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Atom- and Step-Efficient Construction of Five-Membered Carbocycles with Alkenes and Alkynes Catalyzed by $AgSbF_6$

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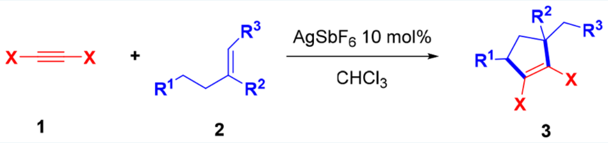
Supporting Information

ABSTRACT: We report a cationic intermolecular cyclization between simple alkenes and alkynes catalyzed by $AgSbF_6$ with great selectivity, involving alkyl C−H bond cleavage. This methodology could supply important multisubstituted cyclopentene scaffolds. The remarkable tolerance of functional groups in the reaction allows great possibility for further transformations.

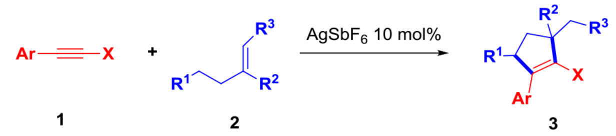


KEYWORDS: *intermolecular cyclization, alkenes, alkynes, cyclopentene derivatives, $AgSbF_6$ catalysis*

The cationic cyclization reactions of alkenes and alkynes are powerful methods to prepare various carbocycles.[1] These types of reactions are normally initiated by proton (involving Lewis or Brønsted acids) or carbocation species (generated in situ) and terminated at π-bonds as electrophilic substitution. In contrast, it was relatively rare for the alkyl C−H bond to trap the carbocation, let alone with great selectivity. When enynes, polyolefins, or polyacetylenes are used as the substrates, polycyclic products could be generated via intramolecular processes, and these types of reactions are applied to synthesize many complex natural products.[2−4] Although these methods are very effective, there is a critical challenge for the intermolecular cyclization between the alkenes and alkynes, because the intrinsic electrophilic properties of these substrates would result in self-dimerization or oligomerization. Another inevitable problem is the control of regioselectivity, in particular, when unsymmetric alkenes or alkynes are involved. Although many efforts have been made in this part, most successful cases are accomplished via the combination of special substrates and a cationic center, such as using allylic alcohols, propargyl alcohols, or acetals as the substrates.[5] In 2010, Echavarren and co-workers reported a gold(I)-catalyzed intermolecular [2 + 2] cycloaddition of terminal alkynes with alkenes leading to cyclobutenes.[6] Inspired by this elegant work, as well as our recent success in electrophilic activation of simple alkynes,[7] we hypothesized that initiation of this process by other catalysts might alter the reaction outcome and/or barrier. Remarkably, a suitable Lewis acid $AgSbF_6$ could catalyze the cationic intermolecular cyclization between simple alkenes and alkynes with great selectivity, involving alkyl C−H bond cleavage and yielding entirely different products and multisubstituted cyclopentene derivatives (see Scheme 1).

Recently, several other groups and our group reported intramolecular cationic cyclization reactions of alkenes and alkynes promoted by super acid through the formation of a C−C bond converted at the alkyl C−H bond.[7a,8] These reactions could supply even polycyclic carbocyles in one step from rather simple starting materials. Here, we envisioned an economic and straightforward synthesis of cyclopentene derivatives with one alkene and one alkyne as the substrates. Treating the mixture of alkyne **1a** and alkene **2a** with the super acid TfOH could generate the desired product **3aa** in 40% yield (see Scheme 2, entry 1). However, the contaminant of generated alkene dimer made the mixture inseparable, and the conversion ratio of alkyne **1a** was merely 60%. The use of Tf_2NH led to lower efficiency (Scheme 2, entry 2), but $HSbF_6$ catalyst could produce the desired product **3aa** in 70% yield, despite some isomers in ∼15% yield (Scheme 2, entry 3). The Lewis acid $AgSbF_6$ then was tested, surprisingly giving desired product **3aa** in 90% yield, meanwhile the dimerization of **2a** was suppressed efficiently (Scheme 2, entry 4). The success of the catalyst $AgSbF_6$ was assumably attributed to the balance between the affinity of the Ag ion with alkynes versus alkenes.[9,10] The utilization of other silver salts or other solvents instead of $CHCl_3$ was not successful to give the desired product (Scheme 2, entries 5−16). And the co-catalyst $PPh_3AuCl/AgSbF_6$ was capable of catalyzing the reaction but resulted in slightly diminished yield (Scheme 2, entry 17).

Scheme 1. Silver-Catalyzed Efficient Cyclization of Alkenes and Alkynes to Five-Membered Carbocycles



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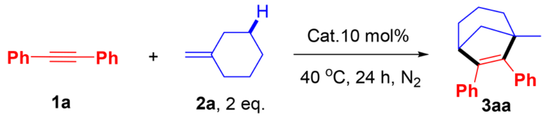
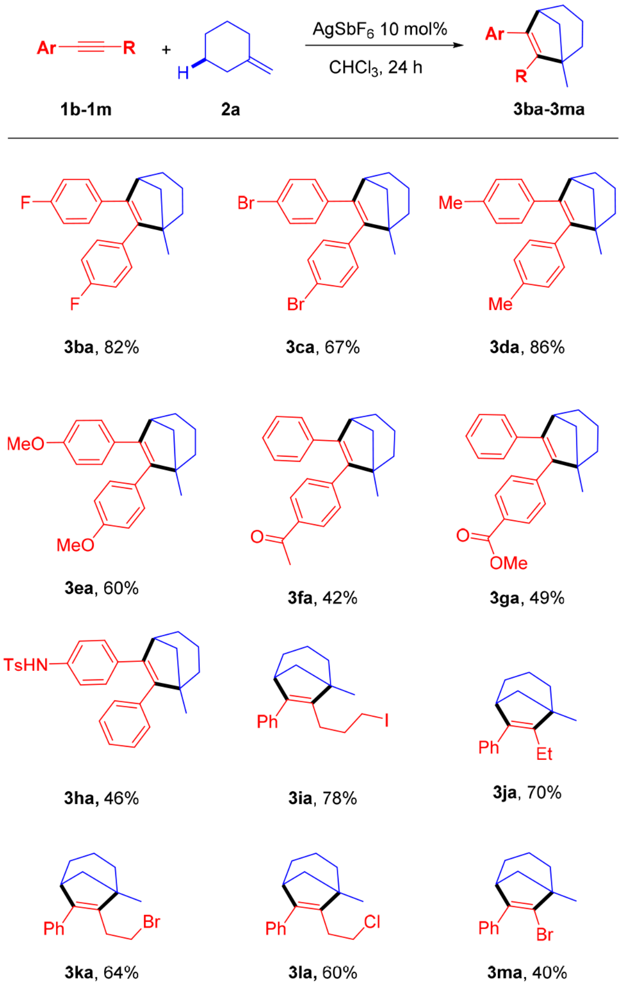
Scheme 2. Condition Optimization of Construction of Five-Membered Carbocycles with 1a and 2a



Entry	Cat.	Solvent	Yield[a]
1	TfOH	$CHCl_3$	40%
2	Tf_2NH	$CHCl_3$	10%
3	$HSbF_6$	$CHCl_3$	70%
4	**$AgSbF_6$**	**$CHCl_3$**	**90% (83%[b])**
5	$AgNTf_2$	$CHCl_3$	0
6	AgOTf	$CHCl_3$	0
7	$AgBF_4$	$CHCl_3$	0
8	$AgNO_3$	$CHCl_3$	0
9	AgOAc	$CHCl_3$	0
10	AgF	$CHCl_3$	0
11	$AgPF_6$	$CHCl_3$	0
12	$AgSbF_6$	DCE	0
13	$AgSbF_6$	DCM	0
14	$AgSbF_6$	CCl_4	0
15	$AgSbF_6$	MePh	0
16	$AgSbF_6$	1,4-Dioxane	0
17[c]	PPh_3AuCl/ $AgSbF_6$	DCE	78%
18	PPh_3AuCl	DCE	0
19	$AgSbF_6$ (5 mo%)	$CHCl_3$	73%
20	$AgSbF_6$ (2.5 mo%)	$CHCl_3$	< 5%

[a] Determined by ^1H NMR versus an internal stardard. [b] Isolated yield. [c] Reaction conditions: $PPh_3AuCl/AgSbF_6$ (5 mol %/6 mol %), 60 °C.

Scheme 3. Reaction Scope of Alkynes with 2a



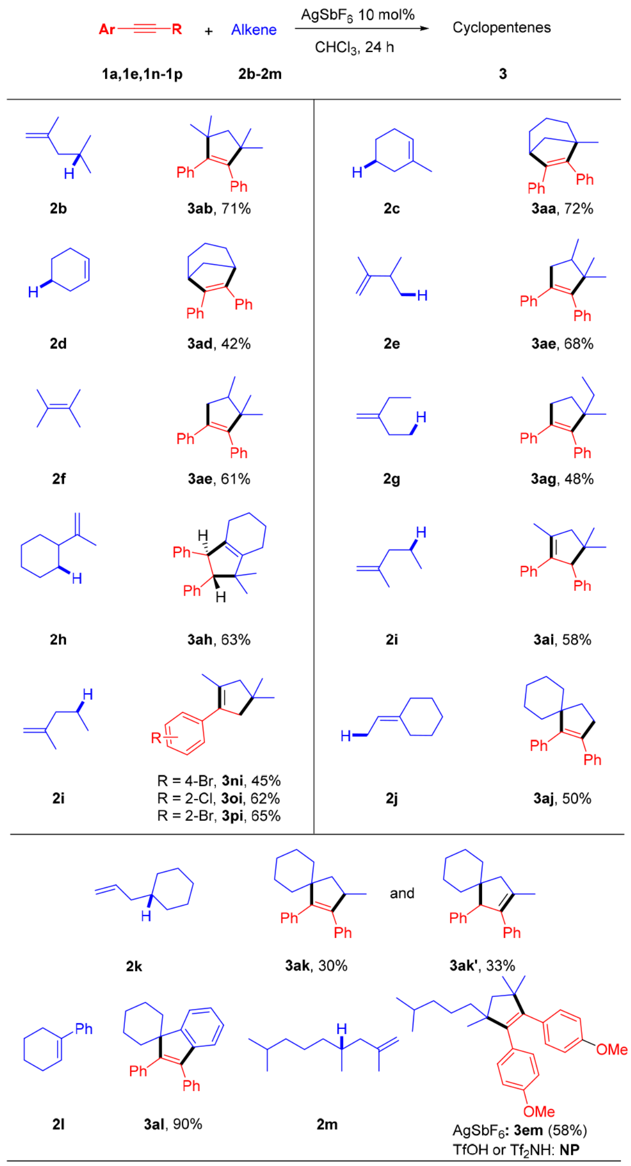
However, alone PPh_3AuCl catalyst failed to initiate the process (Scheme 2, entry 18). Lower catalyst loading led to decreased yields and conversion rate (Scheme 2, entries 19 and 20).

Because of the importance of cyclopentenes,[11] the reactions were extended with more substrates (Scheme 3). First, a range of alkynes with various substitutents were tested in the reactions. As shown in Scheme 3, diaryl acetylenes **1b**−**1e** with the F-, Br-, Me-, and MeO-groups on the phenyl rings all proceeded smoothly under standard conditions to give products **3ba**−**3ea** in good yields. The use of unsymmetric diaryl acetylenes **1f**−**1h** afforded the corresponding products **3fa**−**3ha** with great regioselectivity (>50:1), probably because the generated carbocation center near the electron-rich phenyl is more stable. Remarkably, aryl-alkyl acetylenes **1i**−**1l** also worked well in the cyclization reactions with **2a** to give products **3ia**−**3la**. To our surprise, halogen atoms (including Cl, Br, and I) on the alkyl groups (**1i**, **1k**, and **1l**) all tolerated this $AgSbF_6$-catalyzed reaction. Finally, bromo-phenyl acetylene **1m** also fit this $AgSbF_6$-catalyzed cyclization reaction to form **3ma**, albeit in slightly low yield. The residence of the halogen atoms in the products left the possibility for further useful transformations.

Next, a variety of alkenes were evaluated with symmetric or unsymmetric acetylenes for this $AgSbF_6$-catalyzed cyclization (Scheme 4). Many commercially available alkenes **2b**−**2i** with 2, 3, and 4-substituents were tested with tolane **1a**. The use of different alkenes **2c** and **2a** gave the same product **3aa**, indicating the carbocationic process of this reaction, as well as **2e** and **2f**. When **2h** was employed, the double bond in the product was shifted to the cyclohexyl ring, probably due to the lesser steric hindrence in the product **3ah**. And, interestingly, the two neighboring H atoms on the five-membered ring were transconfigured. The shift of the double bond was also found in the formation of **3ai**. When cyclic substrates **2j** and **2k** were used, spirocycles were easily produced. When phenyl-cyclohexene **2l** reacted with **1a**, indene product was generated via C−C bonds formed on the phenyl ring. Interestingly, when alkene **2i** reacted with terminal alkynes **1n**, **1o**, and **1p**, all the reactions produced cyclopentenes with shifted double bonds. This may be due to the higher stability of the formed tertiary carbocation, in comparison to a secondary carbocation. The reaction of alkyne **1e** and alkene **2m** with long alkyl chain could proceed smoothly with good regioselectivity, leading to the five-membered ring product **3em**, instead of any larger-ring derivatives. When using proton initiator (TfOH or Tf_2NH) for the reaction of **1e** and **2m**, there was no desired cyclopentene product; instead, isomers of alkene **2m** with the double bond shifted to internal were produced. Therefore, $AgSbF_6$ possessed unique advantages, compared to proton catalysts.

Excitingly, this skeleton widely occurs in many biologically active compounds, natural products, and natural productlike molecules.[12] Thus, we examined the possibility of modification of these new products. To our delight, the bromoethyl product **3ka** could be easily transformed via substitution by an azido group (to compound **4**), thiocyano group (to compound **5**), or elimination by KOH (to compound **6**). Moreover, the bromo product **3ma** could be performed with the Sonogashira or

Scheme 4. Reaction Scope of Various Alkenes with 1



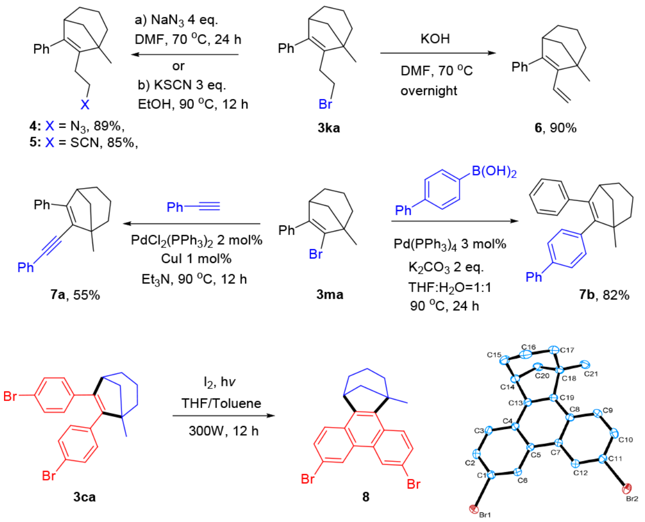
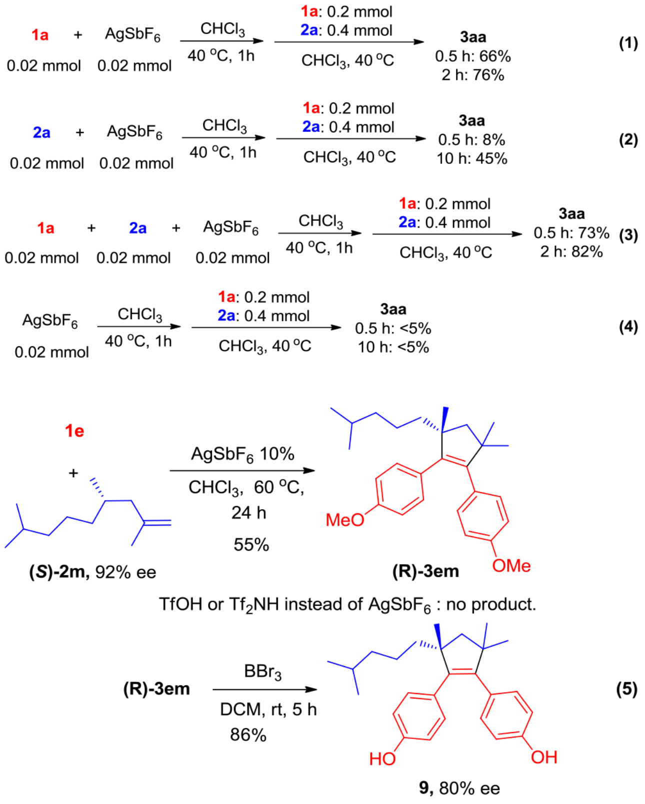


Figure 1. Products derivatization and structure determination of **8** from **3ca**.

Scheme 5. Controlled Experiments for the Catalyst Role



Suzuki coupling reaction to give products **7a** and **7b**.[13] Finally, the product **3ca** could be irradiated to give fused phenanthrene **8**. The structure of **8** was unequivocally confirmed by XRD analysis as well (see Figure 1, Cambridge Crystallographic Data Centre No. CCDC-1584141).

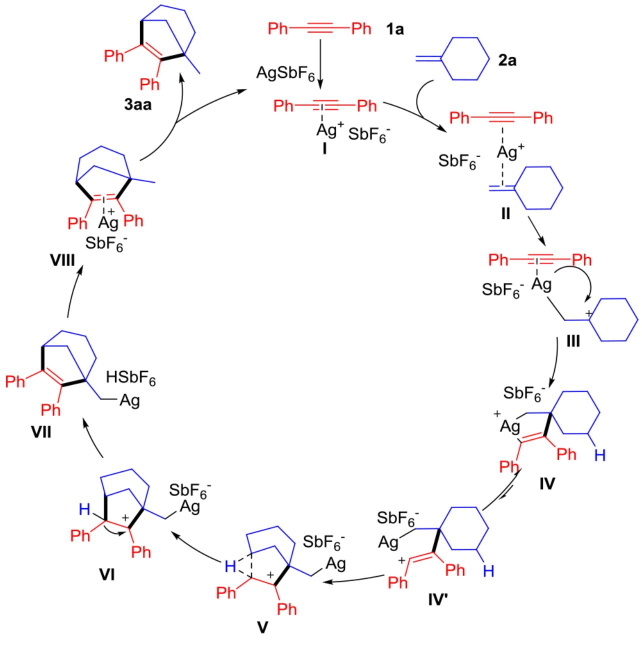
Mechanistically, it is noteworthy to discover the great selectivity between simple alkenes and alkynes in the presence of AgSbF$_6$ catalyst. We were curious about the trigger mode of AgSbF$_6$ catalyst. Thus, monitoring the reaction of **1a** with **2a** under 5 mol % and 10 mol % AgSbF$_6$ by GC analysis showed that the formation of cyclopentene **3aa** under 10 mol % AgSbF$_6$ loading is obviously faster than the reaction with 5 mol AgSbF$_6$ (see Figure S1 in the Supporting Information). So the catalyst loading is very crucial for this transformation. At the same time, there was a dramatic rate increase after 2 h under both conditions. The slow conversion ratio (<20%) within the first 2 h suggests that this reaction requires a long initiation process. Controlled experiments then were conducted [see Scheme 5, eqs 1–4]. Surprisingly, even within 0.5 h, the reaction can reach beyond 60% yield (>70% conversion) [Scheme 5, eqs 1 and 3], and is in sharp contrast to the standard protocol (0.5 h, ~15% conversion). For the pretreatment of AgSbF$_6$ with alkene **2a**, the reaction rate declined slightly, compared with the standard condition [Scheme 5, eq 2]. Whereas for the pretreatment of AgSbF$_6$ in CHCl$_3$, the catalyst could be deactivated and not be capable of catalyzing the cyclization. Through these series of experimental results, we proposed that this reaction was induced by the action of AgSbF$_6$ with alkynes, and the in-situ-generated reactive intermediates could trigger the subsequent cyclization with alkenes.

In addition, we made some attempts to shed more light on the catalyst activation step. Chemical shift had changed obviously via ^{13}C NMR spectra, compared with the alone alkyne **1d** in $CDCl_3$, which revealed the dynamic coordination between **1d** and $AgSbF_6$ and the formed complex was not stable (see Figure S2 in the Supporting Information).[14] Monitoring the reactions of **1a** with **2a** under different substrates concentration via gas chromatography (GC) analysis showed the relative rate of cyclopentene **3aa** formation with higher alkyne concentration was faster (see Figures S4 and S5 in the Supporting Information); but no obvious acceleration was observed with higher alkene concentration. These results further proved the coordination between alkyne and $AgSbF_6$ was more favorable.

Furthermore, for a deep insight into the alkyl C−H cleavage mechanism, (**S**)-**2m** was prepared and subjected to react with **1e**, thus enantioenriched product (**R**)-**3em** was synthesized with some erosion of ee [Scheme 5, eq 5]. The comparation of its derivative **9** with simulating result suggested that the enantiomer ratio was 90:10. This result implied that most of the C-figuration was retained in the cyclization process and suggested the alkyl C−H cleavage was very likely a concerted process.[7b]

Based on the above controlled experiments, plausible catalytic cycles are proposed in Scheme 6. In this reaction, the alkyne (exemplified by **1a**) is very likely to coordinate with a silver salt first,[14] which serves as a template to further react with the alkene (exemplified with **2a**) (see Scheme 6). The template effect enables the C−C bond formation between the alkene and alkyne moiety rather than two alkenes. So when the C−C bond is formed, a vinylic-silver species **IV** is generated and it resembles a vinyl cation **IV′**.[15,7] The subsequent key step is the alkyl C−H cleavage, according to previous work by Gaunt,[15d] Metzger,[15e] and our group,[7b] and the experiment result of Scheme 5, eq 5, a concerted 1,5-hydride shift-carbocation interception or a concerted C−H insertion is preferred via transition state **V**, leading to intermediate **VI**. The intermediate **VI** then can undergo elimination to give an alkyl silver intermediate **VII** and an acid. Finally, the silver intermediate is quenched by the acid to give the product and regenerates the catalyst $AgSbF_6$.[16]

Scheme 6. Proposed Mechanism



In summary, we reported a novel cationic intermolecular cyclization between the alkenes and alkynes catalyzed by $AgSbF_6$. The remarkable tolerance of functional groups in the reaction allowed a great possibility for further transformations. These findings encourage us finding more Ag-catalyzed new reactions based on C−C bond formation on the inert C−H bond.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.8b02448.

Experimental procedures, the data, and the copies of ^{1}H and ^{13}C NMR (PDF)

(CIF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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(16) Although we have received some tips for the reaction mechanism, it is difficult to fully understand the reaction pathway at this stage. No long-life intermediate was observed via IR in situ. To shed more light on the reaction mechanism at the molecular level, density functional theory (DFT) calculations were then conducted. The energies of intermediate **II, IV, IV′**, and **VIII** were estimated, but determination of an ideal pathway, including an appropriate transition state, was not successful; see page S33 in the Supporting Information.

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