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# Discovery of a Robust and Efficient Homogeneous Silver(I) Catalyst for the Cycloaddition of Azides onto Terminal Alkynes

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**Keywords:** Cycloaddition / Azides / Alkynes / Click chemistry / Silver

A highly efficient, chemically stable, and well-defined homogeneous silver(I) catalyst is reported for the cycloaddition of azides onto terminal alkynes (Ag-AAC reaction). The Ag-AAC reaction occurs at room temperature or with heating to deliver exclusively the corresponding 1,4-triazole. A pronounced ligand effect was discovered through systematic modification to the ligand structure resulting in the discovery of a chemically stable active catalyst for this reaction.

## Introduction

Since the concept of "click" chemical reactions was described by Sharpless,[1a] the copper(I)-catalyzed azide–alkyne cycloaddition (Cu-AAC: i.e., the copper-catalyzed Huisgen cycloaddition) reaction has emerged as the most extensively investigated and applied. This reaction permits the chemoselective, regiocontrolled conjugation of a functionalized alkyne **1** to a functionalized azide **2**[1] yielding 1,4- or 1,4,5-substituted 1,2,3-triazole **3** and occasionally 1,5-regioisomer **4** (Figure 1). Applications in many areas ranging from functional materials, drug discovery, biological, and hybrid bioconjugate areas have increased exponentially over the last decade.[2,3] The reaction (Figure 1) mechanism is complex, proceeding through a stepwise process initiated by copper(I) acetylide **A**, which complexes to azide **2**. Complexation of the copper(I) catalyst to the Cu–acetylide/azide leads to intermediate **B**, which undergoes the cycloaddition to generate metalated triazole **C**,[4,5] and this intermediate, upon protonation,[5e] yields 1,4-triazole **3**.

Despite the positive attributes of the 1,4-regioselective Cu-AAC process, several problems persist. From a fundamental viewpoint, isoelectronic gold(I)[6a] and silver(I)[5d,6b] acetylides are known to participate in the AAC reaction; however, the addition of copper(I) salts is *required* to effect the cycloaddition. No competent silver(I) or gold(I) species has been reported to promote the AAC reaction alone.[5d,5f,6b–6d] The rationale for the failure of a competent silver(I) catalyst is not clear.

In addition, reports of problematic Cu-AAC reactions[5g,7a–7f] and the toxicity (including genetoxicity) of redox-active copper(I) species have arisen in relation to biological applications.[9] Many copper-catalyzed processes are heterogeneous and suffer from aggregation problems. Homogeneous copper catalysis has been achieved by using amine and phosphane ligands, allowing low catalyst loadings (<1%).[7g–7j] Despite the unpromising precedents reported for a possible Ag-AAC process, we became interested in exploring homogeneous complexes of type $[Ag^+(L_2)(X^-)]$ for several applications and recently discovered the first homogeneous silver(I) catalyst for the AAC reaction.[8] In accord with issues of copper toxicity, concern

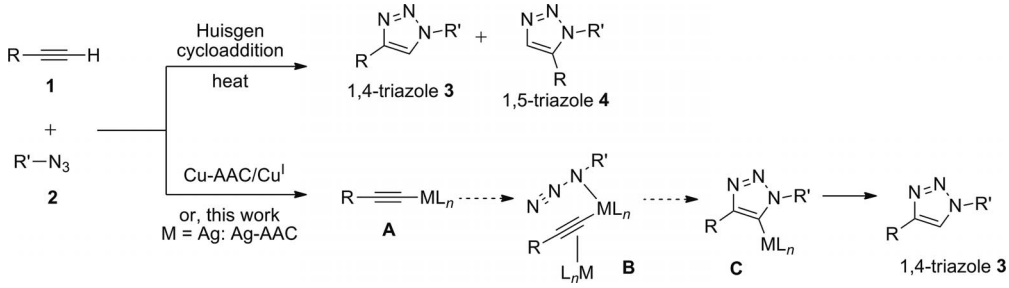


Figure 1. The general Cu-AAC reaction.

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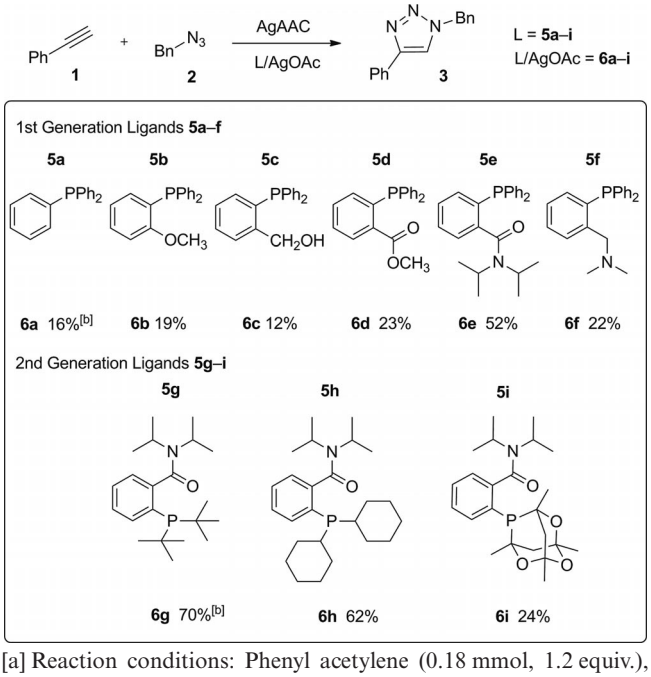
has been raised over the potential toxicity of silver nanoparticles.[10a] Silver complexes have been shown to be significantly less cytotoxic than silver salts.[10b] Silver complexes are not expected to participate in analogous ($Cu^{I}$–$Cu^{II}$) one-electron transfer processes, and we were confident that a stable, catalytically efficient, suitably ligated silver(I) species could be developed that would not precipitate metallic silver or silver halide under the conditions required. In view of these concerns and initial success,[8] we have systematically evaluated structural effects of the ligand in the Ag-mediated AAC process. In this communication, we report the development of an optimized, chemically stable, highly efficient silver(I) homogeneous catalyst for the Ag-AAC process.

## Results and Discussion

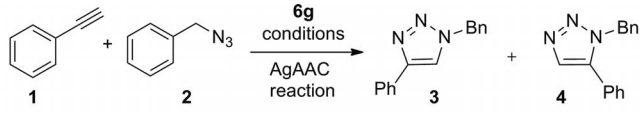
We recently reported a homogeneous, well-defined silver(I) complex derived from silver acetate and *N*,*N*-diisopropyl(2-diphenylphosphanyl)benzamide (**5e**) competent in affecting the Ag-AAC process. Whereas these reactions proceeded at room temperature in toluene, the catalyst was inefficient. Full conversion of the alkyne/azide to triazole required the use of 20 mol-% catalyst and a 4.8-fold excess amount of azide relative to alkyne. Our vision in developing hemilabile ligand **5e** was to enable push–pull effects on the metal center, which would allow progression through the cycle by electrophilic 14-electron to 18-electron intermediates effecting cyclization through nucleophilic ligand-mediated polarization of the complexed alkyne onto the azide (vide infra). To probe ligand effects in the Ag-AAC process, ligands **5a**–**i** (Table 1) were synthesized by using standard methods by employing nucleophilic and electrophilic phosphane coupling (see the Experimental Section). Crystalline complexes **6a**–**i** of ligands **5a**–**i** were formed with silver acetate (1:1) in all cases. The Ag-AAC process was investigated under a standard set of conditions (10 mol-% catalyst, 48 h, r.t. in toluene) with all nine silver complexes (Table 1). The first generation of ligands **5a**–**f** consisted of modifications to the weak donor ability of the *ortho* substituent on the ligand. A slight excess amount of the alkyne (azide/alkyne = 1.0:1.2) was used in contrast to our earlier requirement of an excess amount of the azide (4.8 equiv.). The overall results of screening catalysts **6a**–**f** demonstrated the clear superiority of the *N*,*N*-diisopropylamide substituent, which, fortuitously, was the first ligand investigated in the series.[8]

Table 1. Pronounced ligand effect on the Ag-AAC reaction.[a]




[a] Reaction conditions: Phenyl acetylene (0.18 mmol, 1.2 equiv.), benzyl azide (0.15 mmol, 1.0 equiv.), catalyst (10 mol-%), caprylic acid (20 mol-%), PhMe (1.0 mL), 48 h, r.t. [b] Yield of triazole **3**.

Table 2. Optimization with catalyst **6g** in the Ag-AAC reaction.[a]




| Entry | Cat. loading [mol-%] | Temp. [°C] | Time [h] | Conversion **3**/**4** (% isolated yield of **3**) |
|---|---|---|---|---|
| 1 | 10 | 25 | 48 | 70:0 (70) |
| 2 | 10 | 70 | 48 | 93:0 (92) |
| 3 | 10 | 110 | 48 | 95:5 (94) |
| 4 | 10 | 110 | 24 | 95:5 (92) |
| 5 | 10 | 70 | 24 | 82:0 (80) |
| 6 | 10 | 90 | 24 | 89:0 (86) |
| 7 | 5 | 110 | 24 | 95:5 (92) |
| 8 | 5 | 90 | 24 | 90:0 (ND) |
| 9 | 5 | 90 | 24 | 93:0 (ND) |
| 10 | 2 | 90 | 24 | 62:0 (ND) |
| 11 | 2 | 90 | 24 | 99:0 (98) |
| 12 | 2 | 90 | 12 | 79:0 (ND) |
| 13 | 1 | 90 | 24 | 92:0 (ND) |
| 14 | 0.5 | 90 | 24 | 79:0 (ND) |
| 15 | 1 | 90 | 48 | 99:0 (ND) |
| 16 | 0.5 | 90 | 48 | 99:0 (ND) |

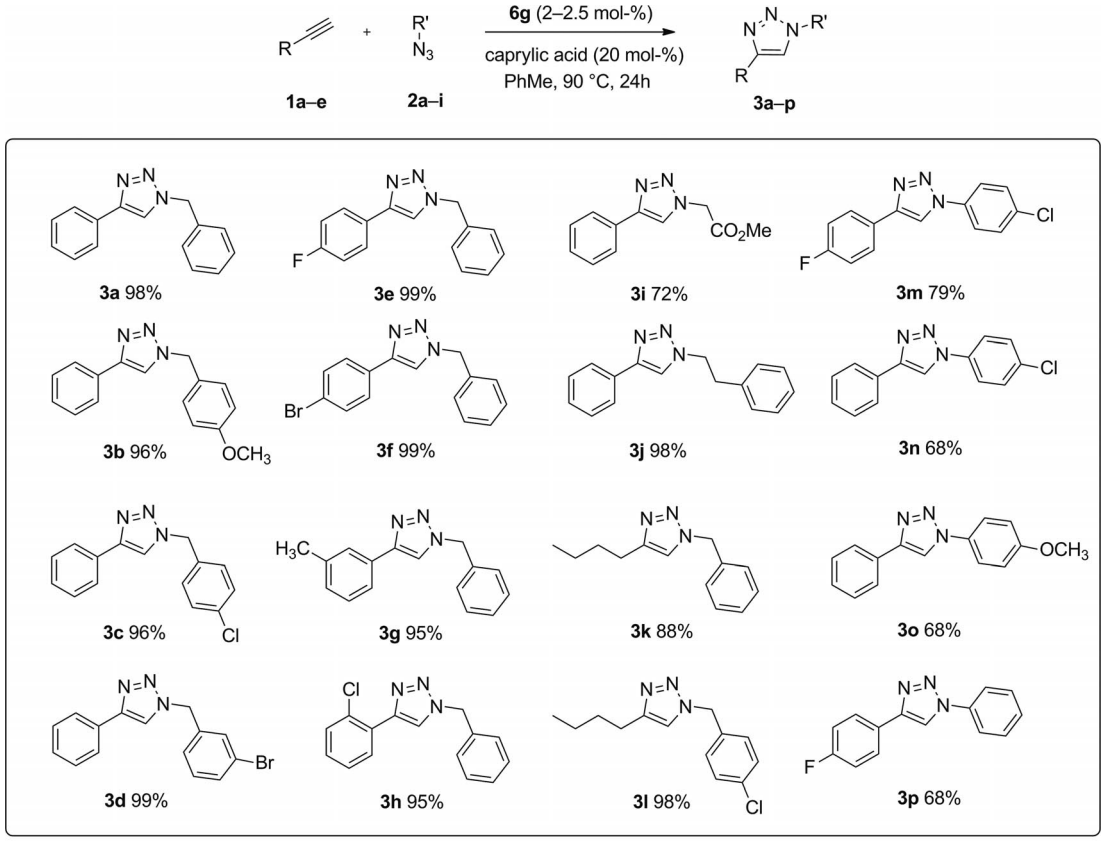
[a] Reaction conditions for entries 1–8, 10: Phenyl acetylene (0.18 mmol, 1.2 equiv.), benzyl azide (0.15 mmol, 1.0 equiv.), caprylic acid (20 mol-%), PhMe (1.0 mL). Reaction conditions for entries 9, 11–16: Phenyl acetylene (0.09 mmol, 1.0 equiv.), benzyl azide (0.14 mmol, 1.5 equiv.), caprylic acid (20 mol-%), PhMe (1.0 mL).

The effect of the *ortho* substituent is sharp, both on catalytic activity and overall stability of the complex. Complex **6e** (most stable) showed only minor silver metal deposition after one reaction cycle, whereas catalyst **6c** (least stable) decomposed rapidly and gave poor conversion. Also, stronger and weaker donor appendages at the *ortho* position appear detrimental with the amide substituent alone exhibiting a superior effect on catalyst stability and turnover. The second generation of ligands **5g**–**i** was therefore prepared retaining the *N*,*N*-diisopropylamide substituent and modulating the phosphane substituent from diphenyl- (i.e., **5e**) to di-*tert*-butyl- (i.e., **5g**) and dicyclohexyl- (i.e., **5h**), in addition to phosphadamantane derivative **5i**.[11] Screening new complexes **6g**–**i** derived from the second-generation ligands in the Ag-AAC reaction (Table 1) demonstrated the superiority of the di-*tert*-butyl- and dicyclohexyl-containing ligands.

On the basis of these ligand effects, catalyst **6g** was chosen with the goals of increased catalyst efficiency and expanding scope in the reaction. Silver complex **6g** is a solvate-free, air-stable white crystalline solid (m.p. 190–200 °C, decomp.) that is very soluble in toluene and most other organic solvents. It produces clear, colorless solutions in organic solvents that remain unaffected for weeks under normal laboratory conditions and through various heating/cooling cycles. No precipitation of silver metal is observed at all. The optimization results for catalyst **6g** are summarized in Table 2. The initial reaction provided seven catalyst turnovers at room temperature over 48 h (Table 2, entry 1). Increasing the temperature allowed higher conversion; however, the formation of trace amounts of minor 1,5-regioisomeric triazole **4** was observed at temperatures above 100 °C, whereas formation of this product was totally suppressed at 90 °C (Table 2, entries 2–7). All other reactions were therefore conducted at 90 °C and the catalyst loading was now reduced (Table 2, entries 8–16). Modification of the alkyne/azide stoichiometry showed that a slight excess amount of the azide (alkyne/azide = 1.0:1.5) was superior to a slight excess amount of the alkyne (Table 2, entry 10 vs. 11). Overall, catalyst **6g** proved to be highly active with loadings as low as 0.5 mol-%, providing quantitative conversion (200 turnovers) within 48 h.

Using 2–2.5 mol-% of catalyst **6g** under otherwise conditions of Table 2 (entry 11), >99% conversion to the 1,4-triazole was observed after 24 h at 90 °C. To check the efficiency of the catalyst, the above reaction was repeated three times on the initial catalyst charge by using identical quantities of azide and alkyne to provide >99, 96, and 95% conversion on subsequent runs. The solution remained completely clear, colorless, and homogeneous, showing no sign of silver metal precipitation after the fourth cycle. Control experiments also demonstrated that no Staudinger-type az-




[a] Reaction conditions: Acetylene (0.09 mmol, 1.0 equiv.), azide (0.14 mmol, 1.5 equiv.), **6g** (2–2.5 mol-%), caprylic acid (20 mol-%), PhMe (1.0 mL), 24 h, 90 °C. For **3m**–**p**, 4–9 % of the 1,5-isomer was detected by $^1$H NMR spectroscopy.

Figure 2. Scope of aryl alkyne participation in Ag-AAC reaction.[a]

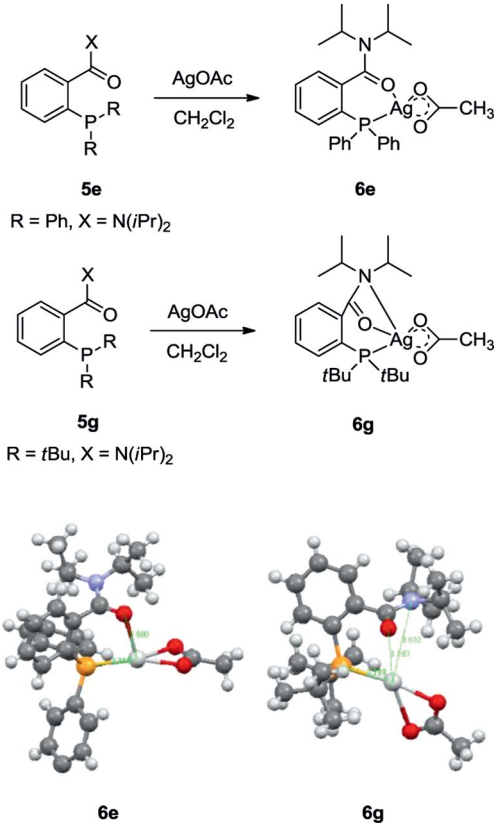
  

ide reduction occurred between catalyst **6g** and benzyl azide under the Ag-AAC reaction conditions, demonstrating further the exceptional stability of this complex.

The silver-mediated AAC reaction proved broad in scope with complex **6g**, as summarized in Figure 2. These reactions were conducted by using 2–2.5 mol-% of catalyst **6g** to achieve high conversions in a 24 h reaction period (i.e., similar to Table 1, entry 11).

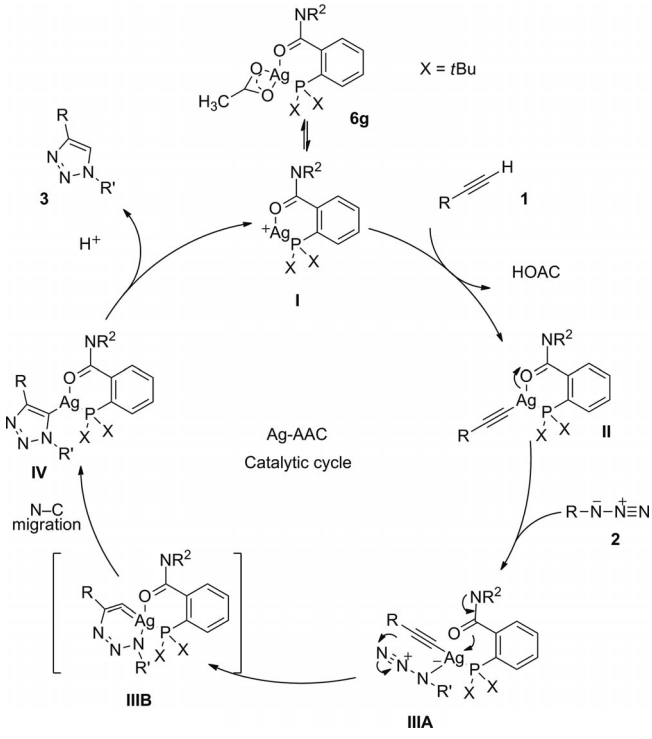
The Ag-AAC reaction catalyzed by **6g** is successful with a wide range of substrates including aryl, benzyl, and alkyl azides coupling with both phenyl and aliphatic acetylenes. No restrictions on the generality have been identified on the process so far.

Earlier, we reported the X-ray crystal structure of complex **6e**.[8] To gain potential insight into the reactivity of complex **6g**, crystals suitable for X-ray analysis were grown, and the crystal structure is shown in Scheme 1. The silver atom of complex **6e** proved to be ligated to the amide donor through one of the non-bonding lone pairs of the oxygen atom (2.680 Å). In contrast, highly active complex **6g** showed weak ligation to the amide HOMO with contacts between Ag–O (3.163 Å) and Ag–N (3.632 Å), whereas other contacts (Ag–P and Ag–acetate) were very similar.




Scheme 1. Synthesis of AgOAc complexes of ligands **5e** and **5g** (top) and ball-and-stick plots of **6e** and **6g** (bottom).

The reaction could readily be followed by NMR spectroscopy in [$D_8$]toluene. Interruption at various times during the progress of the standard reaction and analysis by $^{31}$P NMR spectroscopy showed only the presence of complex **6g**, with no other aggregate species observable. In addition, $^{1}$H NMR spectroscopy showed only clean conversion of the azide/alkyne into the triazole. The role of the ligand in complex **6g** is clearly significant, and we postulate the stepwise catalytic cycle shown in Scheme 2. The proposed catalytic cycle for the Ag-AAC process provides a rationale for the effectiveness of the hemilabile ligand on complex **6g**. Loss of acetate from 18-electron species **6g** yields the active catalyst **I** (14e$^-$), which forms ligated silver(I) acetylide **II**, the electrophilicity of which is modulated by the hemilabile amide substituent.




Scheme 2. Proposed catalytic cycle for the homogeneous Ag$^{I}$-catalyzed AAC reaction.

Nucleophilic attack on **II** by the azide generates intermediate **IIIA**, shown as the 16e$^-$ species. The role of the hemilabile nature of the ligand comes into play again from **IIIA** by complexation of the amide forming an 18e$^-$ intermediate, which transmits polarization of negative charge through the filled d orbitals into the acetylide π* orbitals effecting cyclization onto the tethered azide. This process can proceed through the transient silver metallacycle shown as **IIIB**, from which the nitrogen migrates to carbon carrying both electrons to yield metalated triazole **IV**, leading to product **3** on protonation and regenerating active catalyst **I**. A similar catalytic cycle, without ancillary ligand effects, was postulated for the Cu-AAC process in accord with DFT calculations.[6c]

## Conclusions

In summary, we report a chemically robust and effective general homogeneous catalyst for the Ag-AAC reaction. A pronounced ligand effect is observed and a significant role

is attributed to the hemilabile nature of ligand **5g** in both the stability and efficiency of catalyst **6g**. The catalyst is effective at loadings as low as 0.5 mol-% and is stable thermally over repeated catalytic cycles showing no silver metal precipitation. A mechanism is proposed involving continuous coordination of the phosphane donor of the ligand to silver and proceeding through intermediates that allow coordination and polarization of the acetylide/azide to effect the stepwise cyclization. Further studies to probe the mechanism and extension of the reaction scope are under investigation.

## Experimental Section

**General Information:** All reactions were carried out under a nitrogen atmosphere in oven-dried glassware. Toluene (dry) was distilled from sodium/benzophenone. AgOAc (purity ≥99.0%) and AgOTf (purity = 99.95%) were purchased from Fluka Chemicals, Switzerland, and Sigma–Aldrich, Canada, respectively. DMSO (dry) was obtained from Sigma–Aldrich (Sure-seal), and dichloromethane was distilled from calcium hydride. Phenyl acetylenes were obtained commercially from Sigma–Aldrich or Alfa Aesar. Melting points were recorded in open capillary using a calibrated Büchi melting point B540 apparatus. Thin-layer chromatography (TLC) was carried out by using aluminum sheets precoated with silica gel $60F_{254}$ (Merck) and was visualized under 254 nm UV light. $^1$H NMR and $^{13}$C NMR spectra were recorded with an AV 600 spectrometer in $CDCl_3$ with TMS as internal standard. Chemical shifts ($\delta$) are reported in ppm downfield of TMS.

**General Procedure for the Preparation of Starting Azides 2a–f:**[12] Sodium azide (1.0 g, 15.3 mmol, 1 equiv.) was dissolved in DMSO (25 mL) by stirring in a flame-dried, 100-mL round-bottomed flask under a nitrogen atmosphere for 12 h. A solution of the corresponding benzyl bromide/chloride (13.8 mmol, 0.9 equiv.) was added, and the reaction mixture was stirred for 10 h. Water (20 mL) was added slowly to quench the reaction (exothermic process), and the mixture was stirred until it cooled to room temperature. The mixture was poured into water (50 mL) and extracted with $Et_2O$ (3 × 30 mL). The organic layer was separated, washed with brine, dried with sodium sulfate, filtered, and concentrated in vacuo to afford azides **2a**–**h** as oils.

**1-(Azidomethyl)benzene (2a):**[12] $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.43–7.25 (m, 5 H), 4.35 (s, 2 H) ppm.

**1-(Azidomethyl)-4-methoxybenzene (2b):**[13] $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.28 (d, $J$ = 8.6 Hz, 2 H), 6.94 (d, $J$ = 8.6 Hz, 2 H), 4.30 (s, 2 H), 3.85 (s, 3 H) ppm.

**1-(Azidomethyl)-4-chlorobenzene (2c):**[14] $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.39 (d, $J$ = 8.3 Hz, 2 H), 7.28 (d, $J$ = 8.3 Hz, 2 H), 4.35 (s, 2 H) ppm.

**1-(Azidomethyl)-3-bromobenzene (2d):**[15] $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.51 (d, $J$ = 1.9 Hz, 2 H), 7.28 (d, $J$ = 1.4 Hz, 2 H), 4.35 (s, 2 H) ppm.

**Methyl 2-Azidoacetate (2e):**[16] $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 3.91 (s, 2 H), 3.83 (s, 3 H) ppm.

**1-(2-Azidoethyl)benzene (2f):**[17] $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.37 (t, $J$ = 7.4 Hz, 2 H), 7.33–7.28 (m, 1 H), 7.28–7.24 (m, 2 H), 3.55 (t, $J$ = 7.3 Hz, 2 H), 2.94 (t, $J$ = 7.3 Hz, 2 H) ppm.

**General Procedure for the Preparation of Starting Azides 2g–i:**[18] In a 100-mL round-bottomed flask, 4-methoxyaniline (1.0 g, 8.1 mmol, 1 equiv.) was dissolved in water (2.5 mL) that contained concentrated HCl (4.1 mL). This solution was cooled to below 5 °C in an ice bath and diazotized with a solution of $NaNO_2$ (0.850 g, 12.1 mmol, 1.5 equiv.) in distilled water (2.5 mL). The mixture was stirred in an ice bath for 1 h. A solution of $NaN_3$ (1.05 g, 16.2 mmol, 2 equiv.) in water (6 mL) was added at 0 °C, and the mixture was stirred for 30 min. The mixture was warmed up to room temperature and stirred for an additional 3 h. The reaction mixture was extracted with EtOAc (2 × 50 mL). The combined organic layers was dried with anhydrous $Na_2SO_4$, filtered, and concentrated under reduced pressure. The crude 4-methoxyazidobenzene was further purified by flash column chromatography over a short plug of silica gel (5% EtOAc/hexanes) to afford a yellow liquid in 80% yield. An identical procedure was followed for the synthesis of **2g** and **2i**.

**4-Chlorophenyl Azide (2g):**[18] $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.32 (d, $J$ = 8.2 Hz, 2 H), 6.96 (d, $J$ = 8.2 Hz, 2 H) ppm.

**4-Methoxyphenyl Azide (2h):**[18] $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 6.96 (d, $J$ = 8.8 Hz, 2 H), 6.89 (d, $J$ = 8.8 Hz, 2 H), 3.80 (s, 3 H) ppm.

**Azidobenzene (2i):**[18] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.34 (t, $J$ = 8.0 Hz, 2 H), 7.12 (t, $J$ = 7.2 Hz, 1 H), 7.02 (d, $J$ = 7.6 Hz, 2 H) ppm.

**Synthesis of (2-Methoxyphenyl)diphenylphosphane (5b):**[19] To a clear solution of 1-iodo-2-methoxybenzene (0.100 g, 0.42 mmol) in THF (2.0 mL) was added *n*BuLi (1.6 M in hexanes, 0.530 mL, 0.854 mmol) at –78 °C under a nitrogen atmosphere. The resulting solution was stirred at –78 °C for 1 h. A solution of chlorodiphenylphosphane (76.0 μL, 0.427 mmol) in THF (2.0 mL) was added at –78 °C. Then the mixture was warmed to room temperature and stirred for an additional 3 h. Water was added to quench the reaction, and the mixture was extracted with $Et_2O$ (3 × 15 mL). The organic layers were combined, washed with brine, dried with $Na_2SO_4$, and concentrated. The resulting residue was purified by column chromatography on silica gel to obtain **5b** (0.075 g, 60%) as crystalline white solid. M.p. 120–122 °C (ref.[19] m.p. 124–126 °C). $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 6.40–7.40 (m, 14 H, ArH), 3.65 (s, 3 H, OMe) ppm. $^{31}$P NMR (80 MHz, $CDCl_3$): $\delta$ = –16.74 ppm.

**Synthesis of [2-(Diphenylphosphanyl)phenyl]methanol (5c):**[20] To a suspension of 2-(diphenylphosphanyl)benzoic acid (0.100 g, 0.32 mmol) in THF (2.0 mL) was added lithium aluminum hydride (0.027 g, 0.71 mmol). The resulting reaction mixture was stirred at room temperature for 2 h. The reaction mixture was then quenched by adding saturated solution of sodium potassium tartarate. The mixture was extracted with EtOAc (3 × 15 mL). The organic layers were combined, washed with brine, dried with $Na_2SO_4$, and concentrated. The resulting residue was purified by column chromatography on silica gel to give **5c**[21] (0.076 g) as a colorless oil in 80% yield. $^1$H NMR (200 MHz, $CDCl_3$: $\delta$ = 7.46–7.57 (m, 1 H, ArH), 7.14–7.39 (m, 12 H, ArH), 6.83–6.95 (m, 1 H, ArH), 4.82 (s, 1 H), 2.04 (br. s, 1 H, -OH) ppm. $^{31}$P NMR (80 MHz, $CDCl_3$): $\delta$ = –16.29 ppm.

**Synthesis of Methyl 2-(Diphenylphosphanyl)benzoate (5d):**[20] In a 50-mL flame-dried pear-shaped Schlenk flask equipped with a magnetic stir bar, rubber septum, and an argon inlet, cesium carbonate (0.190 g, 0.58 mmol, 1.25 equiv.) and CuI (10 mol-% with respect to diphenylphosphane) were charged, and the vessel was sealed with a rubber septum. Toluene (5.0 mL), methyl-2-bromobenzoate (0.1 g, 0.46 mmol, 1 equiv.), and diphenylphosphane (0.72 g, 0.38 mmol, 0.8 equiv.) were injected into the tube through

the septum. The rubber septum was replaced with a dry argon flushed reflux condenser. The reaction mixture was then heated at 110 °C for 24 h. The reaction mixture was then cooled to room temperature and filtered with dichloromethane to remove any insoluble residues. The filtrate was concentrated in vacuo; the residue was purified by flash chromatography on silica gel to obtain pure **5d**[22] as a colorless solid in 60% yield. M.p. 97.5–99 °C (ref.[22] m.p. 96 °C). $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 8.10–8.12 (m, 1 H), 7.32–7.37 (m, 12 H), 6.96–6.99 (m, 1 H), 3.78 (s, 3 H) ppm. $^{31}$P NMR (80 MHz, $CDCl_3$): $\delta$ = –4.41 ppm.

**Synthesis of (*N*,*N*-Diisopropyl-2-diphenylphosphanyl)benzamide (5e):**[20] Into a flame-dried flask, containing a magnetic stirring bar, was weighed *N*,*N*-diisopropylbenzamide (0.100 g, 0.48 mmol, 1 equiv.) under an argon atmosphere and anhydrous THF (2 mL) was added. The flask was stirred for 15 min at –78 °C whereupon *s*BuLi (1.4 M in cyclohexane, 0.417 mL, 0.58 mmol, 1.2 equiv.) was added dropwise followed by TMEDA (0.088 mL, 0.58 mmol, 1.2 equiv.). The resultant solution was stirred at –78 °C for 30 min. Chlorodiphenylphosphane (0.090 mL, 0.48 mmol, 1 equiv.) was added dropwise at –78 °C. The reaction mixture was stirred for an additional 1 h at –78 °C and then allowed to reach room temperature with continuous stirring. The reaction mixture was quenched with saturated solution of $NH_4Cl$ and extracted with EtOAc. The organic phase was washed with water followed by brine, dried with sodium sulfate, and concentrated in vacuo. Purification through column chromatography (hexane/EtOAc) gave **5e**[23] as a colorless solid in 91% yield. M.p. 95–97 °C. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 1.07 (m, 6 H), 1.59 (d, 6 H), 3.51 (m, 1 H), 3.71 (d, 1 H), 7.13–7.43 (m, 14 H) ppm. $^{13}$C NMR (51 MHz, $CDCl_3$): $\delta$ = 20.44, 20.78, 20.86, 45.96, 51.10, 125.18, 125.24, 125.70, 128.29, 128.46, 128.56, 129.28, 133.44, 133.56, 133.77, 134.10, 134.21, 134.98, 137.13, 137.68, 145.65, 145.89, 169.99 ppm. $^{31}$P NMR (80 MHz, $CDCl_3$): $\delta$ = –14.13 ppm. HRMS: calcd. for $C_{25}H_{28}NOP$ $[M]^+$ 389.1894; found 389.1909.

**Synthesis of [(2-*N*,*N*-Dimethylaminomethyl)phenyl]diphenylphosphane (5f):**[24] The ligand was synthesized according to a published procedure with slight modification. To a solution of *n*BuLi (1.6 M in hexanes, 10.2 mL, 16.3 mmol, 1.2 equiv.) at room temperature was added dimethylbenzylamine (1.84 g, 13.6 mmol, 1 equiv.). The reaction mixture was diluted with freshly distilled $Et_2O$ (15 mL) and allowed to stand for 24 h. The lithiated benzylamine deposited on the flask as a mass of yellow crystals leaving an orange solution. The crystalline mass was resuspended in solution with vigorous stirring. The solution was cooled in an ice water bath and diphenylchlorophosphane (3.0 mL, 16.3 mmol, 1.2 equiv.) was added slowly. The reaction mixture was stirred for 1 h in an ice bath and then warmed to room temperature over 20 min. The mixture was recooled in ice, and the reaction was cautiously quenched by the slow addition of water. The reaction mixture was partitioned between 2 M HCl and $Et_2O$. The HCl extracts were adjusted to pH 12 with NaOH. The resultant aqueous solution was extracted with $CH_2Cl_2$. The $CH_2Cl_2$ extracts were dried, filtered, and concentrated in vacuo to give an orange oil. The crude product was crystalized by adding ethanol (8.0–10.0 mL) and cooling at –20 °C to give **5f** in 90% yield. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 2.08 (s, 6 H), 3.64 (s, 2 H), 6.90 (m, 1 H), 7.13–7.31 (m, 12 H), 7.48 (m, 1 H) ppm. $^{31}$P (80 MHz, $CDCl_3$): $\delta$ = –15.43 ppm.

**Synthesis of *N*,*N*-Diisopropyl-2-(di-*tert*-butylphosphanyl)benzamide (5g):**[23] To a flame-dried flask with a stirring bar was added *N*,*N*-diisopropylbenzamide (0.454 mg, 2.2 mmol) and THF (4 mL) under an argon atmosphere. The resultant solution was cooled to –78 °C and *n*BuLi (1.6 M in hexanes, 1.66 mL, 2.65 mmol) was added dropwise. The reaction mixture was stirred for 30 min at –78 °C. Chloro-di-*tert*-butylphosphane (0.585 mL, 2.65 mmol) was added to the reaction mixture followed by stirring at –78 °C for 2 h. The reaction mixture was further stirred at 1 h at room temperature. The reaction mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure to give the crude product, which was purified by flash chromatography to afford **5g** as a white solid in 78% yield. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.66 (d, $J$ = 7.4 Hz, 1 H), 7.24 (t, $J$ = 7.4 Hz, 1 H), 7.18 (t, $J$ = 7.3 Hz, 1 H), 7.05 (d, $J$ = 5.9 Hz, 1 H), 3.57 (hept., $J$ = 6.6 Hz, 1 H), 3.38 (hept., $J$ = 6.8 Hz, 1 H), 1.47 (dd, $J$ = 9.6, 6.8 Hz, 6 H), 1.17–1.04 (m, 21 H), 0.95 (d, $J$ = 6.6 Hz, 3 H) ppm. $^{31}$P NMR (243 MHz, $CDCl_3$): $\delta$ = 23.09 ppm.

**Synthesis of *N*,*N*-Diisopropyl-2-(dicyclohexylphosphanyl)benzamide (5h):**[23] To a flame-dried flask with a stirring bar was added *N*,*N*-diisopropylbenzamide (0.454 mg, 2.2 mmol) and THF (4 mL) under an argon atmosphere. The resultant solution was cooled to –78 °C and *n*BuLi (1.6 M in hexanes, 1.66 mL, 2.65 mmol) was added dropwise. The reaction mixture was stirred for 30 min at –78 °C. Chlorodicyclohexylphosphane (0.585 mL, 2.65 mmol) was added to the reaction mixture followed by stirring at –78 °C for 2 h. The reaction mixture was further stirred at 1 h at room temperature. The reaction mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure to give the crude product, which was purified by flash chromatography to afford **5h** as a white solid in 75% yield. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.62–7.41 (m, 1 H), 7.32 (s, 2 H), 7.15 (s, 1 H), 3.56 (d, $J$ = 20.2 Hz, 1 H), 3.52–3.35 (m, 1 H), 2.11–1.03 (m, 34 H) ppm. $^{31}$P NMR (243 MHz, $CDCl_3$): $\delta$ = –9.22 ppm.

**Synthesis of 1,3,5,7-Tetramethyl-2,4,8-trioxa-6-(2′-*N*,*N*-diisopropylbenzamide)-6-phosphaadamantane (5i):** A mixture containing 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphaadamantane (0.152 g, 0.70 mol, 2 equiv.), 2-bromo-*N*,*N*-diisopropylbenzamide (0.100 g, 0.35 mol, 1 equiv.), triethylamine (0.106 g, 0.70 mol, 2 equiv.), nickel acetate tetrahydrate (0.272 g, 1.09 mmol, 3.1 equiv.), and toluene (2.0 mL) was heated to reflux under a nitrogen atmosphere with magnetic stirring. During this time the nickel acetate dissolved, generating a reddish brown solution. After 60 h at reflux, the mixture was filtered through a pad of Celite. The organic solvent was evaporated to yield a crude mass, which was purified by flash chromatography (10–15% EtOAc/hexanes) to yield a colorless, crystalline solid in 60% yield. M.p. 180–183 °C. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 8.26 (d, $J$ = 7.8 Hz, 1 H), 7.38 (t, $J$ = 7.4 Hz, 1 H), 7.33 (td, $J$ = 7.6, 1.5 Hz, 1 H), 7.16 (ddd, $J$ = 7.4, 3.0, 1.3 Hz, 1 H), 3.55–3.43 (m, 2 H), 2.06–1.97 (m, 2 H), 1.92 (dd, $J$ = 25.1, 13.1 Hz, 1 H), 1.60 (d, $J$ = 6.8 Hz, 3 H), 1.57–1.52 (m, 4 H), 1.45 (s, 3 H), 1.41 (s, 3 H), 1.36 (d, $J$ = 12.7 Hz, 3 H), 1.34 (d, $J$ = 12.7 Hz, 3 H), 1.19 (d, $J$ = 6.7 Hz, 3 H), 1.03 (d, $J$ = 6.6 Hz, 3 H) ppm. $^{31}$P NMR (243 MHz, $CDCl_3$): $\delta$ = –35.84 ppm. $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ = 169.97 (d, $J$ = 4.7 Hz), 148.61 (d, $J$ = 37.75 Hz), 133.92 (d, $J$ = 2.8 Hz), 130.3 (d, $J$ = 33.22 Hz), 129.93 (s), 127.85 (s), 125.66 (d, $J$ = 8.7 Hz), 96.84 (s), 96.19 (s), 73.90 (d, $J$ = 4.5 Hz), 73.79 (d, $J$ = 16.61 Hz), 51.04 (s), 45.95 (s), 45.84 (s), 36.45 (s), 28.65 (d, $J$ = 21.3 Hz), 28.10 (s), 27.85 (s), 26.62 (d, $J$ = 10.9 Hz), 20.77 (s), 20.73 (s), 20.55 (s), 20.25 (s) ppm. HRMS: calcd. for $C_{23}H_{34}NO_4P$ $[M]^+$ 419.2223; found 419.2225.

**General Procedure for the Preparation of the Ligand/AgOAc Complex (1:1):**[8] To an oven-dried flask was added the corresponding ligand (0.100 g, 1.00 equiv.), silver acetate (1.00 equiv.), and freshly distilled dichloromethane (5.0 mL), and the solution was stirred at room temperature for 10–12 h in the dark. The resultant homogeneous reaction mixture was filtered through a pad of Celite to re-

move any insoluble impurities. The organic layer was evaporated, further treated with dry pentane (2.0 mL), and concentrated. The complex obtained was dried under high vacuum to yield the silver acetate complex.

**6a:** Yield: 99%. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.49–7.38 (m, 15 H), 2.09 (s, 3 H) ppm. $^{31}$P NMR (243 MHz, $CDCl_3$): $\delta$ = 16.28 (br. s) ppm.

**6b:** Yield: 99%. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.57–7.34 (m, 11 H), 7.00–6.86 (m, 2 H), 6.79–6.65 (m, 1 H), 3.78 (s, 3 H), 2.09 (s, 3 H) ppm. $^{31}$P NMR (243 MHz, $CDCl_3$): $\delta$ = 2.12 (d, $J$ = 670.6 Hz) ppm.

**6c:** Yield: 82%. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.56 (d, $J$ = 6.8 Hz, 1 H), 7.45 (t, $J$ = 7.3 Hz, 3 H), 7.42–7.29 (m, 8 H), 7.22 (t, $J$ = 7.5 Hz, 1 H), 6.84 (t, $J$ = 8.5 Hz, 1 H), 4.75 (s, 2 H), 1.93 (s, 3 H) ppm. $^{31}$P NMR (243 MHz, $CDCl_3$): $\delta$ = 4.21 (s) ppm.

**6d:** Yield: 99%. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 8.17 (ddd, $J$ = 7.7, 4.2, 1.1 Hz, 1 H), 7.56 (t, $J$ = 7.6 Hz, 1 H), 7.50–7.36 (m, 11 H), 6.99–6.87 (m, 1 H), 3.73 (s, 3 H), 2.08 (s, 3 H) ppm. $^{31}$P NMR (243 MHz, $CDCl_3$): $\delta$ = 17.77 (d, $J$ = 833.49 Hz) ppm.

**6e:** Data previously reported.[8]

**6f:** Yield: 99%. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.49–7.38 (m, 6 H), 7.36 (dd, $J$ = 10.5, 4.0 Hz, 4 H), 7.31 (t, $J$ = 7.5 Hz, 1 H), 7.24–7.11 (m, 2 H), 6.84–6.73 (m, 1 H), 3.26 (s, 2 H), 2.09 (s, 6 H), 2.04 (s, 3 H) ppm. $^{31}$P NMR (243 MHz, $CDCl_3$): $\delta$ = 5.29 (d, $J$ = 690.12 Hz) ppm.

**6g:** Yield: 99%. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.81 (d, $J$ = 5.8 Hz, 1 H), 7.44 (d, $J$ = 6.3 Hz, 1 H), 7.37 (t, $J$ = 6.5 Hz, 1 H), 7.20 (d, $J$ = 1.0 Hz, 1 H), 3.60–3.35 (m, 2 H), 1.98 (s, 3 H), 1.76 (d, $J$ = 6.1 Hz, 3 H), 1.44 (d, $J$ = 6.3 Hz, 3 H), 1.39–1.24 (m, 21 H), 1.06 (d, $J$ = 6.0 Hz, 3 H) ppm. $^{31}$P NMR (243 MHz, $CDCl_3$): $\delta$ = 46.63 (d, $J$ = 692.55 Hz) ppm. M.p. >170 °C (complex decomposes slightly at this temperature), melts at 190–200 °C.

**Development of X-ray Crystals of 6g:** Compound **6g** was dissolved in dichloromethane followed by slow addition of pentane (10×) over it. Crystals were developed after slow evaporation of the solvents.

**6h:** Yield: 99%. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.59 (t, $J$ = 7.1 Hz, 1 H), 7.51–7.41 (m, 2 H), 7.25 (dd, $J$ = 3.5, 1.4 Hz, 1 H), 3.67–3.40 (m, 2 H), 2.39–2.24 (m, 1 H), 2.14–1.96 (m, 6 H), 1.87 (t, $J$ = 13.8 Hz, 1 H), 1.82 (d, $J$ = 6.7 Hz, 3 H), 1.71 (m, 4 H), 1.62 (d, $J$ = 11.8 Hz, 1 H), 1.51 (d, $J$ = 6.7 Hz, 5 H), 1.42–1.17 (m, 12 H), 1.13 (d, $J$ = 6.4 Hz, 4 H) ppm. $^{31}$P NMR (243 MHz, $CDCl_3$): $\delta$ = 23.84 (d, $J$ = 711.99 Hz) ppm.

**6i:** Yield: 85% yield. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 8.44 (t, $J$ = 6.6 Hz, 1 H), 7.57–7.51 (m, 1 H), 7.47 (t, $J$ = 7.6 Hz, 1 H), 7.31–7.27 (m, 1 H), 3.64–3.48 (m, 2 H), 2.70 (dd, $J$ = 14.0, 6.4 Hz, 1 H), 2.12–1.97 (m, 5 H), 1.89–1.72 (m, 4 H), 1.57–1.43 (m, 17 H), 1.34 (m, 3 H), 1.15 (m, 3 H) ppm. $^{31}$P NMR (243 MHz, $CDCl_3$): $\delta$ = –9.29 (d, $J$ = 721.71 Hz) ppm.

**General Procedure for the Ag[I] Complex Catalyzed Synthesis of 1,2,3-Triazoles:** To a mixture of phenyl acetylene (0.010 g, 0.09 mmol, 1 equiv.) and benzyl/aryl azide (0.14 mmol, 1.5 equiv.) in toluene (1 mL) was added sequentially catalyst **6g** (2–2.5 mol-%) and caprylic acid (20 mol-%.) The mixture was then stirred with heating at 90 °C for 24 h. The reaction mixture was diluted and extracted with EtOAc (2 × 20 mL), washed with sodium hydrogen carbonate (5 mL) and brine, dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The resulting residue was purified through silica gel column chromatography (10–20% EtOAc/hexanes) to afford the desired product.

**1-Benzyl-4-phenyl-1*H*-1,2,3-triazole (3a):**[5e] $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.79 (dd, $J$ = 8.2, 1.1 Hz, 2 H), 7.65 (s, 1 H), 7.43–7.34 (m, 5 H), 7.34–7.27 (m, 3 H), 5.57 (s, 2 H) ppm. $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ = 148.24, 134.68, 130.51, 129.18, 128.82, 128.20, 128.09, 125.73, 119.48, 54.28 ppm.

**1-(4-Methoxybenzyl)-4-phenyl-1*H*-1,2,3-triazole (3b):**[25] $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.79–7.71 (m, 2 H), 7.58 (s, 1 H), 7.35 (t, $J$ = 7.6 Hz, 2 H), 7.27 (d, $J$ = 7.4 Hz, 1 H), 7.23 (d, $J$ = 8.7 Hz, 2 H), 6.87 (d, $J$ = 8.7 Hz, 2 H), 5.47 (s, 2 H), 3.77 (s, 3 H) ppm. $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ = 159.95, 148.07, 130.50, 129.65, 128.75, 128.11, 126.56, 125.67, 119.22, 114.50, 55.32, 53.80 ppm.

**1-(4-Chlorobenzyl)-4-phenyl-1*H*-1,2,3-triazole (3c):**[25] $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.84–7.76 (m, 2 H), 7.66 (s, 1 H), 7.43–7.38 (m, 2 H), 7.38–7.34 (m, 2 H), 7.32 (dt, $J$ = 9.1, 4.3 Hz, 1 H), 7.25 (s, 2 H), 5.55 (s, 2 H) ppm. $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ = 149.09, 135.55, 133.84, 131.02, 130.05, 130.04, 129.51, 128.96, 126.39, 120.05, 54.17 ppm.

**1-(3-Bromobenzyl)-4-phenyl-1*H*-1,2,3-triazole (3d):**[5e] $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.87–7.80 (m, 2 H), 7.72 (s, 1 H), 7.53 (d, $J$ = 7.7 Hz, 1 H), 7.50 (s, 1 H), 7.44 (t, $J$ = 7.6 Hz, 2 H), 7.39–7.33 (m, 1 H), 7.32–7.23 (m, 2 H), 5.58 (s, 2 H) ppm. $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ = 148.48, 136.88, 131.99, 131.00, 130.74, 130.34, 128.86, 128.33, 126.56, 125.76, 123.16, 119.49, 53.48 ppm.

**1-Benzyl-4-(4-fluorophenyl)-1*H*-1,2,3-triazole (3e):**[26] $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.77 (dd, $J$ = 8.9, 5.3 Hz, 2 H), 7.61 (s, 1 H), 7.42–7.35 (m, 3 H), 7.33–7.30 (m, 2 H), 7.09 (t, $J$ = 8.7 Hz, 2 H), 5.57 (s, 2 H) ppm. $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ = 162.82 (d, $J$ = 247.3 Hz), 147.53 (s), 134.73 (s), 129.34 (s), 129.00 (s), 128.24 (s), 127.59 (d, $J$ = 8.1 Hz), 126.91 (d, $J$ = 2.7 Hz), 119.34 (s), 115.93 (d, $J$ = 21.7 Hz), 54.44 (s) ppm.

**1-Benzyl-4-(4-bromophenyl)-1*H*-1,2,3-triazole (3f):**[27] $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.70 (m, 3 H), 7.58–7.53 (m, 2 H), 7.45–7.38 (m, 3 H), 7.34 (d, $J$ = 6.3 Hz, 2 H), 5.60 (s, 2 H) ppm. $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ = 147.36 (s), 134.63 (s), 132.11 (s), 129.64 (s), 129.37 (s), 129.06 (s), 128.28 (s), 127.38 (s), 122.22 (s), 119.66 (s), 54.49 (s) ppm.

**1-Benzyl-4-m-tolyl-1*H*-1,2,3-triazole (3g):**[25] $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.66 (s, 1 H), 7.64 (s, 1 H), 7.57 (d, $J$ = 7.7 Hz, 1 H), 7.42–7.34 (m, 3 H), 7.33–7.30 (m, 2 H), 7.28 (t, $J$ = 7.7 Hz, 1 H), 7.13 (d, $J$ = 7.6 Hz, 1 H), 5.58 (s, 2 H), 2.38 (s, 3 H) ppm. $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ = 148.46 (s), 138.65 (s), 134.82 (s), 130.46 (s), 129.31 (s), 129.13 (s), 128.90 (d, $J$ = 13.9 Hz), 128.22 (s), 126.55 (s), 122.97 (s), 119.60 (s), 54.42 (s), 21.54 (s) ppm.

**1-Benzyl-4-(2-chlorophenyl)-1*H*-1,2,3-triazole (3h):**[28] $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 8.18 (dd, $J$ = 7.9, 1.6 Hz, 1 H), 8.04 (s, 1 H), 7.37–7.27 (m, 5 H), 7.26–7.22 (m, 2 H), 7.19 (m, 1 H), 5.54 (s, 2 H) ppm. $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ = 144.44, 134.69, 131.18, 130.17, 129.83, 129.23, 129.16, 129.04, 128.77, 127.95, 127.17, 123.19, 54.25 ppm.

**Ethyl 2-(4-Phenyl-1*H*-1,2,3-triazol-1-yl)acetate (3i):**[5c] $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.94 (s, 1 H), 7.90–7.85 (m, 2 H), 7.46 (t, $J$ = 7.7 Hz, 2 H), 7.38 (t, $J$ = 7.4 Hz, 1 H), 5.26 (s, 2 H), 3.86 (s, 3 H) ppm. $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ = 166.72, 148.37, 130.32, 128.87, 128.35, 125.85, 120.90, 53.11, 50.84 ppm.

**1-(2-Phenylethyl)-4-phenyl-1*H*-1,2,3-triazole (3j):**[29] $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.79 (dd, $J$ = 8.3, 1.1 Hz, 2 H), 7.49 (s, 1 H), 7.43 (t, $J$ = 7.7 Hz, 2 H), 7.38–7.31 (m, 3 H), 7.31–7.26 (m, 1 H), 7.17 (d, $J$ = 7.4 Hz, 2 H), 4.67 (t, $J$ = 7.3 Hz, 2 H), 3.29 (t, $J$ = 7.2 Hz, 2 H) ppm. $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ = 147.49,

137.08, 130.63, 128.88, 128.82, 128.75, 128.10, 127.17, 125.72, 119.90, 51.78, 36.82 ppm.

**1-Benzyl-4-butyl-1*H*-1,2,3-triazole (3k):**[30] $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.32–7.25 (m, 3 H), 7.19 (m, 2 H), 7.11 (s, 1 H), 5.42 (s, 2 H), 2.65–2.57 (m, 2 H), 1.62–1.50 (m, 2 H), 1.35–1.22 (m, 2 H), 0.84 (t, $J$ = 7.4 Hz, 3 H) ppm. $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ = 149.14 (s), 135.21 (s), 129.29 (s), 128.85 (s), 128.20 (s), 120.72 (s), 54.25 (s), 31.73 (s), 25.62 (s), 22.55 (s), 14.03 (s) ppm.

**1-(4-Chlorobenzyl)-4-butyl-1*H*-1,2,3-triazole (3l):** $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.36–7.31 (m, 2 H), 7.18 (m, 3 H), 5.46 (s, 2 H), 2.74–2.64 (m, 2 H), 1.67–1.57 (m, 2 H), 1.43–1.31 (m, 2 H), 0.91 (t, $J$ = 7.4 Hz, 3 H) ppm. $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ = 149.23 (s), 134.80 (s), 133.62 (s), 129.40 (s), 120.58 (s), 53.39 (s), 31.60 (s), 25.49 (s), 22.44 (s), 13.92 (s) ppm. HRMS: calcd. for $C_{13}H_{16}ClN_3$ $[M]^+$ 249.1034, found 249.1033. M.p. 52–54 °C.

**1-(4-Chlorophenyl)-4-(4-fluorophenyl)-1*H*-1,2,3-triazole (3m):** $^1$H NMR (600 MHz, DMSO): $\delta$ = 9.33 (s, 1 H), 8.03–7.94 (m, 4 H), 7.77–7.68 (m, 2 H), 7.36 (t, $J$ = 8.9 Hz, 2 H) ppm. $^{13}$C NMR (151 MHz, DMSO): $\delta$ = 162.03 (d, $J$ = 245.0 Hz), 146.56 (s), 135.39 (s), 132.99 (s), 129.92 (s), 127.42 (s), 127.36 (s), 126.67 (d, $J$ = 2.5 Hz), 126.66 (s), 121.64 (s), 119.63 (s), 116.06 (s), 115.92 (s) ppm. HRMS: calcd. for $C_{14}H_9ClFN_3$ $[M]^+$ 273.0479; found 273.0469. M.p. 205–208 °C

**1-(4-Chlorophenyl)-4-phenyl-1*H*-1,2,3-triazole (3n):**[31] $^1$H NMR (600 MHz, DMSO): $\delta$ = 9.34 (s, 1 H), 8.01 (d, $J$ = 8.9 Hz, 2 H), 7.95 (dd, $J$ = 8.2, 1.1 Hz, 2 H), 7.73 (d, $J$ = 8.9 Hz, 2 H), 7.51 (t, $J$ = 7.7 Hz, 2 H), 7.42–7.37 (m, 1 H) ppm. $^{13}$C NMR (151 MHz, DMSO): $\delta$ = 147.44 (s), 135.44 (s), 132.96 (s), 129.92 (s), 129.02 (s), 128.33 (s), 125.34 (s), 121.66 (s), 119.71 (s) ppm.

**1-(4-Methoxyphenyl)-4-phenyl-1*H*-1,2,3-triazole (3o):**[31] $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 8.14 (s, 1 H), 7.93 (d, $J$ = 6.6 Hz, 2 H), 7.71 (dd, $J$ = 7.0, 1.7 Hz, 2 H), 7.48 (t, $J$ = 6.8 Hz, 2 H), 7.39 (s, 1 H), 7.07 (dd, $J$ = 6.9, 1.8 Hz, 2 H), 3.91 (s, 3 H) ppm. $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ = 160.01 (s), 148.37 (s), 130.70 (s), 130.52 (s), 129.04 (s), 128.48 (s), 125.97 (s), 122.35 (s), 117.98 (s), 114.95 (s), 55.79 (s) ppm.

**4-(4-Fluorophenyl)-1-phenyl-1*H*-1,2,3-triazole (3p):** $^1$H NMR (600 MHz, DMSO): $\delta$ = 9.30 (s, 1 H), 8.00 (dd, $J$ = 8.9, 5.5 Hz, 2 H), 7.97–7.93 (m, 2 H), 7.69–7.62 (m, 2 H), 7.54 (dd, $J$ = 10.6, 4.2 Hz, 1 H), 7.36 (t, $J$ = 8.9 Hz, 2 H) ppm. $^{13}$C NMR (151 MHz, DMSO): $\delta$ = 161.99 (d, $J$ = 244.9 Hz), 146.44 (s), 136.61 (s), 129.94 (s), 128.76 (s), 127.38 (d, $J$ = 8.2 Hz), 126.84 (s), 120.01 (s), 119.56 (s), 116.04 (s), 115.89 (s) ppm. HRMS: calcd. for $C_{14}H_{10}FN_3$ $[M]^+$ 239.0850; found 239.0859. M.p. 198–200 °C.

CCDC-843618 (for **6e**) and -882589 (for **6g**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Supporting Information** (see footnote on the first page of this article): Copies of $^1$H, $^{13}$C and $^{31}$P NMR spectra of complex **6g** and $^1$H and $^{13}$C NMR spectra of the triazoles **3a**–**3p**.

## Acknowledgments

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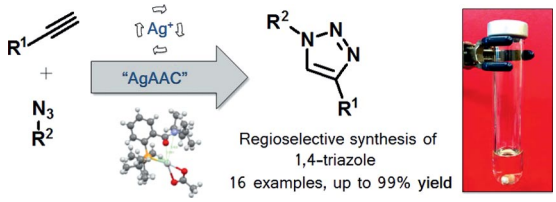


A highly efficient, chemically stable, and well-defined homogeneous silver(I) catalyst is reported for the cycloaddition of azides onto terminal alkynes (Ag-AAC reaction).

**Click Chemistry**

**J. McNulty,* K. Keskar ..... 1–10**

Discovery of a Robust and Efficient Homogeneous Silver(I) Catalyst for the Cycloaddition of Azides onto Terminal Alkynes

**Keywords:** Cycloaddition / Azides / Alkynes / Click chemistry / Silver

  