Green Chemistry

Cite this: *Green Chem.*, 2011, **13**, 3440

www.rsc.org/greenchem

PAPER

Reusable ammonium salt-tagged NHC–Cu(I) complexes: preparation and catalytic application in the three component click reaction†

Wenlong Wang,[a,c] Junliang Wu,[a] Chungu Xia[a] and Fuwei Li*[a,b]

Received 19th July 2011, Accepted 8th September 2011
DOI: 10.1039/c1gc15871f

A series of ammonium salt-tagged SIPr–Cu(I) complexes have been conveniently synthesized and characterized by NMR and HRMS. They are highly active toward the three component click reaction of benzyl bromide, NaN_3 and alkyne with water as solvent at rt. Current water soluble NHC–Cu(I) catalyst could be efficiently used at least four times with an 84% isolated yield of the desired triazole in the last run.

Introduction

Since the first isolation of "free" N-heterocyclic carbene (NHC) by Arduengo in 1990,[1] NHC-transition metal complexes have attracted considerable attention owing to their high stability and outstanding application in homogeneous catalysis.[2] However, most of them are complicated to synthesize through multiple steps and only can be used for one time in the homogeneous reaction. They could not be separated easily from the reaction system and reused, which thus caused not only the waste of expensive transition metal complexes but also a contamination problem in the product. In order to overcome these limitations, a number of reusable NHC-transition metal catalysts have been developed by different supporting strategies such as immobilization of the complexes on the silica gel,[3] polymer,[4] SBA-16,[5] MCM-41[6] and nanoparticle supports[7] or *via* self-coordinative polymerization to be a recyclable catalyst.[8]

Introducing a water soluble moiety such as ammonium salt or sulfonate group onto the ligand to make the resultant metal complex more soluble in water is also an ideal solution for immobilization and recycling of the expensive (or hard to prepare) metal catalyst by using aqueous solvent system; this methodology has been applied in many kinds of ligands where phosphines are by far the ones that have been most widely studied,[9] however it is rather surprising that these types of NHC ligands or metal complexes have rarely been developed for catalytic reactions in water,[9,10] and, to the best of our knowledge, there is no account of the synthesis of ammonium salt-tagged NHC-metal catalysts and their catalytic application using water as a green media.

Click chemistry is a chemical concept introduced by Sharpless and coworkers in 2001,[11] and the Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) has undoubtedly become the most popular click-reaction, and has found a wide application in chemistry, biology and material science because of its mild conditions and high efficiency.[12] Recently, the CuAAC has been proved to be accelerated by Cu(I) species supported by nitrogen,[13] sulfur,[14] phosphine[15] and NHC[16] ligands, since these ligands could stabilize the Cu(I) center and thus enhance its catalytic activity. However, recycling of the CuAAC catalyst is scarcely investigated due to the generally homogeneous nature of these copper catalysts. On the other hand, most of the reported CuAAC studies are two-component (organic azide and alkyne) reaction systems; the organic azides need to be synthesized in advance, and the potential hazards of organic azides especially in isolation or purification processing can be problematic. It is thus desirable to develop an efficient one-pot methodology that uses halides and sodium azide for direct cycloaddition with alkyne.

As part of our continuing studies on the preparation and catalytic application of transition metal-NHC complexes[17] and the three-component CuAAC,[13a] we herein describe the synthesis of a new class of water soluble Cu(I)–NHC complexes and their recyclable application in the three component CuAAC with water as solvent at rt.

Results and discussion

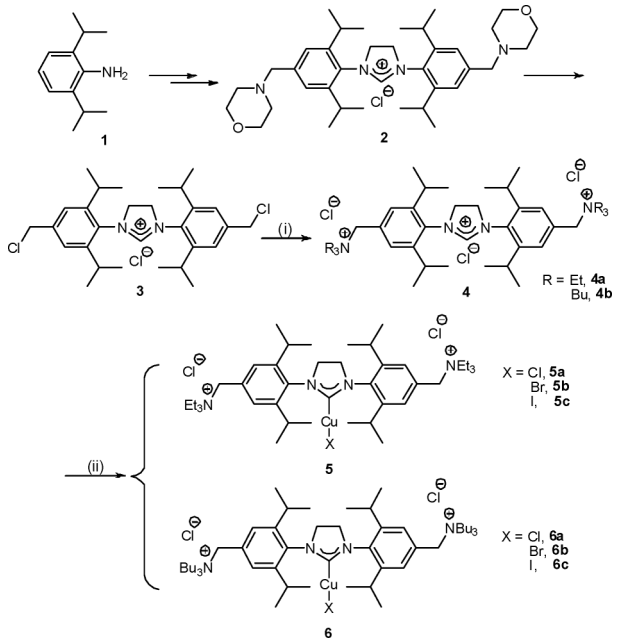
Typical SIPr (SIPr = *N*,*N*′-bis(2,6-diissopropylphenyl)-imidazolidin-2-ylidene) has been applied in many catalytic reactions as an effective ligand with various transition metals.[2] However, Nolan and co-workers found that neutral [(SIPr)CuCl] showed latent reactivity toward the standard two component click reaction of benzyl azide and phenylacetylene only giving

[a]*State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Lanzhou, 730000, China. E-mail: fuweili@licp.cas.cn; Fax: (+86)-931-4968129*
[b]*Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou, 215123, China*
[c]*Chinese Academy of Sciences and Graduate School of Chinese Academy of Sciences, Beiijng 100049, China*

† Electronic supplementary information (ESI) available: ^{1}H NMR, ^{13}C NMR spectra and HRMS analyses for unknown compounds. See DOI: 10.1039/c1gc15871f

26% conversion of substrate after one week of reaction time with water as solvent,[16d] introduction of an ammonium electron withdrawing group (EWG) to the ligand of the complex can alter its physical-chemical properties such as solubility in aqueous media, and will possibly increase the catalyst's activity.[18]

The synthetic route of Cu(I)–NHC catalysts (**5** and **6**) investigated in this work are shown in Scheme 1, commercially available 2,6-diisopropylaniline (**1**) was easily converted to **3** *via* morphine functionalized [SIPr]·HCl (**2**) according to the reported procedure,[19] and subsequent N-alkylation of **3** with triethylamine or tributlyamine gave the desired ammonium salt-tagged NHC-precursor **4a** or **4b** as white solid in high yields (>90%), respectively. The formation of **4a** and **4b** was confirmed by the characteristic downfield signal in the ^{1}H NMR spectra at 9.82 and 9.89 ppm for the NCHN proton and a base peak in the HRMS(ESI) at m/z = 206.5226 and 262.5847 for the ammonium-tagged H[SIPr]$^{3+}$ fragment. Deuteration of the NCHN proton of **4a** and **4b** was also observed when using D_2O as NMR solvent.[20]

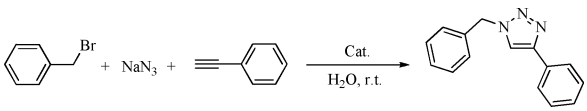


Scheme 1 Synthesis of ammonium salt-tagged SIPr–Cu(I) (**5** and **6**). Reagent and conditions: (i) triethylamine or tributlyamine, MeOH, reflux; (ii) CuCl or CuBr·SMe$_2$ or CuI, KO*t*Bu, MeOH, reflux.

Following the reported methodology,[16a] the initial synthesis of ionically tagged [(SIPr)CuCl] by the reaction of CuCl with *in situ*-generated free NHC from its imidazolium salt and 1.0 equivalent of a strong base (KO*t*-Bu) in THF or toluene at rt only resulted in a low yield of the desired NHC–Cu(I) complex during the prolonged reaction time (48 h), which is possibly caused by the different physical-chemical properties between standard [SIPr]·HCl carbene precursor and the current ionically tagged one, and we did find most of the imidazolium salts was not dissolved during the reaction and a quite number of unreacted starting salt was recovered. Changing solvent to MeOH and performing the reaction in reflux eventually led to a 74% yield of [(NHC)CuCl] (**5a**). As seen in Scheme 1, these optimized reaction conditions could be extended to the synthesis of **5c** in a yield of 77% with CuI as the copper source, however, reaction of carbene precursor **4a** with CuBr in the presence of KO*t*-Bu was found to be particularly inefficient, due to the significant formation of unidentified products. In this case, 80% yield of **5b** could be achieved using CuBr.SMe$_2$ as metal source under the same reaction conditions with that of **5a** and **5c**. Similarly, **6a**, **6b**, and **6c** could be obtained in 71%–82% yield by reaction of **4b** with the corresponding copper source with KO*t*-Bu as a base. All the Cu–NHC coordination was established by the ^{13}C NMR shift at about 201 ppm, assignable to the 2C-imidazolidin-2-ylidene carbon, and absence of the ^{1}H resonance of NCHN proton. It is worth to mention that methanol as solvent and heating are crucial for the efficient synthesis of current ammonium salt-tagged NHC–Cu(I) complexes.

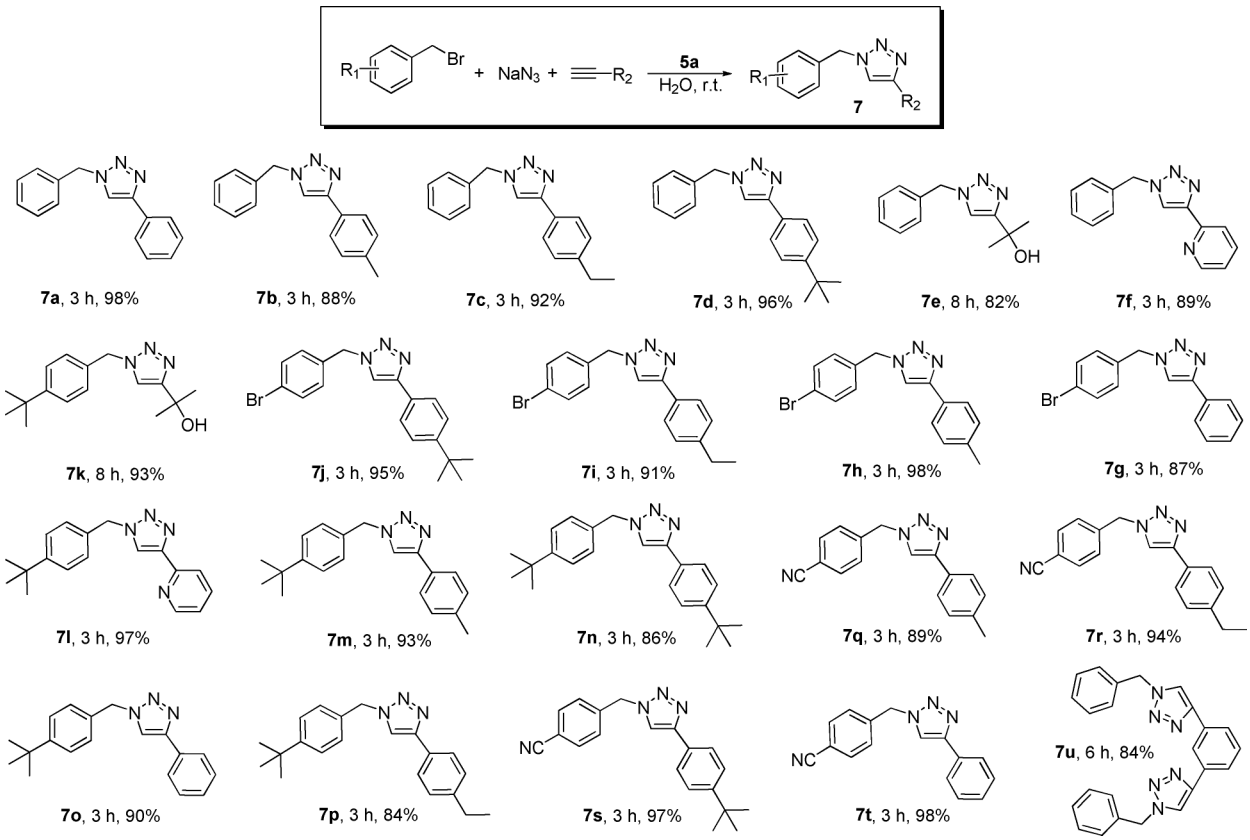
We initially carried out the standard three component click reaction of benzyl bromide and NaN_3 with phenylacetylene in water to investigate the catalyst activity of **5** and **6** (Table 1). Unlike the latent activity of neutral [(SIPr)CuCl] in the two component click reaction of benzyl azide and phenylacetylene at room temperature,[16d] the current ionically tagged [(SIPr)CuCl] (**5a**) showed efficient activity toward the model click reaction affording a 98% isolated yield of triazole (**7a**) within 3 h (entry 1). Unfortunately, replacing the chloride on the copper center by a bromide only gave trace catalytic activity (entry 2), this trend demonstrated by **5b** is opposite to the neutral [(SIMes)CuBr] (SIMes = *N*,*N*′-bis(2,6-dimethylphenyl)imidazolidin-2-ylidene), which showed higher activity than that of [(SIMes)CuCl] in the two component click reaction.[16e] Changing chloride to iodide also resulting in a lower yield of 71% in 3 h and the reactivity could be enhanced to 92% with prolonged reaction time (entry 3). Generally, complexes **6** displayed lower reactivity compared to their corresponding analogues of **5** (entries 4–6), which is possibly due to the catalyst solubility difference in water between **5** and **6** resulted from the longer hydrophobic alkyl chain of the ammonium salt on **6**. Interestingly, Similar trend in reactivity of **5** and **6** with respect to their counterion was found for this reaction (Cl > I ≫ Br). Interestingly, the model click reaction

Table 1 Catalyst screening in the click synthesis of [1,2,3]-triazole (**7a**)[a]



Entry	Catalyst (mol%)	Time (h)	Yield[b] (%)
1	Complex **5a** (5%)	6	98
		3	98
2	Complex **5b** (5%)	6	trace
3	Complex **5c** (5%)	6	92
		3	71
4	Complex **6a** (5%)	6	94
		3	76
5	Complex **6b** (5%)	6	trace
6	Complex **6c** (5%)	6	66
7	Complex **5a** (2%)	24	95
8	Complex **5a** (1%)	36	91
9	Complex **5a** (0.5%)	48	88

[a] Reaction conditions: benzyl bromide (1.0 mmol), sodium azide (1.2 mmol), phenylacetylene (1.2 mmol), catalyst, water (2.0 mL), rt. [b] Isolated yield.



Scheme 2 Ammonium salt-tagged [(SIPr)CuCl]-catalyzed three component synthesis of triazoles. Reaction conditions: benzyl bromide (1.0 mmol), NaN_3 (1.2 mmol), alkyne (1.2 mmol), **5a** (5.0 mol%), H_2O (2.0 mL), rt.

could also proceed smoothly catalyzed by current ammonium-tagged SIPr–u(I) with low catalyst loading (up to 0.5 mol%) and prolonged reaction time. 2.0 mol% of catalyst **5a** gave 95% yield of **7a** in 24 h (Entry 7) and 91% yield of the desired product was obtained in the presence of further reduced catalyst loading (Entry 8, 1.0 mol%). To our delight, catalyst loading could be minimized to 0.5 mol%, affording excellent yield of **7a** within 48 h (Entry 9).

With the optimized catalyst **5a** in hand, we then investigated the scope of this three component catalytic system with pure water as solvent, as shown in Scheme 2. To ensure short reaction duration and minimize any decomposition of starting substrates, 5 mol% of **5a** was used. All reactions proceeded smoothly giving high isolated yield of the desired triazoles (**7**) with good NMR purity (based on ^{1}H NMR spectra, see ESI†) after simple filtration at room temperature. For the organic bromides, benzyl bromides with electron-withdrawing or electron-donating groups all afforded good yields. Electron-rich or electron-poor alkynes all worked efficiently toward this click transformation and the hydroxyl-functionalized alkyne was also a good reaction partner resulting in 82%–93% yield of the corresponding triazole (**7e** and **7k**). Current catalyst system could effectively tolerate the N-containing aryl acetylene (**7f** and **7l**). The double click of diyne also proceeded efficiently affording the desired *meta*-bis-triazole (**7u**) with 84% yield.

To validate the recyclability of current ammonium-tagged SIPr–Cu(I) under lower catalyst loading, the reuse investigation was performed in the model click reaction of benzyl bromide, sodium azide and phenylacetylene with 2 mol% of **5a** for 24 h (Fig. 1). After the completion of reaction, ether was added to the reaction tube, the upper organic phase containing product was easily separated by simple liquid–liquid extraction to produce triazole **7a**, and the residual aqueous catalyst phase was remained and reused for the next run because of the obvious solubility difference of the ammonium salt functionalized [(SIPr)CuX] in ether and water. It is shown in Fig. 1 that current water soluble catalyst could be used at least four times with the fourth run giving an 84% isolated yield of **7a**.

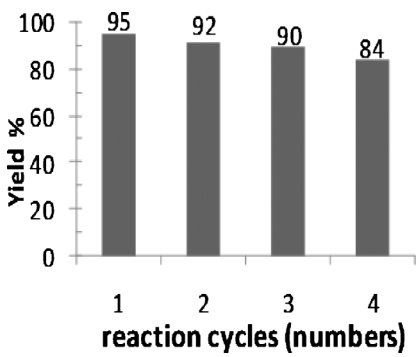


Fig. 1 The recyclability test of complex **5a**.

Conclusions

In summary, we have developed a series of reusable ammonium salt-tagged [(SIPr)CuX] complexes, which showed highly efficient reactivity toward the three component click-reaction of a wide arrange of benzyl bromides and alkynes using water as solvent at rt. The optimized catalyst **5a** could be conveniently recycled up to three times without a significant loss of its activity with catalyst loading as low as 2.0 mol% in the fresh run. The observed higher catalytic activities of this ammonium salt-tagged [(SIPr)CuCl] compared to its standard neutral analogue demonstrates the potential of ionic functionalization of NHC–Cu(I) complex in promoting CuAAC catalysis and achieving catalyst recycle. Current experiments in our laboratory are directed at the synthesis of new recyclable transition metal-NHC complexes and their catalytic applications.

Experimental

All the chemical and solvents were used as received without purification except MeOH, which was dried by distillation over magnesium powder and freshly distilled prior to use. 1,3-Bis(2,6-diisopropyl-4-(chloromethyl)phenyl)-4,5-dihydro-1-H-imidazol-3-ium-chloride (**3**) was synthesized according to the reported procedure.[19] NMR spectra were recorded using a Bruker Avance™ spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C. Chemical shifts are given in ppm relative to TMS or to residual solvent proton resonances. High resolution mass spectra (HRMS) were obtained on a Bruker micrOTOF-Q spectrometer. All the reported yields in the catalytic studies are isolated yields and averaged by at least two runs.

General procedure for the synthesis of ammonium salt-tagged SIPr-carbene precursor (4a and 4b)

10 mL triethylamine or tributylamine was added slowly to a MeOH solution (80 mL) of freshly synthesized intermediate **3** (2 g, 3.82 mmol) at room temperature, the reaction mixture was subsequently refluxed for 24 h. The solvent and excess tertiary amines were evaporated under the reduced pressure, and 100 mL of anhydrous ether was added to precipitate the product, and the resultant white powder was collected and washed with 10 mL of ether three times to give the corresponding ammonium salt-tagged carbene precursor **4a** (2.61 g, 94%) or **4b** (3.14 g, 92%).

1,3-Bis(2,6-diisopropyl-4-((triethylammonio)methyl)phenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (4a). White solid; ^{1}H NMR (D_2O): 1.23 (t, 12 H), 1.35–1.40 (m, 30 H), 3.07–3.14 (m, 4 H, J = 6.8 Hz), 3.16–3.25 (m, 12 H), 4.46 (s, 4 H), 4.59 (s, 4 H), 7.46 (s, 4 H); ^{1}H NMR (DMSO-d_6): 1.21 (d, 12 H, J = 6.8 Hz), 1.31–1.38 (m, 30 H, J = 6.8 Hz), 3.13 (t, 4 H, J = 6.4 Hz), 3.16–3.22 (m, 12 H, J = 7.2 Hz), 4.59 (d, 8 H, J = 10.4 Hz), 7.57 (s, 4H), 9.82 (s,1 H); ^{13}C NMR (D_2O): 7.0, 22.4, 24.2, 28.7, 52.6, 53.6, 59.8, 128.8, 130.5, 131.1, 147.7. HRMS m/z (ESI) calcd for $C_{41}H_{71}N_4$ [cation]$^{3+}$ 206.5221, found 206.5226.

1,3-Bis(2,6-diisopropyl-4-((tributylammonio)methyl)phenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (4b). White solid; ^{1}H NMR (D_2O): 0.95 (t, 18 H, J = 7.2 Hz), 1.21 (d, 16 H, J = 6.8 Hz), 1.36 (d, 20 H, J = 6.8 Hz), 1.79 (s, 12 H), 3.08–3.14 (m, 16 H), 4.48 (s, 4 H), 4.58 (s, 4 H), 7.43 (s, 4 H); ^{1}H NMR (DMSO-d_6): 0.97 (t, 18 H), 1.21 (d, 16 H, J = 6.8 Hz), 1.28–1.37 (m, 20 H), 1.76 (s, 12 H), 3.15 (t, 16 H), 4.58 (s, 4 H), 4.65 (s, 4 H), 7.59 (s, 4 H), 9.89 (s, 1 H); ^{13}C NMR (DMSO-d_6): 13.6, 13.4, 23.3, 24.8, 28.2, 45.4, 53.8, 56.0, 57.9, 60.9, 125.4, 129.4, 131.0, 131.4, 146.8, 160.2. HRMS m/z (ESI) calcd for $C_{53}H_{95}N_4$ [cation]$^{3+}$ 262.5847, found 262.5853.

General procedure for the preparation of ammonium salt-tagged NHC–Cu(I) complexes (5 and 6)

An oven-dried Schlenk flask was charged with **4a** (726 mg, 1.0 mmol), CuCl (109 mg, 1.1 mmol) and KO*t*-Bu (135 mg, 1.0 mmol). The flask was evacuated and backfilled with argon three times before the addition of dried methanol (30 mL), then the mixture was refluxed for 12h. After the completion of reaction, the resultant reaction mixture was filtered through a plug of Celite, and the filtrate was concentrated to about 10 mL under reduced pressure. Upon the addition of pentane to the crude reaction mixture, complex **5a** was slowly precipitated and isolated as a yellow solid (584 mg, 74%).

Complex **5b**, **5c**, **6a**, **6b** and **6c** were synthesized in high yields by similar procedure to the preparation of **5a** from corresponding copper resource and carbene precursor (see Scheme 1 and ESI†).

(1,3-Bis(2,6-diisopropyl-4-((triethylammonio)methyl)phenyl) imidazolidin-2-yl)copper(I) chloride (5a). ^{1}H NMR (D_2O): 1.20–1.30 (m, 42 H), 3.10–3.16 (m, 16 H), 4.14 (s, 4 H), 4.36 (s, 4 H), 7.33 (s, 4 H). ^{13}C NMR (D_2O): 7.1, 22.7, 24.7, 28.3, 52.6, 53.5, 60.3, 128.6, 136.4, 148.7, 201.1. HRMS m/z (ESI) calcd for $C_{41}H_{70}ClCuN_4$ [cation]$^{2+}$ 358.2287, found 358.2295.

(1,3-Bis(2,6-diisopropyl-4-((triethylammonio)methyl)phenyl) imidazolidin-2-yl)copper(I) bromide dichloride (5b). White solid, 77% yield; ^{1}H NMR (D_2O): 1.16–1.20 (m, 24 H), 1.25 (t, 18 H, J = 7 Hz), 3.03–3.13 (m, 16 H), 4.10 (s, 4 H), 4.33 (s, 4 H), 7.30 (s, 4 H). ^{13}C NMR (D_2O): 7.0, 22.7, 24.6, 28.3, 52.6, 53.4, 60.3, 128.5, 136.4, 148.7, 201.3. HRMS m/z (ESI) calcd for $C_{41}H_{70}BrCuN_4$ [cation]$^{2+}$ 380.2034, found 380.2035.

(1,3-Bis(2,6-diisopropyl-4-((triethylammonio)methyl)phenyl) imidazolidin-2-yl)copper(I) iodide dichloride (5c). White solid 80% yield; ^{1}H NMR (D_2O): 1.10–1.15 (m, 24 H), 1.27 (t, 18 H, J = 7 Hz), 3.00–3.07 (m, 16 H), 3.98 (s, 4 H), 4.30 (s, 4 H), 7.21 (s, 4 H). ^{13}C NMR (D_2O): 7.0, 23.2, 24.6, 28.2, 52.3, 53.1, 59.8, 128.0, 137.2, 148.6, 201.4. HRMS m/z (ESI) calcd for $C_{41}H_{70}ICuN_4$ [cation]$^{2+}$ 404.1965, found 404.1950.

(1,3-Bis(2,6-diisopropyl-4-((tributylammonio)methyl) phenyl) imidazolidin-2-yl)copper(I) chloride (6a). Yellow solid, 71% yield; ^{1}H NMR (D_2O): 0.85 (d, 18 H, J = 7.2 Hz), 1.20–1.26 (m, 32 H), 1.68 (s, 12 H), 1.98 (s, 4 H), 3.11 (s, 16 H), 4.12 (s, 4 H), 4.38 (s, 4 H), 7.29 (s, 4 H). ^{13}C NMR (DMSO-d_6): 13.5, 19.3, 23.4, 24.9, 28.1, 53.7, 57.9, 61.5, 129.1, 131.1, 136.2, 147.1, 201.0. HRMS m/z (ESI) calcd for $C_{53}H_{94}ClCuN_4$ [cation]$^{2+}$ 442.3226, found 442.3224.

(1,3-Bis(2,6-diisopropyl-4-((tributylammonio)methyl)phenyl) imidazolidin-2-yl)copper(I) bromide dichloride (6b). White solid, 82% yield; ^{1}H NMR (D_2O): 0.82–0.88 (m, 18 H), 1.19–1.28 (m, 32 H), 1.69 (s, 12 H), 2.05 (s, 4 H), 3.03 (d, 16 H, J =

4.8 Hz), 4.13 (s, 4 H), 4.39 (d, 4 H, J = 5.2 Hz), 7.30 (s, 4 H). ^{13}C NMR (DMSO-d_6): 13.5, 19.4, 23.3, 25.0, 28.2, 53.7, 58.0, 61.2, 129.2, 131.1, 136.2, 147.1, 201.1. HRMS m/z (ESI) calcd for $C_{53}H_{94}BrCuN_4$ [cation]$^{2+}$ 464.2973, found 464.2977.

(1,3-Bis(2,6-diisopropyl-4-((tributylammonio)methyl)phenyl) imidazolidin-2-yl)copper(I) iodide dichloride (6c). White solid, 78% yield; ^{1}H NMR (D_2O): 0.83 (t, 18 H, J = 7.2 Hz), 1.18–1.24 (m, 32 H), 1.67 (s, 12 H), 1.93 (s, 4 H), 3.01 (s, 16 H), 4.12 (s, 4 H), 4.38 (s, 4 H), 7.29 (s, 4 H). ^{13}C NMR (DMSO-d_6): 13.5, 19.4, 23.4, 24.9, 28.1, 53.6, 57.9, 61.5, 129.1, 131.1, 136.2, 147.2, 201.1. HRMS m/z (ESI) calcd for $C_{53}H_{94}ICuN_4$ [cation]$^{2+}$ 488.2904, found 488.2909.

Typical procedure for the three component click-reaction catalyzed by complex 5a

Organic bromide (1.0 mmol), NaN_3 (1.2 mmol), alkyne (1.2 mmol), catalyst **5a** (0.05 mmol) and water (2.0 mL) were introduced to a vial fitted with a screw cap. The reaction was carried out at room temperature and monitored by TLC. After completion of the reaction, 20 mL of water was added to the vial and the mixture was stirred for 10 min to precipitate the product completely, which was collected by suction filtration and washed with 10 mL of water several times affording the desired triazole. All the products can be obtained with NMR purity by this procedure.

Recyclability study

All the recycling operations were carried out in a 25 mL Schlenk tube under argon atmosphere. After the completion of the fresh reaction performed as above typical procedure in the presence of 2 mol% of **5a** for 24 h, the reaction mixture was extracted with ether (4 × 20 mL) to remove the starting substrate and product, and the residual aqueous catalyst phase could be reused for the next run after addition of fresh reactants. The organic extracts were combined and purified to give the desired triazole **7a**.

NMR and HRMS data of new compounds

1-Benzyl-4-(4-ethylphenyl)-1*H*-1,2,3-triazole (7c). White solid; ^{1}H NMR ($CDCl_3$): 1.24 (t, 3 H, J = 7.6 Hz), 2.66 (q, 2 H, J = 7.6 Hz), 5.57 (s, 2 H), 7.22–7.30 (m, 2 H), 7.31 (d, 2 H, J = 2.4 Hz), 7.36–7.41 (m, 3 H), 7.63 (brs, 1 H), 7.72 (d, 2 H, J = 8.4 Hz). ^{13}C NMR ($CDCl_3$): 15.5, 28.7, 54.2, 125.7, 128.0, 128.3, 128.7, 129.1, 131.6, 134.8, 144.4, 148.3. HRMS m/z (ESI) calcd for $C_{17}H_{18}N_3$ [M+H]$^+$ 264.1495, found 264.1489.

1-Benzyl-4-(4-(*tert*-butyl)phenyl)-1*H*-1,2,3-triazole (7d). White solid; ^{1}H NMR ($CDCl_3$): 1.33 (s, 9 H), 5.57 (s, 2 H), 7.28–7.30 (m, 2 H), 7.38 (d, 2 H, J = 7.2 Hz), 7.42 (d, 2 H, J = 8.0 Hz), 7.65 (brs, 1 H), 7.74 (d, 2 H, 8.0 Hz). ^{13}C NMR ($CDCl_3$): 31.3, 34.7, 54.3, 125.5, 125.8, 127.6, 128.0, 128.3, 128.8, 129.1, 134.7, 151.4. HRMS m/z (ESI) calcd for $C_{19}H_{21}N_3Na$ [M+Na]$^+$ 314.1628, found 314.1615.

1-(4-Bromobenzyl)-4-phenyl-1*H*-1,2,3-triazole (7g). White solid; ^{1}H NMR ($CDCl_3$): 5.53 (s, 2 H), 7.18 (d, 2 H, J = 8.4 Hz), 7.31–7.43 (m, 3 H), 7.52 (d, 2 H, J = 8.4 Hz), 7.67 (brs, 1 H), 7.80 (d, 2 H, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$): 53.7, 119.6, 123.1, 125.8, 128.4, 129.0, 129.2, 129.8 130.5, 132.5, 133.8. HRMS m/z (ESI) calcd for $C_{15}H_{12}BrN_3Na$ [M+Na]$^+$ 336.0107, found 336.0096.

1-(4-Bromobenzyl)-4-(*p*-tolyl)-1*H*-1,2,3-triazole (7h). White solid; ^{1}H NMR ($CDCl_3$): 2.36 (s, 2 H), 5.51 (s, 2 H), 7.16–7.22 (m, 4 H), 7.51 (d, 2 H, J = 8.4 Hz), 7.63 (brs, 1 H), 7.68 (d, 2 H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$): 21.4, 53.7, 119.2, 123.1, 125.8, 127.7, 129.7, 129.8, 132.5, 133.9, 138.3. HRMS m/z (ESI) calcd for $C_{16}H_{15}BrN_3$ [M+H]$^+$ 328.0444, found 328.0430.

1-(4-Bromobenzyl)-4-(4-ethylphenyl)-1*H*-1,2,3-triazole (7i). White solid; ^{1}H NMR ($CDCl_3$): 1.25 (t, 3 H, J = 7.6 Hz), 2.67 (q, 2 H, J = 7.6 Hz), 5.52 (s, 2 H), 7.17 (d, 2 H, J = 8.4 Hz), 7.24 (d, 2 H, J = 8 Hz), 7.50–7.52 (m, 2 H), 7.63 (brs, 1 H), 7.71 (d, 2 H, J = 8.4 Hz). ^{13}C NMR ($CDCl_3$): 15.6, 28.8, 53.6, 119.3, 123.0, 125.8, 127.9, 128.4, 129.8, 132.4, 133.9, 144.7. HRMS m/z (ESI) calcd for $C_{17}H_{17}BrN_3$ [M+H]$^+$ 342.0600, found 342.0595.

1-(4-Bromobenzyl)-4-(4-(*tert*-butyl)phenyl)-1*H*-1,2,3-triazole (7j). White solid; ^{1}H NMR ($CDCl_3$): 1.33 (s, 9 H), 5.52 (s, 2 H), 7.16 (d, 2 H, J = 8.4 Hz), 7.43 (d, 2 H, J = 8.4 Hz), 7.51 (m, 2 H), 7.65 (brs, 1 H), 7.73 (d, 2 H, J = 8.4 Hz). ^{13}C NMR ($CDCl_3$): 31.3, 34.7, 53.5, 119.3, 122.9, 125.5, 125.8, 127.4, 129.6, 131.9, 132.3, 133.8, 151.5. HRMS m/z (ESI) calcd for $C_{19}H_{20}BrN_3Na$ [M+Na]$^+$ 392.0733, found 392.0715.

2-(1-(4-(*tert*-Butyl)benzyl)-1*H*-1,2,3-triazol-4-yl)propan-2-ol (7k). White solid; ^{1}H NMR ($CDCl_3$): 1.32 (s, 9 H), 1.61 (s, 6 H), 5.47 (s, 2 H), 7.22 (d, 2 H, J = 8.4 Hz), 7.35 (brs, 1 H), 7.40 (d, 2 H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$): 30.5, 31.4, 34.8, 54.3, 68.5, 126.2, 128.2, 131.3, 152.2, 155.7. HRMS m/z (ESI) calcd for $C_{16}H_{23}N_3NaO$ [M+Na]$^+$ 296.1733, found 296.1723.

2-(1-(4-(*tert*-Butyl)benzyl)-1*H*-1,2,3-triazol-4-yl)pyridine (7l). brown solid; ^{1}H NMR ($CDCl_3$): 1.31 (s, 9 H), 5.55 (s, 2 H), 7.20–7.23 (m, 1 H), 7.28 (d, 3 H, J = 8.8 Hz), 7.40 (dd, 2 H, J = 7.2, 2.0 Hz), 7.75–7.79 (m, 1 H), 8.04 (brs, 1 H), 8.18 (d, 1 H, J = 8.0 Hz), 8.53 (d, 1 H, J = 4.8 Hz). ^{13}C NMR ($CDCl_3$): 31.4, 34.8, 54.4, 121.2, 123.3, 126.3, 128.3, 131.2, 152.2. HRMS m/z (ESI) calcd for $C_{18}H_{20}N_4Na$ [M+Na]$^+$ 315.1586, found 315.1574.

1-(4-(*tert*-Butyl)benzyl)-4-(p-tolyl)-1*H*-1,2,3-triazole (7m). White solid; ^{1}H NMR ($CDCl_3$): 1.31(s, 9 H), 2.36 (s, 3 H), 5.53 (s, 2 H), 7.20 (d, 2 H, J = 7.2 Hz), 7.25 (d, 2 H, J = 8.4 Hz), 7.40 (d, 2 H, J = 6.8 Hz), 7.65 (brs, 1 H), 7.69 (d, 2 H, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$): 21.4, 31.4, 34.8, 54.1, 125.7, 126.2, 128.0, 129.6, 131.8, 132.5, 138.1, 139.6, 152.0. HRMS m/z (ESI) calcd for $C_{20}H_{24}N_3$ [M+H]$^+$ 306.1970, found 306.1947.

1-(4-(*tert*-Butyl)benzyl)-4-(4-(*tert*-butyl)phenyl)-1*H*-1,2,3-triazole (7n). White solid; ^{1}H NMR ($CDCl_3$): 1.31 (s, 9 H), 1.33(s, 9 H), 5.54 (s, 2 H), 7.22–7.43 (m, 7 H), 7.78 (brs, 2 H). ^{13}C NMR ($CDCl_3$): 31.4, 34.8, 54.2, 125.5, 125.9, 126.2, 128.0, 128.9, 131.8, 132.4, 134.9, 151.4, 152.0. HRMS m/z (ESI) calcd for $C_{23}H_{30}N_3$ [M+H]$^+$ 348.2434, found 348.2413.

1-(4-(*tert*-Butyl)benzyl)-4-(4-ethylphenyl)-1*H*-1,2,3-triazole (7p). White solid; ^{1}H NMR ($CDCl_3$): 1.23 (t, 3 H, J = 7.6 Hz), 1.31 (s, 9 H), 2.65 (q, 2 H, J = 7.6 Hz), 5.52 (s, 2 H), 7.21–7.25 (m, 4 H), 7.38–7.40 (m, 4 H), 7.62 (brs, 1 H), 7.71 (d, 2 H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$): 15.6, 28.8, 31.4, 34.7, 54.0, 119.4, 125.8, 126.1, 128.0, 128.1, 128.4, 128.9, 131.8, 144.4, 152.0. HRMS

m/z (ESI) calcd for $C_{42}H_{50}N_6Na$ [2M+Na]$^+$ 661.3995, found 661.3973.

4-((4-(*p*-Tolyl)-1*H*-1,2,3-triazol-1-yl)methyl)benzonitrile (7q). White solid; ^{1}H NMR ($CDCl_3$): 2.29 (s, 3 H), 5.55 (s, 2 H), 7.14 (d, 2 H, J = 8.0 Hz), 7.29 (d, 2 H, J = 8.0 Hz), 7.57–7.63 (m, 5 H). ^{13}C NMR ($CDCl_3$): 21.3, 53.4, 112.7, 118.2, 119.6, 125.7, 127.4, 128.4, 129.6, 132.9, 138.4, 140.1, 148.7. HRMS *m/z* (ESI) calcd for $C_{17}H_{15}N_4$ [M+H]$^+$ 275.1291, found 275.1280.

4-((4-(4-Ethylphenyl)-1*H*-1,2,3-triazol-1yl)methyl)benzonitrile (7r). White solid; ^{1}H NMR ($CDCl_3$): 1.25 (t, 3 H, J = 7.6 Hz), 2.67 (q, 2 H, J = 7.6 Hz), 5.64 (s, 2 H), 7.25 (d, 1 H, J = 8.4 Hz), 7.37 (d, 2 H, J = 8.4 Hz), 7.63–7.74 (m, 6 H). ^{13}C NMR ($CDCl_3$): 15.6, 28.8, 53.6, 112.9, 118.3, 119.5, 125.9, 127.6, 128.5, 129.9, 132.7, 133.0, 140.1, 144.9. HRMS *m/z* (ESI) calcd for $C_{18}H_{17}N_4$ [M+H]$^+$ 289.1448, found 289.1439.

4-((4-(4-(*tert*-Butyl)phenyl)-1*H*-1,2,3-triazol-1-yl)methyl) benzonitrile (7s). Yellow solid; ^{1}H NMR ($CDCl_3$): 1.33 (s, 9 H), 5.52 (s, 2 H), 7.16 (d, 2 H, J = 8.4 Hz), 7.43 (d, 2 H, J = 8.0 Hz), 7.50 (d, 2 H, J = 8.4 Hz, 7.66 (brs, 1 H), 7.74 (d, 2 H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$): 31.4, 34.8, 53.6, 119.3, 123.0, 125.5, 125.9, 127.6, 129.7, 132.0, 132.4, 134.0, 148.5, 151.5. HRMS *m/z* (ESI) calcd for $C_{20}H_{21}N_4$ [M+H]$^+$ 317.1766, found 317.1782.

1,3-Bis(1-benzyl-1*H*-1,2,3-triazol-4-yl)benzene (7u). White solid; ^{1}H-NMR ($CDCl_3$): 5.55 (s, 4 H), 7.29–7.43 (m, 11 H), 7.73–7.78 (m, 4 H), 8.17 (s, 1 H). ^{13}C NMR ($CDCl_3$): 54.5, 123.0, 125.5, 128.3, 129.0, 129.3, 129.5, 131.0, 134.6. HRMS *m/z* (ESI) calcd for $C_{24}H_{21}N_6$ [M+H]$^+$ 398.1822, found 398.1803.

Acknowledgements

We are grateful to the National Natural Science Foundation of China (21002106 and 21133011) and the Chinese Academy of Science for financial support.

References

1 A. J. Arduengo, H. V. R. Dias, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1992, **114**, 5530–5534.
2 For selected carbene reviews in catalysis, see: (*a*) S. Díez-González, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612–3676; (*b*) C. Samojlowicz, M. Bieniek and K. Grela, *Chem. Rev.*, 2009, **109**, 3708–3742; (*c*) R. Corberan, E. Mas-Marza and E. Peris, *Eur. J. Inorg. Chem.*, 2009, 1700–1716; (*d*) S. Díez-González and S. P. Nolan, *Aldrichimica Acta*, 2008, **41**, 43–51; (*e*) E. A. B. Kantchev, C. J. O'Brien and M. G. Organ, *Angew. Chem., Int. Ed.*, 2007, **46**, 2768–2813; (*f*) O. Kuhl, *Chem. Soc. Rev.*, 2007, **36**, 592–607.
3 (*a*) D. P. Allen, M. M. Van Wingerden and R. H. Grubbs, *Org. Lett.*, 2009, **11**, 1261–1264; (*b*) H. Qiu, S. M. Sarkar, D. H. Lee and M. J. Jin, *Green Chem.*, 2008, **10**, 37–40; (*c*) P. H. Deshmukh and S. Blechert, *Dalton Trans.*, 2007, 2479–2491; (*d*) S. Prühs, C. W. Lehmann and A. Fürstner, *Organometallics*, 2004, **23**, 280–287; (*e*) M. Mayr, M. R. Buchmeiser and K. Wurst, *Adv. Synth. Catal.*, 2002, **344**, 712–719.
4 (*a*) D. B. Bagal, Z. S. Qureshi, K. P. Dhake, S. R. Khan and B. M. Bhanage, *Green Chem.*, 2011, **13**, 1490–1494; (*b*) P. Li, L. Wang, Y. Zhang and M. Wang, *Tetrahedron Lett.*, 2008, **49**, 6650–6654.
5 H. Yang, X. Han, G. Li and Y. Wang, *Green Chem.*, 2009, **11**, 1184–1193.
6 H. Zhou, Y. M. Wang, W. Z. Zhang, J. P. Qu and X. B. Lu, *Green Chem.*, 2011, **13**, 644–650.
7 (*a*) H. Yang, Y. Wang, Y. Qin, Y. Chong, Q. Yang, G. Li, L. Zhang and W. Li, *Green Chem.*, 2011, **13**, 1352–1361; (*b*) S. Wittmann, A. Schätz, R. N. Grass, W. J. Stark and O. Reiser, *Angew. Chem., Int. Ed.*, 2010, **49**, 1867–1870; (*c*) K. V. S. Ranganath, J. Kloesges, A. H. Schäfer and F. Glorius, *Angew. Chem., Int. Ed.*, 2010, **49**, 7786–7789.
8 (*a*) M. N. Liu and O. Reiser, *Org. Lett.*, 2011, **13**, 1102–1105; (*b*) J. Choi, H. Y. Yang, H. J. Kim and S. U. Son, *Angew. Chem., Int. Ed.*, 2010, **49**, 7718–7722; (*c*) B. Karimi and P. F. Akhavan, *Chem. Commun.*, 2009, 3750–3752; (*d*) S. J. Connon, A. M. Dunne and S. Blechert, *Angew. Chem., Int. Ed.*, 2002, **41**, 3835–3838.
9 (*a*) K. H. Shaughnessy, *Chem. Rev.*, 2009, **109**, 643–710, and reference therein.
10 (*a*) S. Roy and H. Plenio, *Adv. Synth. Catal.*, 2010, **352**, 1014–1022; (*b*) A. Azua, S. Sanz and E. Peris, *Organometallics*, 2010, **29**, 3661–3664; (*c*) C. Fleckenstein, S. Roy, Leuthau and H. Plenio, *Chem. Commun.*, 2007, 2870–2872; (*d*) S. H. Hong and R. H. Grubbs, *J. Am. Chem. Soc.*, 2006, **128**, 3508–3509; (*e*) M. an der Heiden and H. Plenio, *Chem.–Eur. J.*, 2004, **10**, 1789–1797.
11 H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004–2021.
12 (*a*) M. Meldal and C. W. Tornøe, *Chem. Rev.*, 2008, **108**, 2952–3015; (*b*) J. E. Moses and A. D. Moorhouse, *Chem. Soc. Rev.*, 2007, **36**, 1249–1262; (*c*) J. F. Lutz, *Angew. Chem., Int. Ed.*, 2007, **46**, 1018–1025.
13 (*a*) F. W. Li and T. S. A. Hor, *Chem.–Eur. J.*, 2009, **15**, 10585–10592; (*b*) V. O. Rodionov, S. I. Presolski, S. Gardinier, Y. H. Lim and M. G. Finn, *J. Am. Chem. Soc.*, 2007, **129**, 12696–12704; (*c*) V. O. Rodionov, S. I. Presolski, D. Díaz, V. V. Fokin and M. G. Finn, *J. Am. Chem. Soc.*, 2007, **129**, 12705–12712; (*d*) T. R. Chan, R. Hilgraf, K. B. Sharpless and V. V. Fokin, *Org. Lett.*, 2004, **6**, 2853–2855; (*e*) W. G. Lewis, F. G. Magallon, V. V. Fokin and M. G. Finn, *J. Am. Chem. Soc.*, 2004, **126**, 9152–9153.
14 F. Wang, H. Fu, Y. Jiang and Y. Zhao, *Green Chem.*, 2008, **10**, 452–456.
15 N. Moitra, J. J. E. Moreau, X. Cattoën and M. Wong Chi Man, *Chem. Commun.*, 2010, **46**, 8416–8418.
16 (*a*) S. Diez-Gonzalez, E. C. Escudero-Adan, J. Benet-Buchholz, E. D. Stevens, A. M. Z. Slawin and S. P. Nolan, *Dalton Trans.*, 2010, **39**, 7595–7606; (*b*) M. L. Teyssot, A. Chevry, M. Traïkia, M. EI-Ghozzi, D. Avignant and A. Gautier, *Chem.–Eur. J.*, 2009, **15**, 6322–6326; (*c*) S. Díez-González and S. P. Nolan, *Angew. Chem., Int. Ed.*, 2008, **47**, 8881–8884; (*d*) S. Diez-Gonzalez, E. D. Stevens and S. P. Nolan, *Chem. Commun.*, 2008, 4747–4749; (*e*) S. Díez-González, A. Correa, L. Cavallo and S. P. Nolan, *Chem.–Eur. J.*, 2006, **12**, 7558–7564.
17 (*a*) L. Q. Xue, L. J. Shi, Y. Han, C. G. Xia, H. V. Huynh and F. W. Li, *Dalton Trans.*, 2011, **40**, 7632–7638; (*b*) F. W. Li, J. J. Hu, L. L. Koh and T. S. A. Hor, *Dalton Trans.*, 2010, **39**, 5231–5241; (*c*) F. W. Li, S. Q. Bai and T. S. A. Hor, *Organometallics*, 2008, **27**, 672–677.
18 (*a*) D. Rix, F. CaÏjo, I. Laurent, L. Gulajski, K. Grela and M. Mauduit, *Chem. Commun.*, 2007, 3771–3773; (*b*) A. Michrowska, L. Gulajski, Z. Kaczmarska, K. Mennecke, A. Kirschning and K. Grela, *Green Chem.*, 2006, **8**, 685–688.
19 V. Sashuk, D. Schoeps and H. Plenio, *Chem. Commun.*, 2009, 770–772.
20 S. T. Handy and M. Okello, *J. Org. Chem.*, 2005, **70**, 1915–1918.