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Gold(I)-Catalyzed Intramolecular Tandem Cyclization Reaction of Alkylidenecyclopropane-Containing Alkynes†

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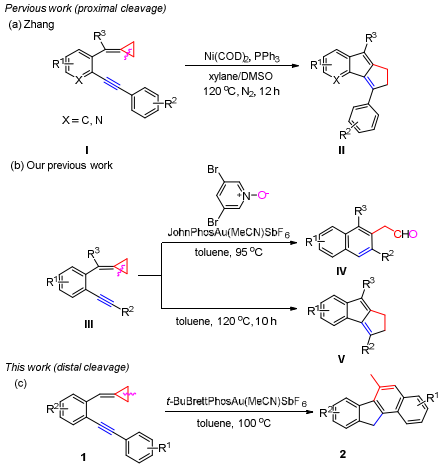
A novel gold(I)-catalyzed intramolecular tandem cyclization reaction of *ortho*-(arylethynyl)arenemethylenecyclopropanes provided an efficient approach to prepare functionalized 11*H*-benzo[a]fluorene derivatives in moderate to good yields. The further transformations as well as application of the product have been presented and a plausible reaction mechanism has been also proposed on the basis of deuterium labeling and control experiments.

Gold catalysis has witnessed a rapid development in the past decades in organic chemistry. Nowadays homogeneous gold catalysis has become one of the most efficient strategies for the construction of carbon-carbon or carbon-heteroatom bonds.[1] Gold-catalyzed transformations[2] have been also widely used in material science, medicinal chemistry and total synthesis in recent years due to the mild reaction conditions and unique catalytic activities. Methylenecyclopropanes (MCPs) or alkylidenecyclopropanes, containing a highly strained cyclopropane ring, are readily accessible and highly reactive molecules that have served as useful building blocks in organic synthesis.[3] Owing to their unique structural features and electronic properties, transition metal-catalyzed (Pd, Rh, Pt, Au, Ni *etc.*) reactions of MCPs have been extensively investigated.[4] For example, in 2010, Zhang's group reported a Ni-catalyzed intramolecular cycloaddition of MCPs to arylalkynes via proximal bond cleavage, giving polycyclic products (Scheme 1, a).[5] Moreover, our group also disclosed a gold(I)-catalyzed tandem cyclization-oxidation of MCP-containing 1,5-enynes with 3,5-dibromopyridine N-oxide via proximal bond cleavage and non-carbene reaction model (Scheme 1, b).[6] On the basis of above information and previous studies, we attempted to utilize substrate **1a** under gold catalysis to examine the reaction outcomes (Scheme 1, c). To our delight, we found that a novel gold(I)-catalyzed intramolecular tandem cyclization reaction took place smoothly via distal bond cleavage, giving the desired 6-methyl-11*H*-benzo[a]fluorene product **2a** in good yield under mild conditions.[7] In this paper, we wish to report this finding.



Scheme 1 Pervious work and this work.

We initially stated to optimize the reaction conditions for the production of **2a** using **1a** as a model substrate and the screening results are shown in Table 1. Substrate **1a** in the presence of IPrAu(MeCN)NTf$_2$ (5.0 mol%) in toluene at 100 °C did not deliver the desired product **2a** after 3 hours (Table 1, entry 1). The use of (2,4-*t*-BuC_6H_3O)$_3$PAu(MeCN)OTf (5.0 mol%) as the catalyst also failed to give **2a** under the same condition (Table 1, entry 2). It was found that **2a** was afforded in 42% yield in the presence of Me$_4$-*t*-BuXphosAuCl/AgSbF$_6$ (5.0 mol%) in toluene at 100 °C within 3 hours (Table 1, entry 3). Cy$_3$PAuCl/AgSbF$_6$ (5.0 mol%) and *t*-BuXphosAuCl/AgSbF$_6$ (5.0 mol%) did not further improve the yield of **2a** (Table 1, entries

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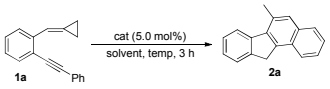
4 and 5). JackiephosAuCl/$AgSbF_6$ (5.0 mol%) provided **2a** in the same yield as that of Me_4-*t*-BuXphosAuCl/$AgSbF_6$ (Table 1, entry 6). Utilizing XphosAuCl/$AgSbF_6$ (5.0 mol%) as catalyst, **2a** was formed in 52% yield in toluene at 100 °C within 3 hours (Table 1, entry 7) and SphosAuCl/$AgSbF_6$ (5.0 mol%) only gave **2a** in 34% yield under the preceding condition (Table 1, entry 8). Delightfully, *t*-BuBrettphosAuCl/$AgSbF_6$ (5.0 mol%) could deliver **2a** in 89% yield in toluene at 100 °C within 3 hours (Table 1, entry 9), although the use of JohnphosAuCl/$AgSbF_6$ (5.0 mol%) only gave **2a** in 50% yield under identical conditions (Table 1, entry 10). Furthermore, (p-$CF_3C_6H_4)_3$PAu(MeCN)SbF_6 (5.0 mol%), IPrAu(MeCN)SbF_6 (5.0 mol%), and Ph_3PAu(MeCN)SbF_6 (5.0 mol%) and $AgSbF_6$ itself (5.0 mol%) did not promote the transformation under the preceding condition (Table 1, entries 11-14). Next, we screened solvent effects in the presence of *t*-BuBrettphosAuCl/$AgSbF_6$ (5.0 mol%). Using 1,2-dichloroethane (DCE), dioxane, MeCN and PhCl as the solvent, **2a** was obtained in lower yields and no reaction could take place in PhOMe (Table 1, entries 15-19). The examination of reaction temperature revealed that carrying out the reaction at 90 or 110 °C did not enhance the yield of **2a** (Table 1, entries 20 and 21). The optimal conditions have been identified as that using *t*-BuBrettphosAu(MeCN)SbF_6 (5.0 mol%) as the catalyst and performing the reaction in toluene at 100 °C within 2 hours afforded **2a** in 90% yield NMR yield (83% isolated yield) within 2 hours (Table 1, entry 22).

Table 1 Optimization of the reaction conditions for the synthesis of **2a**

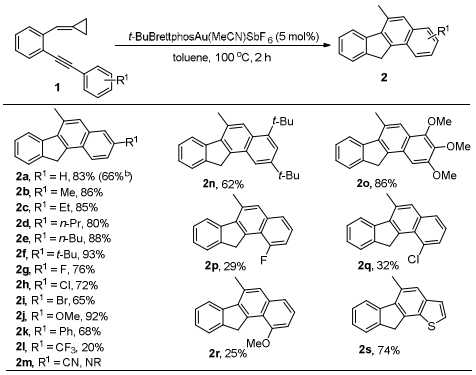


entry	catalyst	solvent	temp (°C)	yield[a] (%)
1	IPrAu(MeCN)NTf_2	toluene	100	NR
2	(2,4-*t*-$BuC_6H_3O)_3$PAu(MeCN)OTf	toluene	100	NR
3	Me_4-*t*-BuXphosAuCl/$AgSbF_6$	toluene	100	42
4	Cy_3PAuCl/$AgSbF_6$	toluene	100	14
5	*t*-BuXphosAuCl/$AgSbF_6$	toluene	100	32
6	JackiephosAuCl/$AgSbF_6$	toluene	100	42
7	XphosAuCl/$AgSbF_6$	toluene	100	52
8	SphosAuCl/$AgSbF_6$	toluene	100	34
9	*t*-BuBrettphosAuCl/$AgSbF_6$	toluene	100	89
10	JohnphosAuCl/$AgSbF_6$	toluene	100	50
11	(p-$CF_3Ph)_3$PAuSbF$_6$	toluene	100	NR
12	IPrAu(MeCN)SbF_6	toluene	100	NR
13	Ph_3PAu(MeCN)SbF_6	toluene	100	NR
14	$AgSbF_6$	toluene	100	NR
15	*t*-BuBrettphosAuCl/$AgSbF_6$	DCE	100	21
16	*t*-BuBrettphosAuCl/$AgSbF_6$	dioxane	100	55
17	*t*-BuBrettphosAuCl/$AgSbF_6$	MeCN	100	20
18	*t*-BuBrettphosAuCl/$AgSbF_6$	PhCl	100	16
19	*t*-BuBrettphosAuCl/$AgSbF_6$	PhOMe	100	NR
20	*t*-BuBrettphosAuCl/$AgSbF_6$	toluene	90	42
21	*t*-BuBrettphosAuCl/$AgSbF_6$	toluene	110	75
22	*t*-BuBrettphosAu(MeCN)SbF_6	toluene	100	90 (83[b])

Reaction conditions: **1a** (0.1 mmol), catalyst (5.0 mol%), solvent (0.5 mL). [a] Yields were determined by ^{1}H NMR spectroscopy. [b] The isolated yield within 2 hours. NR is no reaction.

Having the optimal reaction conditions in hand, we next investigated substrate scope of the reaction with respect to various substituted *ortho*-(arylethynyl)arenemethylenecyclopropanes **1**. Firstly, we examined the substituents R^1 at the aromatic ring and the results are shown in Table 2. As can be seen, the desired products **2b**-**2f** were afforded in good to excellent yields when R^1 was an alkyl group having different steric bulkiness at *para* position. Introducing halogen atoms such as F, Cl and Br at *para* positions afforded the corresponding 6-methyl-11*H*-benzo[a]fluorenes **2g**-**2i** in moderate to good yields. If R^1 was OMe, Ph and CF_3, the corresponding products **2j**-**2l** were obtained in 92%, 68% and 20% yields, respectively, suggesting a significant electronic impact on the reaction proceeding. In the case of R^1 = CN at the *para* position of alkynyl group, no reaction occurred. We also introduced electron-donating substituents such as *t*-Bu and OMe at the *meta* positions of aklynyl group and found that the reaction proceeded smoothly, giving the desired 6-methyl-11*H*-benzo[a]fluorenes **2n** and **2o** in 62% and 86% yields, respectively. However, when substituents such as F, Cl and OMe were introduced at the *ortho* positions of alkynyl group, the corresponding 6-methyl-11*H*-benzo[a]fluorenes **2p**-**2r** were given in 29%, 32% and 25% yield, respectively, indicating a significant steric effect. Notably, introducing a heterocycle at terminal alkyne, such as substrate **1s**, furnished the desired product **2s** in 74% yield. Furthermore, a gram scale synthesis of **2a** was also accessible, affording **2a** in 66% yield. In general, the electron-rich aromatic ring having substituent R^1 is in favour of the transformation.

Table 2 Reaction scope of substituent R^1.[a]



[a] Reactions were carried out by use of **1** (0.2 mmol) in toluene (1.0 mL) with *t*-BuBrettphosAu(MeCN)SbF_6 (9.0 mg, 5.0 mol %) at 100 °C within 2 hours, isolated yields. [b] Reaction was carried out on a 0.900 gram scale of **1a** by use of 32.8 mg *t*-BuBrettphosAu(MeCN)SbF_6 (1.0 mol %). NR is no reaction.

Next, the substituents R^2 at the benzene ring bearing MCP moiety were also examined with substrates **1aa**-**1kk** as shown in Table 3. When R^2 was Me, F and Cl at C4 position, the reactions proceeded smoothly to deliver the corresponding products **2aa**-**2cc** in 82%, 88% and 85% yields, respectively. Introducing Me, F, Cl, CF_3 and NO_2 at C5 position, the corresponding 6-methyl-11*H*-benzo[a]fluorenes **2dd**-**2hh** were formed in 78%, 76%, 80%, 72% and 46% yields, respectively. The structure of **2ff** was assigned by X-ray diffraction (see Supporting Information for the details). CF_3 and NO_2 groups are both tolerated in the reaction. Notably, substrate **1ii** containing benzo[d][1,3]dioxole heterocycle offered the desired product **2ii** in a significantly decreased yield. Furthermore, if utilizing naphthalene or pyridine to replace benzene ring, the reaction did not take place under the standard conditions.

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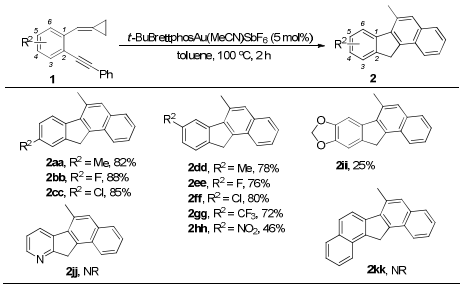
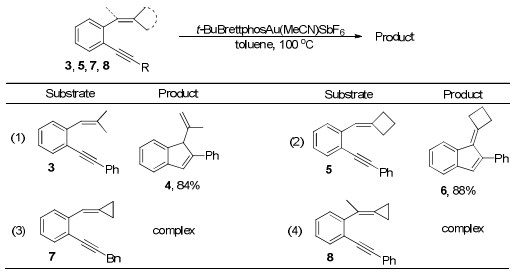
Table 3 Reaction scope of substituent R^2.[a]



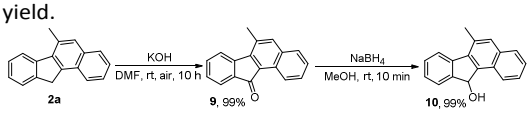
[a] Reactions were carried out by use of **1** (0.2 mmol) in toluene (1.0 mL) with *t*-BuBrettphosAu(MeCN)SbF_6 (9.0 mg, 5.0 mol %) at 100 °C within 2 hours, isolated yields. NR is no reaction.

To further clarify the substrate scope, substrates **3**, **5**, **7** and **8** were prepared and the experimental results are shown in Scheme 2. Substrate **3** bearing an isoproylidene moiety as well as substrate **5** having a cyclobutylidene moiety afforded the corresponding products **4** and **5** in 84% and 88% yields, respectively via a 1,5-enyne 5-*endo-dig* cycloisomerization[8] pathway (Scheme 2, entries 1-2). Substrate **7** bearing an benzyl group and substrate **8** having a methyl group both gave complex product mixtures (Scheme 2, entries 3-4).



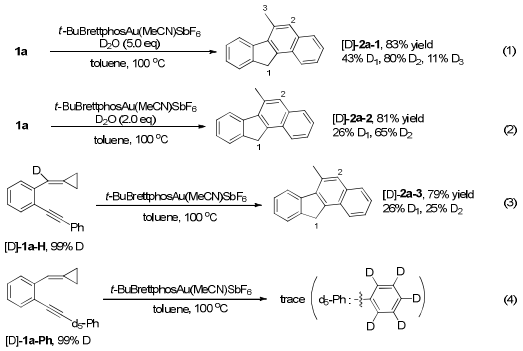
Scheme 2 The supplementary experiment on the substrate scope

To demonstrate the synthetic utility of these functionalized 11*H*-benzo[a]fluorene derivatives, further transformations were performed as shown in Scheme 3. 6-methyl-11*H*-benzo[a]fluorene **2a** was oxidized to 6-methylbenzo[a]fluorene-11-one **9** in 99% yield in the presence of KOH in DMF under air. Product **9** has potential application in material science, including optical materials, organic dyes, organic light emitting materials (OLEDs).[9] Treatment of **9** with $NaBH_4$ provided the corresponding reduction product **10** in 99% yield.



Scheme 3 Further transformations of **2a**

To illuminate the reaction mechanism, four deuterium-labeling experiments were performed under the standard conditions. Adding 5.0 equiv of D_2O into the reaction gave the deuterated product [D]-**2a-1** in 83% yield along with deuterium incorporation at C1 with 43% D content, at C2 with 80% D content and at C3 with 10% D content (Scheme 4, eq. 1). When 2.0 equiv of D_2O was employed, the deuterated product [D]-**2a-2** was given in 81% yield along with deuterium incorporation at C1 with 26% D content and at C2 with 65% D content (Scheme 4, eq. 2). Utilizing deuterated [D]-**1a-H** as substrate, the reaction proceeded smoothly to offer the corresponding partially deuterated product [D]-**2a-3** in 79% yield along with 26% D content at C1 and 65% D content at C2 (Scheme 4, eq. 3). Trace of the desired product was formed when 99% deuterated [D]-**1a-Ph** was used as substrate, probably because the C-D bond is more stable[10] which hindered the form of intermediate **IV** derived from intermediate **III** shown in Scheme 5 and the desired product could not be accessed smoothly (Scheme 4, eq. 4).



Scheme 4 Deuterium labeling experiments

Based on the above experimental results and pervious reports, a plausible mechanism for gold(I)-catalyzed intramolecular tandem cyclization reaction of **1a** is outlined in Scheme 5. At the beginning, substrate **1a** evolves through a 5-*endo-dig* cycloisomerization to give intermediate **I** in the presence of gold catalyst, which produces intermediate **II** through deprotonation. Intermediate **II** undergoes i) protodeauration, ii) reactivation by gold(I) and iii) cyclopropane ring-opening process (distal C-C bond cleavage) to produce allylic carbocation **III**.[11] A subsequent Friedel-Crafts-type cyclization delivers intermediate **IV**, which undergoes dehydro-aromatization to afford intermediate **V**. Following olefinic isomerization, intermediate **VI** is formed. Then, a stable vinyl-gold(I) species **VII** is generated through a 1,3-gold migration.[12] Protonation of intermediate **VII** releases gold(I) catalyst to afford intermediate **VIII**, which undergoes intramolecular 1,3-proton transfer to give the final product **2a**. In the presence of large amount of D_2O (5.0 equiv), the high concentration of D^+ may cause the deuteration at C3 during the reaction proceeding since product **2a** remained unchanged upon treatment with D_2O under identical conditions (see Supporting Information).

Fluorine derivatives have high solution- and solid-state photoluminescence quantum yields and are used in the field of blue-emitting materials.[13] Therefore, compounds **2b** and **2ii** were selected for studying their photonic properties. As shown in Figure 1, **2ii** showed a better fluorescence emission than **2b** when they were excited at λ = 271 nm. The quantum yield (Φ) of **2ii** even reached to 0.59 (see Supporting Information), suggesting that 11*H*-benzo[a]fluorene derivatives could be also realized as the highly promising candidates for blue OLEDs.[14]

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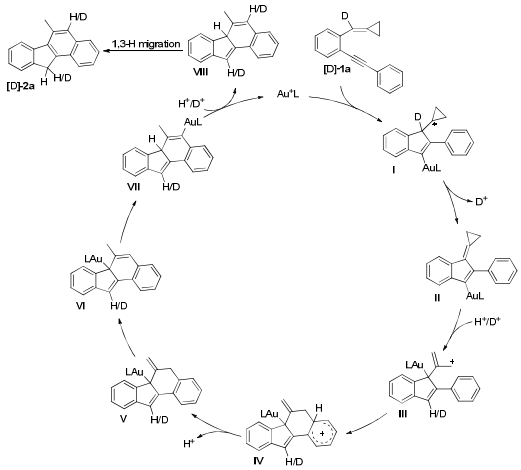

Scheme 5 A plausible reaction mechanism.

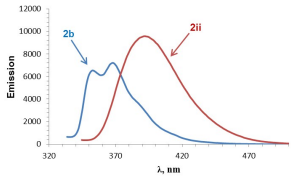

Figure 1 Fluorescence emission of **2b** and **2ii**: samples were measured in CH_2Cl_2, c = 1.0 μM.

In conclusion, we have developed a novel gold(I)-catalyzed intramolecular tandem cyclization reaction of alkylidenecyclopropane-containing alkynes provided an efficient access to 11*H*-benzo[a]fluorene derivatives in moderation to excellent yields under mild conditions. In addition, a plausible mechanism has been proposed on the basis of deuterium-labeling and control experiments and a promising application of these 11*H*-benzo[a]fluorene products for blue OLEDs has been also explored. Further investigations on the mechanistic details and exploration of new methodology based on gold(I)-catalyzed transformations of MCPs are currently underway in our laboratory.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgment

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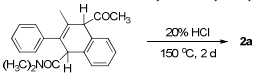

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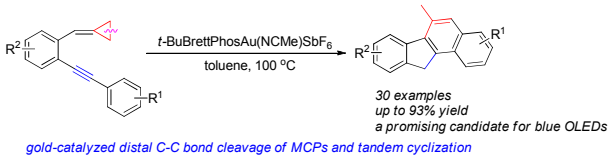
Gold(I)-catalyzed intramolecular tandem cyclization reaction of alkylidenecyclopropane-containing alkynes

A novel strategy for gold(I)-catalyzed intramolecular tandem cyclization reaction of *ortho*-(arylethynyl)arenemethylenecyclopropanes has been developed, providing a facile access to functionalized 11*H*-benzo[a]fluorene derivatives.



gold-catalyzed distal C-C bond cleavage of MCPs and tandem cyclization

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