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Gold(I)-Catalyzed Chloroalkynylation of 1,1-Disubstituted Alkenes via 1,3-Chlorine Shift: A Combined Experimental and Theoretical Study

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ABSTRACT:

The haloalkynylation reaction is of great interest for the synthesis of complex molecules as it represents a carbon-carbon bond-forming reaction where the reactive halide reappears in the product. The latter enables further chemical transformations. However, only a few examples of haloalkynylations have been described so far. By using alkenes as reactant, this reaction is strictly limited to norbornene systems proceeding via a non-classical carbocation. Herein, we show by means of quantum chemical calculations and experiments that the chloroalkynylation of 1,1-disubstituted alkenes can be successfully achieved via gold(I) catalysis. The key step in the reaction mechanism is a 1,3-chlorine shift to a cationic center leading selectively to the corresponding homopropargyl chlorides. As this gold(I)-catalyzed addition can be conducted on a preparative scale and tolerates a broad substrate scope of both alkyne and alkene reactants, the presented chloroalkynylation reaction is an attractive method en route to complex alkynes and their congeners.

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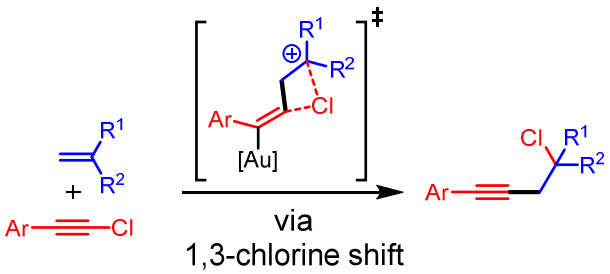
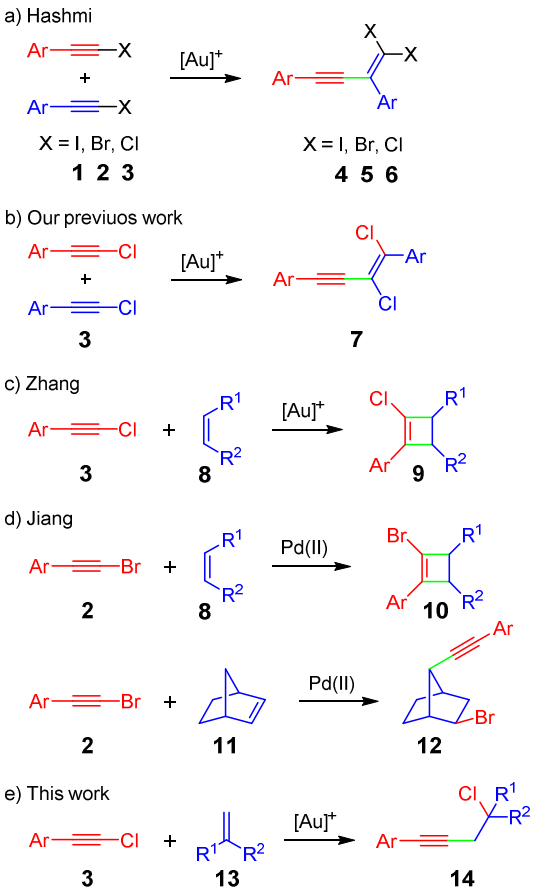


Introduction

The development of new carbon-carbon bond-forming procedures for the synthesis of complex molecules is a challenge and though fundamental task in modern organic chemistry.[1] In this context, alkyl halides are important intermediates, whereby the halogen atom is usually discarded during a carbon-carbon bond-forming reaction, rendering these transformations nonatom economic. Nevertheless, there are some examples for haloacetylenes in carbon-carbon bond formations in which the reactive halide of the starting material is retained (Scheme 1).[2-3] This has the advantage that the reactive halide in the product can be used for further chemical transformations. Furthermore, haloacetylenes are easily accessible from the corresponding terminal alkyne and easy to handle.[2] For example, fluoroalkylacetylenes and chloroarylacetylenes are activated by Bent's rule[4] and only start to oligomerize at temperatures above 100 °C.[5-6] The activation barrier for the thermal dimerization of chloroarylacetylenes is influenced by the substituent at the aromatic unit.[7-9] Unfortunately, this reaction lacks in selectivity and leads to complex product mixtures,[5,7-8] making this thermal dimerization an unattractive method for a preparative application.

However, the dimerization of haloacetylenes via gold(I) catalysis[10-21] can be used on a preparative scale and gives direct access to halogen-substituted enyne systems. For example, Hashmi *et al.* were able to demonstrate that the iodoalkynes **1** dimerize via dual gold(I) catalysis[22] to the corresponding head-to-tail products **4** (Scheme 1a).[23] Besides the iodoalkynes **1**, also one example for both bromoacetylene and chloroacetylene has been presented which gives the corresponding enynes **5** and **6**, respectively. The enynes **4**-**6** are formed via a dual σ,π activation of the corresponding haloacetylenes **1**-**3**.[23] The first step is the formation of a gold acetylide by a metal-halogen exchange (σ activation), followed by the activation of another alkyne unit by the cationic gold complex (π activation). The π complex is subsequently attacked by the gold acetylide (carbon-carbon bond-forming). In the last step, the gold complex is replaced by chlorine via a metal-halogen exchange which exclusively delivers the head-to-tail dimer.[23]

The variation of the gold(I) catalyst has a significant impact on the outcome of the dimerization reaction. Only recently we were able to show that the chloroacetylenes **3** can also be dimerized to the corresponding head-to-head products **7** via mono gold(I) catalysis (Scheme 1b).[24] Here, the key step is the formation of a vinyl cation which is stabilized via an unusual 1,3-chlorine shift. This mechanism enables the stereoselective synthesis of *trans*-1,2-dichloroenynes **7**. From a formal point of view, this reaction can be considered as a *syn* addition of one alkynyl moiety and a chloride to a chloroacetylene, which corresponds to a 1,2-chloroalkynylation of a chloroacetylene.



Scheme 1. Gold(I)-catalyzed dimerization of haloarylacetylenes **1**-**3** (a and b). Palladium(II)- and gold(I)-catalyzed addition of haloarylacetylenes **2** and **3** to alkenes (c-e).

The addition of haloacetylenes to alkyl-substituted alkynes and alkenes via gold(I) catalysis is also possible. However, in this case always a cycloaddition reaction takes place. For example, iododialkynes react via dual gold catalysis in an intramolecular reaction to the corresponding iodofulvenes.[25] L. Zhang *et al.* were able to show, that the non-activated alkenes **8** (mono- and 1,2-disubstituted alkenes) can be reacted with the chloroarylacetylenes **3** to form the cyclobutenes **9** in good yields via a gold-catalyzed intermolecular [2+2] cycloaddition (Scheme 1c).[26] It is noteworthy, that this reaction enables the use of more challenging monosubstituted non-activated alkenes while exhibiting excellent regioselectivities. From the mechanistic point of view the reaction proceeds via mono gold(I) catalysis. In the first step, the gold complex activates the triple bond via formation of a π complex.[26] As the electron-withdrawing nature of chlorine makes this π complex more polarized towards its vinyl cationic resonance structure, it reacts with an alkene to a gold-stabilized cyclopropylmethyl cation. The final step is the enlargement of the three-membered ring and the subsequent E1-type elimination of the gold complex to form the cyclobutenes **9**.[26]

The addition reaction of the bromoacetylenes **2** with the alkenes **8** was achieved via Pd(II) catalysis (Scheme 1d).[27] Here, the outcome of the reaction strongly depends on the alkene substrate. The reaction of different bromoacetylenes with cyclooctene leads selectively to the corresponding cycloaddition products **10** (Scheme 1d).[27] By changing the alkene partner to norbornene (**11**) and its derivates, a 1,7-bromoalkynylation takes places (Scheme 1d).[27] The formation of these products can be explained by an intermediary formed non-classical carbocation. Therefore, only norbornene and its derivates react with haloacetylenes under these conditions. Furthermore, the outcome of this reaction is very sensitive to the alkyne and the reaction conditions. For example, the conversion of iodoacetylenes **1** with norbornene gives the 1,2- and the 1,7-iodoalkynylation product depending on the solvent used.[28] The formation of both products can be explained via the non-classical norbornene cation.

Except for norbornenes, no 1,2-haloalkynylation of alkenes has been described so far to the best of our knowledge. This addition reaction would be of great interest, since it represents a carbon-carbon bond-forming reaction where the reactive halide reappears in the product. Herein, we describe our investigation of the 1,2-chloroalkynylation of disubstituted alkenes. By means of quantum chemical calculations, we are able to show that the mono gold(I)-catalyzed reaction of chlorophenylacetylene with 1,2-disubstituted alkenes leads to the [2+2] cycloaddition products. By contrast, the gold(I)-catalyzed reaction of chlorophenylacetylene with 1,1-disubstituted alkenes results in the desired 1,2-haloalkynylation via a 1,3-chlorine shift. Experimental studies support our calculations, and hence we present the synthesis of a series of homopropargyl chlorides, which are otherwise not easily available. Noteworthy, this transformation is one of the few gold-catalyzed reactions reforming an alkyne by an elimination process.[29-30,24]

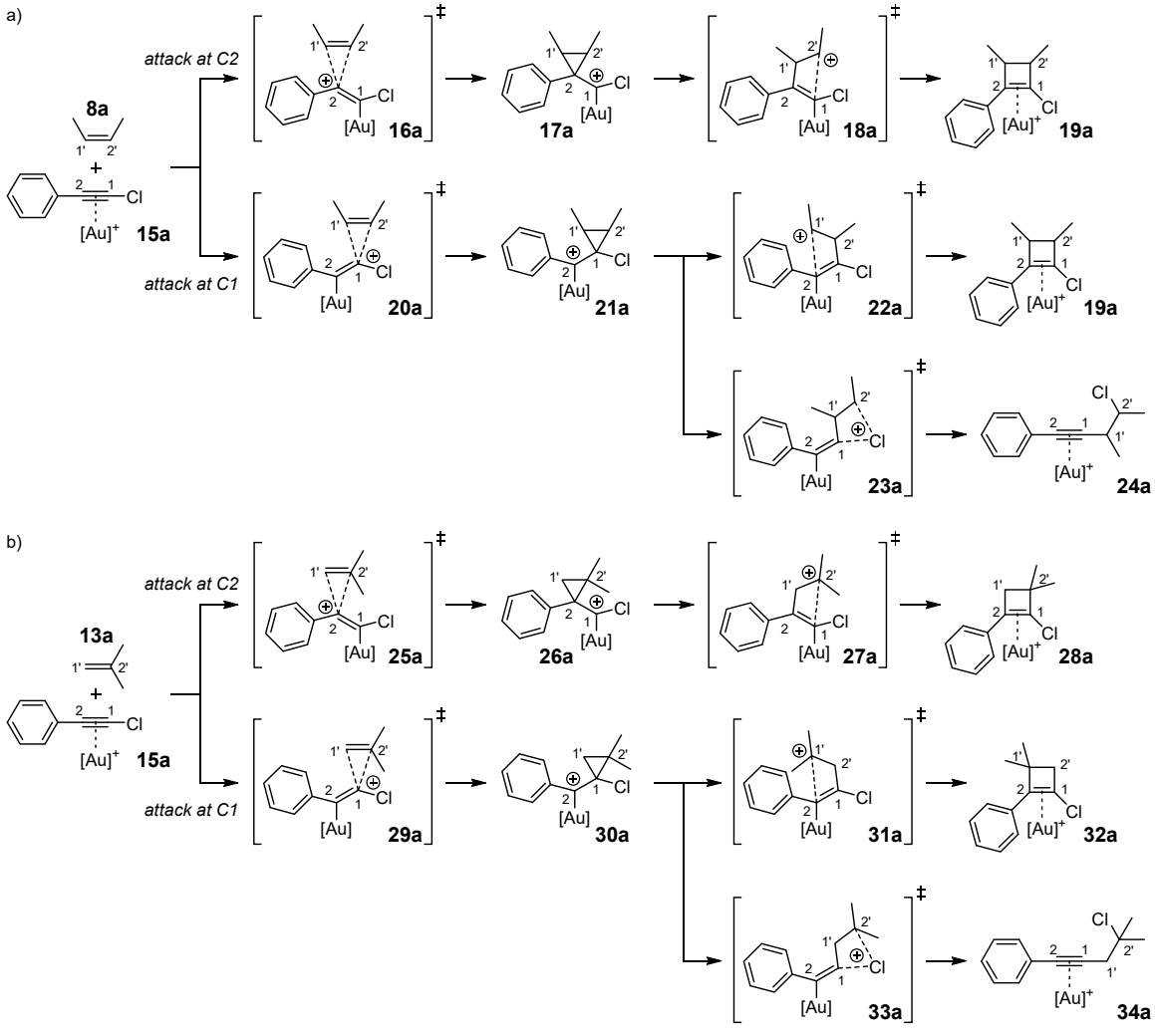
Results and Discussion

a) Quantum Chemical Model Studies

First, we wanted to examine by means of quantum chemical calculations whether a 1,2-chloroalkynylation of alkenes can be achieved via gold(I) catalysis. Chlorophenylacetylene (**3a**; Scheme 2) was chosen as model system, as it is the simplest representative of the chloroarylacetylenes and served well in previous quantum chemical calculations on the dimerization of chloroacetylenes.[8,24] Furthermore, we chose *cis*-2-butene (**8a**) and isobutene (**13a**), as they are the simplest representatives of 1,2- and 1,1-disubstituted alkenes. For the quantum chemical study, we only considered the mono gold(I)-catalyzed reaction as we can rule out a metal-halogen exchange via dual catalysis under these conditions.[23] The isolated alkenes (**8a** and **13a**) and the π complex of chlorophenylacetylene (**15a**) were defined as the

reference system for the comparison of the energetic values. As ligand for the cationic gold complex, the neutral phosphine PMe_3 was chosen ($[Au]^+ = Au^+$-PMe_3).

For the reaction of the complex **15a** with the alkenes **8a** and **13a** we considered in each case three realistic paths (Scheme 2): The nucleophilic attack at the carbon atom C2 of the alkyne complex **15a** leads to the gold-stabilized cyclopropylmethyl cations **17a** (Scheme 2a) and **26a** (Scheme 2b), respectively. The transformation of the alkyne into a cyclopropyl cation is a manifestation of masked dicarbene reactivity.[31] Both cations can be stabilized via a ring enlargement to form the complexes **19a** and **28a**, respectively. This reaction pathway corresponds to the reaction mechanism for the [2+2] cycloaddition of chloroacetylene **3** with alkenes **8** proposed by L. Zhang *et al.* (Scheme 1c).[26]



Scheme 2. The gold(I)-catalyzed reaction of chlorophenylacetylene (**3a**) with the disubstituted alkenes **8a** and **13a** can lead to the cyclobutenes **19a**, **28a** and **32a** as well as to the alkynes **24a** and **34a**. $[Au]^+ = Au^+$-PMe_3.

The other two realistic pathways start with the nucleophilic attack of alkenes **8a** and **13a** at the carbon atom C1 of the alkyne complex **15a** (Scheme 2). Here again the corresponding

cyclopropylmethyl cations **21a** and **30a**, respectively, are formed in the first step. However, these cations can now be stabilized in different ways. On the one hand, both cations can undergo ring enlargement to form the cyclobutene complexes **19a** and **32a**, respectively. On the other hand, a ring-opening process accompanied by a 1,3-chlorine shift can lead to the alkyne complexes **24a** and **34a**, respectively.

For the optimization of the stationary points for all three reaction pathways, B3LYP[32-34] was chosen as density functional with two different basis sets (B1 and B2). For the basis set B1, the small basis set 6-31G(d)[35-36] was used for the atoms C, H, Cl and P. For B2, the 6-311++G(d,p)[37-40] basis set was employed for the same atoms. In both cases (B1 and B2), the def2-TZVP+ECP[41-42] basis set was used for Au. Frequency calculations were carried out at each of the structures to verify the nature of the stationary point. It turned out that all transition states have exactly one imaginary frequency, whereas all other structures have none. Furthermore, single point calculations by means of the density functionals B3LYP, B3LYP-D3[43-44], PBE0[45-46] and M06[47] were performed on the B3LYP optimized structures. To determine the solvent effect, single point calculations on the B3LYP optimized structures were performed using dichloromethane as solvent. For single point calculations, the basis sets B2, B3 and B4 were used. The basis set B2 has been already described above. In case of B3, the large basis set aug-cc-pVTZ[48-52] was employed for all atoms which are directly involved in the reaction (C1, C2, C1' and Cl, for numbering see Scheme 2). For all other atoms (except Au), the 6-311++G(d,p) basis set was used. B4 includes the basis set aug-cc-pVTZ for the atoms C, H, Cl and P. In both cases (B3 and B4) the aug-cc-pVTZ-PP+ECP[53-54] basis set was applied for Au.

Table 1. Free energies (ΔG in kcal/mol) of **16a**-**34a** relative to the starting materials (**8a** and **15a** for **16a**-**24a**; **13a** and **15a** for **25a**-**34a**) as calculated by means of different methods. $[Au]^+ = Au^+\text{-}PMe_3$.

	ΔG^a	ΔG^b	ΔG^c	ΔG^d	ΔG^e	ΔG^f	ΔG^g	ΔG^h
16a	13.9	16.7	17.1	18.3	18.6	9.2	23.1	13.6
17a	-2.5	2.7	2.8	4.8	5.4	-5.1	8.9	-1.5
18a	15.5	21.2	21.3	23.9	24.2	13.9	27.1	16.7
19a	-20.2	-14.9	-14.7	-12.0	-11.7	-23.1	-10.7	-22.1
20a	19.6	21.1	22.1	22.8	23.1	14.1	27.1	18.1
21a	0.5	5.9	5.9	8.4	8.7	-0.4	12.6	3.5
22a	13.6	18.4	18.0	20.7	21.1	10.4	23.9	13.3
23a	18.1	21.2	21.2	22.7	23.3	15.1	25.1	16.9
24a	-22.7	-19.5	-19.4	-17.5	-17.2	-25.8	-15.0	-23.5
25a	14.0	16.6	16.8	17.9	18.2	9.6	22.6	14.0
26a	-0.3	4.1	3.5	5.4	5.9	-4.1	9.0	-1.0

27a	17.4	23.1	23.0	25.8	26.1	15.2	29.3	18.4
28a	-19.6	-14.4	-14.4	-11.6	-11.3	-22.0	-10.1	-20.8
29a	19.6	21.2	22.0	22.6	22.9	14.6	27.0	18.6
30a	3.4	8.8	8.2	10.7	11.1	1.5	15.0	5.4
31a	20.9	26.0	26.1	29.0	29.3	17.5	32.2	20.4
32a	-17.9	-12.6	-13.0	-10.3	-10.0	-21.2	-8.9	-20.1
33a	11.7	14.6	14.4	15.8	16.3	9.3	18.8	11.8
34a	-23.7	-20.8	-20.4	-18.3	-18.1	-26.4	-15.7	-24.0

[a] B3LYP/B1. [b] B3LYP/B2//B3LYP/B1. [c] B3LYP/B2.

[d] B3LYP/B3//B3LYP/B2. [e] B3LYP/B4//B3LYP/B2. [f] B3LYP-D3/B4//B3LYP/B2.

[g] B3LYP(dichloromethane as solvent)/B4//B3LYP/B2.

[h] B3LYP-D3(dichloromethane as solvent)/B4//B3LYP/B2.

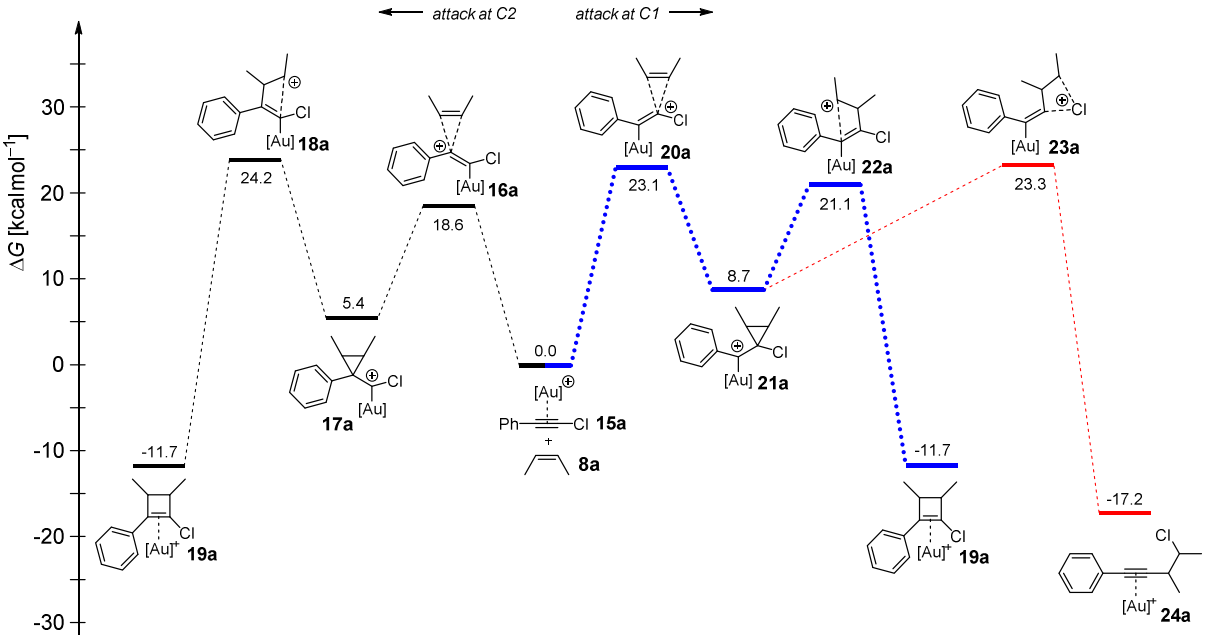


Figure 1. Free energy (Δ*G*) profile for the gold(I)-catalyzed reaction of chlorophenylacetylene (**3a**) with the 1,2-disubstituted alkene **8a** calculated by means of B3LYP/B4//B3LYP/B2. The dominant route to the cycloalkene complex **19a** is highlighted in blue. $[Au]^+ = Au^+\text{-}PMe_3$.

The calculated data are summarized in Tables 1 and S1-S4 and in Figures 1, 2 and S1-S4. If we take a closer look at the data obtained via the B3LYP method, it becomes obvious that the energies strongly depend on the basis set used (Table 1). The difference is most visible for B1 and B2. The values obtained by B3LYP/B2 are throughout higher than the data calculated via B3LYP/B1; the difference amounts in several instances to more than 5 kcal/mol. On the contrary, the differences between the values calculated with B3LYP/B3//B3LYP/B2 and B3LYP/B4//B3LYP/B2 are rather small. Thus, in order to get reliable results for the determination of energies, single point calculations should not be carried out with small basis sets (B1 = 6-31G(d)). Ideally, the very large basis set aug-cc-

pVTZ (B3 and B4) should be used for all atoms directly involved in the reaction. However, for the determination of geometric parameters it is sufficient to use a small basis set, as there is only a slight difference between the data obtained by the methods B3LYP/B2//B3LYP/B1 and B3LYP/B2 (Table 1).

First, we would like to discuss the stationary points for the reaction of the alkyne complex **15a** with alkene **8a**. To consider the loss of entropy during the addition reaction, the free energies (ΔG in kcal/mol) of the stationary points are depicted in Figure 1. Here, the energies derive from single point calculations with B3LYP/B4, while the thermal corrections to the free energy stem from the geometry optimization with B3LYP/B2. It turns out that an attack at the carbon atom C2 of the alkyne via transition state **16a** should be energetically favored over an attack at the carbon atom C1 via transition state **20a** (for numbering of atoms see Scheme 2a). The reason therefore is the stabilization of the positive charge in the transition state: In both cases the gold(I) activation results in a charge separation of the acetylenic carbon atoms.[55] Additionally, in **16a** the positive charge is localized at the carbon atom C2 and stabilized by the phenyl group, whereas in **20a** the positive charge is located at the carbon atom C1 next to the chlorine substituent resulting in less stabilization of the positive charge. Since no additional reactants are involved in the further course of the reaction, the outcome of both reaction pathways is not necessarily determined by the first transition states (**16a** and **20a**), but by the transition states having the highest total free energy. Considering this circumstance, it becomes obvious that transition state **20a** is energetically more favored than transition state **18a**. Thus, the favored attack should occur at the carbon atom C1. As the transition state **22a** exhibits a lower energy compared to **23a**, the cyclobutene **19a** should be formed preferably. This in accordance with experimental results of L. Zhang *et al.* who reported that the gold-catalyzed reaction of chloroacetylenes with 1,2-disubsituted alkenes exclusively delivers the [2+2] cycloaddition products.[26]

Let us now consider the reaction of alkyne complex **15a** with alkene **13a** by using the same level of theory (B3LYP/B4//B3LYP/B2; Figure 2). Here again, the transition state for the attack at the alkynyl carbon atom C2 (**25a**) is energetically more favored than the corresponding transition state **29a** for the attack at the carbon atom C1 (for numbering of atoms see Scheme 2b). However, the rate of the reaction is not determined by the first transition state of a reaction path, but the one showing the highest total free energy through the reaction pathway. Therefore, three transition states (**27a**, **29a** and **31a**) must now be considered when comparing possible reaction pathways. As the transition state **29a** is the most stable amongst them, the reaction is likely to proceed via an attack at the carbon atom C1 of the acetylene. Remarkably, the transition state for the 1,3-chlorine shift (**33a**) is now significantly lower compared to the transition state **31a** for the ring enlargement of the cyclopropylmethyl cation **30a** (Figure 2). This is in contrast to the reaction discussed above

of the 1,2-disubstituted alkene **8a** with chlorophenylacetylene (**3a**), where the ring enlargement of cyclopropylmethyl cation **21a** to form cyclobutene **19a** was energetically favored (see Figure 1). In summary, the energetically favored reaction pathway proceeds via the attack at the alkynyl carbon atom C1 to form the cyclopropylmethyl cation **30a** which is then stabilized by ring opening and a 1,3-chlorine shift to form the highly stable alkyne complex **34a** (Figure 2). According to the B3LYP calculations, the gold(I)-catalyzed reaction of chloroarylacetylenes with 1,1-disubstituted alkenes should preferably lead to a 1,2-chloroalkynylation of the corresponding alkenes.

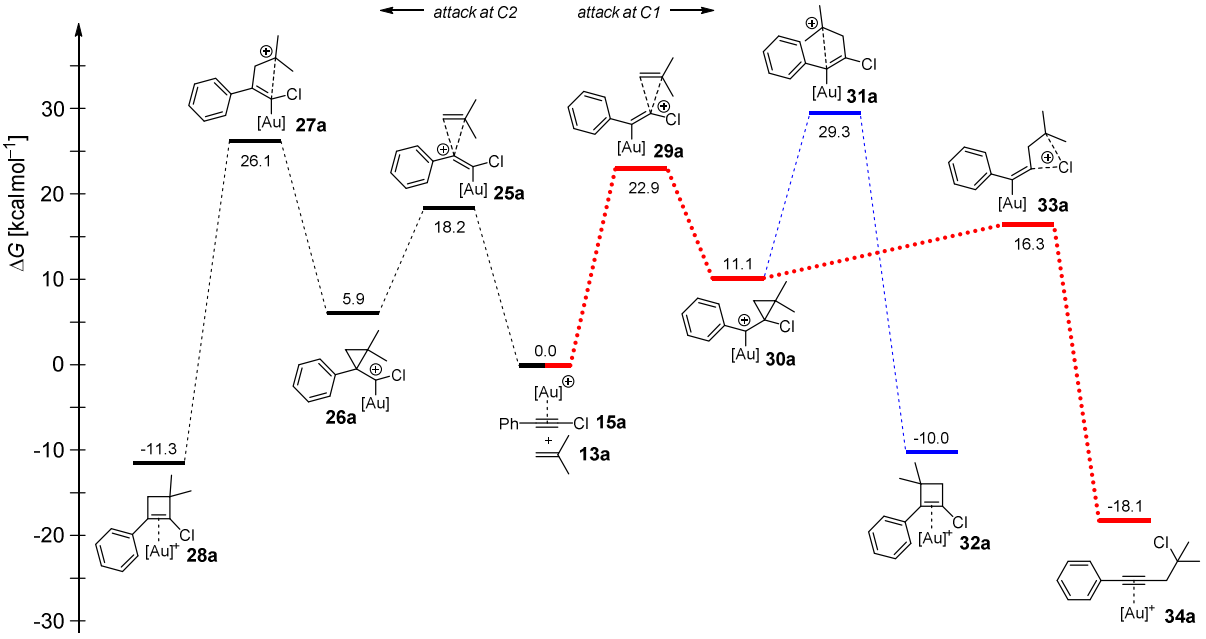


Figure 2. Free energy (Δ*G*) profile for the gold(I)-catalyzed reaction of chlorophenylacetylene (**3a**) with the 1,1-disubstituted alkene **13a** calculated by means of B3LYP/B4//B3LYP/B2. The dominant route to the alkyne complex **34a** is highlighted in red. $[Au]^+ = Au^+\text{-}PMe_3$.

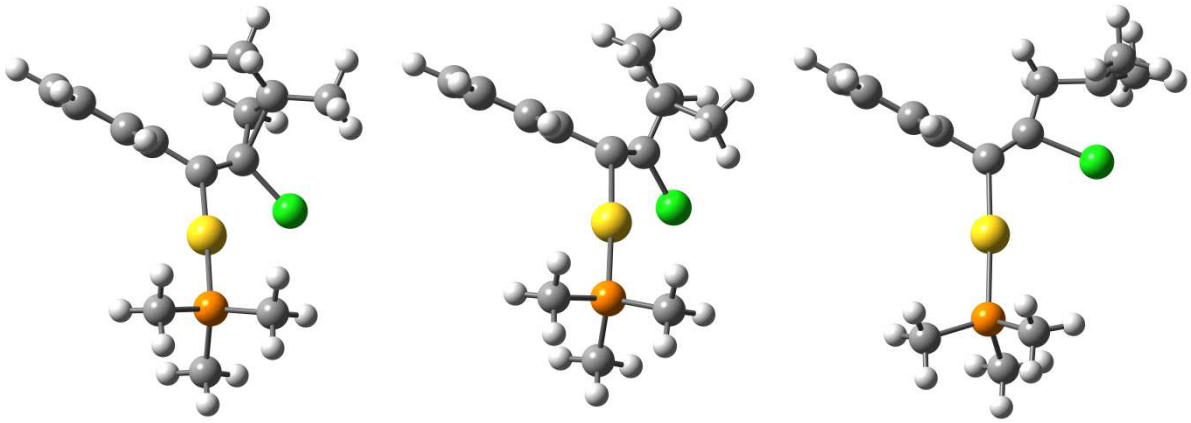


Figure 3. Molecular structures of the intermediate **30a** (left) and the transition states **31a** (middle) and **33a** (right) calculated using B3LYP/6-311++G(d,p)/def2-TZVP+ECP.

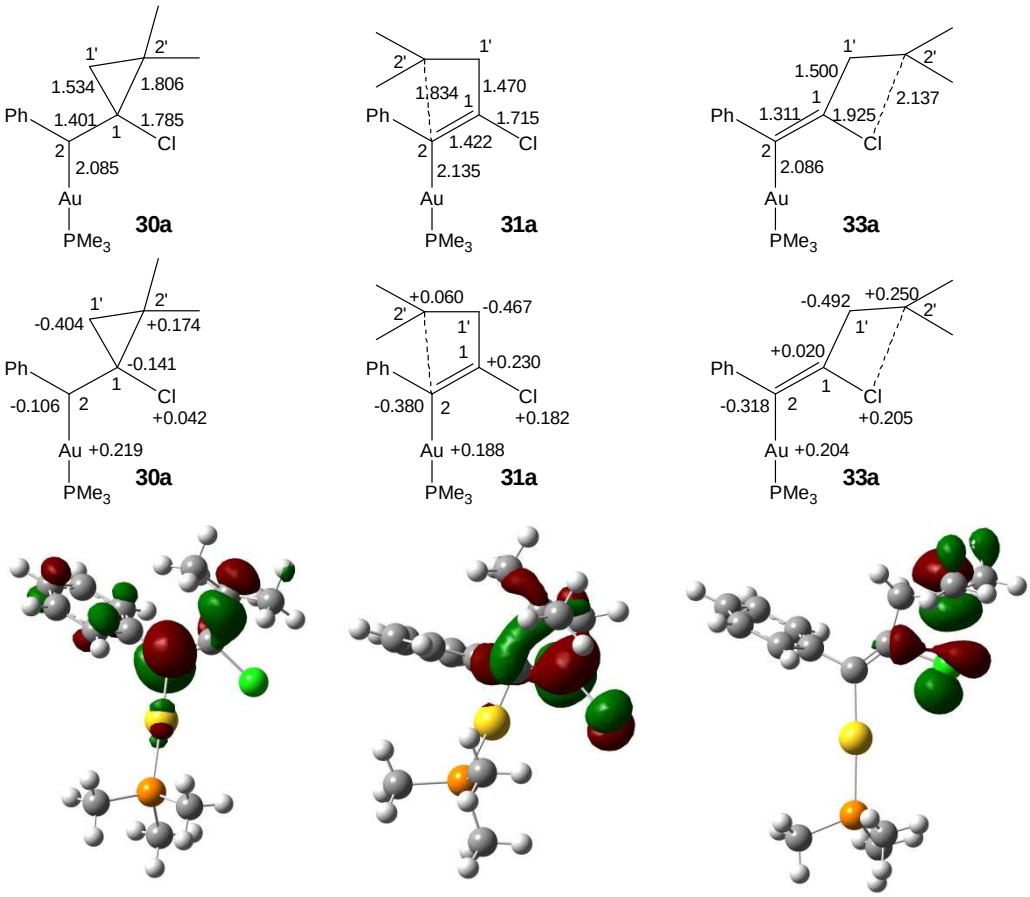


Figure 4. Bond lengths in Ångstrom (top row), natural charges (middle row) and LUMOs (bottom row) of the intermediate **30a** (left) and the transition states **31a** (middle) and **33a** (right) calculated using B3LYP/6-311++G(d,p)/def2-TZVP+ECP.

To clarify why the transition state for the 1,2-chloroalkynylation (**33a**) is significantly lower in energy than the transition state of the [2+2] cycloaddition reaction (**31a**), the structural parameters, natural charges and LUMOs of the intermediate **30a** and of the transition states **31a** and **33a** were examined (Figure 3 and 4). In the intermediate **30a**, the bond length of the C1-C1' bond amounts to 1.534 Å (see top row in Figure 4). This is considerably smaller than the length of the C1-C2' bond (1.806 Å, see Figure 4). Consequently, the C1-C2' bond is more likely to open and initiate one of the two reaction pathways leading to either the [2+2] cycloaddition product **32a** or the 1,2-chloroalkynylation product **34a** (see Figure 2). Of more interest is the distance of the C1-C2 bond: In the transition state **31a** (1.422 Å), this distance is larger than in the intermediate **30a** (1.401 Å). The smallest value is calculated for the transition state **33a** (1.311 Å). Accordingly, these deviations lead to a different charge distribution for the stationary points **30a**, **31a** and **33a**, which can be realized by looking at the natural charges and the size of the coefficients of the LUMOs (see mid and bottom row in Figure 4): For the intermediate **30a** the positive charge is primary localized on the carbon

atom C2. For the transition states the positive charge is located on the carbon atom C1 (natural charge = +0.23) for **31a** and on carbon atom C2' (natural charge = +0.25) for **33a**. This explains the greater stabilization of **33a** in comparison to **23a**. Both stationary points represent the transition state of the 1,3-chlorine shift. For **33a** two methyl groups stabilize the positive charge at the carbon atom C2' (Figure 2) via positive hyperconjugation, whereas the positive charge in **23a** (Figure 1) can be stabilized by only one methyl group. A similar pattern can be observed for the comparison of **22a** and **31a**. For both transition states the positive charge must be stabilized at the carbon atom C1. This is more favorable when an additional methyl group is attached to the carbon atom C1', as is the case in **22a**.

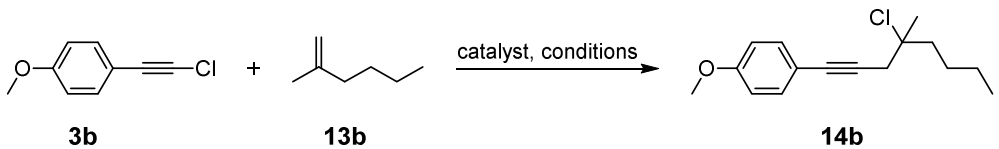
When comparing the calculated B3LYP energies to the data obtained by the B3LYP-D3 approximation, which is a method that describes dispersion interactions more accurately for larger atomic distances, the same tendencies for the reaction kinetics are found (see Table 1). Overall, only a decrease of the energy of both transition states and intermediates can be noticed compared to B3LYP. The additional stabilization amounts to ca. 10 kcal/mol. On the contrary, employing B3LYP and taking solvent effects into account, the energy of both transition states and intermediates increases. The changes amount up to 4.5 kcal/mol.

However, an entirely different picture emerges by looking at the data calculated by means of PBE0 and M06 (Tables S2 and S3, Figures S3 and S4). Here, the transition states **16a**, **20a**, **25a** and **29a** are the stationary points with the highest total free energy along the individual reaction pathways. The rate determining step is now always the first step in the reaction pathway, which is in contrast to the reaction pathway calculated with B3LYP (Figures 1 and 2). The fact that the PBE0 method favors cyclic cationic structures over open geometries has already be found for other gold-catalyzed carbon-carbon bond-forming reactions:[56] For the gold(I)-catalyzed transannular ring-closure reaction of a nonconjugated diyne, the PBE0 method predicts a cyclopropenylmethyl cation as intermediate, whereas B3LYP calculations favor a butadienyl cation as intermediate.[56]

In summary, the model calculations give the following picture: According to the results obtained by the BL3LYP method, the reaction of chlorophenylacetylene with 1,2-disubstituted alkenes should lead to the [2+2] cycloaddition product, whereas the use of 1,1-disubstituted alkenes should enable a 1,2-chloroalkynylation of the alkenes. In both cases, the reaction proceeds via a nucleophilic attack of the alkene at the carbon atom C1 of the alkyne. Contrary to this, the PBE0 method predicts a nucleophilic attack at the carbon atom C2 of the alkyne for the reaction of chlorophenylacetylene with both 1,1- and 1,2-dibsubstituted alkenes, leading only to the [2+2] cycloaddition products.

b) Experimental Studies

The results of the B3LYP calculations encouraged us to investigate the gold-catalyzed reaction of chloroarylacetylenes with 1,1-disubstituted alkenes also experimentally with regard to a 1,2-chloroalkynylation reaction. We chose the reaction which is shown in Scheme 3 as our test model. The experiments were carried out in an NMR tube to directly monitor the course of the reaction. This enables the rapid determination of the conversion of chloroarylacetylene **3b**, the yield of the reaction and the occurrence of possible products and byproducts. Therefore, 1,1,2,2-tetrachloroethane was added as internal standard. The use of chloroarylacetylene **3b** as model compound has two advantages: Firstly, the conversion of **3b** and the yield of possible products can be easily determined via the characteristic ^{1}H NMR signal for the methyl group at around 4 ppm. Additionally, the +M effect of the methoxy group has a stabilizing effect on the intermediary formed cations, which should allow the reaction to occur at ambient temperature. Either way, we wanted to avoid higher temperatures, as the activation barrier for the 1,2-chloroalkynylation is only slightly lower than that for the cycloaddition (Figure 2). The alkene **13b** was chosen as a representative of a 1,1-disubstituted alkene, since it is easy to handle and commercially available in larger quantities. The concentration of **3b** is an important aspect to consider. At lower concentrations there is a risk of the gold-catalyzed hydration of the chloroacetylene as a side reaction.[57,24] At higher concentrations, the dimerization of the chloroacetylene becomes the main reaction.[24] According to B3LYP/B2//B3LYP/B1 calculations, the transition state for the dimerization of **3a** (ΔG = 24.0 kcal/mol) is energetically disfavored compared to the addition of the alkyne **3a** to the alkene **13a** (ΔG = 21.2 kcal/mol). To ensure that the reaction of **3b** and **13b** is the dominant reaction pathway, we chose a concentration of 0.1 M for **3b** and an excess of alkene **13b** (1 to 10 equivalents). The reaction was performed in deuterated dichloromethane (DCM-d_2), as this solvent has a high solubilizing power for the cationic gold complexes and is inert. It should thus react, if at all, very slowly with an intermediary formed cation. To optimize the yields, the experiment was carried out at room temperature by using several cationic gold complexes with different ligands and counterions (Table 2).



3b **13b** **14b**

Scheme 3. Gold(I)-catalyzed 1,2-chloroalkynylation of alkene **13b** with **3b** under different conditions.

Table 2. Optimization of the reaction conditions[a] for the gold(I)-catalyzed chloroalkynylation of the alkene **13b** with chloroarylacetylene **3b.**

entry	ratio **3b** : **13b**	catalyst	yield [%]
1	1 : 1	[JohnPhosAu(NCMe)]SbF_6 (5 mol%)[58]	18
2	1 : 2	[JohnPhosAu(NCMe)]SbF_6 (5 mol%)	39
3	1 : 5	[JohnPhosAu(NCMe)]SbF_6 (5 mol%)	60
4	1 : 10	[JohnPhosAu(NCMe)]SbF_6 (5 mol%)	78
5	1 : 10	JohnPhosAuNTf_2 (5 mol%)[59]	4
6	1 : 10	JohnPhosAuCl (5 mol%), $NaBArF_{24}$ (10 mol%)	0
7	1 : 10	*t*BuXPhosAuNTf_2 (5 mol%)[59]	20
8	1 : 10	BrettPhosAuNTf_2 (5 mol%)[60]	53
9	1 : 10	$(Ph)_3$PAuCl (5 mol%), $AgSbF_6$ (10 mol%)[61]	14
10	1 : 10	$(Ph)_3$PAuCl (5 mol%), $AgNTf_2$ (10 mol%)	0
11	1 : 10	$(Ph)_3$PAuCl (5 mol%), $NaBArF_{24}$ (10 mol%)	57[b]
12	1 : 10	IPrAuCl (5 mol%), $AgSbF_6$ (10 mol%)[62]	0
13	1 : 10	IPrAuNTf_2 (5 mol%)[59]	35
14	1 : 10	IPrAuCl (5 mol%), $NaBArF_{24}$ (10 mol%)	10
15	1 : 10	Dichloro(2-picolinato)gold(III) (5 mol%)[63]	0[b]

[a] Yield determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as internal standard. The reaction was performed in DCM-d_2 (0.1 M for **3b**) at room temperature overnight. [b] No complete conversion.

Based on our previous results for the dimerization of chloroarylacetylenes **3** (see Scheme 1b)[24] we first tested the cationic gold catalyst JohnPhosAu(NCMe)SbF_6. The reaction of chloroarylacetylene **3b** with alkene **13b** in a 1:1 ratio showed the formation of a new addition product with a yield of 18% (entry 1 in Table 2), which might be a product of a 1,2-chloroalkynylation reaction. However, this reaction conditions led to a variety of further unknown products. We assumed the reaction to be strongly dependent upon the equivalents of the alkene **13b**. Therefore, we increased the equivalents of **13b** from one to overall ten. The increase to two equivalents already showed a significantly higher yield of the addition product (entry 2). By using five equivalents of alkene **13b**, the reaction rate increased and led to a cleaner conversion with a higher overall yield for the addition product (entry 3). It should also be mentioned that the product degrades over time in presence of the cationic gold catalyst. We found out that this undesirable process can be slowed down by further increasing the amount of alkene **13b** (entry 4). By using an excess of the alkene **13b** we could ensure the formed product to be stable under the given reaction conditions for a longer period of time.

Next, we screened several cationic gold complexes with different ligands and counterions (entries 5-14) under the optimized reaction conditions (entry 4). Changing to the softer counterion $BArF_{24}^-$ and the more basic NTf_2^- counterion led to almost no addition product (entries 5-6). Other phosphorus-based ligands like triphenylphosphine gold(I) chloride

resulted in barely no addition product with SbF_6^- and NTf_2^- as counterions (entries 9-10), except for $BArF_{24}^-$ (entry 11), which delivered the product in a yield of 57%. It is known that counterions in gold catalysis have a strong influence on the outcome of the reaction.[64-65] We then tested sterically more demanding phosphine ligands such as *t*BuXPhosAuNTf$_2$ (entry 7) and BrettPhosAuNTf$_2$ (entry 8), but these were not superior to JohnPhosAu(NCMe)SbF$_6$ (entry 4). When using *N*-heterocyclic carbene (NHC) ligand complexes (entries 12-14) with different counterions like SbF_6^-, NTf_2^- and $BArF_{24}^-$, the product yield was significantly lower (0-35%) compared to some phosphine-based ligands (see Table 2, entries 4, 5 and 11). The usage of the gold(III) complex dichloro(2-pyridinecarboxylato)gold did not give any addition product at all (entry 15).

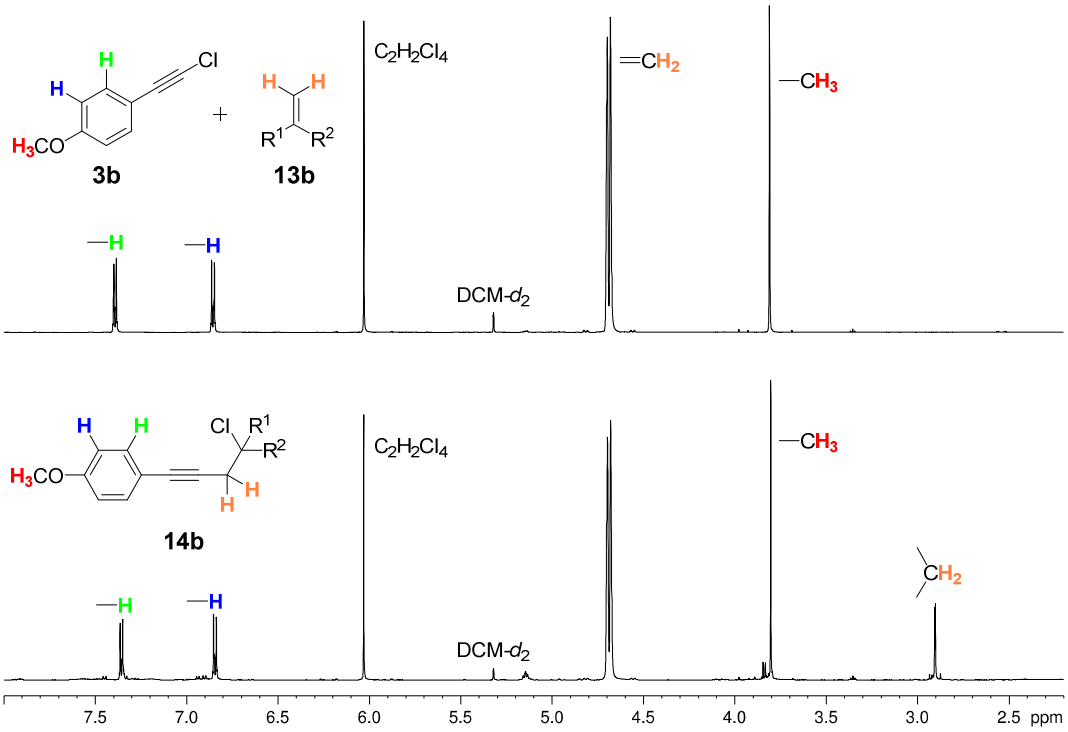
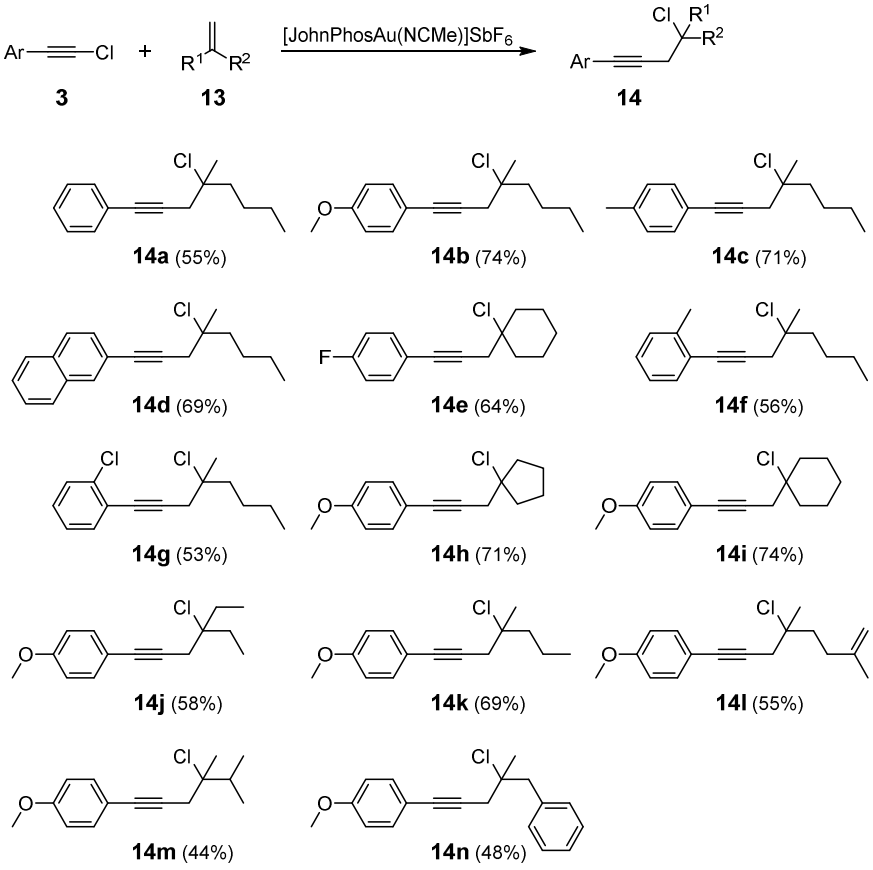


Figure 5. ^{1}H NMR spectra of **3b** (0.1 M), **13b** (1.0 M) and 1,1,2,2-tetrachloroethane as internal standard in dichloromethane-d_2 at 600 MHz before (top) and after (bottom) addition of 5 mol% [JohnPhosAu(NCMe)]SbF$_6$.

The ^{1}H NMR spectra for the addition of **3b** to **13b** under the optimized reaction conditions (entry 4 in Table 2) are depicted in Figure 5. They show a clean conversion of **3b** leading to only one addition product with an overall yield of 78%. No further products with a yield higher than 5% could be identified. The most characteristic signal can be found at δ = 2.9 ppm. As this signal corresponds to two protons, it could stem from the protons of a methylene group, which suggests an addition product. This would be in accordance with the calculated

proposed structure (see above). However, the [2+2] cycloaddition product can only be ruled out by looking at the ^{13}C NMR spectrum: The peaks at δ = 84.2 and 83.0 ppm corroborate the reappearance of the triple bond in the product (see Figure S9 in the Supporting Information) and thus clearly prove the formation of the chloroalkynylation addition product **14b** (Figure 5). It is worth mentioning that the reappearance of the triple bond in the product is uncommon for gold-catalyzed reactions, as the triple bond is normally consumed, and only a few exceptions have been reported so far.[29-30,24] Likewise, the presence of a regioisomer in which the chlorine atom is attached to the former methylene group of the alkene **13b** can be ruled out with the ^{1}H NMR and the HMBC spectra (see Figure S10 in the Supporting Information).

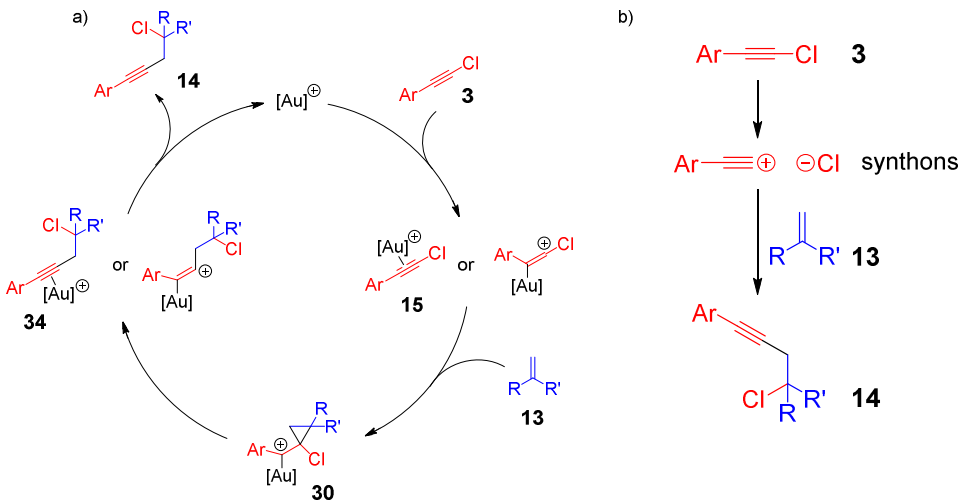


Scheme 4. Substrate scope for the gold(I)-catalyzed chloroalkynylation of alkenes **13** with the chloroarylacetylenes **3**.

To evaluate the scope of the chloroalkynylation of 1,1-disubstituted alkenes, different chloroarylacetylenes **3** were reacted with some alkenes **13** under the optimized reaction conditions (see Scheme 4, entry 4 in Table 2). Besides the methoxy compound **3b**, chloroarylacetylenes with a methyl group or halogen group in both *para* and *ortho* position were also tolerated to form the corresponding homopropargyl chlorides. Changing the phenyl

group to a larger naphthyl backbone led to no decrease of the reaction yield (see yield for **14d** in Scheme 4). Besides open-chain alkenes, like 2-methyl-1-hexene (**13b**), we also tested alkenes with exocyclic double bonds, which had no negative impact on the reaction yield. For example, the reaction of **3b** with methylenecyclohexane delivered the product **14i** with 74% yield (Scheme 4). It turns out that in most cases the products of the 1,2-chloroalkynylation reaction can be isolated in good yields (up to 74%). The preparative reaction of chloroarylacetylenes with electron-withdrawing substituents (**3e** and **3g**) gave significantly lower yields as compared to the conducted ^{1}H NMR experiments. This is due to the fact that the reaction rate of chloroarylacetylenes with electron-withdrawing substituents is slower compared to the reaction of electron-rich chloroarylacetylenes (i.e. **3g**). According to B3LYP/B2//B3LYP/B1 calculations, the transition state for the addition of the fluoro-substituted alkyne **3e** to the alkene **13a** is slightly higher in energy (ΔG = 21.7 kcal/mol) than the value found for the reaction of alkyne **3a** with the alkene **13a** (ΔG = 21.2 kcal/mol). However, we found the reaction of electron-deficient chloroarylacetylenes to be more selective towards the 1,2-chloroalkynylation. For example, the reaction of 1-(chloroethynyl)-4-fluorobenzene (**3e**) with methylenecyclohexane delivers the 1,2-chloroalkynylation product after four days with an overall ^{1}H NMR yield of 99% (see Figure S11 in the Supporting Information). Since this reaction still showed a significant amount of reactant after the same amount of time on a preparative scale, we were forced to stop the reaction by quenching the cationic gold complex with triethylamine.

At this point we would like to note that under the above described conditions, the reaction of **3b** with 1,2-disubstituted alkenes like cycloheptene and cyclooctene led exclusively to the [2+2] cycloaddition product, which is in accordance with the literature.[26]



Scheme 5. a) Possible reaction mechanism for the gold(I)-catalyzed 1,2-chloroalkynylation via 1,3-chlorine shift of alkenes **13** with the chloroarylacetylenes **3**. b) The gold(I)-catalyzed

1,2-chloroalkynylation via 1,3-chlorine shift can be considered as the addition of two ionic synthons to a double bond.

Based on the above-discussed results, we suggest the following mechanism for the 1,2-chloroalkynylation of 1,1-disubsituted alkenes **13** (Scheme 5a): The first step is the coordination of the cationic gold complex to the triple bond of chloroarylacetylene **3** to form the cationic π complex **15** with a highly electrophilic triple bond. The rate determining step is the following nucleophilic attack of the alkene **13** at the carbon atom C1 of the π complex **15**, resulting in the formation of the gold(I)-stabilized cyclopropylmethyl cation **30** as intermediate. The latter can be transformed by a ring opening and subsequent 1,3-chlorine shift to form the stable cationic complex **34**. Notably, the activation barrier for this 1,3-chlorine shift is considerably smaller compared to the activation barrier for the attack of the alkene **13** to the gold alkyne complex **15**. The last step of the catalytic cycle is the removal of the cationic gold(I) complex (desauration), which releases the homopropargyl chloride **14**.

Conclusion

The gold(I)-catalyzed 1,2-chloroalkynylation of 1,1-disubstituted alkenes is presented. Quantum chemical calculations reveal that the choice of the density functional is essential for the reliable prediction of the reaction pathway. While calculations using the B3LYP functional confirm the preferred formation of the experimentally found alkynylation products, the PBE0 method clearly favors the [2+2] cycloaddition reaction. However, no [2+2] cycloaddition products were observed experimentally under the optimized reaction conditions. In formal terms, the reaction can be considered as an addition of two ionic synthons (alkynyl cation and chloride ion; see Scheme 5b) to a double bond. Mechanistically, this reaction proceeds via two steps: The first step is the nucleophilic addition of the alkene to an activated triple bond. The second step is a 1,3-chlorine shift to an intermediary formed cation, which results in the exclusive formation of the homopropargyl chlorides. Notably, the reappearance of one triple bond in the product is rather untypical, as they are normally consumed in gold(I)-catalyzed reactions. Therefore, this chloroalkynylation reaction represents an elegant method to enable a carbon-carbon bond-forming and the simultaneous insertion of a chlorine atom into a double bond. This reaction is an attractive method for the direct synthesis of homopropargyl chlorides which are not readily available by other means. Furthermore, the reaction mechanism for the presented addition of a chloroacetylene to an alkene stresses the importance of the observed 1,3-chlorine shift to a cationic center. We expect this simple and controllable mechanism to be transferable to other chemical transformations, leading to a variety of chloroalkynylation reactions.

Experimental Section

General remarks: Chemicals were purchased from ABCR, Alfa Aesar, Acros Organics, Carbolution, TCI or Sigma-Aldrich. All chemicals were reagent grade and used without further purification. Reactions were monitored by TLC analysis with silica gel 60 F254 thin-layer plates. Flash chromatography was carried out on silica 60 (40–63 µm, 230–400 mesh). ^{1}H and ^{13}C NMR spectra were measured with Bruker Avance DRX 500 and Avance HD 600 spectrometers. All chemical shifts (δ) are given in ppm. The spectra were referenced to the peak for the protium impurity in the deuterated solvents indicated in brackets in the analytical data ($CDCl_3$, ^{1}H: 7.26 ppm, ^{13}C: 77.16 ppm). Signal multiplicity for ^{1}H NMR was determined as s (singlet), d (doublet), t (triplet), sext (sextet), sept (septet), m (multiplet), dd (doublet of doublets) and td (triplet of doublets). ^{13}C NMR spectra were measured with ^{1}H decoupling and the ^{13}C assignment was achieved via DEPT 135, HSQC, HMBC, and COSY spectra. ^{13}C signal multiplicity was determined as p (primary), s (secondary), t (tertiary), q (quaternary). HR-MS spectra were recorded with a Thermo Fisher Scientific Exactive™ Plus Orbitrap MS with APCI as ionization source or with a Bruker BioTOF III Instrument with ESI as ionization source. UV/Vis absorption spectra were obtained with a Jasco V-550 spectrophotometer. IR absorption spectra were recorded with a Shimadzu IR Tracer-100 FTIR spectrophotometer. The 1,1-disubstituted alkenes **13** which were used for the gold(I)-catalyzed chloroalkynylation are all commercially available.

Chlorophenylacetylene (**3a**)[66] was synthesized according to Brandsma[67] from commercially available phenylacetylene. Chloroarylacetylenes **3b**[66], **3c**[66] and **3d**[8] were synthesized via chlorination of the corresponding terminal alkynes according to the literature procedure[68]. 1-(Chloroethynyl)-4-fluorobenzene (**3e**)[68] was obtained via chlorination[68] of commercially available 1-ethynyl-4-fluorobenzene. Chloroarylacetylene **3f**[69] was obtained via direct chlorination[66] of the corresponding TMS-acetylene. 1-Chloro-2-(chloroethynyl)benzene (**3g**)[70] was obtained via chlorination[68] of commercially available 1-chloro-2-ethynylbenzene.

Synthesis of 1-chloro-2-(chloroethynyl)benzene (3g)[70]. A flask was charged with silver carbonate (Ag_2CO_3; 50 mg, 0.18 mmol, 0.1 eq), *N*-chlorosuccinimide (NCS; 489 mg, 3.66 mmol, 2.0 eq) and potassium carbonate (K_2CO_3; 127 mg, 0.92 mmol, 0.5 eq) under argon atmosphere. 1-chloro-2-ethynylbenzene (**S2g**) (250 mg, 1.83 mmol, 1.0 eq) was dissolved in *n*-propanol (4 mL) and added to the flask. The reaction mixture was heated at 50 °C via oil bath for one hour. After removing the solvent in vacuo, ether and brine were added. The phases were separated and the aqueous phase was extracted with ether. The combined organic phases were washed with water and dried over magnesium sulfate. After removing the solvent in vacuo, the residue was adsorbed onto Celite® and purified by flash chromatography (SiO_2, *n*-hexane) to yield **3g** (173 mg, 1.01 mmol, 55%) as a colorless oil. R_f (*n*-hexane) = 0.59. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.49–7.46 (dd, 1 H, $^{3}J_{H,H}$ = 7.7 Hz, $^{4}J_{H,H}$ =

1.6 Hz, CH_{ar}), 7.40–7.37 (dd, 1 H, $^{3}J_{H,H}$ = 8.1 Hz, $^{4}J_{H,H}$ = 1.0 Hz, CH_{ar}), 7.28–7.25 (td, 1 H, $^{3}J_{H,H}$ = 7.8 Hz, $^{4}J_{H,H}$ = 1.7 Hz, CH_{ar}), 7.22–7.19 ppm (td, 1 H, $^{3}J_{H,H}$ = 7.5 Hz, $^{4}J_{H,H}$ = 1.1 Hz, CH_{ar}). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ = 136.5 (q, C_{ar}), 133.9 (t, $C_{ar}H$), 129.7 (t, $C_{ar}H$), 129.5 (t, $C_{ar}H$), 126.6 (t, $C_{ar}H$), 122.3 (q, C_{ar}), 73.4 (q, C≡C), 66.5 ppm (q, C≡C). IR (ATR): $\tilde{\nu}$ = 3069, 2222, 1591, 1559, 1472, 1437, 1425, 1126, 1059, 1032, 945, 893, 748, 708, 642 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (log ε) = 211 (4.46), 244 (4.17), 254 (4.15), 281 nm (2.79). HRMS (APCI) m/z: $[M]^+$ Calcd for $C_8H_4{}^{35}Cl_2$ 169.9685; Found 169.9685.

General Procedure for the gold(I)-catalyzed chloroalkynylation of 1,1-disubstituted alkenes. In a 5 mL screw-capped vial, 1.0 eq. chloroarylacetylene **3** (400 µmol) and 10 eq. alkene **13** (4 mmol) were dissolved in dry DCM (4 mL). Then 5 mol% [JohnPhosAu(NCMe)]SbF_6 (20 µmol) was added. The mixture was stirred at room temperature for 5–96 hours and monitored by TLC. Triethylamine (0.1 mL) was added via syringe to quench the reaction. The solvent and excess alkene were removed under reduced pressure. The crude product was adsorbed onto Celite® and purified by flash chromatography to yield the desired homopropargyl chloride **14**.

Synthesis of (4-chloro-4-methyloct-1-yn-1-yl)benzene (14a). According to the general procedure, chloroarylacetylene **3a** (54.6 mg, 400 µmol, 1.0 eq) and 2-methyl-1-hexene (**13b**) (392.8 mg, 4 mmol, 561 µL, 10.0 eq) were dissolved in dry DCM (4 mL). Then [JohnPhosAu(NCMe)]SbF_6 (5 mol%, 20 µmol, 15.4 mg) was added. The mixture was stirred at room temperature for 41 hours. After removing the solvent and excess alkene in vacuo, the residue was purified by flash chromatography (SiO_2, *n*-hexane) to yield **14a** (51.9 mg, 221 µmol, 55%) as a colorless oil. R_f (*n*-hexane) = 0.25. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.44–7.40 (m, 2 H, CH_{ar}), 7.31–7.28 (m, 3 H, CH_{ar}), 2.93 (d, 1 H, $^{2}J_{H,H}$ = 16.9 Hz, CH_2), 2.90 (d, 1 H, $^{2}J_{H,H}$ = 16.9 Hz, CH_2), 1.97–1.91 (m, 1 H, CH_2), 1.91–1.84 (m, 1 H, CH_2), 1.69 (s, 3 H, CH_3), 1.54–1.46 (m, 2 H, CH_2), 1.37 (sext, 2 H, $^{3}J_{H,H}$ = 7.4 Hz, CH_2), 0.95 ppm (t, 3 H, $^{3}J_{H,H}$ = 7.3 Hz, CH_3). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ = 131.8 (t, $C_{ar}H$), 128.4 (t, $C_{ar}H$), 128.1 (t, $C_{ar}H$), 123.5 (q, C_{ar}), 85.8 (q, C≡C), 83.2 (q, C≡C), 71.8 (q, C-Cl), 43.0 (s, CH_2), 35.6 (s, CH_2), 30.0 (p, CH_3), 27.0 (s, CH_2), 22.9 (s, CH_2), 14.2 ppm (p, CH_3). IR (ATR): $\tilde{\nu}$ = 2957, 2932, 1597, 1489, 1456, 1443, 1379, 1126, 1069, 1044, 1030, 912, 824, 754, 735, 691 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (log ε) = 201 (4.36), 240 (4.19), 249 nm (4.14). HRMS (APCI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{20}{}^{35}Cl$ 235.1248; Found 235.1248.

Synthesis of 1-(4-chloro-4-methyloct-1-yn-1-yl)-4-methoxybenzene (14b). According to the general procedure, chloroarylacetylene **3b** (66.6 mg, 400 µmol, 1.0 eq) and 2-methyl-1-hexene (**13b**) (392.8 mg, 4 mmol, 561 µL, 10.0 eq) were dissolved in dry DCM (4 mL). Then [JohnPhosAu(NCMe)]SbF_6 (5 mol%, 20 µmol, 15.4 mg) was added. The reaction mixture was stirred at room temperature for 17 hours. After removing the solvent and excess alkene in vacuo, the residue was purified by flash chromatography (SiO_2, *n*-hexane/ether 98:2) to

yield **14b** (78.3 mg, 296 µmol, 74%) as a colorless oil. R_f (*n*-hexane/ether 98:2) = 0.29. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.37–7.33 (m, 2 H, CH_{ar}), 6.84–6.81 (m, 2 H, CH_{ar}), 3.80 (s, 3 H, CH_3), 2.91 (d, 1 H, $^2J_{H,H}$ = 16.9 Hz, CH_2), 2.88 (d, 1 H, $^2J_{H,H}$ = 16.9 Hz, CH_2), 1.96–1.90 (m, 1 H, CH_2), 1.89–1.83 (m, 1 H, CH_2), 1.68 (s, 3 H, CH_3), 1.54–1.47 (m, 2 H, CH_2), 1.37 (sext, 2 H, $^3J_{H,H}$ = 7.4 Hz, CH_2), 0.95 ppm (t, 3 H, $^3J_{H,H}$ = 7.3 Hz, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ = 159.5 (q, C_{ar}), 133.1 (t, $C_{ar}H$), 115.7 (q, C_{ar}), 114.0 (t, $C_{ar}H$), 84.2 (q, C≡C), 83.0 (q, C≡C), 72.0 (q, C-Cl), 55.4 (p, OCH_3), 42.9 (s, CH_2), 35.7 (s, CH_2), 30.0 (p, CH_3), 27.0 (s, CH_2), 22.9 (s, CH_2), 14.2 ppm (p, CH_3). IR (ATR): $\tilde{\nu}$ = 2955, 2932, 2837, 1607, 1568, 1508, 1441, 1379, 1289, 1244, 1171, 1126, 1105, 1032, 829, 799, 733, 679 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (log ε) = 201 (4.46), 253 nm (4.35). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{22}{}^{35}ClO$ 265.1354; Found 265.1349.

Synthesis of 1-(4-chloro-4-methyloct-1-yn-1-yl)-4-methylbenzene (14c). According to the general procedure, chloroarylacetylene **3c** (60.2 mg, 400 µmol, 1.0 eq) and 2-methyl-1-hexene (**13b**) (392.8 mg, 4 mmol, 561 µL, 10.0 eq) were dissolved in dry DCM (4 mL). Then [JohnPhosAu(NCMe)]SbF_6 (5 mol%, 20 µmol, 15.4 mg) was added. The reaction mixture was stirred at room temperature for 18 hours. After removing the solvent and excess alkene in vacuo, the residue was purified by flash chromatography (SiO_2, *n*-hexane) to yield **14c** (70.8 mg, 285 µmol, 71%) as a colorless oil. R_f (*n*-hexane/ether 98:2) = 0.61. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.32–7.29 (m, 2 H, CH_{ar}), 7.12–7.08 (m, 2 H, CH_{ar}), 2.91 (d, 1 H, $^2J_{H,H}$ = 16.5 Hz, CH_2), 2.88 (d, 1 H, $^2J_{H,H}$ = 16.5 Hz, CH_2), 2.34 (s, 3 H, CH_3), 1.97–1.90 (m, 1H, CH_2), 1.90–1.84 (m, 1H, CH_2), 1.68 (s, 3 H, CH_3), 1.53–1.47 (m, 2 H, CH_2), 1.37 (sext, 2 H, $^3J_{H,H}$ = 7.4 Hz, CH_2), 0.95 ppm (t, 3 H, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ = 138.1 (q, $C_{ar}CH_3$), 131.6 (t, $C_{ar}H$), 129.1 (t, $C_{ar}H$), 120.4 (q, C_{ar}), 85.0 (q, C≡C), 83.3 (q, C≡C), 71.9 (q, C-Cl), 42.9 (s, CH_2), 35.6 (s, CH_2), 30.0 (p, CH_3), 27.0 (s, CH_2), 22.9 (s, CH_2), 21.6 (p, $C_{ar}CH_3$), 14.2 ppm (p, CH_3). IR (ATR): $\tilde{\nu}$ = 3028, 2957, 2930, 2862, 1609, 1510, 1456, 1379, 1126, 1044, 1020, 814, 733 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (log ε) = 203 (4.40), 244 (4.29), 252 (4.25), 297 nm (2.96). HRMS (APCI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{22}{}^{35}Cl$ 249.1405; Found 249.1405.

Synthesis of 2-(4-chloro-4-methyloct-1-yn-1-yl)naphthalene (14d). According to the general procedure, chloroarylacetylene **3d** (74.7 mg, 400 µmol, 1.0 eq) and 2-methyl-1-hexene (**13b**) (392.8 mg, 4 mmol, 561 µL, 10.0 eq) were dissolved in dry DCM (4 mL). Then [JohnPhosAu(NCMe)]SbF_6 (5 mol%, 20 µmol, 15.4 mg) was added. The reaction mixture was stirred at room temperature for 42 hours. After removing the solvent and excess alkene in vacuo, the residue was purified by flash chromatography (SiO_2, *n*-hexane/DCM 99:1) to yield **14d** (78.9 mg, 277 µmol, 69%) as a colorless oil. R_f (*n*-hexane) = 0.17. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.94 (s, 1 H, CH_{ar}), 7.82–7.75 (m, 3 H, CH_{ar}), 7.50–7.45 (m, 3 H, CH_{ar}), 2.99 (d, 1 H, $^2J_{H,H}$ = 16.9 Hz, CH_2), 2.96 (d, 1 H, $^2J_{H,H}$ = 16.9 Hz, CH_2), 2.01–1.95 (m, 1 H,

CH_2), 1.94–1.88 (m, 1 H, CH_2), 1.73 (s, 3 H, CH_3), 1.59–1.50 (m, 2 H, CH_2), 1.40 (sext, 2 H, $^3J_{H,H}$ = 7.4 Hz, CH_2), 0.97 ppm (t, 3 H, $^3J_{H,H}$ = 7.3 Hz, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ = 133.1 (q, C_{ar}), 132.8 (q, C_{ar}), 131.4 (t, $C_{ar}H$), 128.7 (t, $C_{ar}H$), 128.0 (t, $C_{ar}H$), 127.9 (t, $C_{ar}H$), 127.8 (t, $C_{ar}H$), 126.6 (t, $C_{ar}H$), 120.8 (q, C_{ar}), 86.2 (q, C≡C), 83.6 (q, C≡C), 71.8 (q, C-Cl), 43.0 (s, CH_2), 35.8 (s, CH_2), 30.0 (p, CH_3), 27.0 (s, CH_2), 22.9 (s, CH_2), 14.2 ppm (p, CH_3). IR (ATR): $\tilde{\nu}$ = 3057, 2955, 2930, 1628, 1597, 1501, 1456, 1429, 1379, 1343, 1261, 1221, 1126, 1044, 891, 856, 816, 745, 635 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (log ε) = 245 (4.78), 276 (4.03), 286 (4.08), 297 (3.94), 316 nm (3.07). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{22}{}^{35}Cl$ 285.1405; Found 285.1399, $[M – Cl]^+$ Calcd for $C_{19}H_{21}$ 249.1638; Found 249.1630.

Synthesis of 1-(3-(1-chlorocyclohexyl)prop-1-yn-1-yl)-4-fluorobenzene (14e). According to the general procedure, chloroarylacetylene **3e** (61.8 mg, 400 µmol, 1.0 eq) and methylencyclohexane (384.7 mg, 4 mmol, 481 µL, 10.0 eq) were dissolved in dry DCM (4 mL). Then [JohnPhosAu(NCMe)]SbF_6 (5 mol%, 20 µmol, 15.4 mg) was added. The reaction mixture was stirred at room temperature for three days. After removing the solvent and excess alkene in vacuo, the residue was purified by flash chromatography (SiO_2, *n*-hexane) to yield **14e** (63.6 mg, 254 µmol, 64%) as a colorless oil. R_f (*n*-hexane) = 0.23. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.43–7.38 (m, 2 H, CH_{ar}), 7.02–6.96 (m, 2 H, CH_{ar}), 2.91 (s, 2 H, CH_2), 2.07–1.99 (m, 2 H, CH_2), 1.82–1.74 (m, 4 H, CH_2), 1.73–1.67 (m, 1 H, CH_2), 1.66–1.60 (m, 2 H, CH_2), 1.26–1.18 ppm (m, 1 H, CH_2). ^{19}F NMR (565 Hz, $CDCl_3$): δ = −111.6 ppm (m, 1 F, CF_{ar}). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ = 162.4 (q, $^1J_{C,F}$ = 248.8 Hz, $C_{ar}F$), 133.6 (t, $^3J_{C,F}$ = 8.2 Hz, $C_{ar}H$), 119.7 (q, $^4J_{C,F}$ = 3.3 Hz, $C_{ar}F$), 115.6 (t, $^2J_{C,F}$ = 22.0 Hz, $C_{ar}H$), 85.3 (q, C≡C), 82.5 (q, C≡C), 73.1 (q, C-Cl), 39.0 (s, CH_2), 37.0 (s, CH_2), 25.3 (s, CH_2), 22.4 ppm (s, CH_2). IR (ATR): $\tilde{\nu}$ = 2934, 2862, 1601, 1506, 1447, 1427, 1229, 1155, 1126, 1092, 1015, 932, 876, 833, 814, 783, 669 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (log ε) = 200 (4.37), 238 nm (4.14). HRMS (APCI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{17}{}^{35}ClF$ 251.0997; Found 251.1011.

Synthesis of 1-(4-chloro-4-methyloct-1-yn-1-yl)-2-methylbenzene (14f). According to the general procedure, chloroarylacetylene **3f** (54.0 mg, 359 µmol, 1.0 eq) and 2-methyl-1-hexene (**13b**) (352.5 mg, 3.6 mmol, 503 µL, 10.0 eq) were dissolved in dry DCM (3.6 mL). Then [JohnPhosAu(NCMe)]SbF_6 (5 mol%, 18 µmol, 13.9 mg) was added. The reaction mixture was stirred at room temperature for four days. After removing the solvent and excess alkene in vacuo, the residue was purified by flash chromatography (SiO_2, *n*-hexane) to yield **14f** (49.9 mg, 201 µmol, 56%) as a colorless oil. R_f (*n*-hexane) = 0.26. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.40–7.36 (m, 1 H, CH_{ar}), 7.22–7.17 (m, 2 H, CH_{ar}), 7.14–7.10 (m, 1 H, CH_{ar}), 2.97 (d, 1 H, $^2J_{H,H}$ = 16.9 Hz, CH_2), 2.94 (d, 1 H, $^2J_{H,H}$ = 16.9Hz, CH_2), 2.43 (s, 3 H, CH_3), 2.00–1.93 (m, 1 H, CH_2), 1.92–1.86 (m, 1 H, CH_2), 1.70 (s, 3 H, CH_3), 1.54–1.48 (m, 2 H, CH_2), 1.37 (sext, 2 H, $^3J_{H,H}$ = 7.4 Hz, CH_2), 0.95 ppm (t, 3 H, $^3J_{H,H}$ = 7.3 Hz, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ = 140.3 (q, $C_{ar}CH_3$), 132.1 (t, $C_{ar}H$), 129.5 (t, $C_{ar}H$), 128.1 (t,

$C_{ar}H$), 125.6 (t, $C_{ar}H$), 123.3 (q, C_{ar}), 89.7 (q, C≡C), 82.1 (q, C≡C), 71.8 (q, C-Cl), 43.0 (s, CH_2), 35.7 (s, CH_2), 30.1 (p, CH_3), 27.0 (s, CH_2), 22.9 (s, CH_2), 21.0 (p, $C_{ar}CH_3$), 14.2 ppm (p, CH_3). IR (ATR): $\tilde{\nu}$ = 3061, 3023, 2957, 2930, 2862, 1601, 1485, 1456, 1379, 1225, 1126, 1115, 1044, 939, 826, 754, 733, 716, 644 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (log ε) = 206 (4.42), 242 (4.15), 251 (4.11), 278 (2.92), 285 nm (2.86). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{22}{}^{35}Cl$ 249.1405; Found 249.1399, $[M – Cl]^+$ Calcd for $C_{16}H_{21}$ 213.1638; Found 213.1632.

Synthesis of 1-chloro-2-(4-chloro-4-methyloct-1-yn-1-yl)benzene (14g). According to the general procedure, chloroarylacetylene **3g** (68.6 mg, 400 µmol, 1.0 eq) and 2-methyl-1-hexene (**13b**) (392.8 mg, 4 mmol, 561 µL, 10.0 eq) were dissolved in dry DCM (4 mL). Then [JohnPhosAu(NCMe)]SbF_6 (5 mol%, 20 µmol, 15.4 mg) was added. The reaction mixture was stirred at room temperature for two days. After removing the solvent and excess alkene in vacuo, the residue was purified by flash chromatography (SiO_2, *n*-hexane) to yield **14g** (57.0 mg, 212 µmol, 53%) as a colorless oil. R_f (*n*-hexane) = 0.24. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.47–7.43 (dd, 1 H, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.8 Hz, CH_{ar}), 7.40–7.36 (dd, 1 H, $^3J_{H,H}$ = 7.9 Hz, $^4J_{H,H}$ = 1.0 Hz, CH_{ar}), 7.25–7.21 (td, 1 H, $^3J_{H,H}$ = 7.7 Hz, $^4J_{H,H}$ = 1.8 Hz, CH_{ar}), 7.21–7.17 (td, 1 H, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.3 Hz, CH_{ar}), 3.00 (d, 1 H, $^2J_{H,H}$ = 16.9 Hz, CH_2), 2.96 (d, 1 H, $^2J_{H,H}$ = 16.9 Hz, CH_2), 2.02–1.95 (m, 1 H, CH_2), 1.95–1.88 (m, 1 H, CH_2), 1.72 (s, 3 H, CH_3), 1.54–1.48 (m, 2 H, CH_2), 1.37 (sext, 2 H, $^3J_{H,H}$ = 7.4 Hz, CH_2), 0.95 ppm (t, 3 H, $^3J_{H,H}$ = 7.4 Hz, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ = 136.2 (q, $C_{ar}Cl$), 133.4 (t, $C_{ar}H$), 129.3 (t, $C_{ar}H$), 129.1 (t, $C_{ar}H$), 126.5 (t, $C_{ar}H$), 123.4 (q, C_{ar}), 91.4 (q, C≡C), 80.1 (q, C≡C), 71.7 (q, C-Cl), 42.9 (s, CH_2), 35.7 (s, CH_2), 30.1 (p, CH_3), 27.0 (s, CH_2), 22.9 (s, CH_2), 14.2 ppm (p, CH_3). IR (ATR): $\tilde{\nu}$ = 2957, 2930, 2872, 1560, 1474, 1437, 1427, 1379, 1126, 1065, 1044, 1032, 943, 824, 750, 675, 642 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (log ε) = 211 (4.47), 244 (4.20), 253 (4.18), 281 nm (2.87). HRMS (ESI) m/z: $[M - Cl]^+$ Calcd for $C_{15}H_{18}{}^{35}Cl$ 233.1092; Found 233.1084.

Synthesis of 1-(3-(1-chlorocyclopentyl)prop-1-yn-1-yl)-4-methoxybenzene (14h). According to the general procedure, chloroarylacetylene **3b** (66.6 mg, 400 µmol, 1.0 eq) and methylencyclopentane (328.6 mg, 4 mmol, 421 µL, 10.0 eq) were dissolved in dry DCM (4 mL). Then [JohnPhosAu(NCMe)]SbF_6 (5 mol%, 20 µmol, 15.4 mg) was added. The reaction mixture was stirred at room temperature for 18 hours. After removing the solvent and excess alkene in vacuo, the residue was purified by flash chromatography (SiO_2, *n*-hexane/EtOAc 99:1) to yield **14h** (71.0 mg, 285 µmol, 71%) as a colorless oil. R_f (*n*-hexane/EtOAc 98:2) = 0.26. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.37–7.34 (m, 2 H, CH_{ar}), 6.84–6.81 (m, 2 H, CH_{ar}), 3.80 (s, 3 H, OCH_3), 3.04 (s, 2 H, CH_2), 2.11–2.05 (m, 2 H, CH_2), 2.03–1.95 (m, 2 H, CH_2), 1.82–1.73 ppm (m, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ = 159.5 (q, $C_{ar}OCH_3$), 133.2 (t, $C_{ar}H$), 115.6 (q, C_{ar}), 114.0 (t, $C_{ar}H$), 84.6 (q, C≡C), 82.5 (q, C≡C), 79.2 (q, C-Cl), 55.4 (p, OCH_3), 41.5 (s, CH_2), 34.0 (s, CH_2), 23.7 ppm (s, CH_2). IR (ATR): $\tilde{\nu}$ = 2957, 2874, 2837,

1605, 1568, 1508, 1441, 1289, 1244, 1171, 1105, 1032, 970, 829, 800 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (log ε) = 201 (4.22), 253 nm (4.13). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{18}{}^{35}ClO$ 249.1041; Found 249.1036, $[M - Cl]^+$ Calcd for $C_{15}H_{17}O$ 213.1274; Found 213.1269.

Synthesis of 1-(3-(1-chlorocyclohexyl)prop-1-yn-1-yl)-4-methoxybenzene (14i). According to the general procedure, chloroarylacetylene **3b** (50.0 mg, 300 µmol, 1.0 eq) and methylencyclohexane (288.5 mg, 3 mmol, 361 µL, 10.0 eq) were dissolved in dry DCM (3 mL). Then [JohnPhosAu(NCMe)]SbF_6 (5 mol%, 15 µmol, 11.6 mg) was added. The reaction mixture was stirred at room temperature for 5 hours. After removing the solvent and excess alkene in vacuo, the residue was purified by flash chromatography (SiO_2, *n*-hexane/EtOAc 98:2) to yield **14i** (58.0 mg, 221 µmol, 74%) as a colorless oil. R_f (*n*-hexane/EtOAc 98:2) = 0.25. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.38–7.34 (m, 2 H, CH_{ar}), 6.84–6.81 (m, 2 H, CH_{ar}), 3.80 (s, 3 H, OCH_3), 2.91 (s, 2 H, CH_2), 2.05–1.99 (m, 2 H, CH_2), 1.84–1.73 (m, 4 H, CH_2), 1.72–1.66 (m, 1 H, CH_2), 1.65–1.59 (m, 2 H, CH_2), 1.26–1.18 ppm (m, 1 H, CH_2). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ = 159.4 (q, $C_{ar}OCH_3$), 133.2 (t, $C_{ar}H$), 115.7 (q, C_{ar}), 114.0 (t, $C_{ar}H$), 84.0 (q, C≡C), 83.3 (q, C≡C), 73.4 (q, C-Cl), 55.4 (p, OCH_3), 38.9 (s, CH_2), 37.1 (s, CH_2), 25.3 (s, CH_2), 22.4 ppm (s, CH_2). IR (ATR): $\tilde{\nu}$ = 3038, 3001, 2932, 2861, 2835, 1607, 1568, 1508, 1443, 1289, 1242, 1171, 1126, 1105, 1032, 930, 876, 829, 779, 673, 610 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (log ε) = 202 (4.48), 253 nm (4.40). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{20}{}^{35}ClO$263.1197; Found 263.1190, $[M - Cl]^+$ Calcd for $C_{16}H_{19}O$ 227.1430; Found 227.1423.

Synthesis of 1-(4-chloro-4-ethylhex-1-yn-1-yl)-4-methoxybenzene (14j). According to the general procedure, chloroarylacetylene **3b** (66.6 mg, 400 µmol, 1.0 eq) and 2-ethyl-1-butene (336.6 mg, 4 mmol, 488 µL, 10 eq.) were dissolved in dry DCM (4 mL). Then [JohnPhosAu(NCMe)]SbF_6 (5 mol%, 20 µmol, 15.4 mg) was added. The reaction mixture was stirred at room temperature for 18 hours. After removing the solvent and excess alkene in vacuo, the residue was purified by flash chromatography (SiO_2, *n*-hexane/DCM 90:10) to yield **14j** (57.6 mg, 230 µmol, 58%) as a colorless oil. R_f (*n*-hexane/DCM 80:20) = 0.31. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.36–7.32 (m, 2 H, CH_{ar}), 6.84–6.80 (m, 2 H, CH_{ar}), 3.80 (s, 3 H, OCH_3), 2.88 (s, 2 H, CH_2), 1.98–1.91 (m, 4 H, CH_2), 1.06 ppm (t, 6 H, $^3J_{H,H}$ = 7.3 Hz, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ = 159.5 (q, $C_{ar}OCH_3$), 133.1 (t, $C_{ar}H$), 115.7 (q, C_{ar}), 114.0 (t, $C_{ar}H$), 84.0 (q, C≡C), 82.6 (q, C≡C), 76.7 (q, C-Cl), 55.4 (p, OCH_3), 33.8 (s, CH_2), 31.9 (s, CH_2), 8.9 ppm (p, CH_3). IR (ATR): $\tilde{\nu}$ = 2971, 2938, 2882, 2835, 1607, 1568, 1508, 1458, 1441, 1379, 1287, 1244, 1171, 1105, 1032, 920, 829, 800, 669 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (log ε) = 202 (4.46), 253 nm (4.40). HRMS (ESI) m/z: $[M+ H]^+$ Calcd for $C_{15}H_{20}{}^{35}ClO$ 251.1197; Found 251.1192, $[M - Cl]^+$ Calcd for $C_{15}H_{19}O$ 215.1430; Found 215.1424.

Synthesis of 1-(4-chloro-4-methylhept-1-yn-1-yl)-4-methoxybenzene (14k). According to the general procedure, chloroarylacetylene **3b** (66.6 mg, 400 µmol, 1.0 eq) and 2-methyl-1-pentene (336.6 mg, 4 mmol, 495 µL, 10.0 eq) were dissolved in dry DCM (4 mL). Then [JohnPhosAu(NCMe)]SbF_6 (5 mol%, 20 µmol, 15.4 mg) was added. The reaction mixture was stirred at room temperature for 18 hours. After removing the solvent and excess alkene in vacuo, the residue was purified by flash chromatography (SiO_2, *n*-hexane/EtOAc 98:2) to yield **14k** (68.7 mg, 274 µmol, 69%) as a colorless oil. R_f (*n*-hexane/EtOAc 98:2) = 0.24. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.37–7.33 (m, 2 H, CH_{ar}), 6.84–6.81 (m, 2 H, CH_{ar}), 3.80 (s, 3 H, OCH_3), 2.90 (d, 1 H, $^2J_{H,H}$ = 16.8 Hz, CH_2), 2.87 (d, 1 H, $^2J_{H,H}$ = 16.8 Hz, CH_2), 1.93–1.87 (m, 1 H, CH_2), 1.87–1.81 (m, 1 H, CH_2), 1.68 (s, 3 H, CH_3), 1.60–1.50 (m, 2 H, CH_2), 0.97 ppm (t, 3 H, $^2J_{H,H}$ = 7.4 Hz, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ = 159.5 (q, $C_{ar}OCH_3$), 133.2 (t, $C_{ar}H$), 115.7 (q, C_{ar}), 114.0 (t, $C_{ar}H$), 84.2 (q, C≡C), 83.0 (q, C≡C), 71.9 (q, C-Cl), 55.4 (p, OCH_3), 45.5 (s, CH_2), 35.7 (s, CH_2), 29.9 (p, CH_3), 18.2 (s, CH_2), 14.3 ppm (p, CH_3). IR (ATR): $\tilde{\nu}$ = 2959, 2932, 2872, 2835, 1607, 1568, 1508, 1464, 1443, 1379, 1289, 1244, 1171, 1125, 1105, 1032, 829, 810, 799, 745, 679 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (log ε) = 200 (4.39), 253 nm (4.27). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{20}{}^{35}ClO$ 251.1197; Found 251.1192, $[M – Cl]^+$ Calcd for $C_{15}H_{19}O$ 215.1430; Found 215.1425.

Synthesis of 1-(4-chloro-4,7-dimethyloct-7-en-1-yn-1-yl)-4-methoxybenzene (14l). According to the general procedure, chloroarylacetylene **3b** (66.6 mg, 400 µmol, 1.0 eq) and 2,5-dimethyl-1-butene (440.8 mg, 4 mmol, 596 µL, 10.0 eq) were dissolved in dry DCM (4 mL). Then [JohnPhosAu(NCMe)]SbF_6 (5 mol%, 20 µmol, 15.4 mg) was added. The reaction mixture was stirred at room temperature for 17 hours. After removing the solvent and excess alkene in vacuo, the residue was purified by flash chromatography (SiO_2, *n*-hexane/ether 98:2) to yield **14l** (60.6 mg, 219 µmol, 55%) as a colorless oil. R_f (*n*-hexane/ether 95:5) = 0.46. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.36–7.33 (m, 2 H, CH_{ar}), 6.84–6.81 (m, 2 H, CH_{ar}), 4.74 (s, 2 H, CH_2), 3.80 (s, 3 H, OCH_3), 2.94 (d, 1 H, $^2J_{H,H}$ = 16.9 Hz, CH_2), 2.90 (d, 1 H, $^2J_{H,H}$ = 16.9 Hz, CH_2), 2.29–2.20 (m, 2 H, CH_2), 2.11–2.05 (m, 1 H, CH_2), 2.04–1.97 (m, 1 H, CH_2), 1.77 (s, 3 H, CH_3), 1.71 ppm (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ = 159.5 (q, $C_{ar}OCH_3$), 145.3 (q, C=C), 133.2 (t, $C_{ar}H$), 115.6 (q, C_{ar}), 114.0 (t, $C_{ar}H$), 110.3 (s, CH_2), 84.0 (q, C≡C), 83.1 (q, C≡C), 71.5 (q, C-Cl), 55.4 (p, OCH_3), 41.3 (s, CH_2), 35.6 (s, CH_2), 33.0 (s, CH_2), 30.0 (p, CH_3), 22.8 ppm (p, CH_3). IR (ATR): $\tilde{\nu}$ = 3073, 2932, 2835, 1649, 1607, 1568, 1508, 1441, 1377, 1289, 1244, 1171, 1105, 1078, 1032, 887, 829, 799, 679 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (log ε) = 196 (4.43), 253 nm (4.29). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{22}{}^{35}ClO$ 277.1354; Found 277.1347, $[M – Cl]^+$ Calcd for $C_{17}H_{21}O$ 241.1587; Found 241.1580.

Synthesis of 1-(4-chloro-4,5-dimethylhex-1-yn-1-yl)-4-methoxybenzene (14m). According to the general procedure, chloroarylacetylene **3b** (66.6 mg, 400 µmol, 1.0 eq) and

2,3-dimethyl-1-butene (336.6 mg, 4 mmol, 495 µL, 10 eq.) were dissolved in dry DCM (4 mL). Then [JohnPhosAu(NCMe)]SbF_6 (5 mol%, 20 µmol, 15.4 mg) was added. The reaction mixture was stirred at room temperature for one day. After removing the solvent and excess alkene in vacuo, the residue was purified by flash chromatography (SiO_2, *n*-hexane/ether 98:2) to yield **14m** (43.7 mg, 174 µmol, 44%) as a colorless oil. R_f (*n*-hexane/ether 95:5) = 0.48. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.37–7.33 (m, 2 H, CH_{ar}), 6.84–6.81 (m, 2 H, CH_{ar}), 3.80 (s, 3 H, OCH_3), 2.96 (d, 1 H, $^2J_{H,H}$ = 16.9 Hz, CH_2), 2.89 (d, 1 H, $^2J_{H,H}$ = 16.9 Hz, CH_2), 2.21 (sept, 1 H, $^3J_{H,H}$ = 6.7 Hz, CH), 1.67 (s, 3 H, CH_3), 1.09 (d, 3 H, $^3J_{H,H}$ = 6.7 Hz, CH_3), 1.05 ppm (d, 3 H, 6.7 Hz, CH_3). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 159.5 (q, $C_{ar}OCH_3$), 133.2 (t, $C_{ar}H$), 115.7 (q, C_{ar}), 114.0 (t, $C_{ar}H$), 84.2 (q, C≡C), 82.9 (q, C≡C), 76.2 (q, C-Cl), 55.4 (p, OCH_3), 37.4 (t, CH), 34.6 (s, CH_2), 27.7 (p, CH_3), 18.1 (p, CH_3), 18.0 ppm (p, CH_3). IR (ATR): $\tilde{\nu}$ = 2969, 2934, 2835, 1607, 1568, 1508, 1464, 1441, 1377, 1289, 1244, 1171, 1128, 1105, 1032, 829, 804, 770, 669, 610 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (log ε) = 202 (4.33), 253 nm (4.26). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{20}{}^{35}ClO$ 251.1197; Found 251.1189, $[M – Cl]^+$ Calcd for $C_{15}H_{19}O$ 215.1430; Found 215.1423.

Synthesis of 1-(4-chloro-4-methyl-5-phenylpent-1-yn-1-yl)-4-methoxybenzene (14n). According to the general procedure, chloroarylacetylene **3b** (66.6 mg, 400 µmol, 1.0 eq) and 2-methyl-3-phenyl-1-propene (528.8 mg, 4 mmol, 10 eq.) were dissolved in dry DCM (4 mL). Then [JohnPhosAu(NCMe)]SbF_6 (5 mol%, 20 µmol, 15.4 mg) was added. The reaction mixture was stirred at room temperature for 17 hours. After removing the solvent and excess alkene in vacuo, the residue was purified by flash chromatography (SiO_2, *n*-hexane/ether 98:2) to yield **14n** (56.7 mg, 190 µmol, 48%) as a colorless oil. R_f (*n*-hexane/ether 98:2) = 0.22. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.44–7.40 (m, 2 H, CH_{ar}), 7.40–7.35 (m, 2 H, CH_{ar}), 7.35–7.31 (m, 2 H, CH_{ar}), 7.30–7.27 (m, 1 H, CH_{ar}), 6.87–6.84 (m, 2 H, CH_{ar}), 3.82 (s, 3 H, CH_3), 3.23 (s, 2 H, CH_2), 2.84 (d, 1 H, $^2J_{H,H}$ = 16.9 Hz, CH_2), 2.81 (d, 1 H, $^2J_{H,H}$ = 16.9 Hz, CH_2), 1.70 ppm (s, 3 H, CH_3). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 159.6 (q, $C_{ar}OCH_3$), 136.5 (q, C_{ar}), 133.2 (t, $C_{ar}H$), 131.0 (t, $C_{ar}H$), 128.2 (t, $C_{ar}H$), 127.1 (t, $C_{ar}H$), 115.6 (q, C_{ar}), 114.1 (t, $C_{ar}H$), 84.4 (q, C≡C), 83.8 (q, C≡C), 70.9 (q, C-Cl), 55.5 (p, OCH_3), 48.5 (s, CH_2), 34.9 (s, CH_2), 30.1 ppm (p, CH_3). IR (ATR): $\tilde{\nu}$ = 3028, 2930, 2835, 1605, 1568, 1508, 1454, 1443, 1377, 1289, 1244, 1171, 1105, 1078, 1030, 939, 829, 799, 741, 700, 679 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (log ε) = 200 (4.47), 253 nm (4.30). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{20}{}^{35}ClO$ 299.1197; Found 299.1193, $[M – Cl]^+$ Calcd for $C_{19}H_{19}O$ 263.1430; Found 263.1425.

Computational Details. All calculations were performed by using the program package Gaussian 16[71]. The geometrical parameters of all stationary points were optimized by means of B3LYP[32-34]. For this optimization process two different types of basis sets were used (B1 and B2). In the case of B1 6-31G(d)[35-36] was used for C, H, Cl and P, whereas for B2 the 6-

311++G(d,p)[37-40] basis set was employed for these atoms. For Au the def2-TZVP+ECP[41-42] basis was applied in both cases (B1 and B2). For all stationary points no symmetry restriction was applied. Frequency calculations were carried out at each of the structures to verify the nature of the stationary point. It turned out that all transition states have exactly one imaginary frequency, whereas all other structures have none. Furthermore, the energies of the stationary points were calculated using the density functionals B3LYP-D3[43-44] and PBE0[45-46]. For the single point calculations three different types of basis sets (B2, B3 and B4) were used. In the case of B3 for all atoms, which are involved in the reaction (C1, C2, C1', C2' and Cl; for numbering see Scheme 2), the large basis set aug-cc-pVTZ[48-52] was employed; for all other atoms (except for Au) 6-311++G(d,p) was utilized. In the case of B4 the large basis set aug-cc-pVTZ was used for all atoms except for Au. For Au the aug-cc-pVTZ-PP+ECP[53-54] basis set was employed in both cases (B3 and B4). To determine the solvent effect, the single point calculations on the B3LYP/B2 optimized structures were also performed using dichloromethane as solvent.

Supporting Information

Molecular structures, ^{1}H NMR experiments, cartesian coordinates and absolute energies for all calculated compounds, ^{1}H NMR and ^{13}C NMR spectra.

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