 0.87 mmol g^{-1} based on ICP analysis. The surface area and pore volume of **3b** were found to be 238 $m^2 g^{-1}$ and 0.34 $cm^3 g^{-1}$, respectively. ^{29}Si NMR (solid): δ=−78.5 (br, SiC), −111.5 (br, SiO_2) ppm. IR (KBr): ν=1666, 1498, 1209 cm^{-1}.

4.9. Preparation of SiO_2–NHC–Cu(I) catalyst 3c

In an oven-dried Schlenk flask, freshly prepared CuI (0.190 g, 1.0 mmol), *t*-BuONa (0.096 g, 1.0 mmol), **2c** (1.1 g) and THF (5 mL) were added. The resulting suspension was stirred at room temperature under an inert atmosphere for 6 h. Then the solution was filtered, and the solid was washed with water, methanol, acetone and dried under vacuum at 60 °C for 12 h. The SiO_2–NHC–Cu(I) catalyst **3c** was obtained as a grey-green powder (1.13 g). The copper content of **3c** was found to be 0.85 mmol g^{-1} based on ICP analysis. The surface area and pore volume of **3c** was found to be 231 $m^2 g^{-1}$ and 0.32 $cm^3 g^{-1}$, respectively. ^{29}Si NMR (solid): δ=−78.3 (br, SiC), −111.5 (br, SiO_2) ppm. IR (KBr): ν=1671, 1603, 1551, 1123 cm^{-1}.

4.10. Preparation of SiO_2–NHC–Cu(I) catalyst 3d

In an oven-dried Schlenk flask, freshly prepared CuI (0.190 g, 1.0 mmol), *t*-BuONa (0.096 g, 1.0 mmol), **2d** (1.1 g) and THF (5 mL) were added. The resulting suspension was stirred at room temperature under an inert gas for 6 h. Then the solution was filtered, and the solid was washed with water, methanol, acetone and dried under vacuum at 60 °C for 12 h. The SiO_2–NHC–Cu(I) catalyst **3d** was obtained as a grey-green powder (1.12 g). The copper content of **3d** was found to be 0.82 mmol g^{-1} based on ICP analysis. The surface area and pore volume of **3d** were found to be 227 $m^2 g^{-1}$ and 0.31 $cm^3 g^{-1}$, respectively. ^{29}Si NMR (solid): δ=−78.4 (br, SiC), −111.5 (br, SiO_2) ppm. IR (KBr): ν=1647, 1562, 1402, 1094 cm^{-1}.

4.11. Typical procedure for [3+2] cycloaddition of phenylacetylene and benzyl azide catalyzed by 3b

In a 5 mL Schlenk flask, **3b** (12 mg, contains 0.01 mmol of Cu), phenylacetylene (102 mg, 1.0 mmol), benzyl azide (133 mg, 1.0 mmol) were added. The mixture was stirred at room temperature for 30 min. After the reaction was completed, ethyl acetate

(3 mL×2) was added, and the slurry was stirred, and then filtered using a sintered-glass funnel. The residue was washed with ethyl acetate to ensure removal of the product from the surface of the catalyst. The combined organic layers were washed with water and brine, dried with $MgSO_4$ and evaporated under reduced pressure. The residue was finally purified by flash chromatography on silica gel (eluant: hexane/ethyl acetate, 3:1, v/v) to give the corresponding [3+2] cycloaddition product 1-benzyl-4-phenyl-1*H*-1,2,3-triazole as a colourless crystal (219 mg, 93% yield).

4.12. 1-Benzyl-4-phenyl-1*H*-1,2,3-triazole[12b]

^{1}H NMR (300 MHz, $CDCl_3$): δ=7.80 (d, J=7.1 Hz, 2H), 7.67 (s, 1H), 7.42–7.27 (m, 8H), 5.54 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=147.7, 134.2, 130.0, 126.1, 125.5, 124.7, 119.1, 53.7.

4.13. 1-(4-Methylbenzyl)-4-phenyl-1*H*-1,2,3-triazole[17c]

^{1}H NMR (300 MHz, $CDCl_3$): δ=7.81–7.78 (m, 2H), 7.65 (s, 1H), 7.42–7.30 (m, 3H), 7.21–7.18 (m, 4H), 5.51 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=148.0, 138.6, 131.5, 129.7, 128.7, 128.0, 125.5, 119.4, 53.9, 21.1.

4.14. 1-(4-Nitrobenzyl)-4-phenyl-1*H*-1,2,3-triazole[12b]

^{1}H NMR (300 MHz, $CDCl_3$): δ=8.17–8.15 (m, 2H), 7.74–7.67 (m, 3H), 7.38–7.19 (m, 5H), 5.63 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=148.0, 142.6, 141.7, 130.1, 128.7, 128.6, 125.7, 124.4, 123.9, 119.9, 53.6.

4.15. 1,4-Diphenyl-1*H*-1,2,3-triazole[24]

^{1}H NMR (300 MHz, $CDCl_3$): δ=8.16 (s, 1H), 7.93 (d, J=6.0 Hz, 2H), 7.75 (d, J=6.3 Hz, 2H), 7.50 (t, J=5.7 Hz, 2H), 7.42–7.39 (m, 3H), 7.33–7.26 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=148.7, 137.4, 130.7, 129.9, 128.6, 127.9, 126.0, 125.3, 120.2, 117.7.

4.16. 1-(4-Tolyl)-4-phenyl-1*H*-1,2,3-triazole[24]

^{1}H NMR (300 MHz, $CDCl_3$): δ=8.17 (s, 1H), 7.90 (d, J=7.2 Hz, 2H), 7.67 (d, J=8.1 Hz, 2H), 7.47 (t, J=7.2 Hz, 2H), 7.40–7.31 (m, 3H), 2.40 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=148.4, 139.0, 134.9, 130.4, 129.0, 128.8, 128.5, 126.0, 120.6, 117.9, 21.3.

4.17. 1-(4-Chlorophenyl)-4-phenyl-1*H*-1,2,3-triazole[24]

^{1}H NMR (300 MHz, $CDCl_3$): δ=8.18 (s, 1H), 7.93 (d, J=8.4 Hz, 2H), 7.77 (d, J=8.7 Hz, 2H), 7.54–7.38 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=130.8, 130.5, 130.2, 129.8, 129.1, 128.0, 126.5, 122.9, 122.7.

4.18. 1-Hexyl-4-phenyl-1*H*-1,2,3-triazole[17c]

^{1}H NMR (300 MHz, $CDCl_3$): δ=7.81 (t, J=3.6 Hz, 2H), 7.73 (s, 1H), 7.43–7.38 (m, 2H), 7.34–7.26 (m, 1H), 4.36 (t, J=7.2 Hz, 2H), 1.97–1.87 (m, 2H), 1.35–1.24 (m, 6H), 0.85 (t, J=6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=147.6, 130.6, 128.0, 125.6, 119.5, 50.5, 31.1, 30.2, 26.1, 22.3, 13.9.

4.19. 1-Octyl-4-phenyl-1*H*-1,2,3-triazole[17c]

^{1}H NMR (300 MHz, $CDCl_3$): δ=7.81 (t, J=4.2 Hz, 2H), 7.72 (s, 1H), 7.43–7.37 (m, 2H), 7.33–7.24 (m, 1H), 4.36 (t, J=7.2 Hz, 2H), 1.96–1.87 (m, 2H), 1.32–1.24 (m, 10H), 0.85 (t, J=6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=147.6, 130.6, 128.0, 125.6, 119.4, 50.4, 31.6, 30.3, 28.9, 26.4, 22.5, 14.0.

4.20. 1-Decyl-4-phenyl-1*H*-1,2,3-triazole[17c]

^{1}H NMR (300 MHz, $CDCl_3$): δ=7.84–7.80 (m, 2H), 7.76 (s, 1H), 7.43–7.38 (m, 2H), 7.34–7.25 (m, 1H), 4.37 (t, J=7.2 Hz, 2H), 1.94–1.88 (m, 2H), 1.32–1.25 (m, 14H), 0.87 (t, J=6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=147.7, 130.7, 128.7, 125.6, 119.4, 50.5, 31.7, 30.6, 29.0, 26.6, 22.7, 14.2.

4.21. 4-Phenyl-1-(((*S*)-pyrrolidin-2-yl)methyl)-1*H*-1,2,3-triazole[25]

^{1}H NMR (300 MHz, $CDCl_3$): δ=7.89 (s, 1H), 7.79 (t, J=7.2 Hz, 2H), 7.36–7.24 (m, 3H), 4.46–4.35 (m, 1H), 4.23–4.12 (m, 1H), 3.65–3.53 (m, 1H), 2.91 (t, J=6.6 Hz, 2H), 2.03 (s, 1H), 2.01–1.87 (m, 1H), 1.80–1.60 (m, 2H), 1.52–1.37 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=147.7, 130.9, 129.1, 128.2, 125.8, 120.7, 58.1, 55.7, 46.7, 29.3, 25.9.

4.22. 2-(4-Phenyl-(1,2,3-triazol-1-yl))-cyclohexanol[11a]

^{1}H NMR (300 MHz, DMSO-d_6): δ=8.02 (s, 1H), 7.85–7.79 (m, 2H), 7.49–7.27 (m, 3H), 4.89–4.83 (m, 1H), 4.31–4.18 (m, 1H), 3.92–3.75 (m, 1H), 2.28–1.89 (m, 5H), 1.58–1.30 (m, 3H). ^{13}C NMR (75 MHz, DMSO-d_6): δ=146.1, 131.3, 128.9, 127.8, 125.4, 120.4, 71.9, 66.8, 35.0, 32.1, 25.0, 24.2.

4.23. 1-Benzyl-4-(4-tolyl)-1*H*-1,2,3-triazole[17c]

^{1}H NMR (300 MHz, $CDCl_3$): δ=7.71 (d, J=7.8 Hz, 2H), 7.63 (s, 1H), 7.37–7.26 (m, 5H), 7.21–7.18 (m, 2H), 5.57 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=148.2, 138.0, 134.6, 129.4, 128.7, 127.5, 126.1, 125.6, 119.2, 54.2, 21.2.

4.24. 1-Benzyl-4-(4-chlorophenyl)-1*H*-1,2,3-triazole[17c]

^{1}H NMR (300 MHz, $CDCl_3$): δ=7.73 (d, J=9.0 Hz, 2H), 7.66 (s, 1H), 7.39–7.36 (m, 5H), 7.33–7.29 (m, 2H), 5.57 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=147.0, 134.4, 133.9, 129.1, 128.9, 128.0, 126.9, 119.6, 54.3.

4.25. 1-Benzyl-4-(4-bromophenyl)-1*H*-1,2,3-triazole[17c]

^{1}H NMR (300 MHz, $CDCl_3$): δ=7.70–7.66 (m, 3H), 7.54–7.50 (m, 2H), 7.42–7.40 (m, 2H), 7.33–7.30 (m, 2H), 7.25 (s, 1H), 5.57 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=147.1, 134.9, 134.0, 129.4, 129.0, 128.2, 126.1, 119.4, 54.2.

4.26. 1-Benzyl-4-hexyl-1*H*-1,2,3-triazole[17c]

^{1}H NMR (300 MHz, $CDCl_3$): δ=7.38–7.19 (m, 6H), 5.47 (s, 2H), 2.69 (t, J=7.8 Hz, 2H), 1.68–1.59 (m, 2H), 1.32–1.29 (m, 6H), 0.87 (t, J=6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=148.9, 135.0, 129.0, 127.9, 120.4, 53.9, 31.5, 28.9, 25.7, 22.5, 14.0.

4.27. Ethyl-1-benzyl-1*H*-1,2,3-triazole-4-carboxylate[11a]

^{1}H NMR (300 MHz, $CDCl_3$): δ=7.91 (s, 1H), 7.42–7.23 (m, 5H), 5.56 (s, 2H), 4.36 (q, J=7.2 Hz, 2H), 1.34 (t, J=6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=158.8, 137.7, 134.8, 128.3, 127.9, 127.6, 60.8, 13.7.

4.28. (1-Benzyl-1*H*-1,2,3-triazol-4-yl)methanol[17c]

^{1}H NMR (300 MHz, $CDCl_3$): δ=7.81 (s, 1H), 7.42–7.19 (m, 5H), 5.47 (s, 2H), 4.71 (s, 2H), 4.10 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=146.5, 135.7, 129.5, 128.7, 127.4, 122.1, 55.1, 52.4.

4.29. 1-Benzyl-4,5-diphenyl-1*H*-1,2,3-triazole[26]

^{1}H NMR (300 MHz, $CDCl_3$): δ=7.60–7.49 (m, 2H), 7.46–7.39 (m, 3H), 7.29–7.22 (m, 6H), 7.17–7.13 (m, 2H), 7.05–7.01 (m, 2H), 5.42 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=144.9, 135.6, 134.1, 131.1, 129.7, 128.9, 128.6, 128.2, 128.0, 127.8, 127.6, 126.7, 52.3.

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