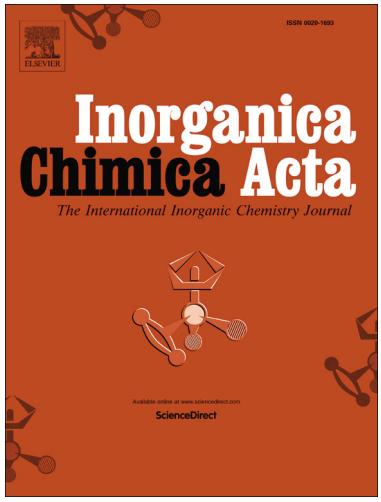

Research paper

An efficient (NHC) Copper (I)-catalyst for azide–alkyne cycloaddition reactions for the synthesis of 1,2,3-trisubstituted triazoles: click Chemistry

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An efficient (NHC) Copper (I)-catalyst for azide–alkyne cycloaddition reactions for the synthesis of 1,2,3-trisubstituted triazoles : click Chemistry

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Abstract

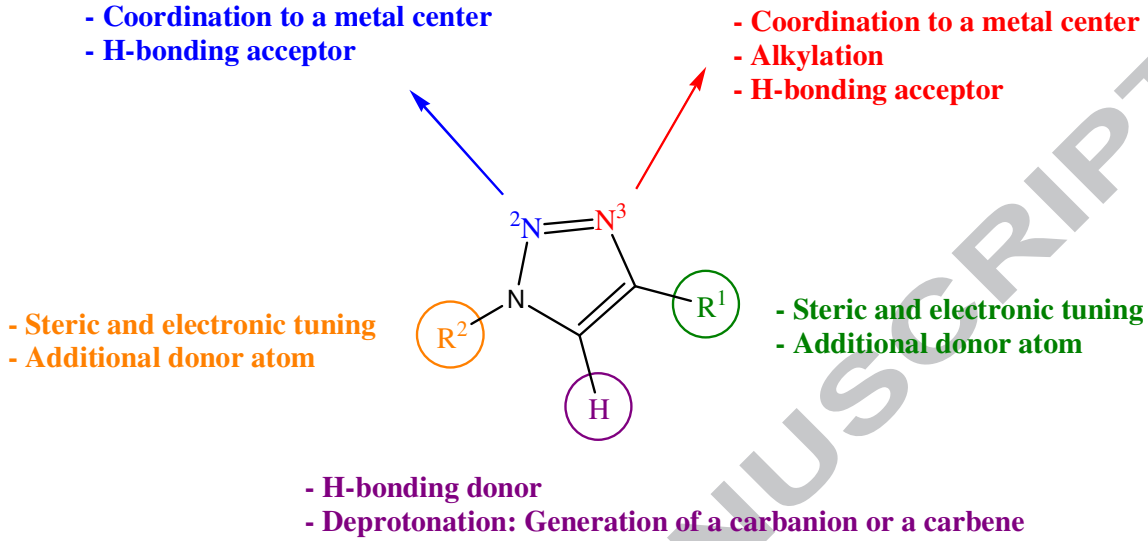
In this study a series of new benzimidazolium salts (**2a–c**) were synthesized from the reaction of 5,6-dimethyl-1-(alkylbenzyl)-1H-benzo[d]imidazole with various alkyl halides. These salts were used to synthesize cupper N-heterocyclic carbene (Cu-NHC) complexes **3-4**. The obtained (NHC) Copper (I) complexes **3-4** were characterized by FT-IR, NMR (^{1}H and ^{13}C) spectroscopic methods, mass spectrometry (EI-MS and HRMS) and elemental analysis. These novel cupper complexes **3-4** were used as a catalyst for alkyne – azide cycloaddition (CuAAC) reaction. Several triazoles **7** have been synthesized. This catalytic system fulfils the requirements of "click chemistry" with its mild and convenient conditions, notably in water at room temperature with low catalyst loading and simple isolation with no purification step.

Keywords: Alkynes, Azides, Click chemistry, Homogeneous catalysis, Copper-N-heterocyclic carbene complex

Introduction

1,2,3-Triazoles are attractive molecules and widely used in organic synthesis, materials sciences, drug development, and bioconjugation chemistry[1]. Thus, the privileged 1,2,3 triazole motif has not only been extensively utilized by synthetic organic chemists, but also by chemists working in fields as diverse as bio-conjugation[2] and anion/cation recognition,[3] just to name a few relevant research fields. A close look at the 1,2,3-triazole ring also shows the

attractive features that this ring, in combination with relevant substituents has to offer to coordination and organometallic chemists (**Scheme 1**).



Scheme 1: Various functionalities of the 1,2,3- triazoles ring

Thus, the 1,2,3-triazole can act as a monodentate ligand by coordination via the N_3 nitrogen, which is the most basic donor atom in the ring.[4]The ring in its deprotonated form (triazolides) can also act as a monodentate carbanionic donor via C^-.[5]However, more interesting are the possibilities of introducing additional donor substituents on the triazole ring for generating chelating ligands, incorporating multi triazole rings within a ligand backbone for generating multi-dentate triazole ligands, or methylating the N_3 nitrogen and deprotonating the triazole C–H ring proton to generate species that have been variously called abnormal N-heterocyclic carbenes (*a*NHC) or mesoionic carbenes (MIC). In addition, the modular synthesis of such substituted triazole rings offers unending possibilities for steric and electronic tuning of the ligands and in turn their metal complexes.

The traditional preparation methods of 1,2,3-triazoles by 1,3-dipolar cycloaddition of azides and alkynes under thermal conditions[6]. Great developments have been realized as click chemistry, copper-catalyzed azide–alkyne cycloaddition (CuAAC), which provides a simple method to join together organic molecules efficiently under mild conditions, has been explored in depth[7]

The copper and ruthenium catalyzed azide alkyne cycloaddition reactions are powerful strategies for the regioselective synthesis of 1,4-disubstituted 1,2,3-triazoles and 1,5-

disubstituted 1,2,3-triazoles. However, internal alkynes are rarely developed [8] and 1,4,5-trisubstituted 1,2,3-triazoles are difficult to synthesize through this strategy. Furthemore functionalized 1,2,3-triazole derivatives have emerged as interesting ligands for transition metals and organometallic species due to their potential to act as N donors.[9] A wide range of mono-, bis-, tris-, and polydentate ligands containing the 1,2,3-triazole skeleton has been synthesized and studied for their coordination chemistry.[10] The preparation of this type of ligands has become more accessible due to the discovery of the 1,3-dipolar Cu(I) catalyzed alkyne–azide cycloaddition (CuAAC) reaction which yields 1,4-disubstituted 1,2,3-triazoles.[11]

Late in the past decade, a new subclass of NHCs, namely 1,2,3-triazol-5-ylidenes (F), was discovered and even isolated in their free form.[12] This new generation of N-heterocyclic carbenes (NHCs) has been termed as "mesoionic carbenes" (MICs) because no uncharged resonance forms can be generated from these systems.[13] Due to the combination of their strong donor character (higher compared to classical NHCs) and the vast synthetic flexibility of their ligand precursors via click chemistry, their use in the area of catalysis has raised a great deal of interest in both academia and industry.

The Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition reaction between alkynes and azides (CuAAC) for constructing triazole cycles, which was independently reported by Sharpless et al.[14] and Meldal et al.[15] in 2002, represents the most efficient essence of "click chemistry" proposed by Sharpless et al.[16] in 2001. This reaction has been widely applied in medicinal, bioorganic, and materials chemistry, as well as many other areas of research over the last decade [17,18]. Although the $CuSO_4$/sodium ascorbate system is still the most frequently used method, numerous efficient catalysts have been developed for improving the present reaction conditions [19]. For example, the use of ligands decreases the amount of Cu catalyst needed and enhances its catalytic activity owing to stabilization of the Cu(I) center[20-28]. Moreover, various Cu complexes, especially Cu(I) complexes bearing different ligands such as amines [20-21], N-heterocycles [22-24], phosphines, and phosphonites [29-30] and N-heterocycle carbenes (NHCs) [31] have been developed and have shown satisfactory results.

Recently, *N*-heterocyclic carbenes (NHC) is firmly occupied an important place in the ancillary ligand for homogeneous catalysis partially for substitution of the phosphine ligands.[32-35] The NHC has superior advantageous due to their high thermal stability, nontoxic chemistry, resistance to oxidation,[36,37] strong σ-donor ligands ability[38] with weak π-acceptor capability, tuneable of electronic and steric properties and easily handling process. The

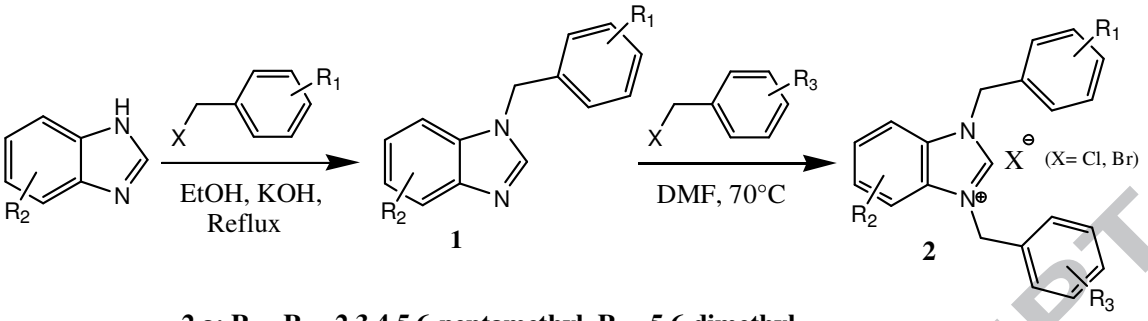
commonly used NHC ligands for transition metals are generating from imidazolium, imidazolidinium and benzimidazolium based salts in presence of strong bases. In 1993, the first NHC–Cu complex was reported by the Arduengo group[39], soon after their ground secceed isolation of a free NHC [40]. Advances in NHC–copper chemistry were then steadily reported, including better synthetic routes to well-defined complexes,[41] and theoretical studies of the NHC–Cu bond that allowed for a better understanding of NHC–metal interactions.[42] Despite these developments, the first known application in catalysis of a NHC–Cu complexes reported in 2001 by Woodward's for conjugate addition.[43] NHC-Cu complexes have been used successfully as effective catalyst in various catalytic reaction such as reduction of carbonyl compounds[44], carbonyl hydrosilylation[45], hydroboration and diboration[46-47], cross-coupling reactions[48-52], Miscellaneous reactions[53-57] and [3 + 2] Cycloaddition reaction [58-60] .

We herein report the synthesis of benzimidazolium salts **2a-c** bearing symmetrical and unsymmetrical ligands and their (NHC) Copper (I) complexes **3-4**. Further we investigate the catalytic activity of these complexes for the Huisgen cycloaddition reaction of insitu generated azides and terminal alkynes to synthesize triazoles.

2. Results and discussion

a- Synthesis and characterization of benzimidazolium salts 2a-c precursors and their (NHC) Copper (I) 3-4

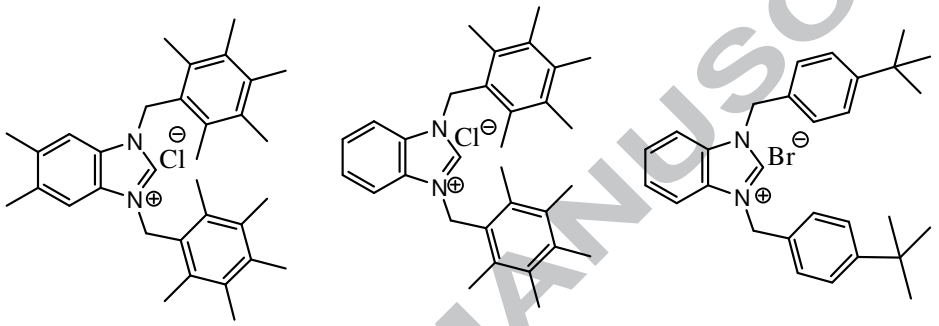
The benzimidazolium salts (**2a–c**) as NHC-precursors, which are stable against light, air and humidity both in the hard form and in the solution state, were obtained by quaternization of 5,6-dimethyl-1-(alkylbenzyl)-1H-benzo[d]imidazole **1** with various alkyl halides in DMF at 70°C for 48h (**Scheme 2**). These salts were soluble in polar solvents such as dichloromethane, ethyl alcohol and methanol but were not soluble in common slightly polar or non polar solvents like diethyl ether and hexane.



1

2

2.a: R_1= R_3= 2,3,4,5,6-pentamethyl, R_2= 5,6-dimethyl
2.b: R_1=R_3= 2,3,4,5,6-pentamethyl, R_2= H
2.c: R_1=R_3= 4-tertbutyl, R_2= H



2.a **2.b** **2.c**

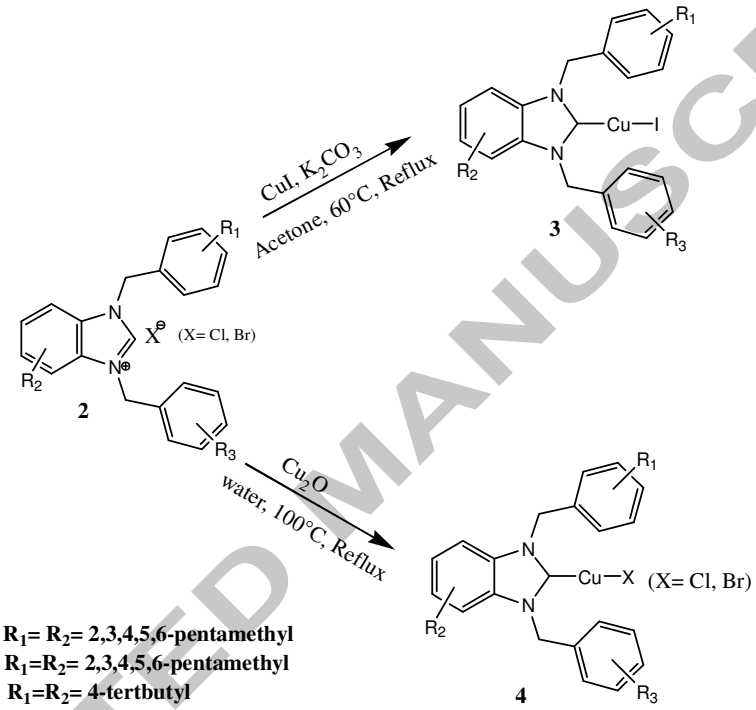
Scheme 2. The Synthesis of N,N- substituted new benzimidazolium salts **2a-c**

The structures of benzimidazolium salts **2a-c** were verified by ^{1}H NMR, ^{13}C NMR, FT_IR and elemental analyses. The ^{1}H NMR spectra of the benzimidazolium salts further supported the assigned structures; the resonances for C(2)–H were observed as sharp singlets at 9.85, 10.34, and 11.83 ppm, respectively, for **2a–c**. ^{13}C NMR chemical shifts were consistent with the proposed structures; the imino carbon are typical singlets in the ^{1}H-decoupled mode at 141.3, 143.0 and 143.1 ppm, respectively, for benzimidazolium chlorides **2a–c**. The IR data for benzimidazolium salts **2a–c** clearly indicate the presence of –C=N– with a ν(C=N) at 1440.9 1454.8 and 1427.8 cm^{-1}, respectively, for **2a–c**. The NMR and IR values are in accordance with the literature [61-62].

b. Synthesis and characterization of (NHC) Copper (I) 3-4

Metal-NHC compounds are in general prepared by treatment of either *in situ* generated NHC or isolated NHC, from the corresponding imidazolium salts using strong bases such as KOBut, NaH/KH or Na[N($SiMe_3$)$_2$], with the corresponding metal precursors[63-65]. The complexes (**3a**–**c**) were synthesized by treatment of benzimidazolium salts **2a-c** with K_2CO_3

in acetone at reflux in the presence of CuI to form the Cu-NHC complexes **3**, in good yields the reaction mixture was mixed for 24 h at 60°C under argon. Treatment of the benzimidazolium salts **2a-c** with Cu_2O in water at reflux afforded quantitatively the expected complexes **4a–c** after 24 h. Cu–NHCs **4a–c** were obtained as white solids in 63–74% yield. The Cu–carbene complexes **3-4** were generally soluble in polar solvents especially in dichloromethane and methanol. **Scheme 3**



Scheme 3. Synthesis of (NHC) Copper (I) **3-4.**

The structures of complexes **3-4** were determined by their characteristic spectroscopic data and elemental analyses. In the ^{1}H NMR spectra, in $CDCl_3$ the lack of a downfield NC*H*N signal shows the successful formation of Cu-NHC complexes **3-4**. The signal of benzylic proton (N–CH_2–Ar) belonging to Cu-NHC **3a-c** complexes was observed as a sharp singlet signal at around δ 5.39 ppm, 5.47ppm and 5.71 respectively. Further, the carbene carbon peaks of Cu-NHC **3a-c** resonates at 184.9, 186.2 and 194.2 ppm respectively. The FT-IR data clearly indicated the presence of ν(CN) at 1448.5, 1419.0 and 1476.5 cm^{-1} for the Cu-NHC complexes **3a-c** respectively. The absence of a peak in the range 8–10 ppm indicates a complete removal of C_2-H proton from the benzimidazolium salt **2a-c** by Cu_2O and the formation of NHC–Cu (I) catalysts **4a-c**. However, the resonances of aromatic, benzylic methylene and aliphatic protons of NHC–Cu (I) catalysts **4** were observed with no or

negligible changes from their respective benzimidazolium **2a-c**. The ^{13}C NMR resonances of the carbene carbons in NHC–Cu (I) catalysts **4a-c** occur in the δ range of 182.6–1861.0 ppm.

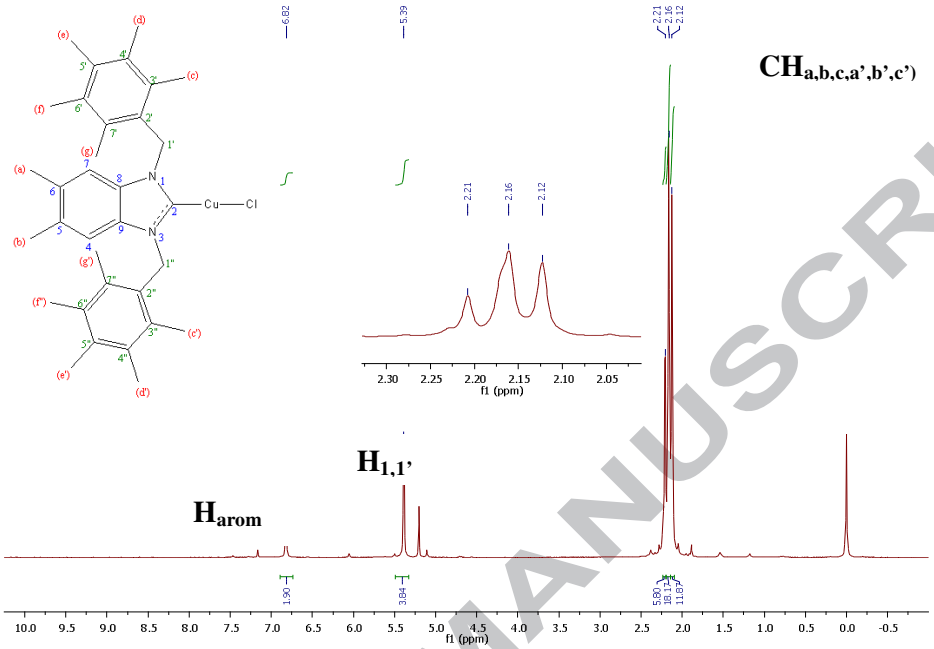


Figure 1: ^{1}HNMR spectra ($CDCl_3$, 400MHz) of (NHC) Copper (I) **4a**

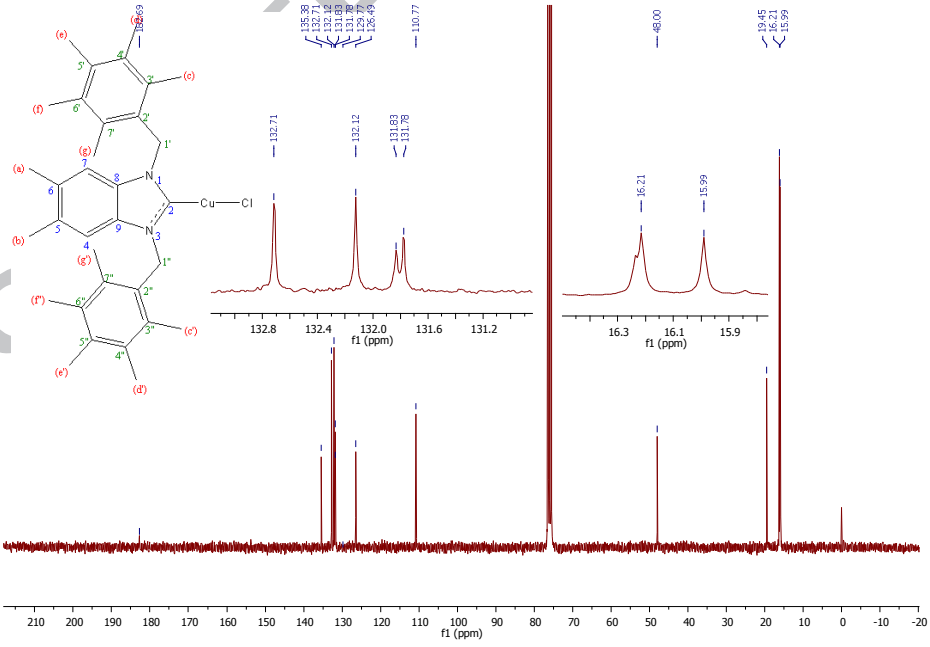
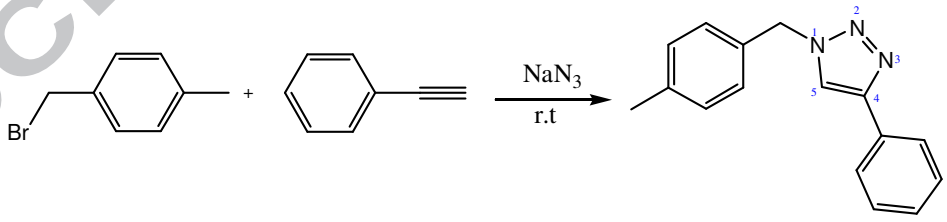


Figure 2: ^{13}C NMR spectra ($CDCl_3$, 100MHz) of (NHC) Copper (I) **4a**

The remarkable stability of the NHC–Cu (I) catalysts **3-4** toward heat, oxygen and moisture prompted us to test them in the Huisgen cycloaddition of benzyl azide and phenyl-acetylene at room temperature in water. Although organic azides are generally safe and stable toward water and oxygen, [66] those of low molecular weight can be difficult to handle.[67] Therefore, a methodology that avoids their isolation is desirable.[68]

The catalytic potential of the complex **3a** was explored in a cycloaddition reaction of an 4-methylbenzyl bromide (1 mmol) and phenylacetylene (1.05 mmol) with NaN_3 (1.05 mmol) at room temperature to form 1,2,3-triazole (**Scheme 4**). Initially, 4-methylbenzyl bromide and phenylacetylene were chosen as a model reactant to optimize the reaction conditions.When the reaction was carried out with 5 mol% catalyst loading **3a** (Table 1, entries 1,2) under room temperature, product is isolated in 100% yield after 24h and 2h respectively. It was observed that the reaction was completed in 2 h using 3 mol % of complex **3a** as a catalyst in water under atmospheric conditions at room temperature. In order to compare the efficacity of complex **3a** with others simple complexes of Copper such us CuCl, CuBr and CuI we have running the following reactions. Using 3 mol% of the copper catalysts CuCl or CuBr or CuI, virtually no conversion of the starting materials was observed in water after 2h. **Table 1** (entries 5,6) when we used CuCl as catalyst, under the same conditions complex CuI afford the triazole with a 27% yiled **(Table 1,** entry 7**)** . Satisfyingly, conversion of benzyl chloride into triazole was obtained on water **(Table 1,** entry 1). However, reactions of 4-methoxy benzylchloride in water were not reproducible to afford the corresponding triazole. Similar results were observed for 4-chlorobenzyl chloride, 4-methoxybenzyl chloride, 4-isopropylbenzyl chloride, 9-chloromethyl anthracene, chloromethyl ethyl ether, bromomethyl cyclohexane and pentaerythritol tetrabromide.



Scheme 4: Cycloaddition reaction of 4-methylbenzyl bromide and phenylacetylene with NaN_3 at room temperature.

Table 1: Synthesis of triazole by using 4-methylbenzyl bromide and phenylacetylene with NaN_3 at room temperature

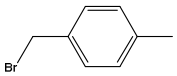
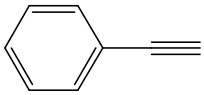
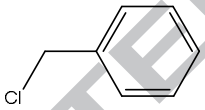
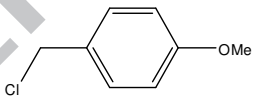
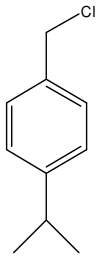
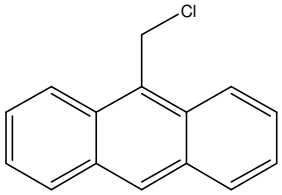
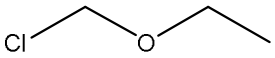
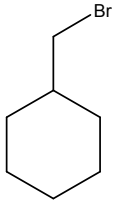
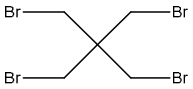
Entry	Benzylbromide	Catalyst	Alkyne	Time	Yield
1		3.a (5 mol %)		24 h	100%
2		3.a (5 mol%)		2h	100%
3		3.a (3 mol%)		24h	100%
4		3.a (3 mol%)		2h	100%
5		CuCl (3 mol%)		2h	No Reaction
6		CuCl (3 mol%)		2h	No Reaction
7		CuI (3 mol %)		2h	27%

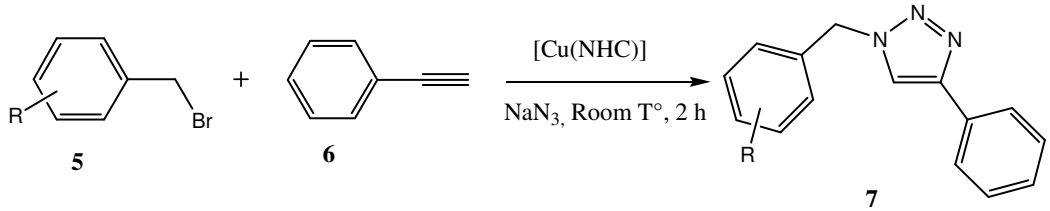
Table 2: Synthesis of triazoles by using differents substrates under the optimum conditions

Entry	Benzylbromide	Catalyst	Alkyne	Time	Yield
1		3.a		2h	32%
2		3.a		2h	No Reaction
3		3.a		2h	No reaction
4					

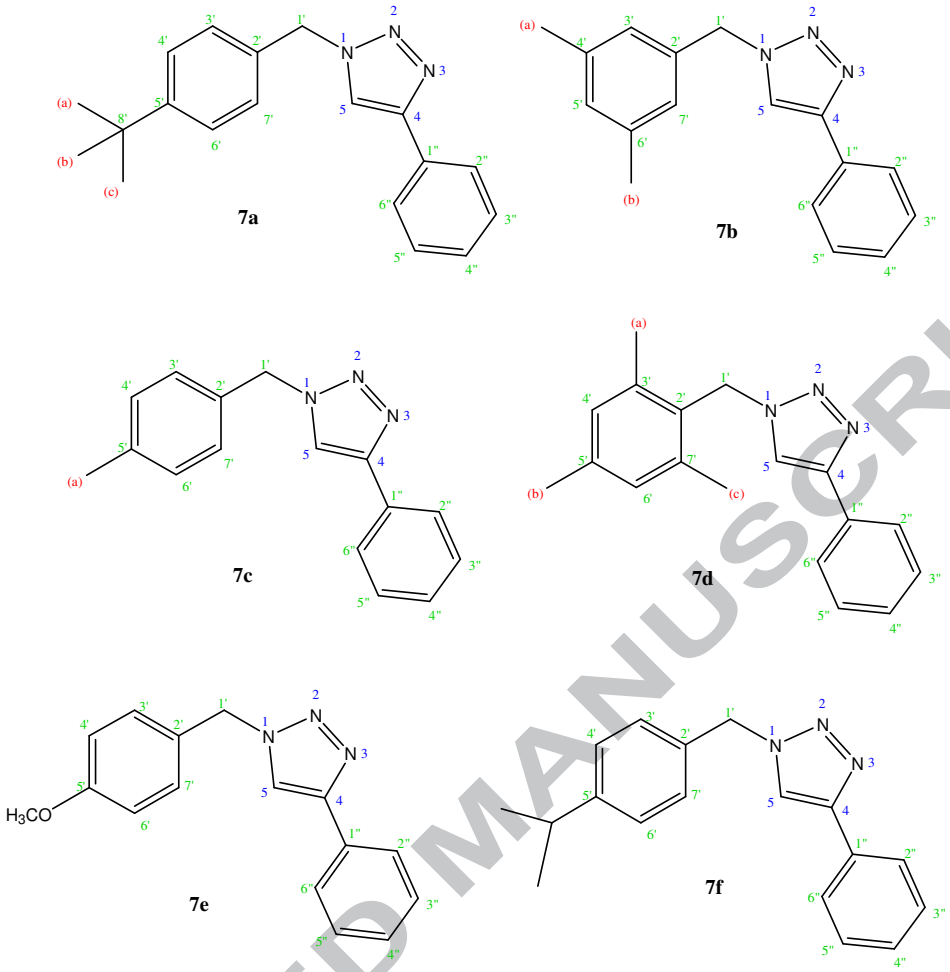
		3.a		2h	No reaction
5		3.a		2h	No raction
6		3.a		2h	No reaction
7		3.a		2h	No reaction

Reaction conditions:[Cu] (3 mol %.), benzylbromide (1 mmol.), sodium azide (1,05 mmol.), phenylacetylen (1,05 mmol) water (1 ml), Room T°, conversion of the triazole was determined by GC

Therefore different substituted benzylbromide bearing electron-donating and one alkyne were used were to synthesize different triazoles. It was found that electron donating groups at para position in benzylbromide could be efficiently converted to the desirable 1.4 triazoles **7** with various NHC copper (I) **3-4** as catalysts at room temperature (**Table 3**, entries 1-6, entries 13-18). On the other hand, between phenylacetylene and respectively 3.5 dimethyl benzylbromide and 2.4.6- trimethyl benzylbromide the later gave better yield (**Table 3**, entries 7-12, entries 19-24) (**Scheme 5**).

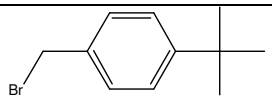
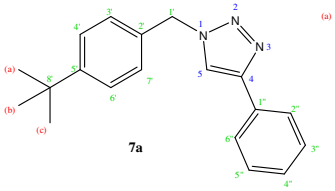


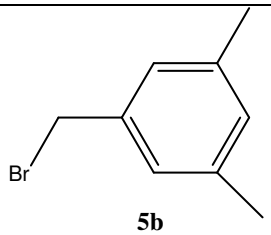
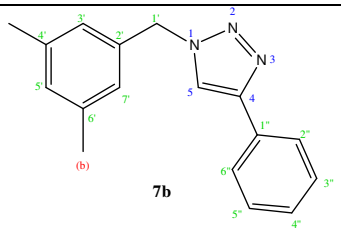
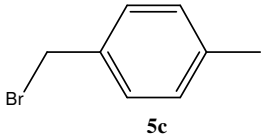
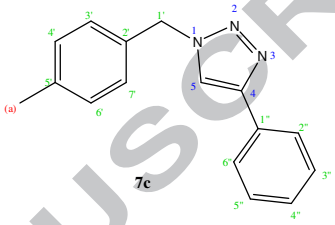
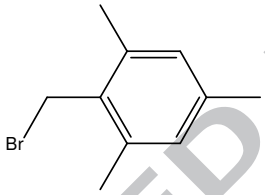
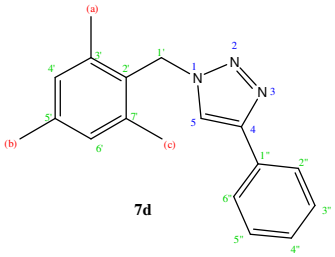
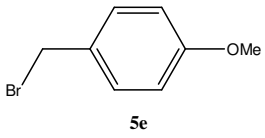
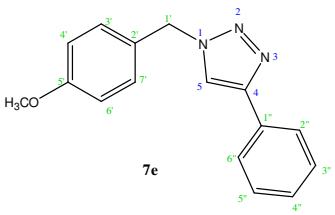
5 **6** **7**

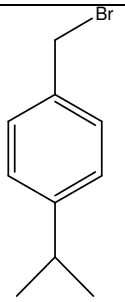
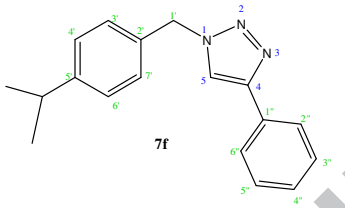


Scheme 5: NHC copper (I) **3-4** catalyzed formation of triazoles **7**

Table 3. NHC copper (I) catalyzed click reaction[a]

Entry	Substrat	Catalyst (Cu-NHC)	Triazole	Yield[b]
1	 **5a**	3a	 **7a**	90%
2		3b		54%
3		3c		94%
4		4a		81%
5		4b		85%
6		4c		64%
7		3a		96%

8	 **5b**	3b	 **7b**	89%
9		3c		59%
10		4a		94%
11		4b		94%
12		4c		76%
13	 **5c**	3a	 **7c**	100%
14		3b		93%
15		3c		88%
16		4a		92%
17		4b		100%
18		4c		95%
19	 **5d**	3a	 **7d**	84%
20		3b		100%
21		3c		99%
22		4a		87%
23		4b		45%
24		4c		100%
25	 **5e**	3a	 **7e**	85%
26		3b		98%
27		3c		97%
28		4a		88%
29		4b		60%
30		4c		100%

31	 **5f**	3a	 **7f**	88%
32		3b		98%
33		3c		95%
34		4a		85%
35		4b		75%
36		4c		100%

[a] [Cu] (3 mol %.), benzylbromide (1 mmol.), sodium azide (1,05mmol.), phenylacetylen (1,05 mmol) water (1 ml), rt. [b] Conversion of the triazole was determined by GC.

The structures of the prepared compounds **7** were confirmed by ^{1}H and ^{13}C-NMR spectroscopic methods, and IR spectra. A singlet observed in the ^{1} HNMR spectrum at δ = 8.10–8.13 ppm confirmed the presence of the triazolyl hydrogen, supported by the signals in the ^{13}CNMR spectrum at δ = 129.34ppm. The signals for the quaternary carbon C_4 of the triazole ring appeared at δ =137.82 ppm in the ^{13}C-NMR spectrum. These chemical shift values are consistent with those reported for 1,4-disubstituted 1,2,3-triazoles [69-72].

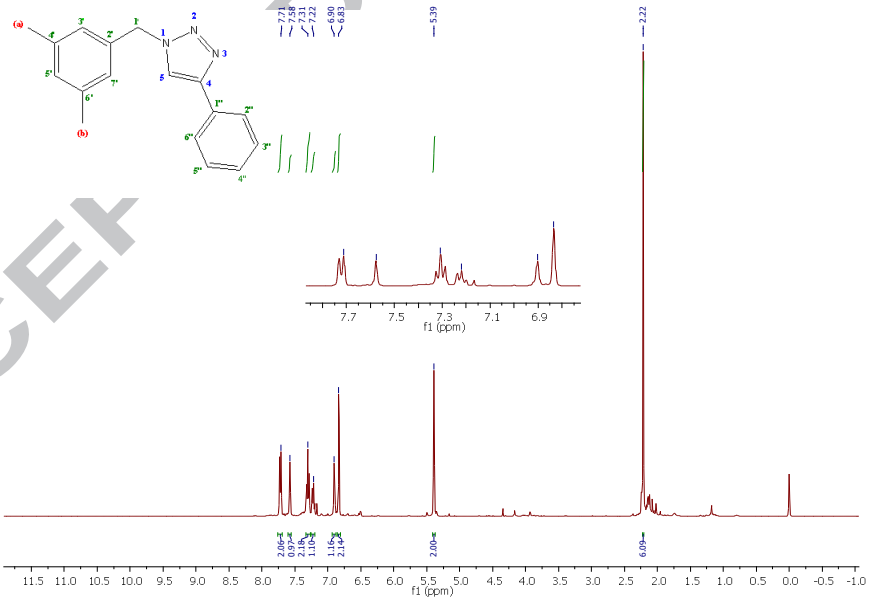


Figure 3: ^{1}HNMR spectra ($CDCl_3$, 400MHz) of (NHC) Copper (I) **7b**

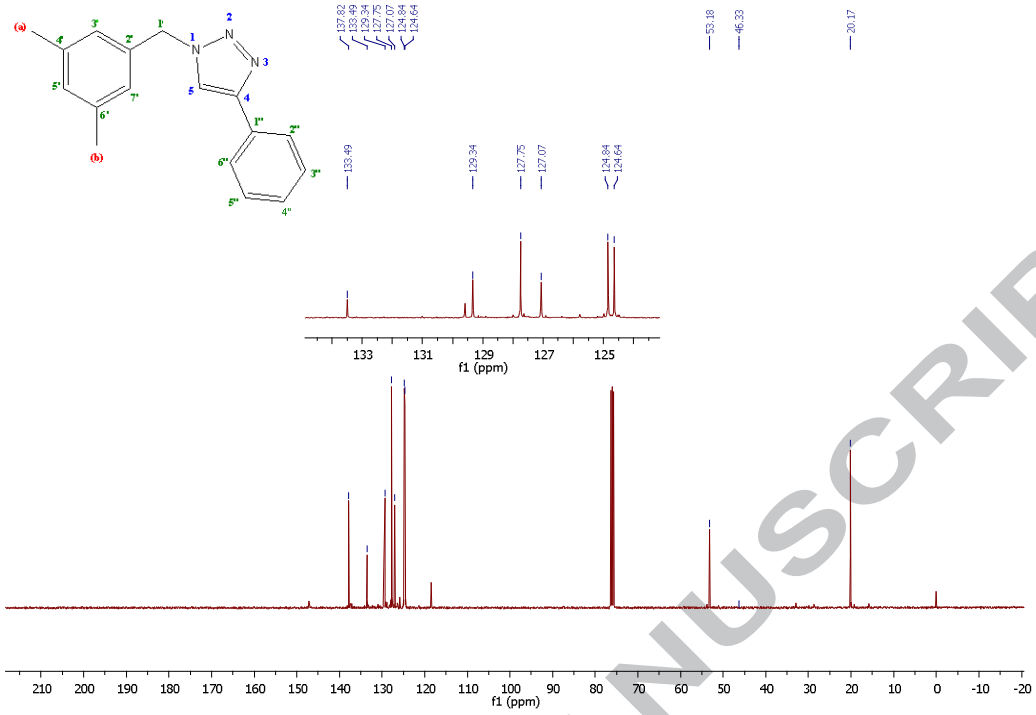
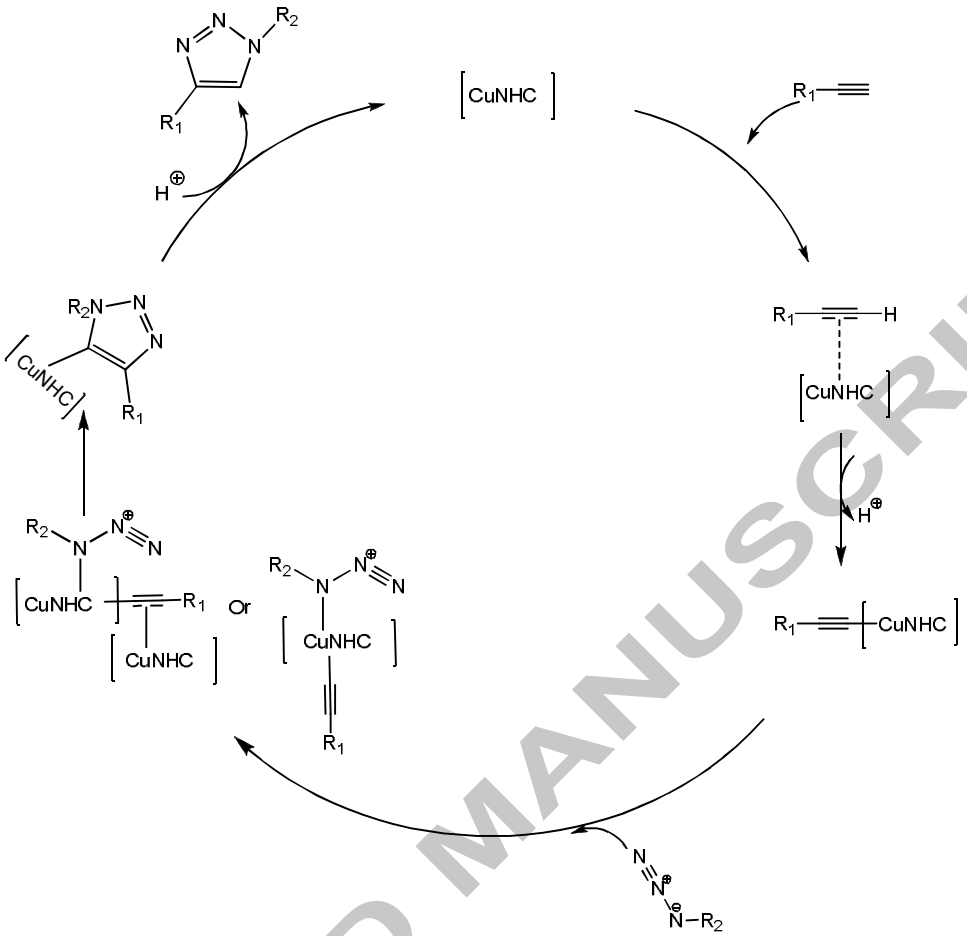


Figure 4: ^{13}C NMR spectra ($CDCl_3$, 100MHz) of (NHC) Copper (I) **7b**

A plausible mechanism for Cu(I)-catalyzed synthesis of 1,4- triazoles cycloaddition is proposed in **Scheme 6**. In a first stage, the starting alkyne would react with the copper(I) species to form an acetylide–copper complex that would interact with the azide activating it toward nucleophilic attack of the acetylide carbon to the 'external' nitrogen atom of the azide and generating a metallacycle. Subsequent ring contraction would generate a copper-triazolide, direct precursor of the reaction product upon protonation. The last step of the catalytic cycle is the exclusion of the Cu(I) through reductive elimination, to give the desired 1,4-disubstituted triazoles.



Scheme 6: Proposed mechanism cycle of the CuAAC

Conclusions

In conclusion air and water stable benzimidazolium salts (**2a–c**) were synthesized and characterized by ^{1}H NMR, ^{13}C NMR, HRMS, FT-IR and elemental analyses. We have developed a versatile and highly efficient catalytic system for the Huisgen cycloaddition. In situ generated azides transformed 1,2,3-triazoles in water at room temperature conditions in extremely short reaction times by Cu-NHC complexes with lower loading than literature. NHC–Cu (I) catalysts **3** showed high catalytic activities tha NHC–Cu (I) catalysts **4**

The unprecedented use of an internal alkyne in this copper-catalyzed transformation has also been described. Further synthetic applications and mechanistic studies addressing the role of the NHC ligand in this transformation are currently ongoing in our laboratories.

Experimental Section

Materials and methods

All procedures were carried out under an inert atmosphere using standard schlenk line techniques. Chemicals and solvents were purchased from Sigma-Aldrich. All solvents were purified and dried by MBraun SPS 800 solvent purification system. ^{1}H NMR and ^{13}C NMR was recorded respectively at 300 and 400 MHz for (^{1}H) and 75 and 101 MHz for (^{13}C) in $CDCl_3$and DMSO-d_6 with TMS as an internal reference. Signals are quoted in parts per million as δ downfield from TMS (δ 0.00) as an internal standard. FT-IR spectra were recorded on a Mattson 1000 spectrophotometer, wavenumbers in cm^{-1}.

Synthesis of ligands (1a-c)

A standard schlenk was charged with 5,6-dimethylbenzimidazole (4.38 g, 30 mmol,), potassium hydroxide (1.68g, 30 mmol) and EtOH (30ml) and stirred at room temperature for 1h. after this time the corresponding aryl bromide or chloride (30 mmol) was added slowly and the resulting mixture was refluxed at 80°C for 2-3 days. After reaction finished, the reaction mixture was allowed to cool down to room temperature then the solvent was removed under reduced pressure. The white solid obtained was washed with DCM (20-30ml) and filtred through filter paper. The CH_2Cl_2 was removed under reduced pressure and the crude product was dried under vaccum.

5,6-dimethyl-1-(2,3,4,5,6-pentamethylbenzyl)-1H-benzo[d]imidazole 1.a

This NHC precursor was synthesized according to published procedure and found NMR data shown below.[62]

m.p. 173°C. Yield (97%). $\nu_{(CN)}$= 1448.65 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ (ppm) 2.11(s, 6H, $CH_{3(c,g)}$), 2.19(s, 6H, $CH_{3(d,f)}$), 2.23(s, 3H, $CH_{3(e)}$), 2.32(s, 3H, $CH_{3(a)}$), 2.37(s, 3H, $CH_{3(b)}$), 5.16(s, 2H, $CH_{2(1')}$), 7.20(s, 1H, $H_{arom(7)}$), 7.24(s, 1H, $H_{arom(4)}$), 7.30(s, 1H, H_2).^{13}C NMR($CDCl_3$, 101MHz)δ (ppm) 16.51($C_{(c,g)}$), 16.87($C_{(d,f)}$), 17.16($C_{(e)}$), 20.33($C_{(a)}$), 20.66($C_{(b)}$), 44.27($C_{1'}$), 109.77(C_7), 120.29(C_4), 127.37($C_{5,8}$), 131.21($C_{4',5',6'}$), 131.97(C_6), 133.38($C_{3',7'}$), 133.56(C_9), 136.13($C_{2'}$), 141.10(C_2).

1-(2,3,4,5,6-pentamethylbenzyl)-1H-benzo[d]imidazole 1.b

This NHC precursor was synthesized according to published procedure and found NMR data shown below.[62]

m.p. 121°C. Yield (95%). $\nu_{(CN)}$= 1454.34 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ (ppm) 2.21(s, 6H, $CH_{3(a,e)}$), 2.27(s, 6H, $CH_{3(b,d)}$), 2.31(s, 3H, $CH_{3(c)}$), 5.31(s, 2H, $CH_{2(1')}$), 7.35(t, 2H, $H_{arom(5,6)}$), 7.43(s, 1H, $H_{arom(7)}$), 7.56(s, 1H, $H_{arom(4)}$), 7.85(s, 1H, H_2).^{13}C NMR($CDCl_3$,

100MHz)δ (ppm) 16.55($C_{(a,e)}$), 16.89($C_{(b,d)}$), 17.19($C_{(c)}$), 44.42($C_{1'}$), 109.77(C_7), 120.29(C_4), 122.37(C_5), 122.87(C_6), 127.12($C_{8,9}$), 133.47($C_{4',5',6'}$), 133.55($C_{3',7'}$), 136.28($C_{2'}$), 141.96(C_2).

1-(4-(tert-butyl)benzyl)-1H-benzo[d]imidazole 1.c

This NHC precursor was synthesized according to published procedure and found NMR data shown below.[63]

m.p. 123.6°C. Yield (92%). $\nu_{(CN)}$= 1457.59 cm^{-1}. ^1H NMR ($CDCl_3$, 400MHz) δ (ppm) 1.22(s, 9H, $CH_{3(a,b,c)}$), 5.25(s, 2H, $CH_{2(1')}$), 7.06(d, 2H, $H_{arom(3',7')}$), 7.20(d, 1H, $H_{arom(5,6)}$), 7.29(d, 1H, $H_{arom(4',6',7)}$), 7.77(s, 1H, $H_{arom(4)}$), 7.88(s, 1H, H_2).^{13}C NMR($CDCl_3$, 100MHz)δ (ppm) 31.28($C_{(a,b,c)}$), 34.60($C_{8'}$), 48.53($C_{1'}$), 110.08(C_7), 120.39(C_4), 122.25(C_5), 123.06(C_6), 125.97($C_{4',6'}$), 126.92($C_{3',7'}$), 132.46($C_{2',8}$), 143.20($C_{2,9}$), 151.40($C_{5'}$).

Synthesis of ligands (2a-c)

A mixture of benzimidazolium salt (1a-1c) (1 g) and the corresponding benzyl bromide or chloride (1eq) in DMF (2 ml) was stirred at 70°C for 2-3 days. After that time, the white solid formed was washed with diethyl ether (20 ml) and stirred for couple hours. Then the reaction mixture was filtred through filter paper and the white solid was dried under vaccum then crystallized with DCM-ether (1:3) for further purification.

5,6-dimethyl-1,3-bis(2,3,4,5,6-pentamethylbenzyl)-1H-benzo[d]imidazol-3-ium chloride 2a

This NHC precursor was synthesized according to published procedure and found NMR data shown below.[62]

m.p. 307.7°C. Yield (96%). $\nu_{(CN)}$= 1440.99 cm^{-1}. ^1H NMR ($CDCl_3$, 400MHz) δ (ppm) 2.22(s, 30H, CH_3), 2.28(s, 6H, $CH_{3(a,b)}$), 5.8(s, 4H, $CH_{2(1',1'')}$), 7.11(s, 2H, $H_{arom(4,7)}$),9.85(s, 1H, H_2). ^{13}CNMR($CDCl_3$, 101MHz) δ (ppm) 17.01(CH_3), 16.92($C_{(c,g,c',g')}$), 17.01 ($C_{(d,f,d',f')}$), 17.28($C_{(e,e')}$), 20.77($C_{(a,b)}$), 48.10($C_{1';1''}$), 113.41($C_{4;7}$), 125.58($C_{8;9}$), 130.42($C_{4';5';6';4'';5'';6''}$), 133.50($C_{3';7';3'';7''}$), 133.74($C_{5;6}$), 136.88($C_{2';2''}$),141.35(C_2).

1,3-bis(2,3,4,5,6-pentamethylbenzyl)-1H-benzo[d]imidazol-3-ium chloride 2b

This NHC precursor was synthesized according to published procedure and found NMR data shown below.[62]

m.p. 210.6°C. Yield (92%). $\nu_{(CN)}$= 1454.84 cm^{-1}. ^1H NMR ($CDCl_3$, 400MHz) δ (ppm) 2.15(s, 12H, $CH_{3(a,e,a',e')}$), 2.18(s, 12H, $CH_{3(b,d,b',d')}$), 2.20(s, 6H, $CH_{3(c,c')}$), 5.84(s, 4H, CH_2), 7.2(d, 2H, $Harom_{(5,6)}$), 7.34(d, 2H, $Harom_{(4,7)}$), 10.34(s, 1H, H_2). ^{13}C NMR($CDCl_3$,100MHz) δ

(ppm) 16.95($C_{a,e,a',e'}$), 17.06($C_{b,d,b',d'}$), 17.30($C_{c,c'}$), 48.58($C_{1';1''}$), 113.72($C_{4;7}$), 125.36($C_{5;6}$), 126.88($C_{8;9}$),131.85($C_{5';5''}$),133.49($C_{4';6';4'';6''}$), 133.82($C_{3';7';3'';7''}$), 137.07($C_{2';2''}$), 143(C_2).

1,3-bis(4-(tert-butyl)benzyl)-1H-benzo[d]imidazol-3-ium bromide 2c

This NHC precursor was synthesized according to published procedure and found NMR data shown below.[63]

m.p. 296.5°C. Yield (89%). $\nu_{(CN)}$= 1427.88 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ (ppm) 1.2 (s, 18H, CH_3), 5.75(s, 4H, CH_2), 7.33(d, 4H, $H_{arom(4',6',4'',6'')}$),7.39(d, 4H, $H_{arom(3';7'3'',7'')}$), 7.46(d, 2H, $Harom_{(5;6)}$), 7.55(d, 2H, $Harom_{(4;7)}$), 11.83(s, 1H, H_2).^{13}CNMR($CDCl_3$,101 MHz) δ (ppm) 31.18(CH_3), 34.67($C_{8';8''}$), 51.27($C_{1';1''}$), 113.78($C_{4;7}$), 126.34($C_{4';6';4'';6''}$), 127.09($C_{5,6}$), 128.17($C_{3';7';3'';7''}$), 129.56($C_{8;9}$),131.41($C_{2';2''}$), 143(C_2),152.46($C_{5';5''}$).

Synthesis of [(NHC)CuI] (3a-c)

A standard schlenk was charged with ligand (1mmol), CuI (1 mmol) and K_2CO_3 (2 mmol). The resulting mixture was refluxed in acetone under Argon at 60°C for 24h. After this time, the mixture was filtered through silica. The pad of silica was concentrated with rotary evaporator and dried under vacuum.

(5,6-dimethyl-1,3-bis(2,3,4,5,6-pentamethylbenzyl)-2,3-dihydro-1H-benzo[d]imidazol-2-yl)copper(II) iodide 3a

m.p. 265.6°C.Yield (68%). $\nu_{(CN)}$= 1448.51 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ (ppm) 2.12(s, 12H, $CH_{3(c,g,c',g')}$), 2.16(s, 12H, $CH_{3(d,f,d'',f')}$), 2.19(s, 6H, $CH_{3(e,e')}$), 2.21(s, 6H, $CH_{3(a,b)}$), 5.39 (s, 4H, $CH_{2(1',1'')}$), 6.86(s, 2H, $H_{arom(4,7)}$). ^{13}C NMR ($CDCl_3$, 100MHz) δ (ppm) 16.10($C_{(c,g,c',g')}$), 16.25($C_{(d,f,d',f')}$), 16.36($C_{(e,e')}$),19.46($C_{(a,b)}$), 47.8($C_{1';1''}$), 110.85($C_{4;7}$), 126.35($C_{8;9}$), 131.79($C_{4';6';4'';6''}$), 131.9 ($C_{5';5''}$), 132.09($C_{5;6}$),132.91($C_{3';7';3'';7''}$), 135.67($C_{2';2''}$), 184.99(C_2). Anal. Calc. for $C_{33}H_{42}N_2ICu$ (%): C, 60.31; H, 6.44; N, 4.26. Found (%): C, 60.39; H, 6.52; N, 4.34. HR-MS(ESI), m/z=529,2614 $[M-I]^+$ (calcd for $C_{33}H_{42}N_2Cu$:529,2644).

(1,3-bis(2,3,4,5,6-pentamethylbenzyl)-2,3-dihydro-1H-benzo[d]imidazol-2-yl)copper(II) iodide 3b

m.p. 245.3°C. Yield (72%). $\nu_{(CN)}$= 1419.02 cm^{-1}.^{1}H NMR ($CDCl_3$, 400MHz) δ (ppm) 2.13(s, 12H, $CH_{3(a,e,a',e')}$), 2.17(s, 12H, $CH_{3(b,d,b',d')}$), 2.22(s, 6H, $CH_{3(c,c')}$), 5.47 (s, 4H, CH_2), 7.08(d, 2H, $Harom_{(5;6)}$), 7.15(d, 2H, $Harom_{(4;7)}$). ^{13}CNMR ($CDCl_3$, 100MHz) δ (ppm)

156.11($C_{(a,e,a',e')}$), 16.26 ($C_{(b,d,b',d')}$), 16.38 ($C_{(c,c')}$), 48.13 ($C_{1';1''}$), 110.61($C_{4;7}$), 122.76($C_{5;6}$), 126.13($C_{5';5''}$), 132.08($C_{4';6';4'';6''}$), 132.98($C_{3';7';3'';7''}$), 133.22($C_{8;9}$), 135.79($C_{2';2''}$), 186.25(C_2). Anal. Calc. for $C_{31}H_{38}N_2ICu$ (%): C, 59.19; H, 6.09; N, 4.45. Found (%): C, 59.25; H, 6.17; N, 4.56.HR-MS(ESI), m/z=501,2398 $[M-I]^+$ (calcd for $C_{31}H_{38}N_2Cu$:501,2331).

(1,3-bis(4-(tert-butyl)benzyl)-2,3-dihydro-1H-benzo[d]imidazol-2-yl)copper(II) iodide 3c

m.p. 208.1°C. Yield (66%). $\nu_{(CN)}$= 1476.56 cm^{-1}. ^1H NMR (DMSO_d6, 400MHz) δ (ppm) 1.20(s, 18H, CH_3), 5.71(s, 4H, CH_2), 7.28(s, 6H, $H_{arom(4',6',4'',6'',5,6)}$), 7.39(d, 4H, $H_{arom(3',7',3'',7'')}$), 7.28(d, 2H, $H_{arom(4,7)}$),^{13}C NMR (DMSO_d6, 101MHz) δ(ppm) 36.23(CH_3), 39.43($C_{8';8''}$), 55.85($C_{1';1''}$), 117.18($C_{4;7}$), 128.74($C_{5;6}$), 130.57($C_{4';6';4'';6''}$), 132.52($C_{3';7';3'';7''}$), 138.63($C_{8;9}$), 138.71($C_{2';2''}$), 155.47($C_{5';5''}$), 194.20(C_2). Anal. Calc. for $C_{29}H_{34}N_2ICu$ (%): C, 57.95; H, 5.70; N, 4.66. Found (%): C, 58.03; H, 5.76; N, 4.74. HR-MS(ESI), m/z=473,2044 $[M-I]^+$ (calcd for $C_{29}H_{34}N_2Cu$:473,2018).

Synthesis of [(NHC)CuX] (4a-c)

A 50 ml bottom flask was charged with ligand (2 mmol), Cu_2O (1.3 mmol) and deionized water (6 ml). The mixture was refluxed for 24h with vigorous stirring. After this time period, the reaction mixture was allowed to cool down to room temperature. The reaction mixture was diluted with CH_2Cl_2 and the organic fraction was extracted. The organic extract was dried with $MgSO_4$ and concentrated with rotary evaporator. The crude product was dissolved in a minimal amount of CH_2Cl_2 and was eluted with CH_2Cl_2 over a silica plug to afford the desired product as an off-white solid.

(5,6-dimethyl-1,3-bis(2,3,4,5,6-pentamethylbenzyl)-2,3-dihydro-1H-benzo[d]imidazol-2-yl)copper(II) chloride 4a

m.p. 265.6°C. Yield (70%). $\nu_{(CN)}$= 1447.07 cm^{-1}. ^1H NMR ($CDCl_3$, 300MHz) δ (ppm) 2.12(s, 12H, $CH_{3(c,g,c',g')}$), 2.16(s, 18H, $CH_{3(d,e,f,d',e',f')}$), 2.21(s, 30H, $CH_{3(a,b)}$), 5.39 (s, 4H, CH_2), 6.82 (s, 1H, $H_{arom(4,7)}$).^{13}CNMR ($CDCl_3$,75MHz) δ (ppm) 15.99($C_{(c,g,c',g')}$), 16.21($C_{(d,e,f,d',e',f')}$), 19.45($C_{(a,b)}$), 48($C_{1';1''}$), 110.77($C_{4;7}$), 126.49($C_{8;9}$), 131.78($C_{4';6';4'';6''}$), 131.83($C_{5';5''}$), 132.13($C_{5;6}$),132.71($C_{3';7';3'';7''}$), 135.38($C_{2';2''}$), 182.69(C_2). Anal. Calc. for $C_{33}H_{42}N_2ClCu$ (%):

C, 70.06; H, 7.48; N, 4.95. Found (%): C, 70.15; H, 7.59; N, 5.05. HR-MS(ESI), m/z=529,2619 $[M-Cl]^+$ (calcd for $C_{33}H_{42}N_2Cu$:529,2644).

(1,3-bis(2,3,4,5,6-pentamethylbenzyl)-2,3-dihydro-1H-benzo[d]imidazol-2-yl)copper(II) chloride 4b

M.P= 238.8°C. Yield (74%). $\nu_{(CN)}$= 1435.31 cm^{-1}.^{1}H NMR ($CDCl_3$, 300MHz) δ (ppm) 2.22(s, 12H, $CH_{3(a,e,a',e')}$), 2.25(s, 12H, $CH_{3(b,d,b',d')}$), 2.30(s, 6H, $CH_{3(c,c')}$), 5.48 (s, 4H, CH_2), 7.04(d, 4H, $H_{arom(5,6)}$), 7.10(d, 4H, $H_{arom(4,7)}$). ^{13}CNMR ($CDCl_3$,75MHz) δ(ppm) 17.05($C_{(a,e,a',e')}$), 17.26 ($C_{(b,c,d,b',c',d')}$), 49.37($C_{1';1"}$), 111.57($C_{4;7}$), 123.72($C_{5;6}$), 127.26($C_{5';5"}$), 133.13($C_{4';6';4";6"}$), 133.84($C_{8;9}$), 134.28($C_{3';7';3";7"}$), 136.58($C_{2';2"}$), 186.03(C_2). Anal. Calc. for $C_{31}H_{38}N_2ClCu$ (%): C, 69.25; H, 7.12; N, 5.21. Found (%): C, 69.37; H, 7.19; N, 5.34. HR-MS(ESI), m/z=501,2391 $[M-Cl]^+$ (calcd for $C_{31}H_{38}N_2Cu$:501,2331).

(1,3-bis(4-(tert-butyl)benzyl)-2,3-dihydro-1H-benzo[d]imidazol-2-yl)copper(II) bromide 4c

M.P= 208.1°C. Yield (63%). $\nu_{(CN)}$= 1479.23 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300MHz) δ (ppm) 1.21(s, 18H, CH_3), 5.55(s, 4H, CH_2), 7.19-7.34(m, 12H, Harom). ^{13}CNMR ($CDCl_3$,75MHz) δ (ppm) 30.23(CH_3), 33.56($C_{8';8"}$), 51.58($C_{1';1"}$), 110.96($C_{4;7}$), 123.00($C_{5;6}$), 124.96($C_{4';6';4";6"}$), 126.27($C_{3';7';3";7"}$), 130.99($C_{8;9}$), 132.79($C_{2';2"}$) 150.49(C_2),184.60($C_{5';5"}$). Anal. Calc. for $C_{29}H_{34}N_2BrCu$ (%): C, 62.87; H, 6.19; N, 5.06. Found (%): C, 62.96; H, 6.26; N, 5.16. HR-MS(ESI), m/z=473,2043 $[M-Cl]^+$ (calcd for $C_{29}H_{34}N_2Cu$:473,2018).

Synthesis of Triazoles 7a-f

A vial was charged with benzimidazolium salt (1 mmol), sodium azide (1.05 mmol), alkyne (1.05 mmol), [Cu(NHC)] (3 mol%) and water (1 ml). The reaction was stirred vigorously at room temperature for 2h. After this time, EtOAc was added and the organic fraction was extracted. The organic extract was dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the expected triazoles.

1-(4-(tert-butyl)benzyl)-4-phenyl-1H-1,2,3-triazole 7a

m.p. 162.8°C. Yield (68%). $\nu_{(C=CH)}$= 2957.93 cm^{-1}, $\nu_{(C(aryl)-N)}$= 1104.93 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ (ppm) 1.22 (s, 9H, CH_3), 5.43 (s, 2H, CH_2), 7.16(d, 2H, $H_{arom(3';7')}$), 7.22(d, 2H, $H_{arom(4';6')}$), 7.31(t, 4H, $H_{arom(3";4";5")}$), 7.58(s, 1H, H_5), 7.72(d, 2H, $H_{arom(2";6")}$). ^{13}C NMR

($CDCl_3$, 101MHz) δ (ppm) 30.22(CH_3), 33.6($C_{8'}$), 52.88($C_{1'}$), 124.65($C_{4';6'}$), 125.02($C_{3';7'}$), 126.85($C_{2";6"}$), 127.07($C_{4"}$), 127.74($C_{3";5"}$), 129.55($C_{1",5}$), 130.62($C_{2'}$), 150.85 ($C_{4,5'}$).

1-(3,5-dimethylbenzyl)-4-phenyl-1H-1,2,3-triazole 7b

m.p. 121.4°C. Yield (76%). $\nu_{(C=CH)}$= 2915.89 cm^{-1},$\nu_{(C(aryl)-N)}$= 1024.62 cm^{-1}. ^1H NMR ($CDCl_3$, 400MHz) δ (ppm) 2.22(s, 6H, CH_3), 5.39(s, 2H, CH_2), 6.83(s, 2H, $H_{arom(3';7')}$), 6.9(s, 2H, $H_{arom(5')}$), 7.22(t, 1H, $H_{arom(4")}$),7.31(t, 3H, $H_{arom(3";5")}$), 7.58(s, 1H, H_5), 7.73(d, 2H, $Harom_{(2";6")}$). ^{13}C NMR ($CDCl_3$, 100MHz) δ (ppm) 20.17 (CH_3), 53.18 ($C_{1'}$), 124.64($C_{2";6"}$), 124.84($C_{3';5';7'}$), 127.07($C_{4"}$), 127.75($C_{3";5"}$), 129.34($C_{1",5}$), 133.49($C_{2';4';6'}$), 137.82(C_4).

1-(4-methylbenzyl)-4-phenyl-1H-1,2,3-triazole 7c

m.p. 108.9°C. Yield (80%). $\nu_{(C=CH)}$= 2970.38 cm^{-1}, $\nu_{(C(aryl)-N)}$= 1075.44 cm^{-1}.^1H NMR ($CDCl_3$, 400MHz) δ (ppm) 2.29 (s, 3H, CH_3), 5.46(s, 2H, CH_2), 7.13(s, 4H, $H_{arom(3',4',6',7')}$), 7.19(s, 1H, H_5), 7.24(t, 1H, $H_{arom(4")}$),7..39(t, 3H, $H_{arom(3";5")}$), 7.74(s, 2H, $H_{arom(2",6")}$). ^{13}C NMR ($CDCl_3$, 100MHz) δ(ppm) 20.14(CH_3), 53.12($C_{1'}$), 124.62($C_{3';7';2";6"}$), 127.10($C_{4"}$), 127.13($C_{3";5"}$), 127.77($C_{4';6'}$), 128.79($C_{1",5}$), 130.60($C_{2'}$), 137.74($C_{4,5'}$).

4-phenyl-1-(2,4,6-trimethylbenzyl)-1H-1,2,3-triazole 7d

m.p. 145.7°C. Yield (72%). $\nu_{(C=CH)}$= 2971.28 cm^{-1}, $\nu_{(C(aryl)-N)}$= 1044.88 cm^{-1}.^1H NMR ($CDCl_3$, 400MHz) δ (ppm) 2.24(s, 6H, CH_3), 5.52(s, 2H, CH_2), 6.87(s, 2H, $H_{arom(4';6')}$), 7.20(t, 2H, $H_{arom(5')}$), 7.25(s, 1H, H_5), 7.25(t, 3H, $H_{arom(3";5")}$), 7.67(d, 2H, $H_{arom(2";6")}$). ^{13}C NMR ($CDCl_3$, 100MHz) δ(ppm) 18.65($CH_{3(a,c)}$), 20.01($CH_{3(b)}$), 47.27($C_{1'}$), 117.52($C_{2";6"}$), 124.59($C_{4';6'}$), 126.99($C_{4"}$), 127.70($C_{3";5"}$), 128.68($C_{1",5}$), 129.61($C_{5'}$), 136.86 ($C_{3';7'}$), 138.04($C_{2'}$), 146.52(C_4).

1-(4-(methoxy)benzyl)-4-phenyl-1H-1,2,3-triazole 7e

m.p. 170°C. Yield (85%). $\nu_{(C=CH)}$= 2956 cm^{-1}, $\nu_{(C(aryl)-N)}$= 1106 cm^{-1}. ^1H NMR ($CDCl_3$, 400MHz) δ (ppm) 3.75 (s, 3H, OCH_3), 5.45 (s, 2H, CH_2), 7.20(d, 2H, $H_{arom(3';7')}$), 7.24(d, 2H, $H_{arom(4';6')}$), 7.35(t, 4H, $H_{arom(3";4";5")}$), 7.61(s, 1H, H_5), 7.74(d, 2H, $H_{arom(2";6")}$). ^{13}C NMR ($CDCl_3$, 101MHz) δ (ppm) 57.22(OCH_3), 33.5($C_{8'}$), 52.82($C_{1'}$), 124.75($C_{4';6'}$), 125.12($C_{3';7'}$), 128.75($C_{2";6"}$), 128.17($C_{4"}$), 127.75($C_{3";5"}$), 129.50($C_{1",5}$), 130.65($C_{2'}$), 150.75 ($C_{4,5'}$).

1-(4-(isopropyl)benzyl)-4-phenyl-1H-1,2,3-triazole 7f

m.p. 175°C. Yield (92%). $\nu_{(C=CH)}$= 2956 cm^{-1}, $\nu_{(C(aryl)-N)}$= 1106 cm^{-1}. ^1H NMR ($CDCl_3$, 400MHz) δ (ppm) 1.22 (s, 6H, CH_3), 5.45 (s, 2H, CH_2), 7.20(d, 2H, $H_{arom(3';7')}$), 7.25(d, 2H, $H_{arom(4';6')}$), 7.35(t, 4H, $H_{arom(3";4";5")}$), 7.60(s, 1H, H_5), 7.75(d, 2H, $H_{arom(2";6")}$). ^{13}C NMR ($CDCl_3$, 101MHz) δ (ppm) 30.20(CH_3), 33.7($C_{8'}$), 52.85($C_{1'}$), 124.75($C_{4';6'}$), 125.22($C_{3';7'}$), 126.75($C_{2";6"}$), 127.17($C_{4"}$), 127.75($C_{3";5"}$), 129.65($C_{1",5}$), 130.65($C_{2'}$), 150.75 ($C_{4,5'}$).

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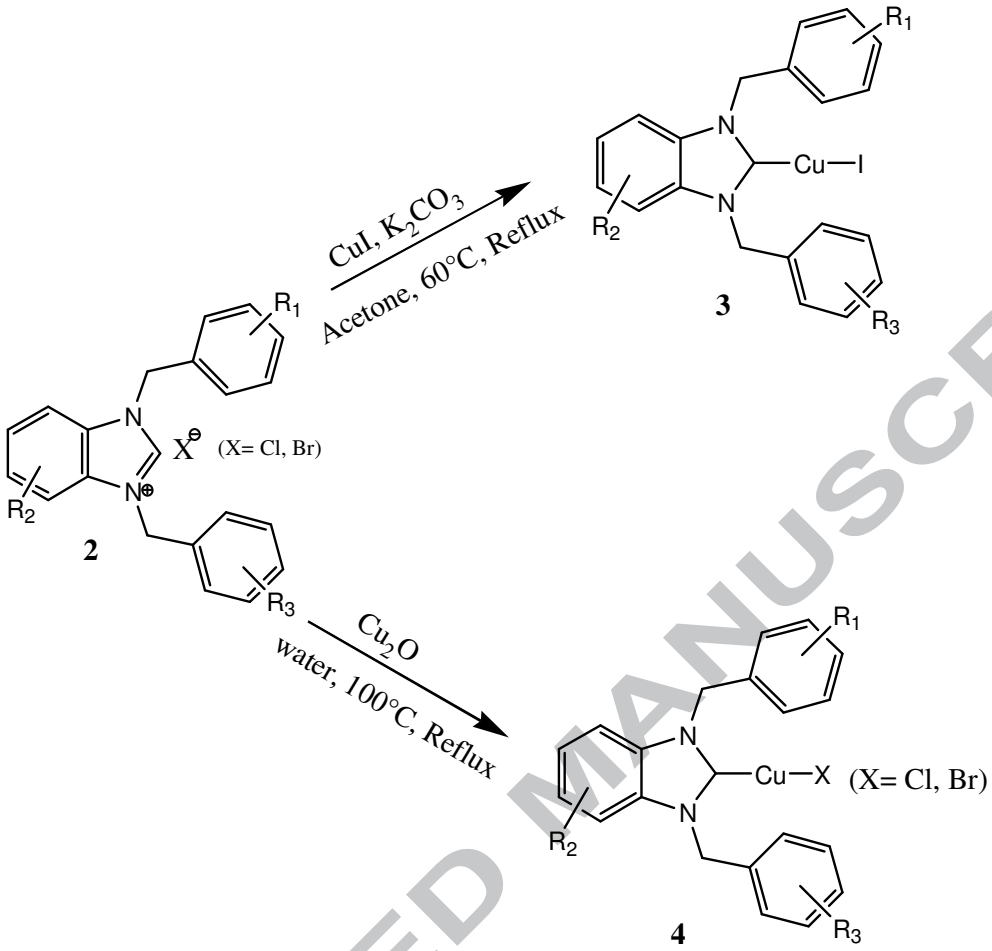
Graphical abstract



In this study

- A series of new benzimidazolium salts (**2a–c**) were synthesized from the reaction of 5,6-dimethyl-1-(alkylbenzyl)-1H-benzo[d]imidazole with various alkyl halides. These salts were used to synthesize cupper N-heterocyclic carbene (Cu-NHC) complexes **3-4**.
- The obtained (NHC) Copper (I) complexes **3-4** were characterized by FT-IR, NMR (^{1}H and ^{13}C) spectroscopic methods, mass spectrometry (EI-MS and HRMS) and elemental analysis.
- These novel cupper complexes **3-4** were used as a catalyst for alkyne – azide cycloaddition (CuAAC) reaction.