Synthetic Methods

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Gold-Catalyzed Cascade Cyclizations of 1,6-Diynyl Carbonates to Benzo[*b*]fluorenes Involving Arylation of Oxocarbenium Ion Intermediates and Decarboxylative Etherification**

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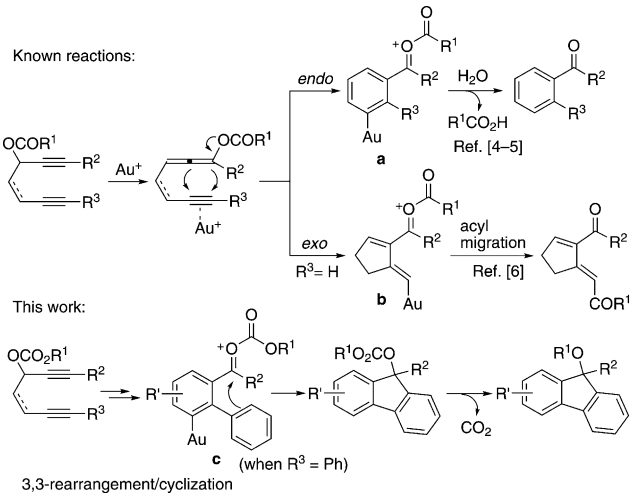
In recent years, the gold-catalyzed rearrangement reactions of propargylic esters have received considerable attention owing to their synthetic utility in a wide variety of fascinating transformations.[1] Two main competitive processes, namely, 1,2-acyloxy migration[2] and 3,3-rearrangement[3] are usually involved in most cases of these gold-catalyzed rearrangement reactions as an initial step, which depends on the substitution patterns on either end of the propargyl moiety. The gold-catalyzed 3,3-rearrangement of propargyl esters leads to the formation of carboxyallenes, which can be further converted into various acyloxocarbenium ion intermediates by activation of the allene moiety by the same gold catalyst. The oxocarbenium ions generated in these reactions show diverse reactivities for further functionalization reactions.[1c] The carboxyallene may also act as a nucleophile to attack carbon–carbon multiple bonds to form similar oxocarbenium ion intermediates showcased in a limited number of reports. For example, propargyl esters tethered with an alkyne moiety undergo tandem 3,3-rearrangement/*endo*-cyclization giving rise to oxocarbenium ion **a**, which can be hydrolyzed by H_2O to yield aromatic ketones as reported by Toste and co-workers[4] and Oh and co-workers (Scheme 1).[5] More recently, Malacria et al. found that the acyl group on the oxonium ion **b** produced through *exo*-cyclization could be trapped intramolecularly by the nucleophilic C–Au bond, thereby resulting in a 1,5-migration of the acyl group (Scheme 1).[6] During our ongoing research on gold-catalyzed cascade reactions[7] of 1,6-diyn-4-en-3-ols,[7a] we envisioned that it is possible for oxocarbenium ions **a** or **b** to further react with a nucleophile owing to their high electrophilicities. Such transformations should be highly dependent on the stability of the oxocarbenium ion.[8] In intermediates **a** or **b**, the acyl group attached to the oxonium ion is highly electron-deficient and thus greatly destabilizes the positive charge on the oxocarbenium ions. We postulated that if the acyl group is replaced by a -$COOR^1$ group, the resulting oxocarbenium ion intermediate like **c** might be more stable, thus a further reaction with a nucleophile could be achieved. To this end, propargyl carbonates would be the right substrates of choice. It should be noted that compared with the intensive development of propargyl esters, little attention has been paid to the gold-catalyzed transformations of propargyl carbonates.[9] Herein, we report our success in gold-catalyzed cascade cyclizations of 1,6-diynyl carbonates leading to benzo[*b*]fluorenes by arylation of oxocarbenium ion intermediates and subsequent decarboxylative etherification (Scheme 1). It is also noted that although decarboxylative etherification has been reported to occur with transition metals such as Pd, Rh, Fe, or Ru etc.,[10] to our knowledge, there is no report with gold.



Scheme 1. Possible transformations of propargylic carboxylates via oxocarbenium ion intermediates.

To test the feasibility of our hypothesis, we initially investigated the cyclization reaction of allyl 3-phenyl-1-[2-(phenylethynyl)phenyl]prop-2-ynyl carbonate (**1a**; Table 1). The reaction of **1a** in the presence of the catalyst [Johnphos-(MeCN)Au]SbF_6 (**A**, 3 mol%) afforded 11-(allyloxy)-11-phenyl-11*H*-benzo[*b*]fluorene **2a** in 77% yield in dichloromethane or in dichloroethane (Table 1, entries 1 and 2). However, in these cases, the products were easily contaminanted with a small amount of impurity, and purification by column chromatography was difficult. To our delight, switching the solvent to toluene allowed the clean formation of **2a** with a yield of 78% (Table 1, entry 3). Other aromatic solvents such as benzene and *o*-xylene afforded **2a** in 74 and 60% yields, respectively (Table 1, entries 4 and 5). A

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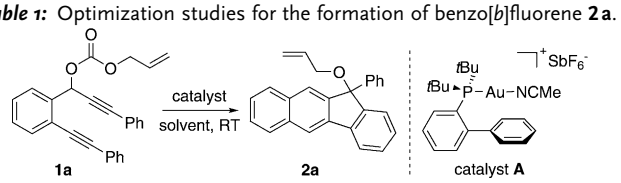
Table 1: Optimization studies for the formation of benzo[*b*]fluorene **2a**.



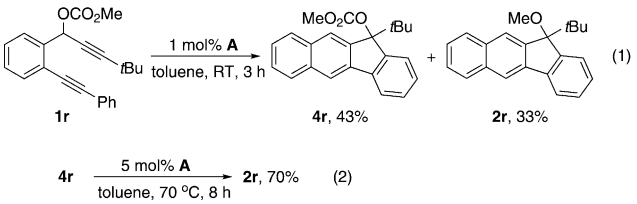
Entry	Catalyst (mol%)	Solvent	*t* [h]	Yield of **2a**[a] [%]
1	**A** (3)	CH_2Cl_2	1	77[b]
2	**A** (3)	$ClCH_2CH_2Cl$	1	77[b]
3	**A** (5)	toluene	2	78
4	**A** (5)	benzene	1	74
5	**A** (5)	*o*-xylene	2	60
6[c]	[JohnphosAuCl]/$AgPF_6$ (5)	toluene	2.5	59
7[d]	[CyJohnphosAuCl]/$AgSbF_6$ (5)	toluene	4	–[e]
8	[PPh_3AuCl]/$AgSbF_6$ (5)	toluene	1	–[e]
9	[tBu_3PAuCl]/$AgSbF_6$ (5)	toluene	1	–[e]
10	$AgSbF_6$ (5)	toluene	12	NR[f]

[a] Yields of isolated product. [b] Contaminanted with a small amount of impurity. [c] Johnphos = (2-biphenyl)di-*t*Bu-phosphine. [d] CyJohnphos = (2-biphenyl)di-cyclohexyl-phosphine. [e] Several products were formed. [f] NR = No reaction.

combination of [JohnphosAuCl] with $AgPF_6$ gave a lower yield of 59% (Table 1, entry 6). We also examined the influence of various phosphine ligands in this transformation. CyJohnphos, PPh_3, and $P(tBu)_3$ all failed to give clean reactions (Table 1, entries 7–9). The results indicate that the nature of the phosphine ligand plays an important role in controlling the chemoselectivity of this reaction. $AgSbF_6$ alone did not promote any transformation (Table 1, entry 10). For comparison, we also prepared the OAc-protected substrate 3-phenyl-1-[2-(phenylethynyl)phenyl]-prop-2-ynyl acetate. It was found that several products were formed catalyzed by catalyst **A** (5 mol%) in toluene by using this substrate; among these products was naphthyl ketone phenyl(3-phenylnaphthalen-2-yl)methanone **3a**, which was derived by hydration of the oxocarbenium ion intermediate and was isolated in 31% yield. The results imply that the protecting group on the alcohol can strongly affect the reaction pathway.

With the optimized reaction conditions in hand, the scope of this cascade cyclization reaction was investigated. As shown in Table 2, the method is applicable to a wide range of suitably substituted 1,6-diynyl carbonates. We first examined the substituent effect (R^1) on the carbonate groups. The allyl, alkyl, and benzyl groups are all compatible under the cyclization conditions, leading to products **2a**–**2c** and **2e** in 66–85% yields. When R^1 is a sterically more demanding alkyl group, the efficiency of this reaction decreased. For example, the methyl-substituted substrate **1b** afforded **2b** in 85% yield. When the methyl group in the carbonate moiety was replaced by an *i*Pr group, the yield of the cyclization product **2c** decreased to 66%. Substrate **1d** with a *tert*-butyl substituent could not deliver the desired benzofluorene product, but only the product 2-naphthyl ketone **3a** in 77% yield. Clearly the bulkiness of the substituent on the carbonate moieties had a detrimental effect on the reactivity. Next, we investigated the electronic effects of the arene substitution (R^3) on the second alkyne terminus. Substrate **1f** with an electron-donating (*p*-Me) group on the aromatic ring worked efficiently and furnished the corresponding product **2f** in 74% yield, whereas substrate **1g** with an electron-withdrawing substituent (*p*-Br) gave the cyclization product **2g** in only 34% yield along with 37% of naphthyl ketone **3g**. The low yield observed for **2g** is attributed to the reduced nucleophilicity of the aromatic ring. The *ortho*-bromo-substituted substrate **1h** did not give the expected product, presumably owing to steric effects. Interestingly, this method could be used for the synthesis of the thienyl-fused polycycle **2i** by using the substrate **1i** with a thienyl sustituent (R^3). The reactions proved to be quite general with respect to substitution of R^2 on the first alkyne terminus, since aryl and alkyl groups were all suitable for this substituent, thereby showing a wide diversity of the products. Functional groups such as -Me, 3,4,5-trimethoxy, 1-naphthyl, -Br, $-CF_3$, and cyclopropyl groups were well tolerated (**2j**–**2n**, **2p**). The reactions with bulky *t*Bu-substituted diynes were also satisfactory and lead to **2q** and **2r** in good yields. Furthermore, substrate **1s**, carrying a fluoro substituent on the parent phenyl ring, was also compatible for this transformation, and 66% yield for product **2s** was realized. It should be noted that in some cases as indicated in Table 2, the addition of molecular sieves was necessary. In the absence of molecular sieves, these reactions were either not clean or resulted in lower yields of the desired products. The structure of benzo[*b*]fluorene was further confirmed by X-ray crystallographic analysis of **2s**.[11]

To understand the reaction mechanism, we tried to determine and isolate the possible reaction intermediates. To our delight, when *t*Bu-substituted compound **1r** was used as a substrate, the carbonate product **4r** was obtained in 43% yield in the presence of catalyst **A** (1 mol%), together with 33% of decarboxylated product **2r** [Scheme 2, Eq. (1)].

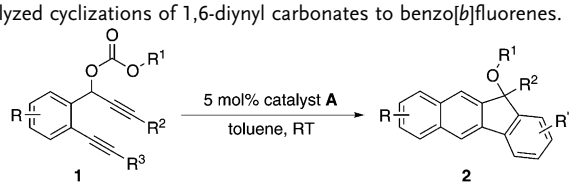


Scheme 2. Determination of the reaction intermediates.

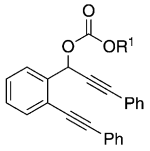
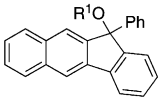
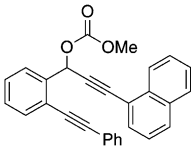
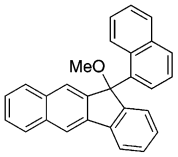
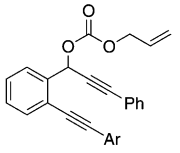
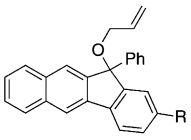
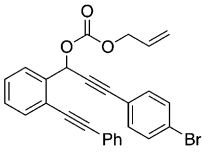
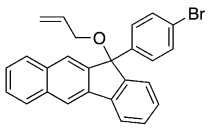
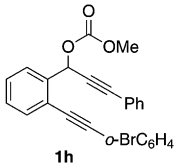
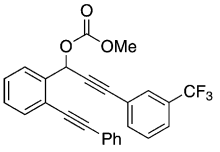
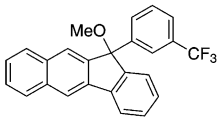
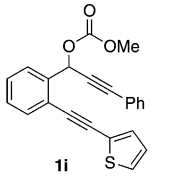
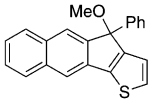
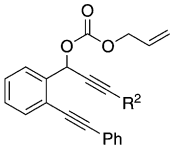
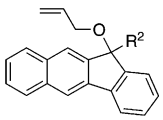
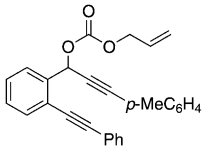
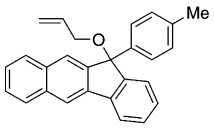
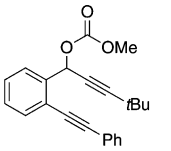
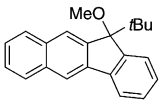
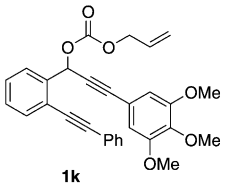
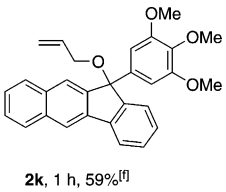
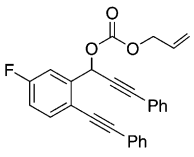
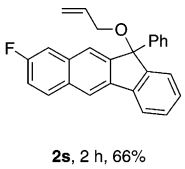
Control experiments with **4r** catalyzed by catalyst **A** (5 mol%) in the presence of 5 Å MS indicated that only a trace amount of **2r** was formed at room temperature; however, upon heating a toluene solution of **4r** at 70 °C, the decarboxylation indeed occurred to give **2r** in 70% yield [Scheme 2, Eq. (2)]. Without the gold catalyst, no reaction occurred. The results disclosed that gold could catalyze the decarboxylative etherification of benzylic carbonates. The reason why a higher reaction temperature than in the one-pot procedure was required is not clear yet.

A crossover experiment was also performed. Treatment of a 1:1 mixture of two diynes, **1a** and **1r**, bearing different protecting groups under the catalytic conditions shown in

Table 2: Gold-catalyzed cyclizations of 1,6-diynyl carbonates to benzo[*b*]fluorenes.



1 2

Substrate	Product[a]	Substrate	Product[a]
			
1a, R^1 = allyl **1b**, R^1 = Me **1c**, R^1 = *i*Pr **1d**, R^1 = *t*Bu **1e**, R^1 = Bn	**2a**, 2 h, 78% **2b**, 1 h, 85% **2c**, 4 h, 66%[b] –[c] **2e**, 5 h, 73%	**1l**	**2l**, 16 h, 50%
			
1f, Ar = *p*-MeC_6H_4 **1g**, Ar = *p*-BrC_6H_4	**2f**, R = Me, 5 h, 74%[b] **2g**, R = Br, 7 h, 34%[b,d]	**1m**	**2m**, 4 h, 73%
	–[e]		
1h		**1n**	**2n**, 3 h, 69%[b]
			
1i	**2i**, 14 h, 48%	**1o**, R^2 = *n*Bu **1p**, R^2 = ---◁ **1q**, R^2 = *t*Bu	**2o**, 5 h, 69%[b] **2p**, 5 h, 47%[g] **2q**, 4 h, 76%[b]
			
1j	**2j**, 4 h, 70%[b]	**1r**	**2r**, 2 h, 76%[b]
			
1k	**2k**, 1 h, 59%[f]	**1s**	**2s**, 2 h, 66%

[a] Yields of isolated products. Unless noted, all the reactions were carried out on 0.2 mmol scale. [b] 5 Å molecular sieves (MS, 50 mg) were added. [c] The hydration product phenyl(3-phenylnaphthalen-2-yl)methanone **3a** was obtained in 77% yield. [d] The hydration product [3-(4-bromophenyl)naphthalen-2-yl](phenyl)methanone **3g** was also formed in 37% yield. [e] The hydration product [3-(2-bromophenyl)naphthalen-2-yl](phenyl)methanone **3h** was obtained in 94% yield. [f] 4 Å MS (25 mg) were added (0.1 mmol scale). [g] 4 Å MS (50 mg) were added.

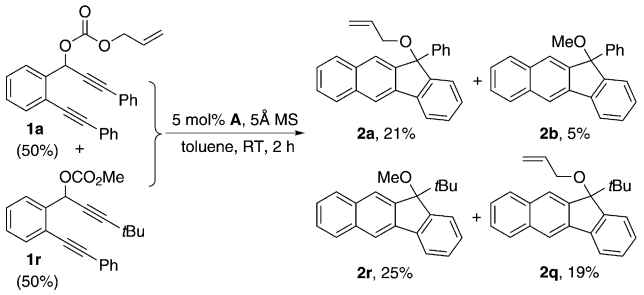
Scheme 3 delivered ethers **2a** and **2r**, as well as the crossover products **2b** and **2q**. The results indicated that the decarboxylative etherification might proceed through the formation of an ion pair of a cationic species and an alkoxide. Dissociation of ion pairs led to rapid exchange of the nucleophilic alkoxides during the process.[12]

A possible reaction mechanism for this cascade cyclization reaction is shown in Scheme 4. π Complexation of the cationic gold complex to the alkyne moiety followed by 3,3-rearrangement results in the formation of allenyl carbonate **6**. Subsequent nucleophilic attack of the allenic moiety to the gold-coordinated triple bond affords oxocarbenium ion intermediate **7**. Intermediate **7** is stable enough to undergo the subsequent intramolecular arylation/deauration to yield carbonate **9**. Decarboxylative etherification of **9**, possibly via benzylic cation intermediate **10** generated by a Au^+-assisted C–O bond cleavage reaction,[13] would finally furnish ether **2**. Alternatively, intermediate **8** may undergo the subsequent reactions directly before protonation.

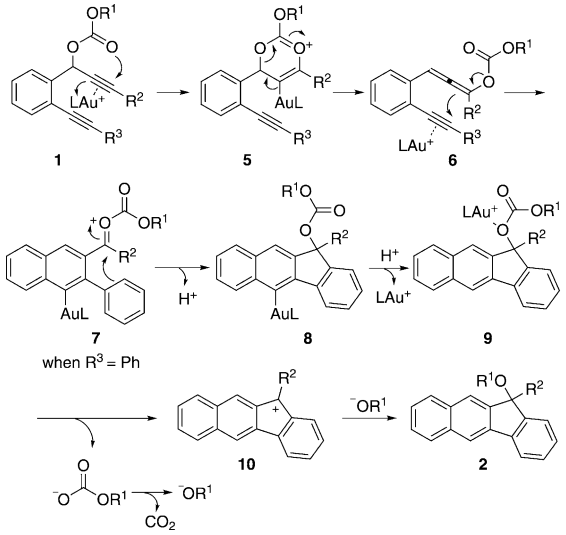
In summary, we have developed a new cascade reaction of 1,6-diynyl carbonates that involves rare reaction patterns of arylation of oxocarbenium ion intermediates and decarboxylative etherification. Our results suggest that when propargyl carbonates are employed instead of carboxylates, it is possible to form more-stable oxocarbenium ion intermediates, which can be further attacked by nucleophiles. The results also indicate that the substituents on the migrating groups may play an important role for defining the reaction pathway in gold-catalyzed rearrangement reactions of propargyl esters. We are now exploiting the new synthetic possibilities by examining the gold-catalyzed reactions of simply substituted propargylic carbonates.

Experimental Section

Typical procedure for the synthesis of benzo[*b*]fluorene **2a**. Catalyst **A**



Scheme 3. Crossover experiment.



Scheme 4. Possible reaction mechanism.

(7.7 mg, 0.010 mmol) was added to a solution of allyl 3-phenyl-1-[2-(phenylethynyl)phenyl]prop-2-ynyl carbonate (**1a**; 78.5 mg, 0.2 mmol) in toluene (2 mL). After stirring at room temperature for two hours, the solvent was evaporated under reduced pressure, and the residue was purified by chromatography on silica gel (petroleum/dichloromethane = 3:1) to afford **2a** (54.4 mg, 78%) as a white solid. m.p. 129–130 °C. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): $\delta = 3.52$–3.62 (m, 2H), 5.06 (dd, $J = 10.2$, 1.5 Hz, 1H), 5.27 (dd, $J = 17.4$, 1.8 Hz, 1H), 5.78–5.90 (m, 1H), 7.18–7.47 (m, 10H), 7.73 (s, 1H), 7.74 (d, $J =$ 6.9 Hz, 1H), 7.83 (d, $J = 7.5$ Hz, 1H), 7.88 (d, $J = 7.8$ Hz, 1H), 8.09 ppm (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si): $\delta = 64.52$, 88.21, 115.58, 118.23, 120.47, 124.65, 126.63, 125.70, 125.86, 126.39, 127.07, 128.07, 128.18, 128.62, 128.86, 129.28, 133.64, 134.29, 135.22, 138.84, 140.22, 144.22, 145.30, 147.53 ppm. HRMS (EI): *m*/*z* calcd for $C_{26}H_{20}O$: 348.1514, found 348.1515.

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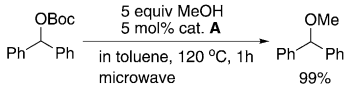
[12] To understand the possible reaction pathway, we also tried the gold-catalyzed decarboxylative etherification reaction of the simple substrate benzhydryl *tert*-butyl carbonate with methanol. It was found that the desired product of (methoxymethylene)-dibenzene was obtained in 99% yield.



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