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Highly Active Dinuclear Copper Catalysts for Homogeneous Azide–Alkyne Cycloadditions

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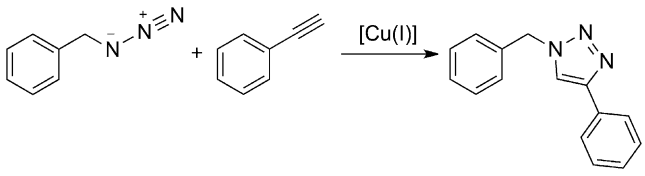
Abstract: The main feature of the herein presented class of molecularly defined catalysts for the copper-catalyzed azide–alkyne cycloaddition reaction is the presence of two copper centres in one catalyst molecule. We report the facile three-step synthesis of two representative bis-NHC-dicopper complexes as well as their catalytic performance in the azide–alkyne cycloaddition. A screening with one of these complexes has proved its wide applicability and excellent performance as homogeneous catalyst in various organic solvents and with different alkyne and azide substrates.

Keywords: click chemistry; copper; cycloaddition; homogeneous catalysis; N-heterocyclic carbenes

The copper-catalyzed azide–alkyne cycloaddition for the synthesis of 1,4-disubstituted 1,2,3-triazoles (CuAAC, Scheme 1)[1] is a variant of Huisgen's 1,3-dipolar cycloaddition[2] which disburdens the thermal reaction from its major drawbacks such as poor regioselectivity, long reaction times and harsh conditions.

Due to its broad applicability and straightforward procedures, the CuAAC reaction has become a popular method in polymer and materials science,[3] bioorganic chemistry[4] and drug discovery.[5] Very often, CuAAC reactions are carried out under "click" conditions,[6] traditionally by *in situ* reduction of copper(II) sulfate with sodium ascorbate in aqueous solution.[1b] However, this procedure is naturally limited to water-tolerant substrates that are inert towards reducing agents. Further research efforts have focused on directly applying copper(I) species together with various additives. These additives act as ligands which do not only stabilize the catalytically active copper(I) ions with regard to oxidation and disproportionation, but can also help increase the salts' solubility and enhance their catalytic performance.[7] A variety of pre-catalyst systems for CuAAC reactions is shown in Figure 1.



Scheme 1. CuAAC reaction of phenylacetylene with benzyl azide.

Fokin and Finn have found the rate order with respect to the concentration of copper(I) ions to be two for both ligand-free[13] and most ligand-containing[7b,14] CuAAC reactions, which suggests the participation of two copper(I) ions in the rate-determining step.[15] This hypothesis is supported by DFT calculations which have predicted the mechanistic route involving dinuclear copper(I) μ-acetylide complexes to be much more favourable than a mononuclear pathway.[16] Based on these findings and the isolation of intermediates,[17] we postulate a consistent mechanism for CuAAC reactions (Scheme 2).

In contrast to the widely used "black box" reagent mixtures, our aim was to rationally construct a molecularly defined, highly active catalyst system for homogeneous CuAAC reactions. In dependence on the postulated mechanism, its most important structural feature is the presence of two copper(I) ions irreversibly bound in the same catalyst molecule in an adequate distance to each other (Figure 2).[18] On the one hand, this feature entropically favours the coopera-

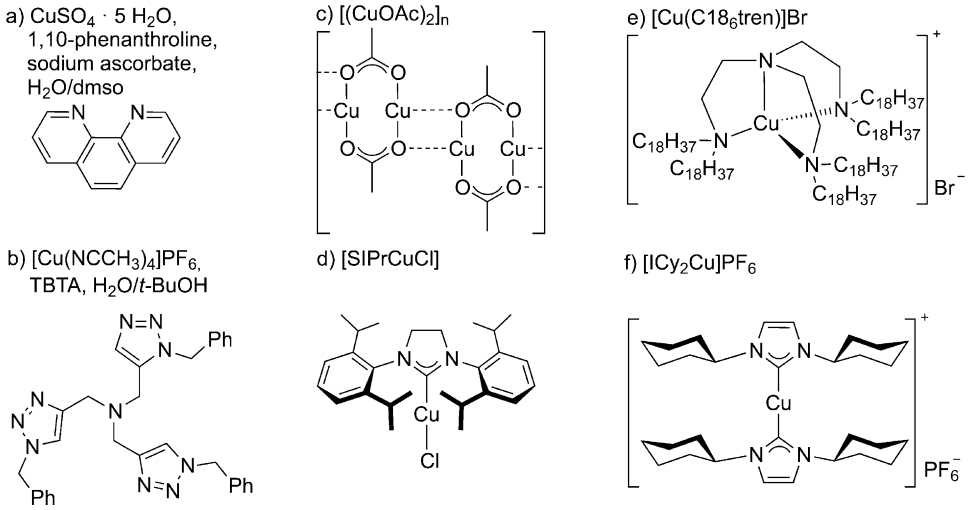
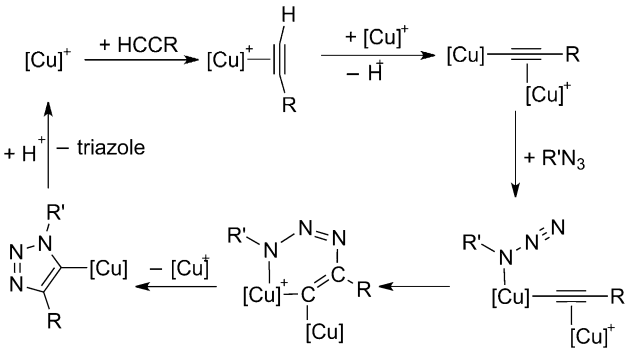


Figure 1. Pre-catalyst systems for CuAAC reactions as reported in literature: a) copper(II) sulfate pentahydrate with sodium ascorbate reducing agent and 1,10-phenanthroline;[7b] b) $[Cu(NCCH_3)_4]PF_6$ with TBTA;[7a,8] c) copper(I) acetate;[9] d) [SIPrCuCl];[10] e) $[Cu(C18_6tren)]Br$;[11] f) $[ICy_2Cu]PF_6$.[12]



Scheme 2. Proposed mechanism for the azide–alkyne cycloaddition based on DFT calculations;[16] [Cu] stands for a copper(I) complex fragment.

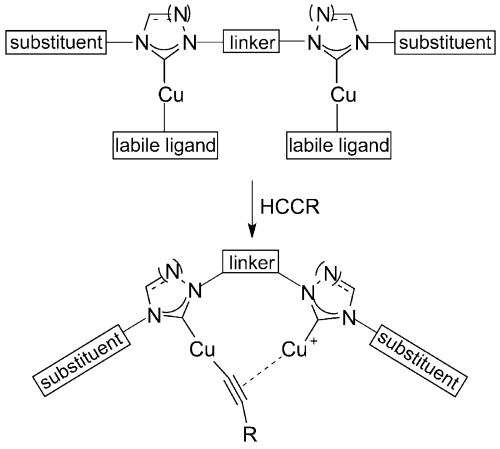
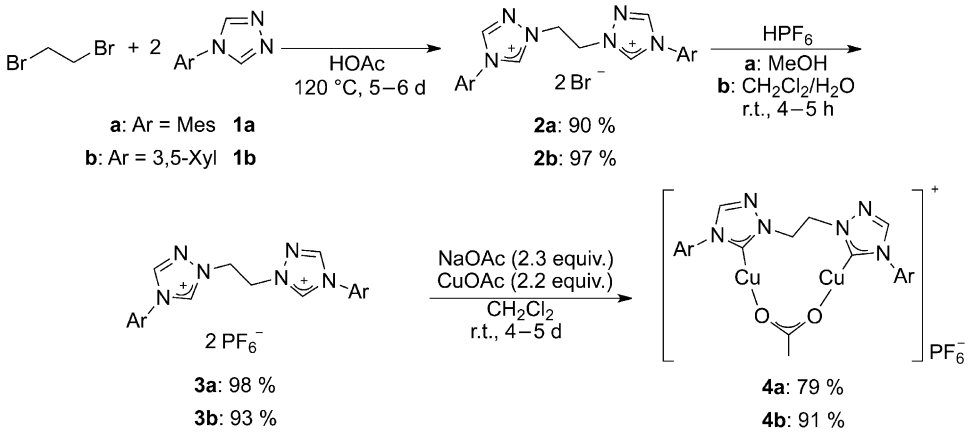


Figure 2. Structural features of target catalyst system and initiation by reaction with alkyne substrate to give the μ-acetylide intermediate.

tion of the two copper(I) centres compared to mononuclear catalysts, which is particularly important with low catalyst concentrations. On the other hand, the enthalpically profitable formation of a bridged μ-acetylide intermediate is facilitated. It should thus be possible to effectively catalyze CuAAC reactions in aprotic solvents under homogeneous conditions with low catalyst loadings. Moreover, the catalysts' structure is modular so that its structural components such as the nature of the NHC ligands, their substituents and the "sacrificial" labile ligands can be easily varied.

Although it has long been acknowledged that two copper(I) ions participate in the CuAAC's crucial mechanistic steps, we are aware of only two references to dinuclear copper complexes as pre-catalysts in this reaction. On the one hand, Finn et al. have realized the potential of dinuclear copper(I) complexes.[19] On the other hand, Williams et al. have explained Fokin's observation that the rate law of a CuAAC test reaction in the presence of TBTA is first order with respect to the concentration of catalytically active copper(I) ions[14] by crystallizing a dinuclear TBTA-copper(I) complex.[8]

In this context, we present the synthesis of well-defined bis-triazolylidene dicopper(I) complexes corresponding to the structural outline given in Figure 2 as well as their application in CuAAC test reactions. The synthesis of complexes **4a**/**b** (Scheme 3) starts from the corresponding triazoles **1a**/**b**.[20] The introduction of the linker unit proceeds *via* a double S_N2-reaction with 1,2-dibromoethane in acetic acid. In order to avoid the presence of halide ions as inhibitory ligands for copper(I),[1c,18] a salt metathesis of **2a**/**b** with hexafluorophosphoric acid yields the bis-triazolium hexafluorophosphate salts **3a**/**b**. The last



Scheme 3. Modular synthesis of catalytically active complexes **4**.

step is the reaction with copper(I) acetate and sodium acetate as an additional base in order to deprotonate the cationic triazolium moieties and form the bis-triazolylidene copper(I) acetate complexes **4a**/**b**, in which the acetate ligand μ-coordinates to both copper(I) centres. The great advantage of triazolylidene ligands as compared to imidazolylidene or imidazolinylidene ligands is the effortlessness with which their precursors, the triazolium salts, can be deprotonated. A base as weak as sodium acetate is sufficient to produce the desired complexes under notably mild conditions. Complexes **4a**/**b** are air-stable as solids for several days, but are oxidized in solution.

A single crystal X-ray structure of compound **4b** is displayed in Figure 3. However, this image only shows one monomeric cation of a more complex coordination polymer. In fact, half the number of copper(I) ions is not only coordinated *via* the ligands' carbene carbon atoms, but also by the N-2 atoms of proximate 1,2,4-triazolylidenes. Thus, the coordination number of these copper(I) centres is three and the C(carbene)–Cu–O(acetate) angle was found to be 146°. As a consequence of this aggregation, the xylyl-substituted complex **4b** is only slightly soluble in solvents such as tetrahydrofuran or dichloromethane and quite robust. In contrast, the sterically more encumbered mesityl-substituted complex **4a** is very well soluble in all polar aprotic solvents and more sensitive than its xylyl-substituted analogue **4b**, which hints at a less aggregated structure in the solid state. Complex **4a** decomposes in coordinating solvents such as acetone or tetrahydrofuran, but is stable in dichloromethane for several hours. Saturated solutions of **4b** in dichloromethane or tetrahydrofuran are stable for weeks.

In order to compare the intrinsic catalytic activities with the help of continuous NMR spectroscopy, catalytic transformations were carried out in the non-interfering solvent deuterated dichloromethane under inert gas (Figure 4). The catalyst loading was 0.5 mol% for the dinuclear species **4a**/**b**, and 1.0 mol% of the mononuclear reference catalyst $[ICy_2Cu]PF_6$ in order to have the same net concentration of copper(I). Even though **4b** is less soluble than **4a**, a homogeneous stock solution with the desired concentration of **4b** in deuterated dichloromethane was obtained. Upon addition of the catalyst solutions **4a**/**b**, $[ICy_2Cu]PF_6$ or copper(I) acetate, all reaction

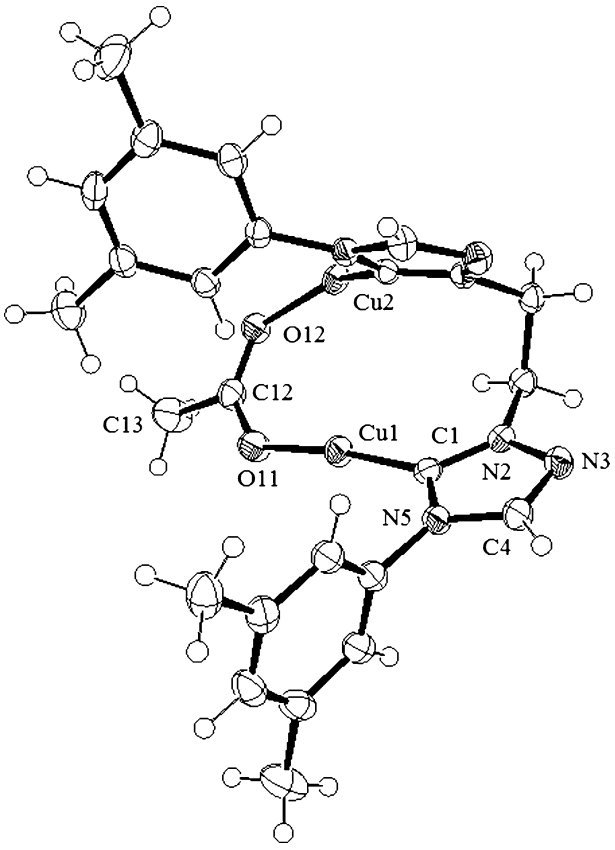


Figure 3. ORTEP ellipsoid model of the single crystal X-ray structure of complex **4b**;[21] the hexafluorophosphate counterion is omitted for clarity.

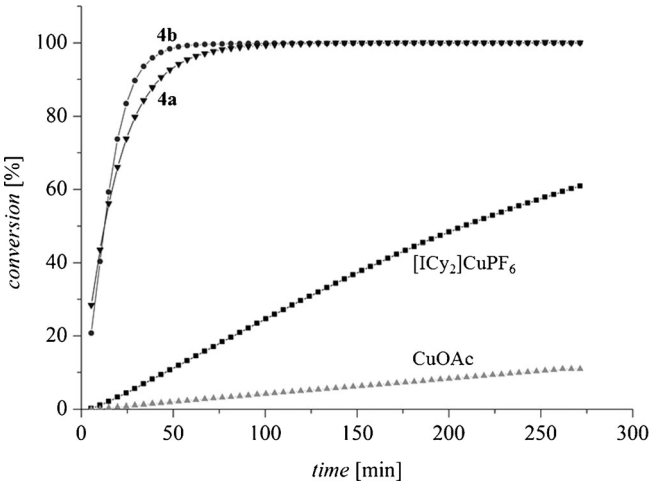


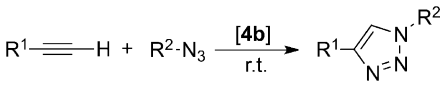
Figure 4. Reaction of benzyl azide with phenylacetylene in CD_2Cl_2 at 23 °C; dots: **4b** (0.5 mol%); triangles: **4a** (0.5 mol%); squares: $[ICy_2Cu]PF_6$ (1.0 mol%); grey triangles: CuOAc (homogeneous solution).

mixtures turned slightly yellow before they quickly returned to being colourless. We attribute the yellow colour to the formation of transient alkyne or acetylide copper complexes. During the course of reaction, no precipitation was observed, but after several days, the product triazole crystallized. With catalyst **4a**, the reaction reaches 50% conversion within 15 min and is completed within 100 min. The catalytic performance of catalyst **4b** is even slightly better with 60% conversion after 15 min and full conversion within 65 min. On the other hand, mononuclear catalyst $[ICy_2Cu]PF_6$ is significantly slower; after 15 min, only 3% conversion is observed, and only about 60% after 4.5 h. A comparison with the catalytic activity of copper(I) acetate is difficult due to its poor solubility. Adding a saturated solution of copper(I) acetate in dichloromethane to the substrate mixture under the same strictly homogeneous conditions gave poor conversion, indicating that copper(I) acetate is a heterogeneous catalyst under the conditions reported in literature.[9]

According to Figure 4, catalyst **4a** is more active at the beginning of the reaction, but due to its greater robustness, complex **4b** presumably is the overall more efficient catalyst. Thus, a series of catalytic test reactions was carried out with **4b** using various solvents and substrates. These reactions were monitored by gas chromatography and are summarized in Table 1

These results indicate that catalyst **4b** can be used in a variety of common organic solvents. In general, non-coordinating solvents such as dichloromethane favour the catalytic performance more than coordinating solvents such as tetrahydrofuran or acetone. In acetonitrile (entry 2), the reaction proceeds comparably fast, which might be due to the precipitation of the product, 1-benzyl-4-phenyl-1*H*-1,2,3-triazole, whereas the reaction mixtures in acetone (entry 3) and dichloromethane (entry 4) remain homogeneous during the whole course of the reaction. Using tetrahydrofuran as solvent (entry 1), the reaction mixture is cloudy during the course of the reaction between benzyl azide and phenylacetylene and clarifies when

Table 1. Catalytic transformations with catalyst **4b**.



Entry	mol% **4b**	R^1	R^2	Solvent	Reaction time [min][a]	Yield [%][b]
1	0.50	Ph	Bn	THF	270	quantitative (n.d.)
2	0.50	Ph	Bn	acetonitrile	35	quantitative (n.d.)
3	0.50	Ph	Bn	acetone	135	quantitative (n.d.)
4	0.50	Ph	Bn	DCM	45	quantitative (96)
5	0.50	*n*-hexyl	Bn	DCM	50	quantitative (96)
6	0.50	CMe_2OH	Bn	DCM	70	quantitative (96)
7	0.12	CO_2Et	Bn	DCM	105	quantitative (n.d.)
8	0.25	CO_2Et	Bn	DCM	40	quantitative (n.d.)
9	0.37	CO_2Et	Bn	DCM	20	quantitative (n.d.)
10	0.50	CO_2Et	Bn	DCM	15	quantitative (98)
11	0.62	CO_2Et	Bn	DCM	7	quantitative (n.d.)
12	0.74	CO_2Et	Bn	DCM	5	quantitative (n.d.)
13	0.50	Ph	$CHTol_2$	DCM	225	quantitative (98)
14	0.50	CO_2Et	$CHTol_2$	DCM	13	quantitative (98)

[a] Reaction time (at room temperature, i.e., 26 ± 3 °C) until neither alkyne nor azide could be detected anymore by gas chromatography.

[b] Yields were determined by gas chromatographic measurements with an internal standard; isolated yields determined after short column chromatography are given in parentheses.

conversion is completed. Variation of the alkyne substrate shows that the electron-withdrawing ester group in ethyl propiolate speeds up the transformation (entry 10), whereas the electron-donating 2-hydroxypropan-2-yl group in 2-methylbut-3-yn-2-ol decelerates the reaction (entry 6). With the sterically encumbering azide 4,4′-(azidomethylene)bis(methylbenzene), the catalytic reaction with phenylacetylene is dramatically slower (entry 13), but not so with ethyl propiolate as reactant (entry 14).

In summary, we have presented a highly active class of catalysts for CuAAC reactions whose main structural feature is the coordination of two copper(I) ions by the ancillary ligand system. These dinuclear complexes are composed of modular components (NHCs, linker unit, substituents, sacrificial ligands, counterion), so as to enable the tuning of their characteristics according to specific demands. Furthermore, they are molecularly defined and allow for strictly homogeneous CuAAC reactions in a variety of organic solvents. We are currently working on the isolation and characterization of reaction intermediates as well as on the synthesis of water-soluble catalysts.

Experimental Section

Attention: We strongly advise against the use of catalysts **4** in CuAAC reactions under neat conditions on a gram substrate scale!

Case example: In a three-necked flask equipped with a hook-up to the Schlenk line for equalization of pressure, catalyst **4b** (40 mg, 0.06 mmol) was kept under inert gas. A neat mixture of benzyl azide (533 mg, 500 μL, 4.00 mmol) and phenylacetylene (409 mg, 440 μL, 4.01 mmol) was added over a septum *via* syringe while stirring. The thermal excursion of the reaction was observed by a rise in temperature and a pressure build-up that finally caused the ejection of the secured stopcock.

Catalytic Tests with Continuous NMR Monitoring

Stock Solution A: Phenylacetylene (286 mg, 2.80 mmol), benzyl azide (373 mg, 2.80 mmol) and 1,4-dioxane (0.08 mL) were dissolved in CD_2Cl_2 (2.00 mL) ($c_{alkyne} = c_{azide} = 1.0\ mmol\,mL^{-1}$).

Stock Solution B: Complex **4a** (8 mg, 0.01 mmol) was dissolved in CD_2Cl_2 (1.00 mL) in a Schlenk flask ($c_{4a} = 0.01\ mmol\,mL^{-1}$).

Stock Solution C: Complex **4b** (7 mg, 0.01 mmol) was dissolved in CD_2Cl_2 (1.00 mL) in a Schlenk flask ($c_{4b} = 0.01\ mmol\,mL^{-1}$).

Stock Solution D: $[ICy_2Cu]PF_6$ (14 mg, 0.02 mmol) was dissolved in CD_2Cl_2 (1.00 mL) in a Schlenk flask ($c_{Nolan's\ cat.} = 0.02\ mmol\,mL^{-1}$).

Saturated Solution of Copper(I) Acetate: Copper(I) acetate (10 mg, 0.08 mmol) was suspended CD_2Cl_2 (1.00 mL) in a Schlenk flask and stirred overnight. The suspension was centrifuged to give a saturated solution of copper(I) acetate in CD_2Cl_2.

NMR Experiments

In a J. Young NMR tube, an aliquot of **stock solution A** (0.42 mL, 0.42 mmol phenylacetylene, 0.42 mmol benzyl azide) was diluted with CD_2Cl_2 (0.08 mL). A ^1H NMR spectrum was taken to reassess the purity of the substrates' solution. An aliquot of catalyst **stock solution B**, **C**, or **D** (0.20 mL, 0.002 mmol catalyst **4a**/**b**, 0.004 mmol $[ICy_2Cu]PF_6$) was added. Likewise, the saturated solution of copper(I) acetate was added (0.20 mL, concentration unknown). The samples were brought to the NMR spectrometer immediately after addition of the catalyst (down time: approximately 3 min). All reactions were continuously monitored on a Bruker Avance DRX 300 MHz machine at 23 °C.

Catalytic Tests with GC Monitoring

Catalyst Stock Solution (i–iv): Complex **4b** (14.0 mg, 0.02 mmol) was dissolved in the solvent (4.00 mL; **i**: THF; **ii**: acetonitrile; **iii**: acetone; **iv**: DCM) in a Schlenk flask under inert gas ($c_{4b} = 0.005\ mmol\,mL^{-1}$).

Substrate Solution 1 (i–iv): Phenylacetylene (310 μL, 288 mg, 2.82 mmol), benzyl azide (350 μL, 373 mg, 2.80 mmol) and dodecane (350 μL) were dissolved in the solvent (1.80 mL; **i**: THF; **ii**: acetonitrile (use of toluene instead of dodecane); **iii**: acetone; **iv**: DCM) ($c_{alkyne} = c_{azide} = 1.00\ mmol\,mL^{-1}$).

Substrate Solution 2: Ethyl propiolate (284 μL, 275 mg, 2.80 mmol), benzyl azide (350 μL, 373 mg, 2.80 mmol) and dodecane (350 μL) were dissolved in DCM (1.80 mL) ($c_{alkyne} = c_{azide} = 1.01\ mmol\,mL^{-1}$).

Substrate Solution 3: 1-Octyne (410 μL, 308 mg, 2.82 mmol), benzyl azide (350 μL, 373 mg, 2.80 mmol) and dodecane (350 μL) were dissolved in DCM (1.80 mL) ($c_{alkyne} = c_{azide} = 1.00\ mmol\,mL^{-1}$).

Substrate Solution 4: 2-Methylbut-3-yn-2-ol (274 μL, 236 mg, 2.80 mmol), benzyl azide (350 μL, 373 mg, 2.80 mmol) and dodecane (350 μL) were dissolved in DCM (1.80 mL) ($c_{alkyne} = c_{azide} = 1.01\ mmol\,mL^{-1}$).

Substrate Solution 5: Phenylacetylene (320 μL, 347 mg, 1.46 mmol), 4,4′-(azidomethylene)bis(methylbenzene) (160 μL, 1.46 mmol) and dodecane (280 μL) were dissolved in DCM (700 μL) ($c_{alkyne} = c_{azide} = 1.00\ mmol\,mL^{-1}$).

Substrate Solution 6: Ethyl propiolate (150 μL, 145 mg, 1.48 mmol), 4,4′-(azidomethylene)bis(methylbenzene) (320 μL, 339 mg, 1.43 mmol) and dodecane (250 μL) were dissolved in DCM (710 μL) ($c_{alkyne} = 1.03\ mmol\,mL^{-1}$, $c_{azide} = 1.00\ mmol\,mL^{-1}$).

Exemplary Procedure for 0.5 mol% Catalyst Concentration

An aliquot of the catalyst stock solution (**i–iv**, 200 μL, 1.00 μmol) was filled into a GC vial equipped with a magnetic stir bar and diluted with DCM (100 μL) under inert gas. At t = 0, the substrate mixture [**1(i–v)–6**, 200 μL, 0.20 mmol] was added *via* syringe. The reaction mixture was stirred at room temperature. In regular intervals, samples (10 μL) of this reaction mixture were taken over the septum by micro-

liter syringe. These samples were diluted with DCM (5 mL), filtered over glass Pasteur pipettes filled with cotton and celite and analyzed by gas chromatography.

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