EurJOC
European Journal of Organic Chemistry

A Journal of
ChemPubSoc Europe

Accepted Article

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To be cited as: *Eur. J. Org. Chem.* 10.1002/ejoc.201700523

Link to VoR: http://dx.doi.org/10.1002/ejoc.201700523

Supported by
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10.1002/ejoc.201700523

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Synthesis, structural characterization and catalytic activities of sulfur-functionalized NHC copper(I) complexes

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Abstract: The synthesis of a family of *N*-heterocyclic copper carbene complexes bearing sulfur moiety using different copper(I) halides and convenient route procedures have been reported. The solid state structures of presented copper compounds were elucidated using X-Ray crystallography. Next, obtained complexes were examined in various catalytic transformations including 1,3-dipolar cycloaddition of alkynes and azides, A^3 coupling reaction and β-hydroboration.

Introduction

A discovery of a first neutral copper carbene complex by Arduengo and Raubenheimer became the turning-point in the development of metal catalytic systems based of NHC ligands.[1] Since this disclosure, various complexes containing a metal centre and NHC moiety have been presented.[2] In particular, NHC complexes based on copper have proven to be important class of initiators in the organic synthesis.[3],[4] Studies on these compounds have shown, that modification of NHC ligand cause considerable differences in reactivity and may have profound impact on the performance of copper catalysts in various organometallic reactions.[5]

To date, numerous modifications of the NHC ligands with various substituents and heteroatoms have been reported.[6] However, the examples of copper complexes containing together "mixed" – alkyl and aryl moieties are still relatively rare in the literature.[7] This change in steric crowding of NHC ligand by replacement of one of the traditional functional group by less steric can influence on the catalyst activity. This trend has been already shown in case of other NHC metal complexes.[8] Based on these remarks, NHC copper complexes bearing this less bulkiness substituents are worth to explore and to examine in more detail.[9] Herein, we present our findings on the preparation of series of unsymmetrical NHC copper(I) complexes with a less constrained thioether ligand and screening of their catalytic activity in various transformations.

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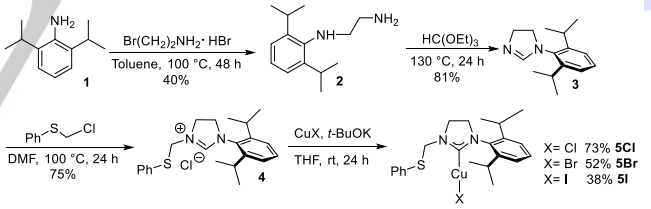
Results and Discussion

SYNTHESIS AND CATALYTIC ACTIVITY

The synthesis of sulfur-containing copper(I) NHC complexes followed the route presented on **Scheme 1**. At the beginning of our project, we focused on the examination of saturated NHC copper analogues containing a thioether chain. In the first two steps, the preparation of NHC precursor **4** relied on the application of the dihydroimidazole **3**, which was obtained according to the well-established procedures.[10] In third step, the treatment of compound **3** with an excess of (phenylthio)methyl chloride at elevated temperature allowed to obtain the expected NHC salt **4** with 75% yield (**Scheme 1**). Subsequently, the non-symmetrically sulfur-containing NHC precursor **4** was used in the direct preparation of the copper complexes. The treatment of the solution of carbene precursor **4** in THF with potassium *tert*-butoxide and in the presence of different copper(I) halides gave the NHC copper complexes: **5Cl**, **5Br** and **5I** as white powders (**Scheme 1**).

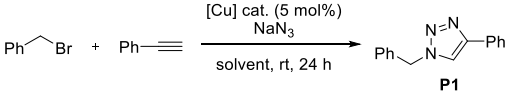


Scheme 1. Synthesis of new copper(I) complexes containing saturated NHC ligands with sulfur moiety.

The compounds bearing halogen atoms: chlorine (**5Cl**) and bromine (**5Br**) were isolated with acceptable yields: 73% and 52%, respectively. In contrary to **5Cl** and **5Br**, the iodo-derivative (**5I**) was obtained with poor yield (38%) and tended to decompose at fast rate. The structures of these three copper complexes were verified by ^{1}H and ^{13}C NMR measurements. Additionally, suitable single crystals of **5Cl** and **5Br** compounds for X-Ray diffraction studies were received by slow diffusion of *n*-pentane from concentrated solutions of these complexes in dichloromethane. The molecular structures of **5Cl** and **5Br** were presented subsequently, in the paragraph describing the crystallographic studies (**Figure 1** and **Figure 2**).

Having in hand, the NHC copper complexes containing sulfur moiety, we began the initial examination of their catalytic activity. As the model reaction, we chose three component click reaction of benzyl bromide, phenylacetylene and NaN_3 using 5 mol% of **5Cl**, **5Br** and **5I** in various solvents at room temperature (**Table 1**).[11], [12], [13]

Table 1. Activity of saturated NHC copper complexes containing sulfur moiety in CuAAC reaction in various solvents.

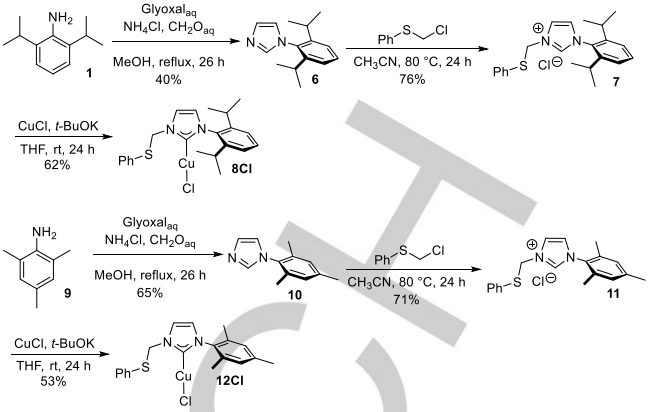


Entry	[Cu] cat.	Solvent	Yield of **P1**(%) [a]
1	**5Cl**	MeOH	73
2	**5Br**	MeOH	48
3	**5I**	MeOH	Traces
4	**5Cl**	DCM	32
5	**5Br**	DCM	Traces
6	**5I**	DCM	n. d.
7	**5Cl**	DMSO	18
8	**5Br**	DMSO	Traces
9	**5I**	DMSO	n. d.
10	**5Cl**	*n*-hexane	n. d.
11	**5Cl**	EtOAc	7
12	**5Cl**	THF	15
13	**5Cl**	Toluene	n. d.

[a] Reaction conditions: benzyl bromide **S1** (1.0 eq), phenylacetylene **S2** (1.2 eq), NaN_3 (1.2 eq), solvent (1 mL), 24 h.

Preliminary studies revealed that, obtained copper complexes with bromine (**5Br**) and iodine (**5I**) ions indicated considerably different activity compared to chlorine analogue (**5Cl**). Moreover, it turned out that among tested solvents, methanol was chosen as the best reaction media. After 24 hours of the conduction of 1,3-dipolar cycloaddition reaction of azides and alkynes in MeOH, the product **P1** was isolated with 73% yield using the catalyst **5Cl** (**Table 1**, entry 1). Replacement of the anionic ligand from chlorine to bromine resulted in much lower yield (48%) of the product **P1** (**Table 1**, entry 2). Finally, the iodo copper complex (**5I**) was inactive at applied conditions, probably due to its low stability (**Table 1**, entry 3). Other attempts to improve the catalytic performance of new complexes proved to be definitely ineffective in examined solvents such as: DCM, DMSO, EtOAc, THF, toluene and *n*-hexane (**Table 1**, entries 4-13).

Based on the initial activity results of the saturated NHC copper(I) complexes, we also decided to prepare unsaturated analogues containing chlorine ions, because the best activity and stability was observed for the copper compound (**5Cl**). The synthetic approach to unsaturated NHC copper(I) complexes **8Cl** and **12Cl** followed a straightforward strategy similar to the saturated derivatives (**Scheme 2**).



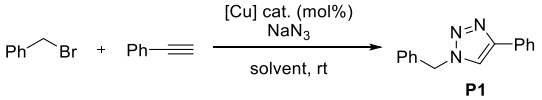
Scheme 2. Synthesis of new copper(I) complexes containing unsaturated NHC ligands with sulfur moiety.

The preparation of the complex **8Cl** consisted of three steps. At the first stage, the commercially available 2,6-diisopropylaniline **1** was converted into the 1-(2,6-diisopropylphenyl)-1*H*-imidazole **6** with 40% yield under standard conditions.[14] Next, the alkylation reaction of the product **6** using (phenylthio)methyl chloride under elevated temperature in dry acetonitrile resulted in the formation of the NHC precursor **7** with high yield (76%). Subsequently, the construction of sulfur-NHC copper complex **8Cl** was successfully accomplished by the treatment the ligand precursor **7** with potassium *tert*-butoxide in the presence of CuCl in THF at room temperature. The desired complex **8Cl** was provided with a good yield (62%).

In case of the synthesis of the unsaturated copper complex **12Cl**, the starting material was 2,4,6-trimethylaniline **9**, which was used in the first step to obtain 1-(2,4,6-trimethylphenyl)-1*H*-imidazole **10** (**Scheme 2**).[14],[15] Next, the imidazole derivative **10** was reacted with an excess of (phenylthio)methyl chloride to give the unsymmetrical salt **11** with 71% yield. In analogy to previous syntheses, the sulfur-functionalized NHC copper(I) complex **12Cl** was gained in the reaction with KO^{t}Bu and copper(I) chloride. The expected product **12Cl** was isolated with 53% yield. The complexes **8Cl** and **12Cl** were received as white powders and were fully characterized by spectral techniques. Moreover, the solid-state structure of the compound **8Cl** was elucidated using X-Ray crystallography analysis with the mixture of dichloromethane and *n*-pentane. More details about crystallographic data of **8Cl** can be found in the section on crystallographic studies (**Figure 1** and **Figure 2** and **Table 5**).

To expand more knowledge about properties of the unsaturated copper analogues with a thioether chain, we next examined their catalytic performance in three component click reaction. Obtained results were showed in **Table 2**.

Table 2. Effect of solvent and catalyst loading on CuAAC reaction.



Entry	[Cu] cat.	Mol (%)	Solvent	Yield of **P1**(%)

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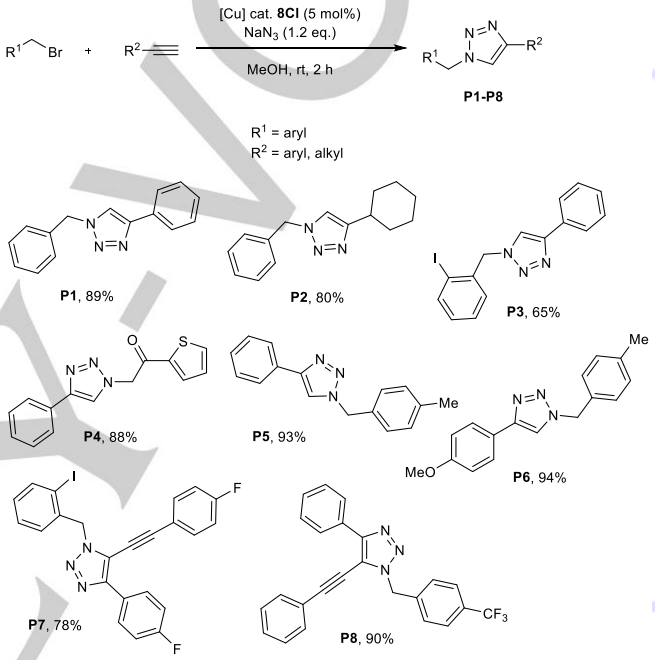
1	**8Cl**	5.0	MeOH	89[a]
2	**8Cl**	5.0	EtOH	82[a]
3	**8Cl**	5.0	DCM	41[a]
4	**8Cl**	5.0	DMSO	27[a]
5	**8Cl**	5.0	THF	n. d.[a]
6	**12Cl**	5.0	MeOH	74[a]
7	**8Cl**	2.0	MeOH	88[a]
8	**12Cl**	2.0	MeOH	72[a]
9	**8Cl**	1.0	MeOH	80[a]
10	**12Cl**	1.0	MeOH	68[a]
11	**5Cl**	2.0	MeOH	73[a]
12	**SIPrCuCl**	2.0	DMSO/Water	98[b]
13	**IPrCuCl**	5.0	Water/*t*-BuOH	18[c]
14	**IMesCuCl**	5.0	Water/*t*-BuOH	65[c]

[a] Reaction conditions: benzyl bromide (1.0 eq), phenylacetylene (1.2 eq), NaN_3 (1.2 eq), solvent (1 mL), rt, 24 h, isolated yields. [b] Reaction conditions: rt, 1 week, 60° C, 1 h, isolated yield. [c] Reaction conditions: rt, 18 h, isolated yields.

In analogy to the examination conducted for the saturated complexes with thioether NHC ligand (**5Cl**, **5Br** and **5I**), we first investigated the effect of various solvents using 5 mol% of compound **8Cl**. It was interesting to note, that the reaction proceeded well only in MeOH and EtOH (**Table 2**, entries 1 and 2), however the yield of product **P1** in methanol was slightly higher (89%). Continuing the study, low yields (41% and 27%) were observed for DCM and DMSO within 24 h (**Table 2**, entries 3 and 4). Moreover, in case of using THF as the reaction media, no product **P1** was detected (entry 5). When comparing the activity between unsaturated complexes **8Cl** and **12Cl**, higher yield of the product **P1** was isolated using the catalyst with 2,6-di*iso*propyl substituent (**Table 2**, entries 1 and 6). After selecting methanol as the best solvent, next studies were related to find out the optimal amount of unsaturated complexes for CuAAC reaction. Decreasing the amount of initiators: **8Cl** and **12Cl** from 5 mol% to 2 mol% led to obtain 1,4-disubstituted triazole **P1** with constantly high yields (88% and 72% respectively, **Table 2**, entries 7 and 8). However, further reduction in application of catalysts **8Cl** and **12Cl** to 1 mol% resulted in lower yields of the product **P1** (80% and 68%, **Table 2**, entries 9 and 10). At this stage, the optimal conditions to perform three component CuAAC reaction were designated as: 5 mol% of catalyst **8Cl** and the use of MeOH as the solvent of choice. To confirm eventually, which copper initiator bearing the thioether chain is the best performer for this transformation, we carried out one more control experiment to compare the reactivity of **8Cl** and **5Cl**. It turned out that using the unsaturated analogue with 2,6-diisopropyl substituent **8Cl**, the highest yield of 1,4-disubstituted triazole **P1** (89%, **Table 2**, entry 1) was determined, than the initiator **5Cl** (73%, **Table 2**, entry 11). In order to compare activity of new copper catalysts with standard NHC copper catalytic systems, we also presented examples of some results from literature in **Table 2** (entries 12-14).[5i],[12],[13] As can be seen, the standard NHC copper complexes were active in the mixture of polar solvents such as water/*t*-BuOH and DMSO/water. In some cases, high temperature and extension of reaction time were required to activate these catalysts to obtain the expected product **P1** (**Table 2**, entry 12).

To demonstrate the applicability of the **8Cl** catalyst we turned our attention into three component click reaction (**Scheme 3**). Series of varied benzyl bromides and alkynes were subjected to optimal reaction conditions described above. The final outcomes were presented in **Scheme 3**.



Scheme 3. Three component synthesis of various substituted triazoles catalyzed by **8Cl**.

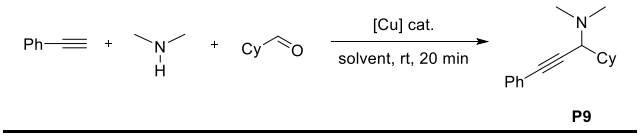
As shown, applied terminal alkynes and benzyl bromides in the presence of sodium azide can be transformed to the corresponding triazoles using the complex **8Cl** with good to high yields after 2 hours. In most cases, we isolated 1,4-disubstituted 1,2,3-triazoles as the only products (**Scheme 3**). These compounds **P1-P6** containing non-substituted and electron donating groups were obtained with very good yields (65-94%) (**Scheme 3**).

In contrary to these examples, for reactions of starting materials bearing electron withdrawing groups, we were surprised to observe exclusively the formation of 1,4,5-trisubstituted 1,2,3-triazoles **P7-P8** with high yields (78-90%). This observation might be the result of consecutive reactions: Glaser coupling and 1,3-dipolar cycloaddition. Such regioselective formation of different substituted 1,4,5-trisubstituted 1,2,3-triazoles was previously reported by Gerard et al.[16] The same outcome can be also explained by the fact that the complex **8Cl** may activate the 5-position in 1,4-disubstituted 1*H*-1,2,3-triazole, such as it has been shown in the publication by F. Alonso et al.[17]

To gain more information about activity of obtained copper complexes, we investigated their properties in another three

component transformation known as A^3 coupling reaction. Products of this multicomponent one-pot synthesis are suitable synthetic building blocks of amino derivatives.[18],[19],[20] In order to identify the best performing copper catalyst containing sulfur moiety, the model reaction was carried out including phenylacetylene and *N*,*N*-dimethylamine with cyclohexenecarboxaldehyde as starting materials (**Table 3**).

Table 3. Effects of solvent and catalysts loading on A^3 coupling reaction.



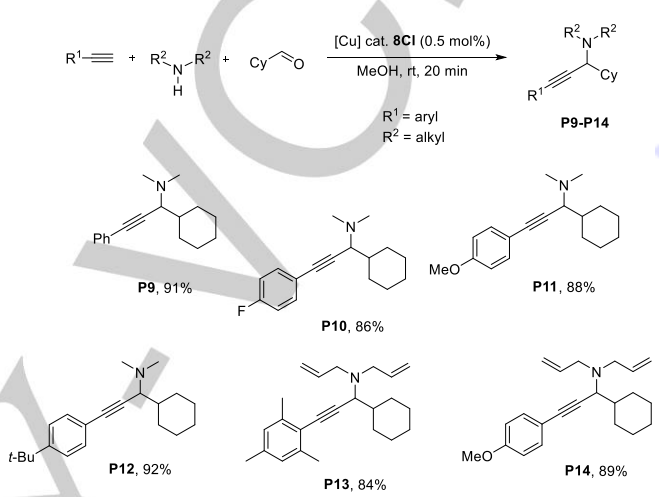
P9

Entry	[Cu] cat.	(mol %)	Solvent	Yield of **P9**(%)[a]
1	**8Cl**	1.0	DCM	Traces
2	**8Cl**	1.0	*n*-hexane	Traces
3	**8Cl**	1.0	Toluene	Traces
4	**8Cl**	1.0	DMSO	n. d.
5	**8Cl**	1.0	MeOH	89
6	**5Cl**	1.0	MeOH	70
7	**12Cl**	1.0	MeOH	81
8	**8Cl**	1.0	THF	28
9	**5Cl**	1.0	THF	5
10	**12Cl**	1.0	THF	16
11	**8Cl**	0.5	MeOH	91
12	**8Cl**	0.2	MeOH	76
13	**SIPrCuCl**	0.5	MeOH	90
14	**IPrCuCl**	0.5	MeOH	79
15	**IMesCuCl**	0.5	MeOH	8

[a] Reaction conditions: phenylacetylene (1.1 eq), *N*,*N*-dimethylamine (1.1 eq), cyclohexenecarboxaldehyde (1.0 eq), solvent (1 mL), 20 min, isolated yields.

The examination of optimal conditions for the synthesis of the propargylamine **P9** was held in the presence of three copper complexes: **5Cl**, **8Cl** and **12Cl**. Among tested solvents, methanol proved to be the most convenient reaction medium (**Table 3**, entries 1-10). The A^3 coupling reactions that were proceeded in DCM, DMSO, *n*-hexane and toluene have shown no formation of the expected product **P9** (**Table 3**, entries 1-4). Results of the reactions carried out in THF were also unsatisfactory (5-28%) (**Table 3**, entries 8-10). Finally, this search revealed that the initiator **8Cl** has been promoted studied transformation in the most efficient way to give the product **P9** with 91% yield (**Table 3**, entry 11). Subsequently, we investigated also the most suitable loading of the catalyst (**Table 3**, entries 11-12). For this propose, we conducted two more experiments using 0.5 mol% and 0.2 mol% of the complex **8Cl**. In both cases, these reactions proceeded smoothly to give the product **P9** in 91% and 76% yields, respectively. In **Table 3**, we also placed outcomes for the model A^3 coupling reaction, when standard NHC copper catalytic systems were applied. As can be seen from entries 13-15, the saturated complex SIPrCuCl was able to promote A^3 coupling reaction similarly well as the complex **8Cl** (90%), whereas unsaturated analogue IPrCuCl gave lower yield (79%). The complex IMesCuCl failed as the suitable catalyst of this transformation (yield 8%).

With the optimized conditions in hand for A^3 coupling reaction, the scope containing various propargylamines was presented on **Scheme 4**.

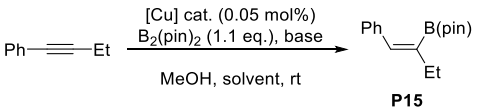


Scheme 4. Three component synthesis of substituted propargylamines catalyzed by **8Cl**.

As displayed on **Scheme 4**, the complex **8Cl** promoted A^3 coupling reaction smoothly in methanol, giving high yields for all six products **P9-P14** (84-92%). Using only 0.5 mol % of **8Cl**, electron-rich and electron-deficient alkynes were transformed into desired propargylamines in very short time (20 minutes) at room temperature. We also carried out some additional experiments of A^3 coupling reaction, when different benzaldehydes were used as substrates. Unfortunately, similarly to Wang and Navarro's studies, significant decrease in reactivity was observed, even in higher reaction temperatures (60° C) and extension of reaction time (3 days).[19] No expected products were identified in these reactions.

In a survey of catalytic activity of obtained copper complexes bearing a thioether chain, we also employed hydroboration reaction of triple and double bonds. Based on efficient methodology presented by Cazin's group, we followed their general conditions in our experiments (**Table 4**).[21]

Table 4. Study of NHC copper complexes in hydroboration reaction.



P15

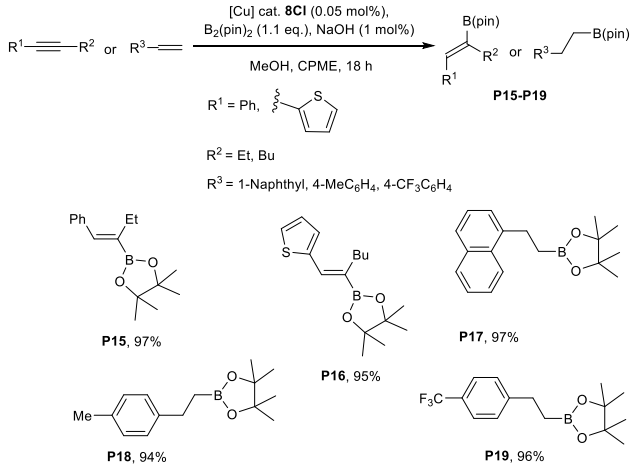
Entry	[Cu] cat.	Solvent	Yield of **P15**(%)

1	**5Cl**	CPME	93[a]
2	**8Cl**	CPME	97[a]
3	**12Cl**	CPME	96[a]
4	**IPrCuCl**	*i*-PrOH	34[b]
5	**IMesCuCl**	CPME	98[c]

[a] Reaction conditions: [Cu] cat. (0.05 mol%), $B_2(pin)_2$ (1.1 eq), NaOH (1 mol%), MeOH (0.1 mL), CPME (1 mL), 18 h, isolated yields, only *β* isomer was detected. [b] Reaction conditions: [Cu] cat. (0.04 mol%), $B_2(pin)_2$ (1.1 eq), NaO*t*-Bu (1 mol%), MeOH (0.18 mL), *i*-PrOH (2.4 mL), 16 h, isolated yields. [c] Reaction conditions: [Cu] cat. (0.04 mol%), $B_2(pin)_2$ (1.1 eq), NaOH (5 mol%), MeOH (0.05 mL), CPME (0.6 mL), 16 h, isolated yield.

For the evaluation step as representative substrate, we used 1-phenyl-1-butyne as the benchmark substrate. At 0.05 mol% catalysts loading, we compared the three NHC copper catalyst containing sulfur moiety (**5Cl**, **8Cl** and **12Cl**) with activity data from literature for well-known copper systems (IPrCuCl and IMesCuCl) (**Table 4**).[21] As shown, in most cases, the product **P15** was formed in very good yields (93-98%) and with high regioselectivity. Only one exception was revealed in entry 4, when Cazin's group used *i*-PrOH as the reaction media (34% yield).[21] The β-hydroboration reaction proceeded well in air using the green solvent CPME and 1 mol% of NaOH. These mild conditions were applied for further examination. All novel examples of NHC copper(I) complexes with a thioether ligand were very efficient in hydroboration reaction, however the highest performance was noticed for initiator **8Cl** (**Table 4**, entry 2).

Based on the initial results presented in **Table 4**, we continued the scope of hydroboration using few examples of alkynes and alkenes (**Scheme 5**).



Scheme 5. Hydroboration reaction of alkynes and alkenes catalyzed by **8Cl**.

This methodology gave good outcomes in the presence of various groups including phenyl (**P15**, 97%), naphthyl (**P17**, 97%), heterocyclic (**P16**, 95%), electron donating substituent (**P18**, 94%) and electron withdrawing substituent (**P19**, 96%) (**Scheme 5**). Furthermore, the compounds **P15** and **P16** were isolated as the only isomers, what emphasizes good regioselectivity and high functionality tolerance of NHC copper complex containing sulfur moiety **8Cl** similar to well-known copper NHC catalytic systems.

CRYSTALLOGRAPHIC STUDIES

Investigated copper compounds form monoclinic crystals in *Cc* (**8Cl**) or $P2_1/c$ (**5Cl** and **5Br**) space group with one molecule in the asymmetric unit of the crystal lattice (**Figure 1** and **Figure 2**). The crystallographic data and selected bond lengths and valence angles are presented in **Table 5**.

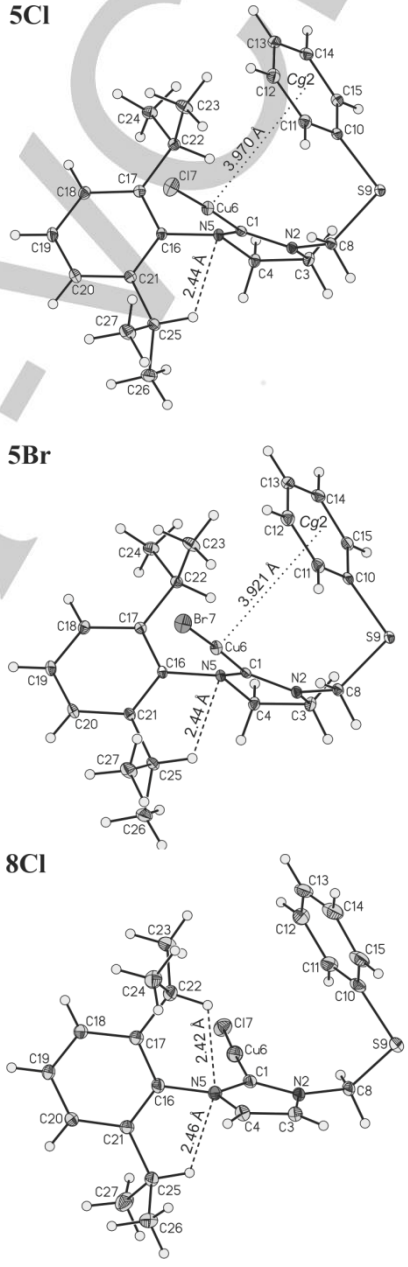


Figure 1. The molecular structure of **5Cl**, **5Br** and **8Cl** – showing the atom labelling scheme. Displacement ellipsoids are drawn at the 25% probability level and H-atoms are shown as small spheres of arbitrary radius. The hydrogen bonds and Cu···π interactions are respectively represented by dashed and dotted lines. *Cg*2 represents the centre of gravity of the C10–C15 aromatic ring.

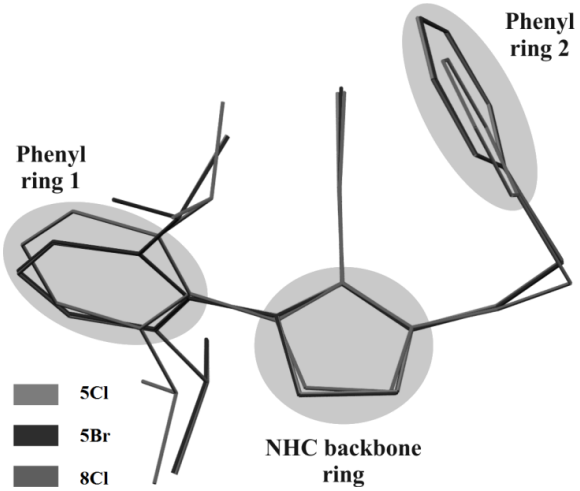


Figure 2. Structural alignment of **5Cl**, **5Br** and **8Cl** (hydrogen atoms were omitted for clarity).

All three complexes have two-coordinated copper(I) center in a near linear environment. The value of C–Cu–X angle lies in the range of 175.7(2)–176.6(1)º. The C–Cu and Cu–X bond lengths are ranging 1.883(2)–1.893(6) and 2.098(2)–2.216(1) Å, respectively (**Table 5**). Above-mentioned values quite well correspond with those observed in similar (NHC)CuX systems.[12],[13]

Compounds **5Cl** and **5Br** are isostructural, whereas **8Cl** indicates observable change of the ligand geometry. This phenomenon is caused by the appearing of a double bond in the NHC backbone ring, which is manifested by increasing of the angles between mean-square planes delineated by the non-hydrogen atoms of phenyl rings and NHC backbone (**Figure 1**). In case of **5Cl** and **5Br** planes of respective phenyl rings are inclined to the NHC backbone by the angles of approximately 77º (ring 1) and 55º (ring 2).

In **8Cl** both phenyl rings are more twisted – respective angles for ring 1 and 2 are ca. 88º and 64º. The above-described mutual arrangement has an impact on the occurrence of intramolecular interactions. In case of **8Cl** the structure is stabilized by two intramolecular C–H···N hydrogen bonds, whereas in **5Cl** and **5Br** there is only one interaction of this type. However specific substituent arrangement in **5Cl** and **5Br** promotes appearance of the Cu··· π interaction, which is not observed in **8Cl** (**Figure 2**).

Table 5. Selected bond lengths and angles of **5Cl**, **5Br** and **8Cl**.

	5Cl	5Br	8Cl
Cu6-X7 [Å]	2.105(4)	2.216(1)	2.098(2)
Cu6-C1 [Å]	1.883(2)	1.885(2)	1.893(6)
C1-N2 [Å]	1.340(2)	1.341(3)	1.349(7)
N2-C8 [Å]	1.441(2)	1.444(3)	1.460(7)
C8-S9 [Å]	1.826(1)	1.829(2)	1.801(5)
C1-N5 [Å]	1.343(2)	1.344(3)	1.347(6)
N5-C16 [Å]	1.439(2)	1.442(3)	1.438(7)
C3-C4 [Å]	1.530(2)	1.530(3)	1.355(9)
N2-C1-N5 [°]	108.1(1)	108.1(2)	105.4(4)
Cu6-C1-N2 [°]	125.1(9)	127.1(2)	126.3(4)
C10-S9-C8 [°]	100.4(6)	100.4(1)	101.0(3)
C1-Cu-X7 [°]	176.6(1)	176.1(7)	175.7(2)

Conclusions

In summary, we have presented an easily-prepared and active copper catalytic systems containing a thioether chain. The preparation of novel family of NHC copper analogues was consisted of three to four steps and used readily available reagents. This class of sulfur-functionalized non-symmetrical copper(I) NHC complexes were fully characterized and tested in three various transformations. X-Ray measurements revealed typical bond lengths and valence angles for standard (NHC)CuX systems. Moreover, in the structure of copper analogue **8Cl** was observed additional interaction involving two intra molecular C–H···N hydrogen bonds. Based on activity examinations, unsaturated complex **8Cl** with a 2,6-diisopropylphenyl substituent displayed the best catalytic performance in three component click reaction, A^3 coupling and hydroboration in air. This copper complex proved to be an efficient catalyst with enhanced stability properties and a good activity profile. Further research on NHC copper complexes bearing sulfur moiety will be demonstrated and reported in due course.

Experimental Section

The procedure for the preparation of compound 2: In the flask, to the solution of 2,6-diisopropylaniline **1** (20 mL, 0.11 mol) in toluene (20 mL) was added 2-bromoethylamine hydrobromide. The reaction mixture was refluxed at 100 °C for 48 hours. After the completion of reaction, the mixture was cooled to rt and poured into a solution of 2M KOH (100 mL). The residue was extracted with Et_2O (2 x 80 mL), and then dried over anhydrous $MgSO_4$. After concentration by evaporation the resulting compound **2** was purified by column chromatography. The product **2** was obtained as dark-brown oil in 40% yield (18.9 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12–7.01 (m, 3H), 3.37–3.24 (m, 2H), 2.99–2.89 (m, 4H), 1.30–1.19 (m, 12H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 123.7, 123.5, 54.1, 42.5, 27.6, 24.3, 24.3 ppm. Spectroscopic data for the compound **2** were consistent with the previously reported ones.[9]

The procedure for the preparation of compound 3: An argon flushed flask was charged with the appropriate diamine **2** (10 g; 45 mmol) and triethyl orthoformate (28 mL, 167 mmol) and *p*-toluenesulfonic acid (0.16 g). The reaction was carried out at 130 °C under argon atmosphere and monitored by TLC (dichloromethane/methanol, v/v = 20:1). After completion of the reaction, the mixture was cooled, dissolved in water (50 mL) and extracted with Et_2O (2 x 35 mL). The combined organic phases were dried over anhydrous magnesium sulfate and the solvent was evaporated under the reduced pressure. The resulting compound **3** was purified by column chromatography using dichloromethane/methanol (v/v = 20:1) as eluent to give the brown solid in 81% yield (7.9 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.19 (dd, *J* = 15.6, 7.7 Hz, 2H), 6.96 (s, 1H), 4.08 (t, *J* = 10.4, 1.6 Hz, 2H), 3.66–3.57 (m, 2H), 3.13–2.98 (m, 2H), 1.30–1.08 (m, 12H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 148.2, 128.9, 128.7, 125.9, 124.7, 124.2, 51.7, 28.4, 28.2, 24.9, 24.1 ppm. Spectroscopic data for the compound **2** were consistent with the previously reported ones.[21]

The procedure for the preparation of compound 6: 2,6-Diisopropylaniline **1** (8.9 g, 9.4 mL, 50 mmol) and 30% glyoxal (8 mL) were stirred in methanol (45 mL) at room temperature, for 24 h. Next, ammonium chloride (5.4 g), 37% solution of formaldehyde (8 mL) and methanol (200 mL) were added the reaction mixture and refluxed for 1 h. Subsequently, a solution of 85% H_3PO_4 (7 mL) was added the reaction mixture and refluxed for another 1 h. The reaction was monitored by TLC (*n*-hexane/ethyl acetate, v/v = 1:1). After completion of reaction the solvent was evaporated. The reaction mixture was poured into 300 g of crushed ice and 40% solution of KOH was gradually added until the pH = 9. The resulting mixture was extracted with Et_2O (5 x 75 mL). The collected organic layers were dried over anhydrous $MgSO_4$. After concentration by evaporated under the reduced pressure, the crude product was purified by column chromatography (*n*-hexane/ethyl acetate, v/v = 1:1). The product **6** was obtained as a dark brown solid in 40% yield (4.55 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49–7.36 (m, 2H), 7.28–7.14 (m, 3H), 3.44 (s, 1H), 2.45–2.32 (m, 2H), 1.11 (d, *J* = 6.9 Hz, 12H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 146.5, 129.8, 129.4, 123.7, 122.8, 28.1, 24.4, 24.3 ppm. Spectroscopic data for the compound **6** were consistent with the previously reported ones.[22]

The procedure for the preparation of compound 10: 2,4,6-trimethylaniline **9** (6.8 g, 7.0 mL, 50 mmol) and 30% glyoxal (8.1 mL) were placed into a round bottom flask and were stirred in methanol (30 mL) at room temperature for 24 h. Next, ammonium chloride (5.4 g), 37% solution of formaldehyde (8 mL) and methanol (200 mL) were transferred to the flask and refluxed for 1 h. After this time, 85% solution of H_3PO_4 (7 mL) was added to the reaction mixture and was refluxed for another 1 h. The reaction was monitored by TLC (*n*-hexane/ethyl acetate, v/v = 1:1). After completion of reaction the solvent was evaporated. The reaction mixture was poured into 300 g of crushed ice and 40% solution of KOH was gradually added until the pH = 9. The resulting mixture was extracted with Et_2O (5 x 75 mL). The collected organic layers were dried over anhydrous $MgSO_4$. After concentration by evaporated under the reduced pressure the crude product was purified by column chromatography (*n*-hexane/ethyl acetate, v/v = 1:1) to give yellow solid (65%, 6.0 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (t, *J* = 1.0 Hz, 1H), 7.22 (t, *J* = 1.1 Hz, 1H), 7.00–6.92 (m, 2H), 6.88 (t, *J* = 1.2 Hz, 1H), 2.33 (s, 3H), 1.98 (s, 6H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 138.8, 137.5, 135.4, 133.4, 129.5, 128.9, 120.0, 28.1, 21.0, 17.3 ppm. Spectroscopic data for the compound **10** were consistent with the previously reported ones.[23],[24]

The procedure for the preparation of compound 4: To the solution of compound **3** (0.7 g, 3 mmol) in dry DMF (4 mL), chloromethyl phenyl sulfide (0.5 g, 0.4 mL, 3.2 mmol) was slowly added at room temperature. The reaction was conducted at 100 °C under an inert atmosphere and was monitored by TLC (dichloromethane/methanol, v/v = 9:1). After completion of the reaction, the solvent was evaporated and the resulting compound **4** was purified by column chromatography (dichloromethane/methanol, v/v = 9:1). The product **4** was obtained as a dark brown oil which slowly crystallized at low temperature (5 °C) in 75% yield (0.85 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.73–7.68 (m, 2H), 7.40–7.28 (m, 4H), 7.14 (d, *J* = 7.8 Hz, 2H), 5.75 (s, 2H), 4.32 (d, *J* = 11.6 Hz, 2H), 4.03 (d, *J* = 11.6 Hz, 2H), 2.51 (m, 2H), 1.13 (dd, *J* = 11.7, 6.8 Hz, 12H) ppm; ^{13}C{1H} NMR (101 MHz, CD_2Cl_2): δ 159.4, 146.3, 131.8, 131.0, 130.5, 129.7, 129.5, 128.3, 124.8, 52.9, 51.5, 28.6, 24.7, 23.9 ppm; HRMS-ESI (m/z) calcd for $C_{22}H_{28}N_2S$ [M–H–Cl]$^+$: 353.2046, found 353.2045; IR (diamond tip): v 2963, 1673, 1620, 1440, 1345, 1265, 805, 745, 479, 421 cm^{-1}.

The procedure for the preparation of compound 7: A 25 mL flask, was charged with compound **6** (2 g, 0.0087 mol) and chloromethyl phenyl sulfide (1.45 g; 1.2 mL; 0.009 mol) then dry DMF (6 mL) was added. The reaction was carried out at 100 °C under an inert atmosphere The reaction was monitored by TLC (dichloromethane/methanol v/v = 9:1). After completion of reaction the solvent was evaporated, the resulting compound **7** was purified by column chromatography (dichloromethane/methanol, v/v = 9:1). Then crystallisation was carried out with dichloromethane/*n*-pentane. The product was obtained as a dark brown solid in 76% yield (2.65 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.48 (s, 1H), 7.88 (br, 1H), 7.70–7.65 (m, 2H), 7.50–7.40 (m, 1H), 7.38–7.27 (m, 3H), 7.25–7.18 (m, 2H), 6.39 (s, 2H), 1.96 (dd, *J* = 13.5, 6.8 Hz, 2H), 1.05 (dd, *J* = 25.7, 6.8 Hz, 12H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 145.2, 139.0, 132.0, 131.8, 129.9, 129.7, 129.6, 128.7, 124.6, 124.0, 122.0, 52.8, 28.5, 24.3, 24.1 ppm; HRMS-ESI (m/z) calcd for $C_{22}H_{26}N_2S$ [M–H–Cl]$^+$: 351.1889, found 351.1888; IR (diamond tip): v 2964, 2868, 1669, 1544, 1459, 1438, 1386, 1365, 1294, 1178, 1112, 1064, 1025, 930, 810, 748, 691, 672, 633, 558, 493, 461 cm^{-1}. M. p. = 185.6 °C

The procedure for the preparation of compound 11: A Schlenk flask was charged with compound **10** (2 g, 0.0087 mol) and chloromethyl phenyl sulfide (1.45 g; 1.2 mL; 0.009 mol). Next, dry DMF (6 mL) was added to the reaction mixture. The reaction was carried out at 100 °C under an argon atmosphere and was monitored by TLC (dichloromethane/methanol v/v = 9:1). After completion of reaction the solvent was evaporated and the resulting compound **11** was purified by column chromatography (dichloromethane/methanol, v/v = 9:1). Then, crystallisation was carried out with dichloromethane/*n*-pentane. The product was obtained as a yellow solid in 71% yield (2.67 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.33 (s, 1H), 7.81–7.79 (m, 1H), 7.60–7.55 lub 7.57 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.34–7.20 (m, 4H), 7.05 (s, 2H), 6.88 (d, *J* = 0.5 Hz, 2H), 6.29 (s, 2H), 2.26 (s, 2H), 1.79 (s, 6H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 141.3, 138.7, 134.1, 132.5, 130.4, 129.8, 129.7, 128.2, 123.1, 122.05, 53.0, 21.0, 17.3 ppm; HRMS-ESI (m/z) calcd for $C_{19}H_{20}N_2S$ [M–H–Cl]$^+$: 309.1420, found 309.1427; IR (diamond tip): v 2970, 2919, 1557, 1544, 1482, 1438, 1199, 1159, 1103, 1066, 1023, 890, 859, 766, 745, 693, 670, 627, 580, 555, 485, 444 cm^{-1}. M. p. = 182–185 °C

The procedure for the preparation of copper complex 5Cl: A dry and argon flushed a Schlenk flask was charged with copper(I) chloride (0.14 g; 1.4 mmol), 1-(2,6-di*i*sopropylphenyl)-3-((phenylthio)methyl)imidazolinium chloride **4** (0.5 g; 1.3 mmol), and potassium *tert*-butoxide (0.15 g; 1.4 mmol), then was added dry THF (20 mL). The mixture was stirred for 20 h at room temperature under an inert atmosphere of argon. The reaction was monitored by TLC (*n*-hexane/ethyl acetate, v/v = 1:1 and 7:3). After completion of reaction the solvent was evaporated. The crude product was purified by column chromatography (*n*-hexane/ethyl acetate, v/v = 1:1). Then crystallization from dichloromethane/*n*-pentane was carried out to give the complex **5Cl** as an white solid in 73% yield (0.43 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.56 (m, 2H), 7.43–7.26 (m, 4H), 7.11 (m, 2H), 5.17 (s, 2H), 3.97–3.88 (m, 2H), 3.77–3.67 (m, 2H), 2.62–2.49 (m, 2H), 1.13 (dd, *J* = 10.6, 6.9 Hz, 12H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$):

δ 146.4, 134.0, 133.2, 130.7, 129.8, 129.7, 128.6, 124.5, 56.0, 54.0, 46.5, 28.2, 25.3, 24.2 ppm; HRMS-ESI (m/z) calcd for $C_{22}H_{28}N_2SCu$ $[M–H–Cl]^+$: 415.1264, found 415.1251; IR (diamond tip): v 2951, 2921, 2862, 1674, 1584, 1484, 1471, 1447, 1411, 1383, 1362, 1340, 1315, 1265, 1238, 1216, 1184, 1099, 1056, 1023, 935, 906, 888, 847, 806, 765, 751, 704, 695, 647, 613, 594, 560, 527, 493, 466 cm^{-1}.

The procedure for the preparation of copper complex 8Cl: In a dry and argon flushed a Schlenk flask were placed copper(I) bromide (0.059 g; 0.41 mmol), 1-(2,6-diisopropylphenyl)-3-((phenylthio)methyl)imidazolinium chloride **4** (0.15 g; 0.39 mmol), and potassium *tert*-butoxide (0.046 g; 0.41 mmol). To these was added dry THF (6 mL). The mixture was stirred for 20 h at room temperature under an inert atmosphere of argon. The reaction was monitored by TLC (*n*-hexane/ethyl acetate, v/v = 1:1 and 7:3). After completion of reaction the solvent was evaporated. The crude product was purified by column chromatography (*n*-hexane/ethyl acetate, v/v = 1:1). Then was carried out crystallization from dichloromethane/*n*-pentane to give the complex **5Br** as an off-white solid in 52% yield (0.1 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.47 (m, 2H), 7.31–7.23 (m, 3H), 7.19 (ddd, *J* = 8.5, 6.4, 1.8 Hz, 1H), 7.13 (d, *J* = 7.7 Hz, 2H), 4.90 (s, 2H), 3.69–3.61 (m, 2H), 3.58–3.49 (m, 2H), 2.79 (dt, *J* = 13.7, 6.9 Hz, 2 H), 1.14 (dd, *J* = 13.6, 6.9 Hz, 12H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 146.4, 133.9, 133.2, 130.6, 129.8, 129.7, 128.6, 124.5, 55.9, 54.0, 46.5, 28.2, 25.3, 24.2 ppm; HRMS-ESI (m/z) calcd for $C_{22}H_{28}N_2SCu$ $[M–H–Br]^+$: 415.1264, found 415.1273; IR (diamond tip): v 2920, 1677, 1580, 1485, 1473, 1449, 1381, 1360, 1313, 1264, 1236, 1215, 1188, 1095, 1055, 1021, 932, 901 , 843, 805, 762, 753, 695, 648, 594, 561, 528 cm^{-1}.

The procedure for the preparation of copper complex 5I: In a dry and argon flushed a Schlenk flask were placed copper(I) iodine (0.077 g; 0.41 mmol), 1-(2,6-diisopropylphenyl)-3-((phenylthio)methyl)imidazolinium chloride **4** (0.15 g; 0.39 mmol), and potassium *tert*-butoxide (0.045 g; 0.41 mmol). To these was added dry THF (6 mL). The mixture was stirred for 20 h at room temperature under an inert atmosphere of argon. The reaction was monitored by TLC (*n*-hexane/ethyl acetate, v/v = 1:1 and 7:3). After completion of reaction the solvent was evaporated. The crude product was purified by column chromatography (*n*-hexane/ethyl acetate, v/v = 1:1). Then, the crystallization was carried out using dichloromethane/*n*-pentane as solvents to give the complex **5I** as a yellowish solid in 38% yield (0.074 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57–7.46 (m, 2H), 7.32–7.23 (m, 3H), 7.22–7.16 (m, 2H), 7.13 (d, *J* = 7.7 Hz, 2H), 4.90 (s, 2H), 3.70–3.60 (m, 2H), 3.58–3.48 (m, 2H), 2.79 (dt, *J* = 13.7, 6.9 Hz, 2H), 1.14 (dd, *J* = 13.6, 6.9 Hz, 12H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 148.0, 134.1, 133.0, 130.5, 129.0, 128.7, 126.7, 124.0, 49.3, 46.0, 41.2, 28.4, 24.5, 24.2 ppm; IR (diamond tip): v 2950, 2918, 2855, 1673, 1584, 1485, 1473, 1445, 1342, 1310, 1263, 1236, 1215, 1182, 1054, 935, 886, 848, 801, 764, 746, 695, 667, 614, 550, 515, 465 cm^{-1}.

The procedure for the preparation of copper complex 5Br: In dry and argon flushed Schlenk flask were placed copper(I) chloride (0.14 g; 1.4 mmol), ligand precursor **7** (0.5 g; 1.3 mmol), potassium *tert*-butoxide (0.16 g; 1.4 mmol). All reagents were dissolved in dry THF (20 mL). The mixture was stirred for 20 h at room temperature under argon atmosphere. The reaction was monitored by TLC (*n*-hexane/ethyl acetate, v/v = 7:3). After completion of the reaction the solvent was evaporated. The crude product was purified by column chromatography (*n*-hexane/ethyl acetate, v/v = 7:3). Subsequently, the crystallization from dichloromethane/*n*-pentane was carried out to give the complex **8Cl** as a white solid in 62% yield (0.38 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.05 (m, 10H), 6.85 (d, *J* = 1.8 Hz, 1H), 5.57 (s, 2H), 2.20–2.00 (m, 2H), 1.07 (dd, *J* = 28.8, 6.9 Hz, 12H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 145.5, 134.1, 133.2, 130.4, 130.0, 129.6, 129.0, 124.3, 124.1, 119.6, 55.4, 28.1, 24.5, 24.2 ppm; HRMS-ESI (m/z) calcd for $C_{22}H_{26}N_2SCu$ $[M–H–Cl]^+$: 413.1107, found 413.1112; IR (diamond tip): v 2965, 1459, 1405, 1284, 1245, 1221, 1177, 1057, 810, 769, 748, 707, 692, 491 cm^{-1}.

The procedure for the preparation of copper complex 12Cl: Under an atmosphere of argon imidazolium salt **11** (0.5 g; 1.45 mmol) and potassium *tert*-butoxide (0.17 g; 1.52 mmol) were dissolved dry THF (20 mL). Next, copper(I) chloride (0.15 g; 1.52 mmol) was added to the reaction. The mixture was stirred for 20 h at room temperature under an atmosphere of argon. The reaction was monitored by TLC (*n*-hexane/ethyl acetate, v/v = 7:3). After completion of reaction the solvent was evaporated. The crude product was purified by column chromatography (*n*-hexane/ethyl acetate, v/v = 7:3). Then crystallization was carried out using mixture of solvents: dichloromethane/*n*-pentane to give the complex **12Cl** as a white solid in 53% yield (0.32 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85–7.15 (m, 5H), 6.88 (s, 2H), 5.57 (s, 2H), 6.40 (bs, 1H), 6.08 (bs, 1H), 5.52 (bs, 1H), 5.08 (bs, 1H), 2.27 (bs, 3H), 2.10–1.55 (m, 6H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 151.5, 133.6, 131.7, 129.7, 129.6, 129.3, 129.1, 129.0, 121.1, 109.9, 47.0, 21.0, 17.8, 17.6 ppm; IR (diamond tip): v 2916, 2848, 1685, 1486, 1472, 1438, 1405, 1233, 1213, 1022, 851, 741, 729, 710, 692, 656, 584, 489, 480 cm^{-1}.

Typical procedure for the three component CuAAC reaction: Organic halide (0.013 mmol, 1.0 eq), NaN_3 (1.2 mmol), alkyne (0.16 mmol, 1.2 eq.), the appropriate copper complex (5 mol%) and solvent (1 mL) were introduced to the vial fitted with a screw cap. The reaction was carried out at room temperature for 2 h and controlled by TLC (*n*-hexane/ethyl acetate, v/v = 7:3). After completion of the reaction, the solvent was evaporated. The crude product was purified by column chromatography (*n*-hexane/ethyl acetate, v/v = 8:2). The isolated product was dried under vacuum.

1-benzyl-4-phenyl-1*H*-1,2,3-triazole, **P1**, white solid, yield 89%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83–7.75 (m, 2H), 7.65 (s, 1H), 7.46–7.34 (m, 5H), 7.33–7.27 (m, 3H), 5.57 (s, 2H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 148.2, 134.6, 130.5, 129.1, 128.8, 128.1, 125.7, 119.4, 54.2 ppm. Spectroscopic data for the compound **P1** were consistent with the previously reported ones.[25]

1-benzyl-4-cyclohexyl-1*H*-1,2,3-triazole, **P2**, light-yellow solid, yield 80%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.28 (m, 3H), 7.26–7.22 (m, 2H), 7.13 (s, 1H), 5.47 (s, 2H), 2.72 (m, 1H), 2.05–1.97 (m, 2H), 1.81–1.64 (m, 3H), 1.43–1.28 (m, 4H), 1.26–1.15 (m, 1H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 154.2, 135.0, 128.5, 128.0, 119.1, 54.0, 35.3, 33.0, 26.1 ppm. Spectroscopic data for the compound **P2** were consistent with the previously reported ones.[26]

1-(2-iodobenzyl)-4-phenyl-1*H*-1,2,3-triazole, **P3**, light-yellow solid, yield 65%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.84–7.78 (m, 2H), 7.76 (s, 1H), 7.43–7.37 (m, 2H), 7.36–7.28 (m, 2H), 7.12 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.08–7.02 (m, 1H), 5.66 (s, 2H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 148.1, 139.9, 137.4, 130.4, 129.6, 129.1, 128.8, 128.2, 125.7, 119.8, 98.6, 58.5 ppm. Spectroscopic data for the compound **P3** were consistent with the previously reported ones.[27]

4-phenyl-1-(2-(thiophen-2-yl)ethan-2-on-1-yl)-1*H*-1,2,3-triazole, **P4**, yellow solid, yield 88%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.89–7.83 (m, 3H), 7.79 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.45–7.40 (m, 2H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.22 (dd, *J* = 5.0, 3.9 Hz, 1H), 5.78 (s, 2H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 183.2, 146.7, 135.9, 133.2, 131.0, 128.8 (d, *J* = 7.2 Hz), 128.3, 125.8, 121.2, 119.8, 104.1, 55.4 ppm. Spectroscopic data for the compound **P4** were consistent with the previously reported ones.[28]

1-(4-methylbenzyl)-4-phenyl-1*H*-1,2,3-triazole, **P5**, yellow solid, yield 93%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.74 (m, 2H), 7.62 (s, 1H), 7.38 (ddd, *J* = 6.4, 1.3 Hz, 2H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.22–7.15 (m, 4H), 5.51 (s, 2H), 2.35 (s, 3H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 148.1, 138.7, 131.6, 130.6, 129.8, 128.8, 128.1, 125.7, 119.4, 54.0, 21.2 ppm.Spectroscopic data for the compound **P5** were consistent with the previously reported ones.[29]

4-(4-methoxyphenyl)-1-(4-methylbenzyl)-1*H*-1,2,3-triazole, **P6**, white solid, yield 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.67 (m, 2H), 7.53 (s, 1H), 7.19 (d, *J* = 1.8 Hz, 4H), 6.96–6.87 (m, 2H), 5.50 (s, 2H), 3.81 (s, 3H), 2.34 (s, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 159.5, 148.0, 138.7, 131.7, 129.8, 128.1, 127.0, 123.3, 118.5, 114.1, 55.3, 54.0, 21.2 ppm. Spectroscopic data for the compound **P6** were consistent with the previously reported ones.[30]

4-(4-fluorophenyl)-5-((4-fluorophenyl)ethynyl)-1-(2-iodobenzyl)-1*H*-1,2,3-triazole, **P7**, white solid, yield 78%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22–8.1 (m, 2H), 7.89 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.48–7.39 (m, 2H), 7.29 (td, *J* = 7.6 Hz, 1.3 Hz, 1H), 7.19–7.12 (m, 2H), 7.10–6.97 (m, 3H), 6.88 (dd, *J* = 7.8 Hz, 1.6 Hz, 1H), 5.74 (s, 2H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 164.6, 164.2, 162.0, 139.6, 137.2, 133.8, 130.0, 128.9, 128.2, 128.1, 128.0, 126.3, 117.4, 115.9 (d, *J* = 10.8 Hz), 115.7, 101.8, 97.5, 74.7, 57.3 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -107.8, -112.2 ppm; IR (diamond tip): ν 2226, 1604, 1563, 1514, 1494, 1461, 1432, 1359, 1230, 1218, 1154, 1039, 1012, 1001, 841, 829, 808, 752, 739, 700, 680, 650, 610, 585, 573, 549, 526, 437, 427, 404 cm^{-1}.

4-phenyl-5-(phenylethynyl)-1-(4-(trifluoromethyl)benzyl)-1*H*-1,2,3-triazole, **P8**, white solid, yield 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20–8.13 (m, 2H), 7.66–7.59 (m, 2H), 7.52–7.33 (m, 10H), 5.73 (s, 2H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 148.3, 138.5, 131.5, 129.9 (d, *J* = 10.9 Hz), 128.8, 128.7, 128.6, 128.3, 126.2, 125.9 (d, *J* = 3.8 Hz), 121.1, 102.7, 52.3 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.8 ppm; IR (diamond tip): ν 2944, 2919, 2848, 2826, 1504, 1468, 1450, 1217, 1156, 1093, 1046, 1016, 983, 846, 830, 814, 606, 582, 529, 471 cm^{-1}.

Typical procedure for the A^3 coupling reaction: In a vial fitted with a screw cap, aldehyde (1.3 mmol, 1.0 eq), alkyne (1.4 mmol, 1.1 eq) and amine (1.3 mmol, 1.1 eq) were dissolved in methanol (1 mL). Next, the appropriate copper catalyst (0.5 mol%) was introduced to the reaction mixture. The reaction was performed at room temperature and was monitored by TLC (*n*-hexane/ethyl acetate, v/v = 7:3). After completion of the reaction (20 minutes), the reaction mixture was extracted with diethyl ether (3 x 1 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and concentrated on a rotary evaporator. The crude product was purified by column chromatography (*n*-hexane/ethyl acetate, v/v = 8:2). The isolated product was dried under vacuum.

1-cyclohexyl-*N*,*N*-dimethyl-3-fenylprop-2-yn-1-amine, **P9**, light-yellow oil, yield 91%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47–7.40 (m, 2H), 7.33–7.26 (m, 3H), 3.15 (d, *J* = 10 Hz, 1H), 2.28 (s, 6H), 2.15–2.07 (m, 1H), 2.04–1.96 (m, 1H), 1.80–1.71 (m, 2H), 1.70–1.63 (m, 1H), 1.54 (ddd, *J* = 14.5, 11.0, 6.1 Hz, 2H), 1.29–1.16 (m, 2H), 0.99 (ddd, *J* = 24.0, 11.9, 3.2 Hz, 2H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 131.7, 128.2, 127.7, 123.6, 86.5, 64.2, 41.6, 40.1, 31.1, 30.3, 26.7, 26.1 ppm; HRMS-ESI (m/z) $[M+H]^+$ calcd for $C_{17}H_{23}N$ $[M+H]^+$: 242.1903, found 242.1907; IR (diamond tip): ν 2921, 2850, 2822, 2779, 1488, 1448, 1338, 1316, 1276, 1259, 1224, 1177, 1157, 1121, 1086, 1069, 1044, 1023, 982, 941, 911, 890, 850, 824, 753, 689, 600, 529, 488 cm^{-1}.

(1-cyclohexyl-3-(4-fluorophenyl)-*N*,*N*-dimethyl-2-yn-1-amine, **P10**, light-yellow oil, yield 86%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.37 (m, 2H), 7.01–6.94 (m, 2H), 3.13 (d, *J* = 10.0 Hz, 1H), 2.27 (s, 6H), 2.07 (dd, *J* = 8.0, 6.5 Hz, 1H), 1.98 (dd, *J* = 8.2, 6.6 Hz, 1H), 1.78–1.70 (m, 2H), 1.69–1.61 (m, 2H), 1.52 (dd, *J* = 10.1, 3.5 Hz, 1H), 1.29–1.15 (m, 3H), 1.06–0.89 (m, 2H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 162.13 (d, *J* = 248.6 Hz), 133.47 (d, *J* = 8.3 Hz), 119.59 (d, *J* = 3.6 Hz), 115.49 115.27, 86.15, 85.45, 64.11, 41.63, 40.03, 31.11, 30.24, 26.63, 26.05 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -112.0 ppm; HRMS-ESI (m/z) calcd for $C_{17}H_{22}NF$ $[M+H]^+$: 260.1809, found 260.1807; IR (diamond tip): ν 2944, 2919, 2848, 2826, 1597, 1503, 1468, 1451, 1319, 1259, 1217, 1196, 1172, 1156, 1120, 1093, 1046, 1016, 983, 846, 829, 814, 606, 582, 529, 471, 433 cm^{-1}.

1-cyclohexyl-3-(4-methoxyphenyl)-*N*,*N*-dimethylprop-2-yn-1-amine, **P11**, light-yellow oil, yield 88%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.32 (m, 2H), 6.85–6.77 (m, 2H), 3.79 (s, 3H), 3.12 (d, *J* = 9.9 Hz, 1H), 2.27 (s, 6H), 2.15–2.05 (m, 1H), 2.03–1.95 (m, 1H), 1.79–1.71 (m, 2H), 1.70–1.63 (m, 1H), 1.55–1.45 (m, 1H), 1.30–1.14 (m, 3H), 1.07–0.88 (m, 2H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 159.1, 133.0, 115.7, 113.8, 86.2, 84.8, 64.2, 55.3, 41.6, 40.1, 31.1, 30.3, 26.7, 26.1 ppm; HRMS-ESI (m/z) calcd for $C_{18}H_{25}NO$ $[M+H]^+$: 272.2009, found 272.2006; IR (diamond tip): ν 3038, 2930, 2851, 2822, 2779, 2667, 2536, 2214, 20151, 1884, 1703, 1657, 1606, 1570, 1509, 1467, 1450, 1414, 1339, 1317, 1289, 1247, 1226, 1173, 1122, 1104, 1086, 1035, 984, 942, 891, 850, 830, 803, 698, 644, 606, 584, 535, 488, 440 cm^{-1}.

3-(4-(*tert*-butyl)phenyl)-1-cyclohexyl-*N*,*N*-dimethylprop-2-yn-1-amine, **P12**, yellow oil, yield 92%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.35 (m, 2H), 7.33–7.29 (m, 2H), 3.13 (d, *J* = 9.9 Hz, 3H), 2.27 (s, 6H), 2.15–2.05 (m, 2H), 2.03–1.95 (m, 2H), 1.28 (s, 9H), 1.23–1.12 (m, 2H), 1.05–0.92 (m, 2H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 150.9, 133.5, 131.4, 125.2, 115.5, 86.5, 85.7, 64.2, 41.6, 40.1, 34.7, 31.1, 30.3, 26.7, 26.7, 26.1 ppm; HRMS-ESI (m/z) calcd for $C_{21}H_{31}N$ $[M+H]^+$: 298.2529, found 298.2539; IR (diamond tip): ν 2922, 2851, 2822, 2779, 1505, 1448, 1405, 1363, 1338, 1316, 1262, 1224, 1194, 1171, 1155, 1108, 1087, 1044, 1020, 984, 890, 850, 832, 736, 654, 605, 560, 527, 472 cm^{-1}.

N-allyl-*N*-(1-cyclohexyl-3-mesitylprop-2-yn-1-yl)prop-2-en-1-amine, **P13**, yellow oil, yield 84%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (d, *J* = 0.5 Hz, 2H), 5.82 (dddd, *J* = 17.2, 10.1, 8.3, 4.1 Hz, 2H), 5.21 (dtd, *J* = 17.2, 2.1, 1.0 Hz, 2H), 5.12–5.06 (m, 2H), 3.44 (d, *J* = 10.2 Hz, 1H), 3.34 (dt, *J* = 4.0, 1.9 Hz, 1H), 3.30 (dt, *J* = 4.0, 1.9 Hz, 1H), 2.94 (dd, *J* = 14.3, 8.3 Hz, 2H), 2.40 (s, 6H), 2.26 (s, 3H), 2.16–2.08 (m, 2H), 1.78–1.70 (m, 2H), 1.68–1.57 (m, 2H), 1.29–1.17 (m, 3H), 1.09–0.97 (m, 1H), 0.95–0.83 (m, 1H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 139.9, 137.0, 127.5, 120.5, 116.7, 95.3, 83.0, 59.0, 54.1, 40.4, 31.4, 30.4, 26.7, 26.2, 26.0, 21.4, 21.2 ppm; HRMS-ESI (m/z) calcd for $C_{24}H_{33}N$ $[M+H]^+$: 336.2686, found 336.2693; IR (diamond tip): ν 2920, 2850, 2813, 1641, 1610, 1478, 1446, 1416, 1375, 1351, 1319, 1262, 1240, 1216, 1186,

1156, 1106, 1032, 993, 973, 916, 889, 850, 728, 711, 594, 573, 471 cm^{-1}.

N-allyl-*N*-(3-(4-(*tert*-butyl)phenyl)-1-cyclohexylprop-2-yn-1-yl)prop-2-en-1-amine, **P14**, yellow oil, yield 89%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.34 (m, 2H), 7.33–7.29 (m, 2H), 5.82 (dddd, *J* = 17.2, 10.2, 8.2, 4.2 Hz, 2H), 5.21 (dtd, *J* = 17.2, 2.0, 1.0 Hz, 2H), 5.09 (ddd, *J* = 10.2, 1.9, 1.2 Hz, 2H), 3.35–3.26 (m, 3H), 2.92 (dd, *J* = 14.3, 8.2 Hz, 2H), 2.15–2.03 (m, 2H), 1.79–1.66 (m, 3H), 1.60–1.50 (m, 2H), 1.30 (s, 9H), 1.22–1.12 (m, 2H), 1.05–0.95 (m, 1H), 0.90–0.80 (m, 1H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 150.9, 137.0, 131.4, 125.2, 120.7, 120.7, 116.6, 86.8, 86.6, 58.8, 53.9, 40.2, 34.7, 31.3, 31.2, 30.4, 26.7, 26.2, 26.0 ppm; HRMS-ESI (m/z) calcd for $C_{25}H_{35}N$ $[M+H]^+$: 350.2842, found 350.2856; IR (diamond tip): v 2922, 2850, 1502, 1446, 1363, 1318, 1265, 1107, 993, 917, 890, 833, 643, 599, 560, 521 cm^{-1}.

Typical procedure for the β-hydroboration of internal alkynes and alkenes: In dry and argon flushed a 5 mL flask were added the appropriate copper complex (0.05 mol%), alkyne or alkene (1.3 mmol, 1.0 eq), $B_2(pin)_2$ (1.5 mmol, 1.1 eq) and NaOH (1 mol%, 0.0013 mmol). Then was added dry methanol (0.1 mL) and CPME (1 mL). The reaction mixture was stirred at room temperature for 18 h under an inert atmosphere of argon. The reaction was monitored by TLC (*n*-hexane/ethyl acetate, v/v = 7:3). After completion of the reaction, the solvent was removed in vacuo, and the product was purified by column chromatography (*n*-hexane/ethyl acetate, v/v = 9:1). The isolated product was dried under vacuum.

2-(1-phenylhex-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, **P15**, colourless oil, 18 h, yield 97%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.33–7.29 (m, 4H), 7.19 (s, 1H), 2.38 (dd, *J* = 7.5, 0.9 Hz, 2H), 1.30 (s, 12H), 1.09 (d, *J* = 7.5 Hz, 1H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 141.3, 137.9, 128.9, 128.0, 127.0, 83.4, 24.8, 22.7, 22.3, 14.7, 14.1 ppm. Spectroscopic data for the compound **P15** were consistent with the previously reported ones.[31]

4,4,5,5-tetramethyl-2-(1-(thiophen-2-yl)-hex-1-en-2-yl)-1,3,2-dioxaborolane, **P16**, colourless oil, yield 95%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.28 (m, 2H), 7.11 (ddd, *J* = 3.6, 1.1, 0.6 Hz, 1H), 7.00 (dd, *J* = 5.1, 3.6 Hz, 1H), 2.56–2.46 (m, 2H), 1.52–1.36 (m, 4H), 1.28 (bs, 12H), 0.93 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 140.8, 133.9, 129.6, 126.7, 126.6, 83.4, 31.4, 30.0, 24.7, 23.1, 14.1 ppm. Spectroscopic data for the compound **P16** were consistent with the previously reported ones.[32]

4,4,5,5-tetramethyl-2-(naphthalen-1-ylmethyl)-1,3,2-dioxaborolane, **P17**, colourless oil, yield 97%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.85–7.81 (m, 1H), 7.70–7.65 (m, 1H), 7.47 (ddd, *J* = 9.2, 7.8, 1.4 Hz, 2H), 7.41–7.34 (m, 2H), 3.23–3.17 (m, 2H), 1.24 (s, 12H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 140.4, 133.8, 131.7, 128.6, 126.3, 125.5, 125.3, 125.0, 123.9, 83.1, 26.9, 25.0, 24.8 ppm. Spectroscopic data for the compound **P17** were consistent with the previously reported ones. [33]

4,4,5,5-tetramethyl-2-(4-methylbenzyl)-1,3,2-dioxaborolane, **P18**, colourless oil, yield 94%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (dt, *J* = 8.5, 4.4 Hz, 4H), 2.72–2.65 (m, 2H), 2.29 (d, *J* = 3.4 Hz, 3H), 1.26 (bs, 12H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 141.4, 134.8, 128.9, 128.8, 127.8, 125.4, 83.1, 29.8, 25.0, 24.8, 24.5, 21.0 ppm. Spectroscopic data for the compound **P18** were consistent with the previously reported ones.[31]

4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)benzyl)-1,3,2-dioxaborolane, **P19**, colourless oil, yield 96%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.47 (m, 2H), 7.34–7.27 (m, 2H), 2.82–2.75 (m, 2H), 1.20 (bs, 12H) ppm; ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 148.5, 128.3, 125.7, 125.1 (q, *J* = 3.8 Hz), 83.2, 29.8, 25.0, 24.8, 24.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.27 ppm. Spectroscopic data for the compound **P19** were consistent with the previously reported ones.[31]

Acknowledgements

Authors are generously grateful to the Foundation for Polish Science for financial support (Homing Plus programme /2013/8-13, "Novel approaches to transition metal complexes based on ligands containing sulfur moiety and their direct application in C-H bond transformations"). The project was co-financed by the European Union by the European Regional Development Fund, Operational Program Innovative Economy 2009-2013. Project was carried out using the infrastructure of Biological and Chemical Research Centre of University of Warsaw.

Keywords: Copper Catalysis • NHC Ligands • CuAAC reaction • A^3 coupling reaction • β-hydroboration reaction

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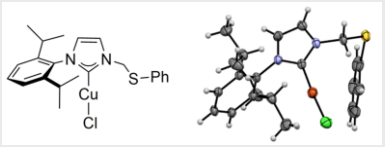
Layout 1:

FULL PAPER

A facile and efficient synthesis of novel family of NHC copper(I) complexes is described. Presented initiators promote actively various transformations at room temperature in high yields.



Copper Catalysis*

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Synthesis, structural characterization and catalytic activities of sulfur-functionalized NHC copper(I) complexes