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Dinuclear Copper(I) Complexes of Phenanthrolinyl-Functionalized NHC Ligands

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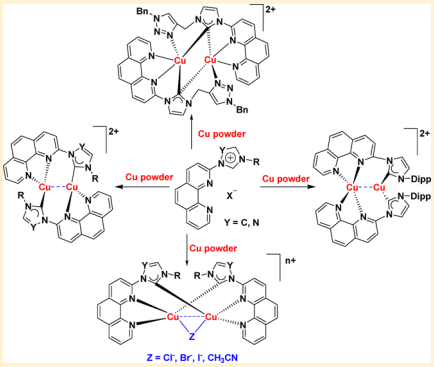
Supporting Information

ABSTRACT: We have prepared a number of phenanthroline-functionalized imidazolium and triazolium salts from 2-iodo-1,10-phenanthroline and imidazole and triazole derivatives. Simple reactions of these imidazolium salts with copper powder at room temperature have afforded a series of dinuclear copper(I)-NHC complexes doubly bridged by *N*-(1,10-phenanthrolin-2-yl)imidazolylidene ligands in excellent yields. The two phen-NHC ligands are either head-to-head or head-to-tail arranged depending upon the steric repulsion of the substituents. Reactions of imidazolium halides and copper yielded dinuclear complexes $[Cu_2(\mu\text{-}X)(L6)_2]X$ (X = Cl, Br, I) in nearly quantitative yields. The dinuclear $[Cu_2(L10)_2(\mu\text{-}MeCN)]^{2+}$ was similarly obtained through 1,2,4-triazolium salts and copper, and the compound consists of a bridging CH_3CN molecule, representing the first example of Cu-NHC complexes with a 3c−2e bond. These Cu(I) complexes have been characterized by NMR spectra and elemental analysis and further confirmed by X-ray diffraction analysis. These dinuclear copper-NHC complexes are highly active for cycloaddition reaction of alkynes and azides at room temperature. $[Cu_2(\mu\text{-}X)(L6)_2]X$ are the most efficient catalysts among these dinuclear complexes in acetonitrile, which are superior to the commonly used copper catalysts for click reaction.



INTRODUCTION

Due to the unique properties of N-heterocyclic carbenes (NHCs), transition metal complexes of NHCs have been the focus of intense research in the fields of medicine, materials, and homogeneous catalysis.[1] Polydentate NHC ligands containing both C and N donating atoms are suitable for the construction of bi- and multinuclear organometallic complexes. NHCs bearing one or more heteroarenes including pyridine,[2] pyridazine,[3] pyrazole,[4] triazole,[5] naphthyridine,[2a,6] etc., have been extensively studied as ligands in transition-metal-catalyzed organic synthesis. Phenanthroline is a commonly used ligand in coordination chemistry and homogeneous catalysis. We have reported that *N*-(1,10-phenanthrolin-2-yl)imidazolylidenes are able to form pincer-type nickel(II), palladium(II), platinum(II), and ruthenium(II) complexes, and these complexes have shown excellent catalytic activities in Kumada, Sonogashira, and hydrosilylation reactions.[7] As a continuation, herein we report the synthesis of dinuclear copper(I) complexes supported by *N*-(1,10-phenanthrolin-2-yl)imidazolylidenes, their properties, and catalytic application in the CuAAC reaction.

RESULTS AND DISCUSSION

Preparation of NHC Precursors. A number of NHC precursors including imidazolium, 1,2,4-triazolium, pyrazolium, and 2-methylimidazolium salts bearing various side chain groups and anions were prepared, and their structures are shown in Scheme 1.

The imidazolium salts $[HL1](PF_6)$−$[HL7](PF_6)$ were prepared from 2-iodo-1,10-phenanthroline and corresponding N-substituted imidazole according to our reported procedure.[7a] [HL6]X (X = Cl, Br, I) were obtained via anion exchange of $[HL6](PF_6)$ with tetrabutylammonium halides (TBAX) in acetone. $[HL8](PF_6)$ was synthesized from 2-(1*H*-imidazol-1-yl)-1,10-phenanthroline, 3-bromopropyne, and benzyl azide. These salts have been characterized by NMR spectroscopy, and their characterization data are given in the Supporting Information. In the ^{1}H NMR spectra of these imidazolium salts, the chemical shifts of C2−H are located between 10.15 and 10.74 ppm. Reaction of 2-(1*H*-1,2,4-triazol-1-yl)-1,10-phenanthroline and 3-bromopropene gave a mixture of 1,2,4-triazolium salt $[HL9](PF_6)$ and phenanthrolinium in the molar ratio of 1: 0.7, which cannot be isolated through simple recrystallization. In contrast, $[HL10](PF_6)$ was obtained as the only product of the reaction of 2-(1*H*-1,2,4-triazol-1-yl)-1,10-phenanthroline and benzyl bromide. The C2−H of the triazolium salt is more acidic than that of the imidazolium salt, as indentified by the chemical shift at 11.30 and 11.47 ppm, respectively. Similarly, pyrazolium salt 2-allyl-1-(1,10-phenanthrolin-2-yl)-1*H*-pyrazol-2-ium hexafluorophosphate was synthesized from 2-(1*H*-pyrazol-1-yl)-1,10-phenanthroline and 3-bromopropene in 85% yield, and its C5−H appears at 9.62

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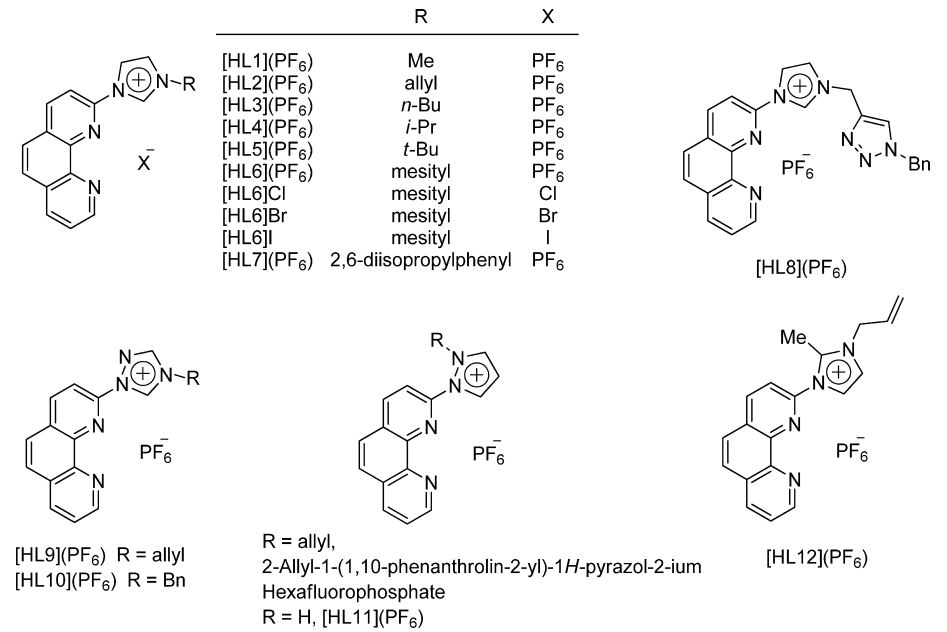
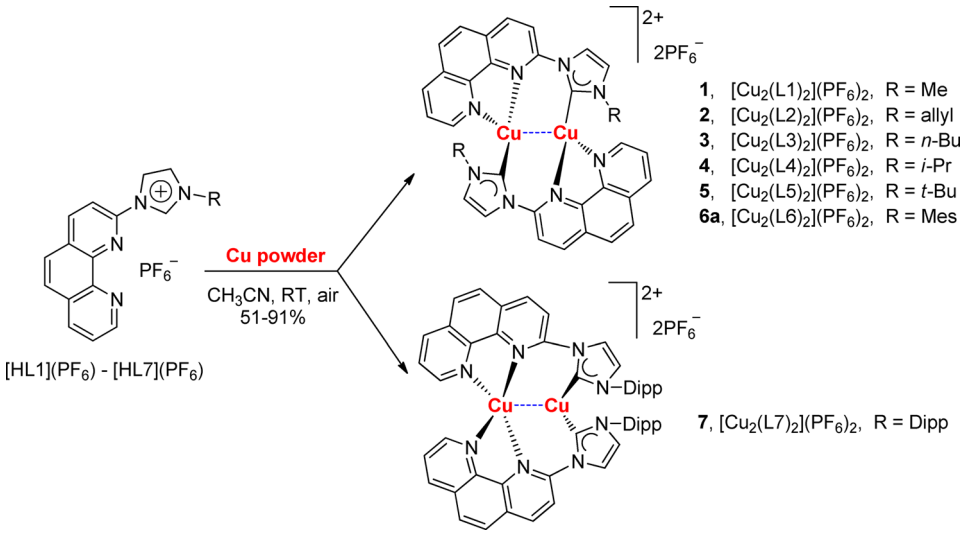
Scheme 1. Schematic Illustration of N-Heterocyclic Carbene Precursors



Scheme 2. Synthesis of Cu(I)-NHC Complexes 1−5, 6a, and 7



ppm. However, the same reaction with benzyl bromide yielded only protonated salt [HL11](PF$_6$) in 70% yield. Additionally, we also synthesized 2-methylidazolium salt [HL12](PF$_6$), and the chemical shift of C5−H is at 9.15 ppm.

Synthesis and Characterization of Cu(I)-NHC Complexes. According to our previous reported method,[8] copper NHC complexes can be directly obtained from the reaction of the corresponding imidazolium salts with copper powder. Treatment of the imidazolium salts listed in Scheme 1 with an excess of copper powder in CH_3CN at room temperature for 3−5 h afforded complexes **1**−**5**, **6a**, and **7** as red solids in 51−91% yields (Scheme 2). Although these binuclear complexes can also be obtained from the reactions of the corresponding imidazolium salts and Cu_2O,[9] the reactions have to be performed at higher temperature (ca. 60 °C) and the yields are significantly lower.

Complexes **1**−**5**, **6a**, and **7** have been characterized by ^{1}H NMR, ^{13}C NMR, and elemental analysis. The elemental analyses show that the ratios of copper and *N*-(1,10-phenanthrolin-2-yl)imidazolylidene are 1:1. The ^{1}H NMR spectra of complexes **1**−**4** and **7** display only one set of ligand signals, whereas in the spectra of **5** and **6a** two sets of proton resonance signals were observed in 1.0/1.6 and 1.0/1.0 ratios, respectively. We speculate that the tridentate NNC ligands may form two isomeric dinuclear copper(I) complexes in which two ligands are arranged in a head−tail or head−head manner. The NNC ligands with N-substituents of less steric hindrance would prefer head−tail isomers, whereas bulky NNC ligands would form head−head isomers due to steric repulsion. For complexes **5** and **6a** bearing bulkier N-substituents, both isomers would exist in solutions (Scheme 3). In their ^{13}C NMR spectra, the chemical shifts of the carbenic carbon of complexes **1**, **2**, **4**, **5**, **6a**, and **7** appear at ca. 180 ppm, similar to that of other reported Cu(I)-NHC complexes.[10] A satisfactory ^{13}C NMR spectrum of **3** was not obtained.

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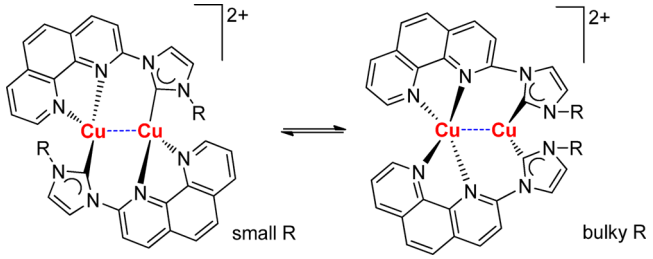
Scheme 3. Interconversion of Head−Tail and Head−Head Isomers



Suitable crystals for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether to the product CH_3CN solution at room temperature. The structures of **2**, **4**, **5**, **6a**, and **7** were unambiguously identified by X-ray single-crystal diffraction analysis. The molecular structures of **2**, **4**, **5**, and **6a** are essentially identical, and thus only **6a** is shown in Figure 1, and other complexes are given in the Supporting Information. The complex consists of two copper(I) ions bridged by two L6 ligands. The two ligands are arranged in head-to-tail manner; thus each copper is coordinated by a phenanthroline and a NHC of the second ligand. The bond distances of Cu−C bond are 1.880(4) and 1.881(4) Å, which are comparable to the known Cu(I)-NHC complexes.[9a,10b,c,11] The separation of Cu(1) and Cu(2) is 2.7081(8) Å, showing weak metal−metal interaction.

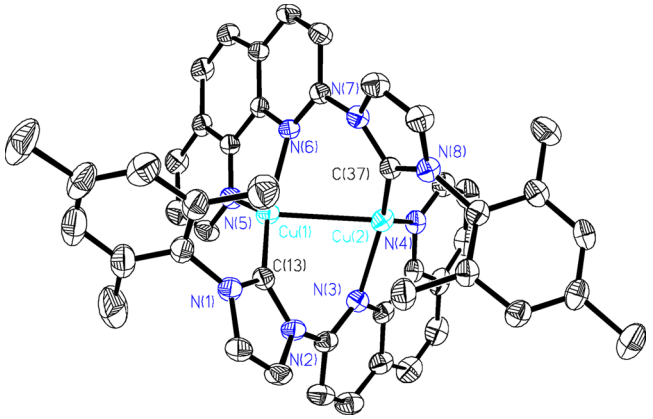


Figure 1. ORTEP drawing of the cationic section of $[Cu_2(L6)_2](PF_6)_2$ (**6a**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms, counteranions, and solvent molecules have been removed for clarity. Selected bond distances (Å) and angles (deg): Cu(1)−C(13) 1.880(4), Cu(1)−N(5) 2.039(3), Cu(1)−N(6) 2.069(3), Cu(2)−C(37) 1.881(4), Cu(2)−N(4) 2.025(4), Cu(2)−N(3) 2.109(4), C(13)−Cu(1)−N(5) 132.17(17), C(13)−Cu(1)−N(6) 144.88(17), N(5)−Cu(1)−N(6) 81.61(14), C(37)−Cu(2)−N(4) 133.36(17), C(37)−Cu(2)−N(3) 144.46(16), N(4)−Cu(2)−N(3) 80.86(15).

Unlike complexes **1**−**5** and **6a**, $[Cu_2(L7)_2](PF_6)_2$ (**7**) has a structure with two ligands head-to-head arranged (Figure 2). Thus, in the molecule one copper is linearly bicoordinated by two NHCs, and the other is tetracoordinated by two phenanthroline moieties in a distorted tetrahedral coordination sphere. The Cu−C bond distances in **7** are comparable to those of complexes **2**, **4**, **5**, and **6a**, but the Cu−Cu sepration in **7** is 2.653(1) Å, shorter than those of **2**, **4**, **5**, and **6a**. In the ^{1}H NMR spectrum of **7**, four resonance signals at 1.00, 0.24, 0.05, and −0.61 ppm in 1:1:1:1 ratio due to methyl were observed, illustrating that the rotation of the bulky 2,6-diisopropylphenyl groups is inhibited. Two sets of CH_3 groups sit above the phenanthroline ring. As a result of the shielding effect, these protons are upfield shifted. The structural analysis reveals that head−head arrangement of two ligands may reduce the geometric repulsion. Thus complexes **1**−**4** tend to be head−tail arranged, and complexes **5** and **6a** have two isomers in their solutions (Scheme 3).

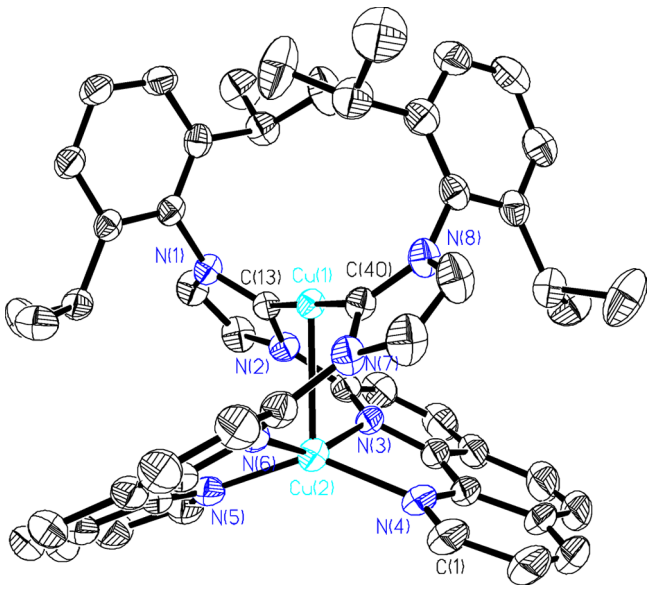


Figure 2. ORTEP drawing of the cationic section of $[Cu_2(L7)_2](PF_6)_2$ (**7**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms, counteranions, and solvent molecules have been removed for clarity. Selected bond distances (Å) and angles (deg): Cu(1)−C(13) 1.905(4), Cu(1)−C(40) 1.910(4), Cu(2)−N(4) 2.043(4), Cu(2)−N(5) 2.047(4), Cu(2)−N(3) 2.094(4), Cu(2)−N(6) 2.102(4), C(13)−Cu(1)−C(40) 178.97(17), N(4)−Cu(2)−N(5) 139.01(17), N(4)−Cu(2)−N(3) 80.96(19), N(5)−Cu(2)−N(3) 109.68(18), N(4)−Cu(2)−N(6) 107.2(2), N(5)−Cu(2)−N(6) 80.98(18), N(3)−Cu(2)−N(6) 153.71(14).

Reactions of [HL6]X with copper powder in CH_3CN gave dark red complexes $[Cu_2(\mu\text{-}X)(L6)_2]X$ (X = Cl (**6b**), Br (**6c**), I (**6d**)) in more than 90% yields (Scheme 4). Treatment of **6a** with 4 equivalents of $^nBu_4NX$ (X = Cl, Br) in MeCN for 30 min quickly generated complexes **6b** and **6c** in 93% and 77% yields. Reaction of **6a** with $^nBu_4NI$ gave a mixture of **6d** and imidazolium salts due to partial decomposition in a molar ratio of 1.15:1. Complexes **6b**−**6d** were fully characterized by NMR, elemental anlysis, and X-ray single-crystal diffraction. In their ^{1}H NMR spectra, only one set of ligands was observed. ^{13}C NMR spectra show that the chemical shifts of the carbenic carbon of **6b**, **6c**, and **6d** at 182.9, 183.0, and 182.6 ppm are similar to other non-halide complexes.

The structure of complex **6d** is shown in Figure 3. Two copper centers are bridged by two L6 in a head−tail manner and one bridging iodide ion. Each copper center is tetracoordinated in a severely distorted INNC tetrahedral geometry. Due to the bridging iodide ion, the Cu−Cu distance of **6d** is shortened from 2.708(1) Å in **6a** to 2.598(1) Å. Meanwhile, the corresponding Cu−C and Cu−N bond distances are slightly longer than those of **6a**. In the ^{1}H NMR spectrum of **6d**, the resonances of methyl groups appear at 1.72, 1.46, and 1.27 ppm, illustrating that the rotation of

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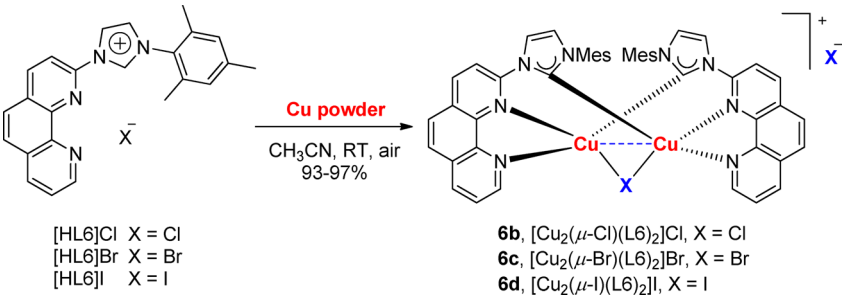
Scheme 4. Synthesis of $[Cu_2(\mu\text{-}X)(L6)_2]X$ (X = Cl (6b), Br (6c), I (6d))



[HL6]Cl X = Cl
[HL6]Br X = Br
[HL6]I X = I

6b, $[Cu_2(\mu\text{-Cl})(L6)_2]Cl$, X = Cl
6c, $[Cu_2(\mu\text{-Br})(L6)_2]Br$, X = Br
6d, $[Cu_2(\mu\text{-I})(L6)_2]I$, X = I

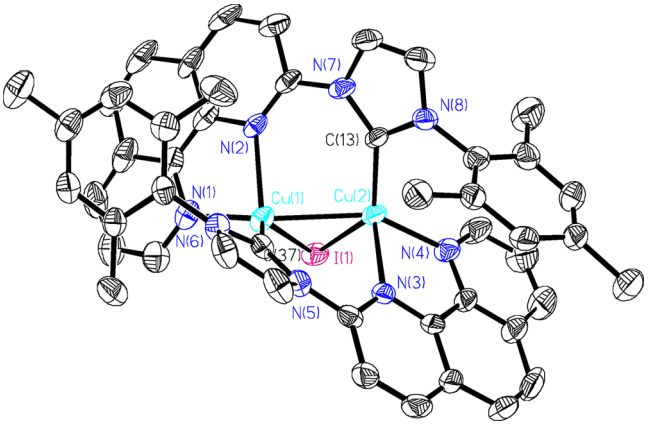


Figure 3. ORTEP drawing of the cationic section of $[Cu_2(\mu\text{-I})(L6)_2]I$ (**6d**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and counteranions have been removed for clarity. Selected bond distances (Å) and angles (deg): Cu(1)−C(37) 1.914(6), Cu(1)−N(1) 2.083(7), Cu(1)−N(2) 2.219(6), Cu(1)−I(1) 2.6778(9), Cu(2)−C(13) 1.922(7), Cu(2)−N(4) 2.094(6), Cu(2)−N(3) 2.174(6), Cu(2)−I(1) 2.7144(11), C(37)−Cu(1)−N(1) 119.9(3), C(37)−Cu(1)−N(2) 115.9(3), N(1)−Cu(1)−N(2) 79.8(3), C(37)−Cu(1)−I(1) 131.9(2), N(1)−Cu(1)−I(1) 91.22(16), N(2)−Cu(1)−I(1) 104.37(13), C(13)−Cu(2)−N(4) 119.4(3), C(13)−Cu(2)−N(3) 119.9(3), N(4)−Cu(2)−N(3) 79.1(2), C(13)−Cu(2)−I(1) 131.4(2), N(4)−Cu(2)−I(1) 90.50(19), N(3)−Cu(2)−I(1) 101.83(15).

mesityl groups of the ligand is restricted. The molecular structures of complexes **6b** and **6c** are similar to **6d**, and they are listed in the Supporting Information.

Reaction of $[HL8](PF_6)$ with copper powder was also exmained, and complex **8** was generated in 73% yield (Scheme 5). Complex **8** is dinuclear, and the carbenic carbon was observed at 181.5 ppm in its ^{13}C NMR spectroscopy.

The structure of complex **8** was further confirmed by X-ray single-crystal diffraction analysis, shown in Figure 4. Unlike the dinuclear copper complexes mentioned above, each NHC

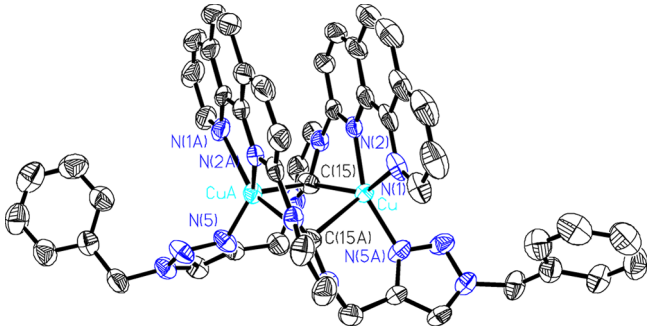


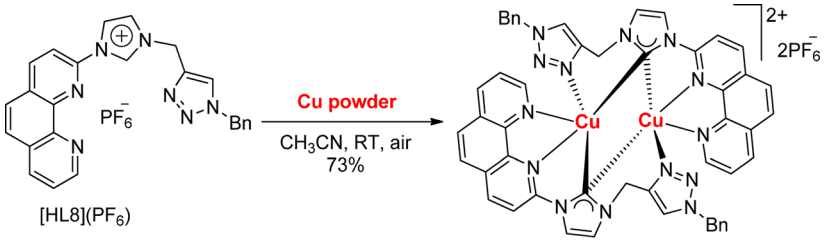
Figure 4. ORTEP drawing of the cationic section of $[Cu_2(L8)_2](PF_6)_2$ (**8**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms, counteranions, and solvent molecules have been removed for clarity. Selected bond distances (Å) and angles (deg): Cu−N(1) 2.210(4), Cu−N(2) 1.931(4), Cu−N(5A) 1.976(3), Cu−C(15) 2.623(0), Cu−C(15A) 2.357(4), N(2)−Cu−N(5A) 151.27(15), N(2)−Cu−N(1) 81.43(16), N(5A)−Cu−N(1) 103.64(17), N(2)−Cu−C(15A) 119.88(14), N(5A)−Cu−C(15A) 88.76(15), N(1)−Cu−C(15A) 87.61(15), C(15)−Cu−N(2) 72.320, C(15)−Cu−N(1) 151.000, C(15)−Cu−C(15A) 94.780, C(15)−Cu−N(5A) 105.300. Symmetry code: A $-x+1, y, -z+1/2$.

carbenic carbon of **8** binds two copper ions in μ_2 mode with Cu−C bond distances of 2.357(4) and 2.623(0) Å, which are remarkably longer than normal Cu−C bonds of Cu(I)-NHC complexes (ca. 1.80−2.20 Å).[12] Such a coordination mode of NHC has been found in a few silver, copper, and nickel complexes.[3b,8b,10c,13] The dangling triazole is only bonded to one copper ion.

Treatment of triazolium salts $[HL9](PF_6)$ and $[HL10](PF_6)$ with copper at room temperature gave dinuclear copper complexes **9** and **10** in 65% and 97% yields, respectively (Scheme 6). The ^{13}C NMR spectra of **9** and **10** display peaks at 181.0 and 180.1 ppm assigned to the crabenic carbons.

The molecular structures of complexes **9** and **10** are shown in Figures 5 and 6. Complex **9** has the same structure as the analogous imidazolylidene complex **2**. The most striking feature

Scheme 5. Synthesis of $[Cu_2(L8)_2](PF_6)_2$ (8)



[HL8](PF6)

8, $[Cu_2(L8)_2](PF_6)_2$

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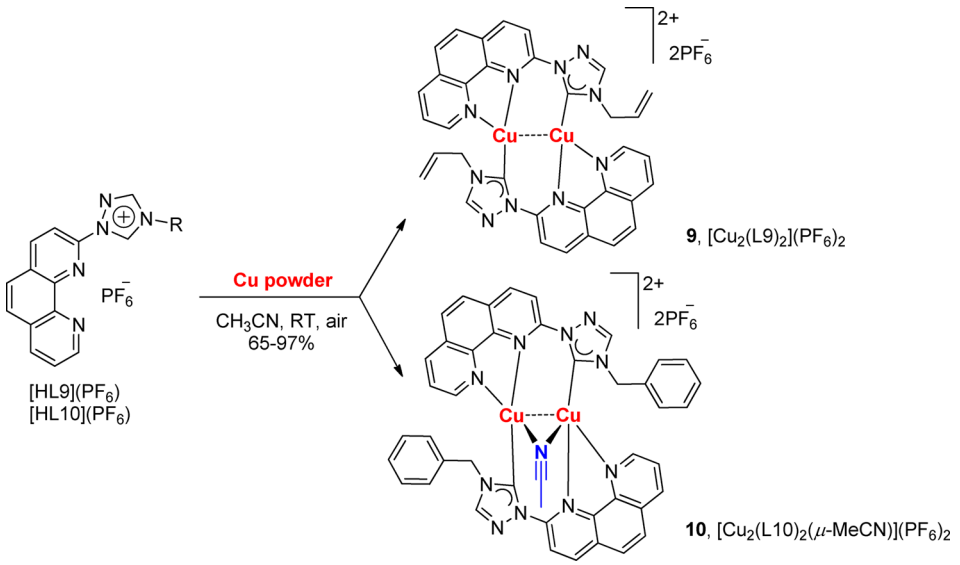
Scheme 6. Synthesis of $[Cu_2(L9)_2](PF_6)_2$ (9) and $[Cu_2(L10)_2(\mu\text{-MeCN})](PF_6)_2$ (10)



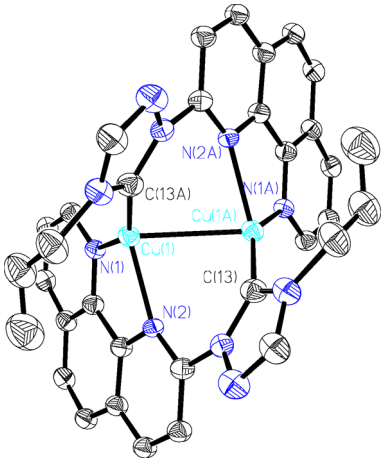


Figure 5. ORTEP drawing of the cationic section of $[Cu_2(L9)_2](PF_6)_2$ (**9**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and counteranions have been removed for clarity. Selected bond distances (Å) and angles (deg): Cu(1)−C(13A) 1.891(7), Cu(1)−N(1) 2.011(5), Cu(1)−N(2) 2.143(5), C(13A)−Cu(1)−N(1) 146.2(3), C(13A)−Cu(1)−N(2) 131.5(3), N(1)−Cu(1)−N(2) 80.3(2). Symmetry code: A $-x+1, y, -z+1/2$.

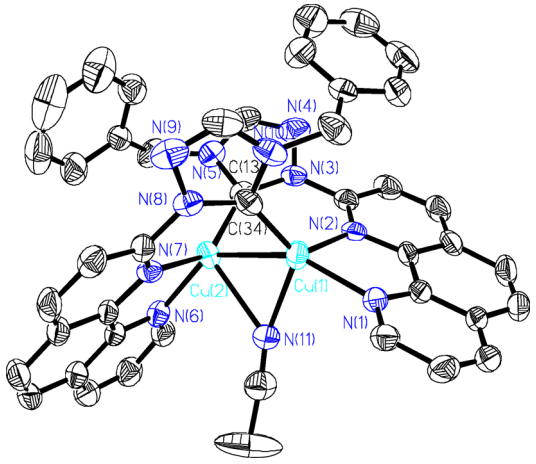


Figure 6. ORTEP drawing of the cationic section of $[Cu_2(L10)_2(\mu\text{-MeCN})](PF_6)_2$ (**10**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and counteranions have been removed for clarity. Selected bond distances (Å) and angles (deg): Cu(1)−C(34) 1.917(10), Cu(1)−N(1) 2.072(8), Cu(1)−N(2) 2.133(7), Cu(1)−N(11) 2.204(10), Cu(2)−C(13) 1.884(10), Cu(2)−N(6) 2.071(9), Cu(2)−N(7) 2.099(7), Cu(2)−N(11) 2.471(10), C(34)−Cu(1)−N(1) 124.9(4), C(34)−Cu(1)−N(2) 127.4(3), N(1)−Cu(1)−N(2) 80.4(3), C(34)−Cu(1)−N(11) 124.4(4), N(1)−Cu(1)−N(11) 88.9(3), N(2)−Cu(1)−N(11) 97.8(3), C(13)−Cu(2)−N(6) 128.0(4), C(13)−Cu(2)−N(7) 137.4(4), N(6)−Cu(2)−N(7) 80.6(3), C(13)−Cu(2)−N(11) 121.9(4), N(6)−Cu(2)−N(11) 86.3(3), N(7)−Cu(2)−N(11) 86.3(3).

of **10** is that the two Cu(I) centers are bridged by a CH_3CN molecule, forming a 3c−2e bond. The distances between two copper ions and acetonitrile are 2.204(10) and 2.471(10) Å. The $Cu-N_{actonitrile}$ distances are significantly longer than $Cu-N_{phen}$ in the same complex. To the best of our knowledge, this bridging coordination mode of acetonitrile is the first example in the family of Cu-NHC complexes and is even scarce for copper compounds.[14] In the ^1H NMR spectrum of **10**, the chemical shift of the methyl of acetonitrile is 2.06 ppm, which is not much different from that of a free acetonitrile molecule.[15] In the structure, each Cu center is located in a distorted tetrahedral geometry. The Cu−C bond distances are 1.917(10) and 1.884(10) Å.

We also briefly examined the possibility to synthesize the abnormal NHC complexes of copper from the direct reaction of pyrazolium salt 2-allyl-1-(1,10-phenanthrolin-2-yl)-1*H*-pyrazol-2-ium hexafluorophosphate and copper powder. Unfortunately, we did not obtain the expected abnormal NHC complex. $[Cu_3(L11)_4(MeCN)_2](PF_6)_3$ (**11**) was obtained as a red solid in 51% yield from reaction of protonated salt $[HL11](PF_6)$ with copper powder (Scheme 7). Complex **11** is less stable than the dinuclear Cu(I)-NHC complexes. It was slowly oxidized, as evidenced by the color change from red to green in acetonitrile. The reaction of 2-methylimidazolium salt $[HL12](PF_6)$ with copper powder generated ionic compound **12** instead of the expected abnormal NHC complex (Scheme 8). The structures of **11** and **12** were identified by ^1H NMR and X-ray single-crystal analysis (see Supporting Information).

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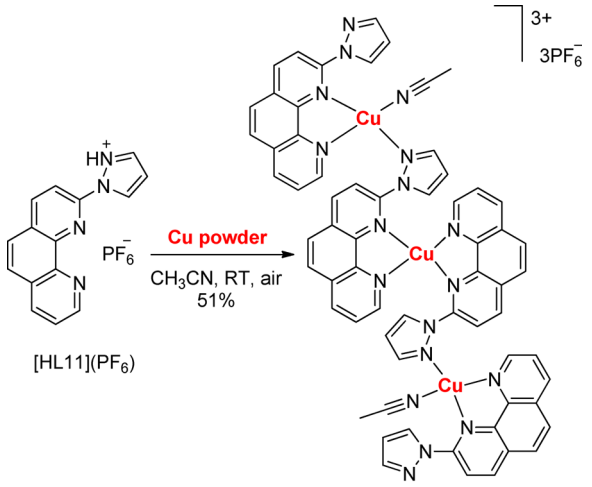
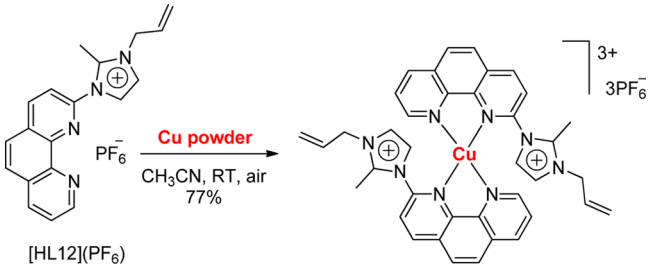
Scheme 7. Synthesis of $[Cu_3(L11)_4(MeCN)_2](PF_6)_3$ (11)



11, $[Cu_3(L11)_4(MeCN)_2](PF_6)_3$

Scheme 8. Synthesis of $[Cu(HL12)_2](PF_6)_3$ (12)



12, $[Cu(HL12)_2](PF_6)_3$

Electrochemistry. The redox behavior of the above-mentioned Cu(I)-NHC complexes was studied by cyclic voltammetry in CH_3CN. The experiments were performed with a three-electrode system (glass carbon working electrode, platinum counter electrode, and Ag/AgCl reference electrode) using Bu_4NPF_6 (0.10 M) as the supporting electrolyte. Oxidation involves the removal of an electron from a metal d orbital. The half-wave potentials of the redox processes and the peak separations vary over a wide range depending on the nature of the ligands and ligand arrangement mode. The cyclic voltammetry of **6a**, **6c**, **7**, **8**, and **10** is shown in Figure 7. Complexes **1**−**5** and **6a** can undergo a quasi-reversible redox process with close half-wave potentials and peak separations. Complexes **6b**−**6d** show two redox processes and lower half-wave potentials at 0.10−0.20 and 0.50−0.80 V compared to **1**−**5** and **6a**, illustrating that these complexes bearing additional halo bridges are more easily oxidized. The oxidation potential of complex **7** is relatively higher, indicating the stability of its head−head structure. Cyclic voltammetry of complex **8** in CH_3CN shows a fully reversible redox process at a half-wave potential of 0.142 V, and the peak−peak separation ΔE_p was ca. 68 mV, corresponding to the oxidation to a stable tricationic species. Complexes **9** and **10** exhibit two similar one-electron oxidation processes at 0.44−0.45 and 0.70−0.75 V.

Catalytic Application in CuAAC Reactions. The mononuclear copper-NHC complexes have been known to catalyze the click reaction between azide and alkyne.[10c,16] However, bimetallic catalysts have not been well explored. At first the present copper complexes **1**−**12** were screened for

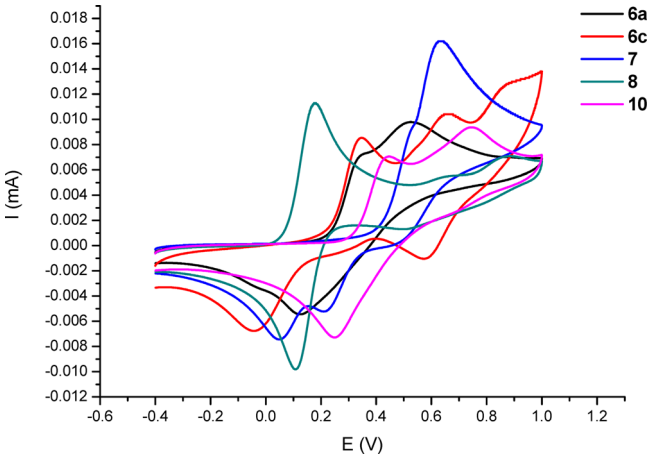


Figure 7. Cyclic voltammetry of complexes **6a**, **6c**, **7**, **8**, and **10** solubilized in CH_3CN at 25 °C at a concentration of 5.5×10^{-4} M.

CuAAC reaction of benzyl azide and phenylacetylene (Table 1). All the dinuclear copper-NHC complexes are active at catalyst loadings of 0.05 mol %. Among these complexes, **6a**−**d**, containing an N-mesityl substituent, are the most active, giving the target product in up to 90% yields (entries 6−9). When the catalyst loading of **6a**−**d** was reduced to 0.005 mol %, the yields of the triazole were sharply decreased to less than 30% (entries 19−22). Complex **12**, in which the copper is chelated by two phen groups, is totally inactive (entry 15). For comparison, other commonly used catalyst systems were also investigated under the same conditions and the same loading of copper. The classical CuAAC catalyst system gave the triazole product in only 10% yield (entry 16). When 0.10 mol % $Cu(MeCN)_4(PF_6)$ was used as the catalyst, only a trace amount of triazole was obtained (entry 17). The copper-NHC complex [(IMes)CuCl] also showed much lower activity (entry 18). Obviously, the dinuclear Cu-NHC complexes are superior to the commonly used copper catalysts.

We also examined the catalytic activity of **6b** at a loading of 0.05 mol % in different solvents (entries 7, 23−32). The reaction could take place at room temperature in alcohols, acetonitrile, or mixed solvents. ^{t}BuOH is better than MeOH, EtOH, and their mixed alcohol/water solvent. The nonprotonic solvent CH_3CN is also suitable for the reaction, and the yield of triazole was 100% (entry 7). But the reaction yield was decreased when a CH_3CN/H_2O mixed solvent was used (entries 30−31). The reaction can be carried out in moderate yield in water (entry 32). Considering the solubility of the reaction substrates, CH_3CN was selected as the optimized solvent.

Under the optimum reaction conditions, we expanded the CuAAC reaction to other azides and alkynes, and the results are listed in Table 2. For example, (azidomethyl)benzene, 1-(azidomethyl)-4-(*tert*-butyl)benzene, and 1-(azidomethyl)-4-nitrobenzene could react with phenylacetylene, generating the corresponding triazoles in more than 91% yields (entries 1−3). Reaction of 2-(azidomethyl)pyridine with phenylacetylene could yield 2-((4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl)pyridine in 93% yield (entry 4). The reaction of 1,4-bis(azidomethyl)-benzene and 2.4 equivalents of phenylacetylene generated a mixture of monocycloaddition and dicycloaddition products in a ratio of 1.5:1.0, probably because the relatively poor solubility of the monocycloaddition product in MeCN prevented its further reaction (entry 5). The electron-deficient 1-azido-4-

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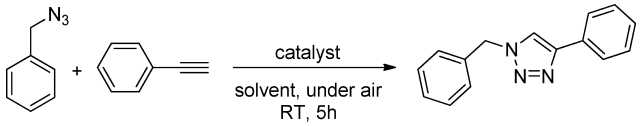
Table 1. Optimization of Solvent and Catalyst for CuAAC Reaction[a]



entry	catalyst	loading (mol %)	solvent (v/v)	yield (%)[b]
1	$[Cu_2(L1)_2](PF_6)_2$ (**1**)	0.05	CH_3CN	28
2	$[Cu_2(L2)_2](PF_6)_2$ (**2**)	0.05	CH_3CN	31
3	$[Cu_2(L3)_2](PF_6)_2$ (**3**)	0.05	CH_3CN	42
4	$[Cu_2(L4)_2](PF_6)_2$ (**4**)	0.05	CH_3CN	34
5	$[Cu_2(L5)_2](PF_6)_2$ (**5**)	0.05	CH_3CN	48
6	$[Cu_2(L6)_2](PF_6)_2$ (**6a**)	0.05	CH_3CN	100
7	$[Cu_2(\mu\text{-}Cl)(L6)_2]Cl$ (**6b**)	0.05	CH_3CN	100
8	$[Cu_2(\mu\text{-}Br)(L6)_2]Br$ (**6c**)	0.05	CH_3CN	89
9	$[Cu_2(\mu\text{-}I)(L6)_2]I$ (**6d**)	0.05	CH_3CN	98
10	$[Cu_2(L7)_2](PF_6)_2$ (**7**)	0.05	CH_3CN	36
11	$[Cu_2(L8)_2](PF_6)_2$ (**8**)	0.05	CH_3CN	28
12	$[Cu_2(L9)_2](PF_6)_2$ (**9**)	0.05	CH_3CN	25
13	$[Cu_2(L10)_2(\mu\text{-}MeCN)](PF_6)_2$ (**10**)	0.05	CH_3CN	4
14	$[Cu_3(L11)_4](PF_6)_3$ (**11**)	0.033	CH_3CN	11
15	$[Cu(HL12)_2](PF_6)_3$ (**12**)	0.10	CH_3CN	trace
16	$CuSO_4{\cdot}5H_2O$ (sodium ascorbate)	0.10 (5.0[c])	$^tBuOH/H_2O$ (2:1)	10
17	$Cu(MeCN)_4(PF_6)$	0.10	CH_3CN	2
18	[(IMes)CuCl]	0.10	CH_3CN	3
19	$[Cu_2(L6)_2](PF_6)_2$ (**6a**)	0.005	CH_3CN	3
20	$[Cu_2(\mu\text{-}Cl)(L6)_2]Cl$ (**6b**)	0.005	CH_3CN	28
21	$[Cu_2(\mu\text{-}Br)(L6)_2]Br$ (**6c**)	0.005	CH_3CN	7
22	$[Cu_2(\mu\text{-}I)(L6)_2]I$ (**6d**)	0.005	CH_3CN	15
23	$[Cu_2(\mu\text{-}Cl)(L6)_2]Cl$ (**6b**)	0.05	$^tBuOH/H_2O$ (1:1)	35
24	$[Cu_2(\mu\text{-}Cl)(L6)_2]Cl$ (**6b**)	0.05	^tBuOH	95
25	$[Cu_2(\mu\text{-}Cl)(L6)_2]Cl$ (**6b**)	0.05	MeOH	55
26	$[Cu_2(\mu\text{-}Cl)(L6)_2]Cl$ (**6b**)	0.05	$MeOH/H_2O$ (2:1)	24
27	$[Cu_2(\mu\text{-}Cl)(L6)_2]Cl$ (**6b**)	0.05	$MeOH/H_2O$ (1:1)	65
28	$[Cu_2(\mu\text{-}Cl)(L6)_2]Cl$ (**6b**)	0.05	EtOH	50
29	$[Cu_2(\mu\text{-}Cl)(L6)_2]Cl$ (**6b**)	0.05	$EtOH/H_2O$ (1:1)	61
30	$[Cu_2(\mu\text{-}Cl)(L6)_2]Cl$ (**6b**)	0.05	CH_3CN/H_2O (2:1)	35
31	$[Cu_2(\mu\text{-}Cl)(L6)_2]Cl$ (**6b**)	0.05	CH_3CN/H_2O (1:1)	10
32	$[Cu_2(\mu\text{-}Cl)(L6)_2]Cl$ (**6b**)	0.05	H_2O	76

[a]Reaction conditions: benzyl azide 1.0 mmol, phenylacetylene 1.1 mmol, catalyst, solvent 3 mL, RT, 5 h. [b]Isolated yields. [c]The loading of sodium ascorbate.

bromobenzene showed relatively lower activity, and the yield of the desired product is 74% (entry 6). Even with steric hindrance, the reaction of mesityl azide afforded the corresponding product in 96% yield upon extension to 10 h (entry 7). However, the more sterically hindered 2,6-diisopropylphenyl azide gave the product in only 25% yield (entry 8). In addition, both electron-rich 1-ethynyl-4-methylbenzene and electron-deficient 2-ethynylpyridine could participate in the reaction, and the corresponding triazoles were isolated in more than 80% yields (entries 9, 10).

CONCLUSION

We have prepared a number of dinuclear Cu(I)-NHC complexes via simple reactions of corresponding imidazolium salts with copper powder at room temperature. On the basis of crystal diffraction analysis, complex **7** is a head-to-head isomer, while the other complexes **1**−**5** and **6a** are head-to-tail isomers with the two $C_{carbene}$ atoms bound to different copper atoms depending on the steric repulsion of the N-substituents. Changing the PF_6^- anion of the imidazolium with the halide ion X^-, dinuclear Cu(I)-NHC complexes **6b**−**6d** containing a bridging halide ion were obtained. In complex **9**, each $C_{carbene}$ atom binds two copper atoms. Complex **11** exhibits a rare bridging CH_3CN molecule, representing the first example of a 3c−2e bond in the family of copper NHC complexes. These dinuclear copper-NHC complexes are efficient catalysts for cycloaddition of alkynes and azides even at room temperature, and the turnover number for **6b** can reach up to 2000. The preparative procedure is simple, and the starting materials are easily available. The two copper ions in these dinuclear complexes are tightly held together with approximate one-bond distance, offering opportunities to investigate potential cooperative catalysis. The reactivities and catalytic properties will be further studied.

EXPERIMENTAL SECTION

All chemicals were obtained from commercial suppliers and used without further purification. The copper powder (200 mesh, with purity ≥99.7 wt %) was purchased from Sinopharm Chemical Reagent Co., Ltd., China, and was used directly without any pretreatment. The detailed synthetic procedures of NHC precursors are given in the Supporting Information. The elemental analyses were performed on a Flash EA 1112 instrument. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm downfield from TMS at $\delta = 0$ ppm, and coupling constants (J) are expressed in Hz. Suitable crystals for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether to the product CH_3CN solution at room temperature. Single-crystal X-ray diffraction data were collected at 293(2) K on a Siemens Smart/CCD area-detector diffractometer with Mo Kα radiation (λ = 0.71073 Å). CV measurements were performed at room temperature under nitrogen in CH_3CN with 0.1 M Bu_4NPF_6 as the supporting electrolyte at a scan rate of 50 mV s^{-1} using a CHI610D electrochemical analyzer.

General Procedure for Preparation of Cu(I)-NHC Complexes 1−10 and Noncarbene Cu(I) Complexes 11 and 12. Cu(I) complexes **1**−**12** were synthesized by the following route: a solution of ligand precursors (0.20 mmol) in 3 mL of CH_3CN was treated with an excess of copper powder (32 mg, 0.50 mmol). The mixture was allowed to react at room temperature for 3−5 h under air. After the reaction, the solution was filtered through Celite. Then the filtrate was concentrated to ca. 1 mL. The compounds were obtained by adding diethyl ether to the filtrate.

$[Cu_2(L1)_2](PF_6)_2$, ***1***. This complex was synthesized from $[HL1](PF_6)$ (81 mg, 0.20 mmol) and Cu powder (32 mg, 0.50 mmol). Yield: 85 mg (91%), orange powder. ^1H NMR (400 MHz, DMSO-d_6): δ 9.20 (d, J = 8.4 Hz, 2H), 8.64 (d, J = 8.0 Hz, 2H), 8.54 (d, J = 8.4 Hz, 2H), 8.36 (s, 2H), 8.33 (d, J = 9.2 Hz, 2H), 8.25 (s, 2H), 8.17 (d, J = 8.8 Hz, 2H), 7.70 (s, 2H), 7.64 (m, 2H), 3.42 (s, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 181.3 (Cu-*C*), 150.4, 149.5, 142.5, 142.0, 141.1, 138.8, 128.9, 127.8, 126.9, 126.6, 125.5, 124.2, 120.1, 119.8, 37.6. Anal. Calcd for $C_{32}H_{24}Cu_2F_{12}N_8P_2$: C, 40.99; H, 2.58; N, 11.95. Found: C, 41.22; H, 2.52; N, 12.21.

$[Cu_2(L2)_2](PF_6)_2$, ***2***. This complex was synthesized from $[HL2](PF_6)$ (86 mg, 0.20 mmol) and Cu powder (32 mg, 0.50 mmol). Yield: 82 mg (83%), red powder. ^1H NMR (400 MHz, DMSO-d_6): δ 9.22 (d, J = 8.4 Hz, 2H), 8.18−8.78 (m, 12H), 7.50−7.83 (m, 4H), 3.74−5.50 (m, 10H, NC_3H_5). ^{13}C NMR (100 MHz, DMSO-d_6): δ 180.1 (Cu-*C*), 150.3, 149.7, 142.3, 141.4, 138.8, 132.7, 129.1, 127.9, 127.0, 126.6,

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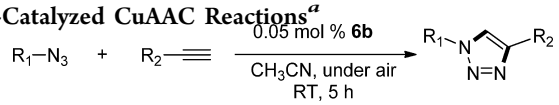
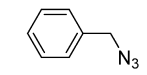
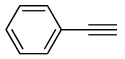
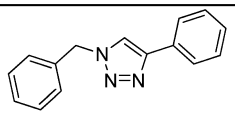
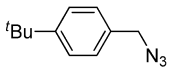
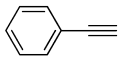
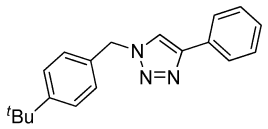
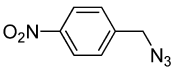
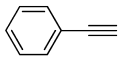
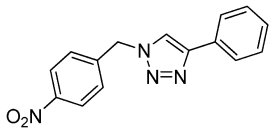
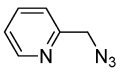
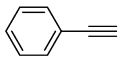
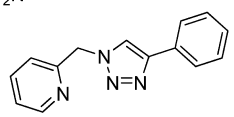
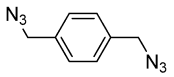
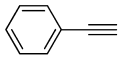
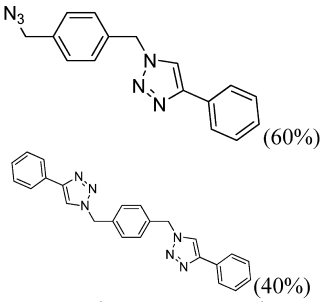
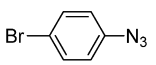
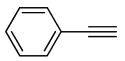
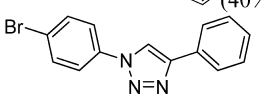
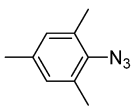
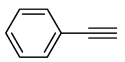
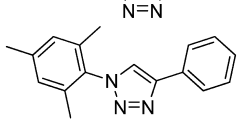
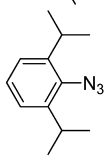
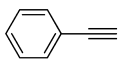
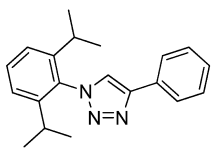
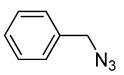
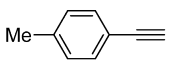
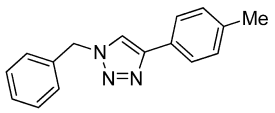
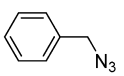
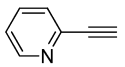
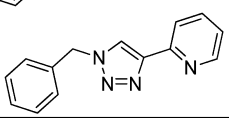
Table 2. The Substrate Scope of 6b-Catalyzed CuAAC Reactions[a]



entry	substrate	substrate	product	yield (%)[b]
1				100
2				91
3				97
4				93
5			 (60%) (40%)	97[c]
6				74
7				96[d]
8				25[d]
9				81
10				80

[a]Reaction conditions: azide 1.0 mmol, alkyne 1.1 mmol, **6b** 0.05 mol %, CH_3CN 3 mL, RT, 5 h. [b]Isolated yields. [c]Phenylacetylene 2.4 mmol. [d]Reaction time 10 h.

125.5, 123.6, 120.6, 119.9, 119.1, 116.3, 64.8. Anal. Calcd for $C_{36}H_{28}Cu_2F_{12}N_8P_2$: C, 43.69; H, 2.85; N, 11.32. Found: C, 43.87; H, 2.82; N, 11.31.

$[Cu_2(L3)_2](PF_6)_2$, ***3***. This complex was synthesized from $[HL3](PF_6)$ (90 mg, 0.20 mmol) and Cu powder (32 mg, 0.50 mmol). Yield: 89 mg (87%), red powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.24 (br, 2H), 8.18−8.79 (m, 12H), 7.84 (br, 2H), 7.61 (m, 2H), 3.80−3.91 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.03−1.08 (m, 4H, $NCH_2CH_2CH_2CH_3$), 0.65−0.73 (m, 4H, $NCH_2CH_2CH_2CH_3$), −0.01 (m, 6H, $NCH_2CH_2CH_2CH_3$). Anal. Calcd for $C_{38}H_{36}Cu_2F_{12}N_8P_2$: C, 44.67; H, 3.55; N, 10.97. Found: C, 44.84; H, 3.62; N, 10.65. No satisfactory ^{13}C NMR spectrum of **3** was obtained.

$[Cu_2(L4)_2](PF_6)_2$, ***4***. This complex was synthesized from $[HL4](PF_6)$ (86 mg, 0.20 mmol) and Cu powder (32 mg, 0.50 mmol). Yield: 90 mg (91%), red powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.22 (d, J = 8.4 Hz, 2H), 8.63 (d, J = 7.6 Hz, 2H), 8.55 (d, J = 8.8 Hz, 2H), 8.48 (s, 2H), 8.34 (d, J = 8.0 Hz, 2H), 8.23 (s, 2H), 8.17 (d, J = 8.4 Hz, 2H), 7.95 (s, 2H), 7.63 (dr, 2H), 4.52 (m, 2H), 1.23 (d, J = 4.8 Hz, 6H, CH_3), 1.02 (d, J = 4.8 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 178.4 (Cu-*C*), 150.3, 149.9, 142.4, 142.3, 141.4, 138.9,

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129.0, 127.8, 126.8, 126.6, 125.5, 120.8, 120.7, 120.0, 53.4, 22.6, 22.3. Anal. Calcd for $C_{36}H_{32}Cu_2F_{12}N_8P_2$: C, 43.51; H, 3.25; N, 11.28. Found: C, 43.51; H, 3.23; N, 11.08.

[Cu$_2$(L5)$_2$](PF$_6$)$_2$, **5**. This complex was synthesized from [HL5](PF$_6$) (90 mg, 0.20 mmol) and Cu powder (32 mg, 0.50 mmol). Yield: 52 mg (51%), red powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.26 (d, J = 8.8 Hz, 1.6H), 9.23 (d, J = 8.8 Hz, 1H), 8.83 (d, J = 8.4 Hz, 1.6H), 8.66 (d, J = 4.4 Hz, 1.6H), 8.61 (d, J = 8.4 Hz, 1H), 8.53−8.58 (m, 2.6H), 8.50 (s, 1H), 8.43 (d, J = 8.8 Hz, 1.6H), 8.35 (d, J = 9.2 Hz, 1.6H), 8.30 (d, J = 9.6 Hz, 2.6H), 8.18 (d, J = 4.4 Hz, 1H), 8.14 (d, J = 9.2 Hz, 1H), 8.08 (s, 1H), 7.89 (dd, J = 4.8 Hz, J = 4.4 Hz, 1.6H), 7.71 (s, 1.6H), 7.63 (dd, J = 4.8 Hz, J = 4.8 Hz, 1H), 1.39 (s, 9H), 0.80 (s, 14.4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 177.4 (Cu-*C*), 173.9 (Cu-*C*), 150.4, 150.1, 149.3, 148.3, 142.6, 142.0, 141.8, 141.3, 141.1, 139.1, 137.8, 129.3, 128.9, 128.5, 127.9, 127.3, 127.0, 126.5, 125.7, 125.6, 122.1, 121.5, 120.7, 120.3, 120.1, 57.7, 57.3, 29.8, 29.4. Anal. Calcd for $C_{38}H_{36}Cu_2F_{12}N_8P_2$: C, 44.67; H, 3.55; N, 10.97. Found: C, 44.73; H, 3.52; N, 11.14.

[Cu$_2$(L6)$_2$](PF$_6$)$_2$, ***6a***. This complex was synthesized from [HL6](PF$_6$) (102 mg, 0.20 mmol) and Cu powder (32 mg, 0.50 mmol). Yield: 89 mg (78%), red powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.28 (d, J = 8.0 Hz, 1H), 9.17 (d, J = 8.0 Hz, 1H), 8.96 (s, 1H), 8.83 (m, 2H), 8.73 (s, 1H), 8.53−8.65 (m, 4H), 8.46 (d, J = 8.4 Hz, 1H), 8.37 (d, J = 8.8 Hz, 1H), 8.32 (d, J = 8.4 Hz, 1H), 8.26 (d, J = 8.0 Hz, 1H), 7.92 (m, 2H), 7.86 (s, 1H), 7.65 (s, 1H), 6.89 (s, 1H), 6.51 (s, 1H), 6.13 (s, 1H), 5.85 (s, 1H), 2.09 (s, 3H), 1.66 (s, 3H), 1.59 (s, 3H), 1.57 (s, 3H), 1.48 (s, 3H), 0.39 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 181.2 (Cu-*C*), 177.6 (Cu-*C*), 150.3, 149.0, 148.5, 147.2, 142.1, 141.7, 141.4, 141.1, 138.9, 138.7, 138.3, 138.1, 135.4, 134.5, 134.0, 133.7, 133.1, 129.5, 129.3, 128.8, 128.7, 128.4, 127.7, 127.4, 126.9, 126.5, 125.9, 125.3, 124.6, 121.5, 121.0, 120.2, 118.7, 118.7, 20.2, 19.8, 17.1, 16.8, 16.7, 14.2. Anal. Calcd for $C_{48}H_{40}Cu_2F_{12}N_8P_2$: C, 50.31; H, 3.52; N, 9.78. Found: C, 50.23; H, 3.69; N, 10.16.

[Cu$_2$(μ-Cl)(L6)$_2$]Cl, ***6b***. This complex was synthesized from imidazolium salt [HL6]Cl (80 mg, 0.20 mmol) and Cu powder (32 mg, 0.50 mmol). Yield: 89 mg (96%), red powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.99 (m, 2H), 8.83 (m, 2H), 8.62 (m, 2H), 8.44 (s, 2H), 8.36 (m, 2H), 8.12 (m, 4H), 7.86 (m, 2H), 7.55 (s, 2H), 5.69 (s, 4H), 1.71 (s, 6H), 1.47 (s, 6H), 1.28 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 182.9 (Cu-*C*), 149.1, 148.2, 141.8, 141.3, 140.0, 136.8, 135.8, 133.9, 133.5, 128.9, 127.4, 126.5, 125.8, 124.4, 123.4, 121.8, 119.0, 118.9, 19.9, 17.4, 16.8. Anal. Calcd for $C_{48}H_{40}Cl_2Cu_2N_8$: C, 62.20; H, 4.35; N, 12.09. Found: C, 62.17; H, 4.50; N, 12.24.

[Cu$_2$(μ-Br)(L6)$_2$]Br, ***6c***. This complex was synthesized from [HL6]Br (89 mg, 0.20 mmol) and Cu powder (32 mg, 0.50 mmol). Yield: 95 mg (93%), red powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.00 (d, J = 8.8 Hz, 2H), 8.83 (d, J = 4.0 Hz, 2H), 8.62 (d, J = 7.6 Hz, 2H), 8.43 (s, 2H), 8.40 (d, J = 8.8 Hz, 2H), 8.17 (q, J = 8.8 Hz, 4H), 7.87 (dd, J = 4.8 Hz, J = 4.4 Hz, 2H), 7.55 (s, 2H), 5.70 (s, 4H), 1.71 (s, 6H, CH_3), 1.47 (s, 6H, CH_3), 1.28 (s, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 182.6 (Cu-*C*), 149.2, 148.3, 141.7, 141.1, 140.1, 136.8, 135.9, 135.8, 134.2, 133.6, 128.9, 127.5, 126.7, 126.6, 126.3, 125.9, 124.5, 123.5, 122.1, 119.2, 19.9, 17.7, 16.7. Anal. Calcd for $C_{48}H_{42}Br_2Cu_2N_8$: C, 56.64; H, 4.16; N, 11.01. Found: C, 56.51; H, 4.21; N, 11.14.

[Cu$_2$(μ-I)(L6)$_2$]I, ***6d***. This complex was synthesized from [HL6]I (99 mg, 0.20 mmol) and Cu powder (32 mg, 0.50 mmol). Yield: 108 mg (97%), red powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.00 (d, J = 8.8 Hz, 2H), 8.87 (s, 2H), 8.61 (d, J = 7.6 Hz, 2H), 8.39−8.46 (m, 4H), 8.18 (q, J = 8.8 Hz, 4H), 7.86 (dd, J = 4.8 Hz, J = 4.8 Hz, 2H), 7.56 (s, 2H), 5.71 (s, 2H), 5.68 (s, 2H), 1.72 (s, 6H, CH_3), 1.46 (s, 6H, CH_3), 1.27 (s, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 182.3 (Cu-*C*), 149.4, 148.5, 141.6, 140.8, 140.2, 136.9, 135.9, 135.7, 134.2, 133.6, 129.0, 127.7, 126.9, 126.6, 126.3, 125.9, 124.5, 123.6, 122.5, 119.4, 19.9, 17.7, 16.7. Anal. Calcd for $C_{48}H_{40}Cu_2I_2N_8$: C, 51.95; H, 3.63; N, 10.10. Found: C, 51.93; H, 3.77; N, 10.26.

[Cu$_2$(L7)$_2$](PF$_6$)$_2$, **7**. This complex was synthesized from [HL7](PF$_6$) (111 mg, 0.20 mmol) and Cu powder (32 mg, 0.50 mmol). Yield: 111 mg (90%), purple powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.35 (d, J = 8.4 Hz, 2H), 8.87 (d, J = 8.0 Hz, 2H), 8.73 (d, J = 8.8 Hz, 2H), 8.66 (s, 2H), 8.57 (d, J = 4.0 Hz, 2H), 8.50 (d, J = 8.8 Hz, 2H), 8.42 (d, J = 8.8 Hz, 2H), 7.95 (s, 2H), 7.91 (dd, J = 4.8 Hz, J = 4.8 Hz, 2H), 7.25 (t, J = 8.0 Hz, 2H), 7.13 (d, J = 7.6 Hz, 2H), 6.88 (d, J = 8.0 Hz, 2H), 1.79 (m, 2H, CH(CH$_3$)$_2$), 1.63 (m, 2H, CH(CH$_3$)$_2$), 1.00 (d, J = 6.4 Hz, 6H, CH_3), 0.24 (d, J = 6.4 Hz, 6H, CH_3), 0.05 (d, J = 6.8 Hz, 6H, CH_3), −0.61 (d, J = 6.0 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 177.6 (Cu-*C*), 148.7, 146.8, 145.0, 142.8, 142.0, 141.7, 138.2, 134.2, 130.0, 129.4, 127.6, 127.1, 126.8, 125.8, 124.3, 123.0, 121.8, 120.8, 27.5, 27.5, 23.8, 23.6, 22.7, 19.5. Anal. Calcd for $C_{55}H_{53.5}Cu_2F_{12}N_{8.5}P_2$ (**7**·0.5CH$_3$CN): C, 52.82; H, 4.31; N, 9.52. Found: C, 52.40; H, 4.32; N, 9.51.

[Cu$_2$(L8)$_2$](PF$_6$)$_2$, **8**. This complex was synthesized from [HL8](PF$_6$) (113 mg, 0.20 mmol) and Cu powder (32 mg, 0.50 mmol). Yield: 91 mg (73%), red powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.00 (d, J = 8.0 Hz, 2H), 8.59 (d, J = 8.0 Hz, 2H), 8.31 (d, J = 7.2 Hz, 2H), 8.20−8.26 (m, 4H), 8.12 (d, J = 8.8 Hz, 2H), 8.08 (d, J = 4.0 Hz, 2H), 7.99 (s, 2H), 7.62−7.69 (m, 4H), 7.23−7.29 (m, 6H), 7.04−7.13 (m, 4H), 5.25−5.34 (m, 4H), 5.21 (d, J = 16.0 Hz, 2H), 5.05 (d, J = 15.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 181.5 (Cu-*C*), 149.1, 148.9, 142.1, 141.6, 141.0, 140.9, 137.8, 135.1, 128.8, 128.6, 128.2, 127.8, 127.7, 126.7, 126.3, 125.1, 123.7, 119.6, 119.2, 52.8, 44.9. Anal. Calcd for $C_{54}H_{50}Cu_2F_{12}N_{14}O_2P_2$ (**8**·Et$_2$O·H$_2$O): C, 48.25; H, 3.75; N, 14.59. Found: C, 47.92; H, 3.45; N, 14.29.

[Cu$_2$(L9)$_2$](PF$_6$)$_2$, **9**. This complex was synthesized from [HL9](PF$_6$) (87 mg, 0.20 mmol) and Cu powder (32 mg, 0.50 mmol). Yield: 64 mg (65%), yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.20−9.26 (m, 4H), 8.73 (d, J = 8.0 Hz, 2H), 8.63 (d, J = 8.8 Hz, 2H), 8.56 (d, J = 4.4 Hz, 2H), 8.39 (d, J = 8.8 Hz, 2H), 8.25 (d, J = 8.4 Hz, 2H), 7.78 (dd, J = 4.8 Hz, J = 4.8 Hz, 2H), 5.48 (m, 2H, CH$_2$CH=CH$_2$), 4.62−4.85 (m, 8H, CH_2CH=CH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 181.0 (Cu-*C*), 150.7, 149.3, 145.7, 142.6, 142.3, 141.2, 138.9, 132.1, 129.1, 128.3, 127.3, 126.6, 125.6, 119.5, 119.0, 50.4. Anal. Calcd for $C_{34}H_{28}Cu_2F_{12}N_{10}OP_2$ (**9**·H$_2$O): C, 40.45; H, 2.80; N, 13.87. Found: C, 40.79; H, 2.53; N, 13.64.

[Cu$_2$(L10)$_2$(μ-MeCN)](PF$_6$)$_2$, **10**. This complex was synthesized from [HL10](PF$_6$) (97 mg, 0.20 mmol) and Cu powder (32 mg, 0.50 mmol). Yield: 110 mg (97%), red powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.36 (s, 2H), 9.20 (d, J = 8.8 Hz, 2H), 8.67 (q, J = 8.0 Hz, 4H), 8.46 (s, 2H), 8.36 (d, J = 8.8 Hz, 2H), 8.23 (d, J = 8.4 Hz, 2H), 7.75 (m, 2H), 6.80 (m, 4H), 6.55 (m, 6H), 5.39 (d, J = 14.8 Hz, 2H), 5.05 (d, J = 14.8 Hz, 2H), 2.06 (s, 3H, CH_3CN). ^{13}C NMR (100 MHz, DMSO-d_6): δ 180.1 (Cu-*C*), 150.5, 149.3, 146.1, 142.5, 142.0, 141.1, 138.8, 134.4, 129.1, 128.2, 127.8, 127.5, 127.2, 126.5, 125.5, 119.4, 117.9, 51.6, 1.0. Anal. Calcd for $C_{44}H_{33}Cu_2F_{12}N_{11}P_2$: C, 46.65; H, 2.94; N, 13.60. Found: C, 46.82; H, 2.84; N, 13.33.

[Cu$_3$(L11)$_4$(MeCN)$_2$](PF$_6$)$_3$, **11**. This complex was synthesized from [HL11](PF$_6$) (79 mg, 0.20 mmol) and Cu powder (32 mg, 0.50 mmol). Yield: 43 mg (51%), red powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.92−9.07 (m, 12H), 8.75−8.86 (m, 4H), 8.47−8.59 (m, 4H), 8.19−8.35 (m, 8H), 7.93−8.06 (m, 4H), 7.55−7.85 (m, 4H), 6.35−6.57 (m, 4H), 2.08 (s, 6H, CH_3CN). Anal. Calcd for $C_{64}H_{46}Cu_3F_{18}N_{18}P_3$: C, 45.41; H, 2.74; N, 14.89. Found: C, 45.64; H, 2.57; N, 14.76. A satisfactory ^{13}C NMR spectrum of **11** was not obtained.

[Cu(HL12)$_2$](PF$_6$)$_3$, **12**. This complex was synthesized from [HL12](PF$_6$) (90 mg, 0.20 mmol) and Cu powder (32 mg, 0.50 mmol). Yield: 85 mg (77%), red powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.27 (d, J = 5.6 Hz, 2H), 8.93−9.06 (m, 4H), 8.46−8.53 (m, 4H), 8.41 (d, J = 7.2 Hz, 2H), 8.07−8.19 (m, 2H), 7.59−7.68 (m, 2H), 6.71−6.83 (m, 2H), 5.46−5.64 (m, 2H, CH$_2$CH=CH$_2$), 5.28 (d, J = 10.0 Hz, 2H, CH$_2$CH=CH_2), 5.19 (d, J = 18.0 Hz, 2H, CH$_2$CH=CH_2), 4.23−4.55 (m, 4H, CH_2CH=CH$_2$), 3.33 (s, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 149.8, 145.3, 144.2, 142.4, 142.3, 142.0, 138.2, 129.8, 129.6, 128.8, 127.0, 126.7, 126.5, 123.1, 121.6, 120.7, 49.7, 9.8. Anal. Calcd for $C_{38}H_{34}CuF_{18}N_8P_3$: C, 41.45; H, 3.11; N, 10.18. Found: C, 41.39; H, 3.04; N, 10.32.

General Procedure for the Copper-Catalyzed CuAAC Reaction. Azide (1.0 mmol), alkyne (1.1 mmol), 3.0 mL of CH$_3$CN, and 200 μL of the CH$_3$CN solution of complex **6b** (2.5 × 10^{-3} M) were added to a 10 mL Schlenk with a magnetic stirrer bar.

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Then the mixture was stirred at RT under air for a required duration. H_2O (2 mL) and CH_2Cl_2 (10 mL) were added to the resultant mixture, and the organic layer was separated from the aqueous phase. The organic extract was dried over $MgSO_4$ and filtered. It was then concentrated under vacuum and purified by column chromatography (silica gel, petroleum ether/ethyl acetate, 3:1).

■ ASSOCIATED CONTENT

Supporting Information

Structural drawings of **2**, **4**, **5**, **6b**,**c**, **11**, and **12**; crystallographic data for **2**, **4**, **5**, **6a**−**d**, and **7**−**12** in CIF format; UV−vis absorption spectra; emission spectra; and CV data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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