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Gold-Catalyzed Cascade Oxidative Cyclization and Arylation of Allenoates

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Keywords: Synthetic methods / Homogeneous catalysis / Oxidation / Arylation / Cyclization / Gold / Allenes

An Au^{I}/Au^{III} catalytic system was found to be effective for the cascade oxidative arylation and cyclization of allenoates with arylboronic acids to give the corresponding cyclic adducts in moderate yields. This reaction system constitutes a new method for the synthesis of β-aryl-γ-butenolides under mild conditions. Based on the previous mechanistic studies, a proposed Au^{I}/Au^{III} redox catalytic cycle has been outlined.

Introduction

Gold was long deemed to be an inert metal until the first gold-catalyzed reaction was reported in 1972.[1] Since then, homogeneous gold-catalyzed reactions have attracted significant attention.[2–4] Gold catalysts are typically been used as soft π-acids for activation of C–C multiple bonds to initiate various novel transformations in organic synthesis.[5,6] However, lately, Hashmi, Zhang, Toste, Gouverneur and other groups have reported several interesting gold-catalyzed homo- and cross-coupling reactions through a proposed Au^{I}/Au^{III} redox catalytic cycle by using an external F^{+} oxidant.[7–10] For example, in 2009, Hashmi and co-workers first prepared the corresponding vinyl Au^{I} complexes to examine their reactivity in a stoichiometric manner; they found that the corresponding vinyl Au^{III} complex could be formed upon treatment of vinyl Au^{I} complex with *N*-fluoro-*N*-(phenylsulfonyl)benzenesulfonamide (NFSI).[7a] In the mean time, Hammond and Xu first proved by XPS measurements the Selectfluor-mediated oxidation of Au^{I} to Au^{III} in the functionalization of alkynes upon hydration.[9a] Moreover, Gouverneur and co-workers also clearly showed that Selectfluor could oxidize Au^{I} to Au^{III}, and the generated Au^{III} species could undergo intramolecular Friedel–Crafts arylation smoothly.[9b] Subsequently, Zhang and Toste's research groups independently described the aminoarylation reaction of olefins with an Au^{I}/Au^{III} redox catalytic cycle. However, Toste and co-workers proposed a bimolecular reductive elimination mechanism proceeding via a five-membered cyclic transition state to explain the reaction outcome.[8a–8c] These findings have remarkably extended the synthetic usefulness of gold catalysis in organic synthesis.

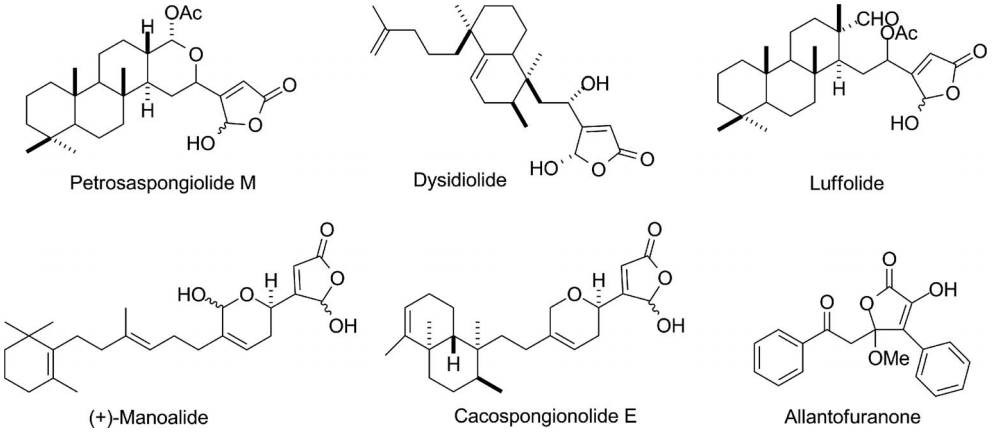

Figure 1. Examples of biologically active β-substituted γ-butenolides.

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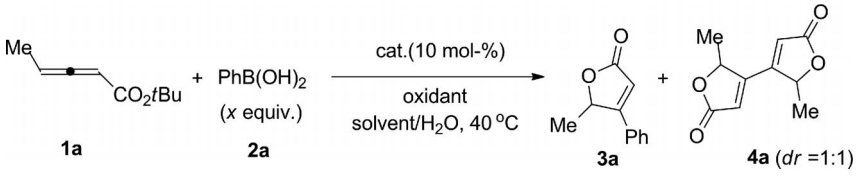
In 2008, Hammond and co-workers first synthesized and isolated the stable organogold(I) compound and disclosed evidence for the reaction mechanism in the gold-catalyzed cyclization of allenoate.[11] Because β-substituted γ-butenolides are very important building blocks in organic synthesis and are widely found in a variety of natural products and medicinally important compounds (Figure 1),[12] the development of a simple synthetic method that allows access to this important structural motif is highly desirable. Currently, these compounds are almost always obtained through a two-step process: cyclization of allenoate and subsequent β-substitution.[11,13] On the basis of the above findings, we attempted to further explore a straightforward new synthetic approach for the construction of the β-aryl-γ-butenolide structure motif by applying an Au^{I}/Au^{III} catalytic process to allenoates. Herein, we wish to report a novel cascade oxidative arylation and cyclization of allenoates with arylboronic acids, affording the corresponding β-aryl-γ-butenolides in moderate yields under mild conditions.

Results and Discussion

Initial studies using allenoate **1a** as substrate with phenylboronic acid (**2a**; 10 equiv.) in the presence of [PPh_3AuCl] (10 mol-%) in CH_3CN/H_2O were aimed at establishing the optimal conditions; the results of these experiments are summarized in Table 1. We found that the desired β-aryl-γ-butenolide **3a** was isolated in 60% yield along with oxidative homo-coupling product **4a** derived from allenoate **1a** in 35% yield as a pair of diastereoisomers (1:1). An examination of solvent effects revealed that CH_3CN was the best solvent with respect to the yield of **3a** (Table 1, entries 1–5). Elevating the reaction temperature to 60 °C dramatically decreased the yield of **3a** (Table 1, entry 6). When the reaction temperature was reduced to room temperature, the desired product **3a** was obtained in trace amounts (Table 1, entry 22). The yield of **3a** was increased to 65% when **1a** in CH_3CN (1.0 mL) was slowly added into the reaction mixture over two hours by using a syringe pump (Table 1, entry 7). Reducing the amount of phenylboronic acid employed also decreased the yield of **3a** (Table 1, entries 8 and 9). An examination of various gold catalysts established that [PPh_3AuCl] was the best choice for this transformation (Table 1, entries 1 and 10–16). Notably, $AuCl_3$ could also promote the reaction, but it was less efficient, delivering **3a** in 15% yield along with **4a** in 70% yield (Table 1, entry 16). It was found that Selectfluor was the best oxidant, affording

Table 1. Optimization of the reaction conditions for oxidative cyclization and arylation.[a]



Entry	Cat.	*x*	Oxidant	Solvent	Yield (%)[b]	
					3a	**4a**
1	PPh_3AuCl	10.0	Selectfluor	CH_3CN/H_2O	60	35
2[c]	PPh_3AuCl	10.0	Selectfluor	acetone/H_2O	49	40
3[c]	PPh_3AuCl	10.0	Selectfluor	toluene/H_2O	18	53
4[c]	PPh_3AuCl	10.0	Selectfluor	DCE/H_2O	33	57
5[c]	PPh_3AuCl	10.0	Selectfluor	THF/H_2O	55	20
6[d]	PPh_3AuCl	10.0	Selectfluor	CH_3CN/H_2O	37	45
7[e]	PPh_3AuCl	10.0	Selectfluor	CH_3CN/H_2O	65	26
8[e]	PPh_3AuCl	3.0	Selectfluor	CH_3CN/H_2O	35	42
9[e]	PPh_3AuCl	5.0	Selectfluor	CH_3CN/H_2O	51	28
10[e]	$(p\text{-}CF_3C_6H_4)_3PAuCl$	10.0	Selectfluor	CH_3CN/H_2O	60	16
11[e]	$(p\text{-}MeC_6H4)_3PAuCl$	10.0	Selectfluor	CH_3CN/H_2O	33	37
12[e]	tBu_3PAuCl	10.0	Selectfluor	CH_3CN/H_2O	trace	60
13[e]	PPh_3AuNTf_2	10.0	Selectfluor	CH_3CN/H_2O	59	15
14[e]	$(dppm)Au_2Br_2$	10.0	Selectfluor	CH_3CN/H_2O	52	21
15[e]	(1,1′-biphenyl-2-yl)tBu_2AuCl	10.0	Selectfluor	CH_3CN/H_2O	26	16
16	$AuCl_3$	10.0	Selectfluor	CH_3CN/H_2O	15	70
17[e]	PPh_3AuCl	10.0	NFSI	CH_3CN/H_2O	46	44
18[e]	PPh_3AuCl	10.0	$PhI(OAc)_2$	CH_3CN/H_2O	trace	trace
19[e]	PPh_3AuCl	10.0	*t*BuOOH	CH_3CN/H_2O	trace	trace
20[f,c]	PPh_3AuCl	2.0	Selectfluor	THF/H_2O	30	10
21[g,c]	PPh_3AuCl	2.0	Selectfluor	THF/H_2O	29	12
22[h]	PPh_3AuCl	10.0	Selectfluor	CH_3CN/H_2O	trace	trace
23	$PPh_3AuCl/AgNTf_2$	2.0	Selectfluor	CH_3CN/H_2O	41	20
24	$PPh_3AuCl/Pd_2(dba)_3$	2.0	Selectfluor	CH_3CN/H_2O	complex	

[a] Reaction conditions: allenoate **1a** (0.2 mmol), catalyst (10 mol-%), $PhB(OH)_2$ **2a** (*x* equiv.), oxidant (2.5 equiv.), solvent (2.0 mL), H_2O (36 μL), stirred at 40 °C, 2 h. [b] Isolated yield. [c] The reaction mixture was stirred for 24 h. [d] The reaction mixture was stirred at 60 °C. [e] Allenoate **1a** (in 1.0 mL CH_3CN) was added to the reaction mixture over 2 h by using a syringe pump. [f] THF (1.0 mL), H_2O (36 μL) used. [g] THF (0.5 mL), H_2O (36 μL). [h] The reaction mixture was stirred at room temperature.

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the desired product **3a** in 65% yield, compared with the other oxidants such as NFSI, $PhI(OAc)_2$ or *t*BuOOH

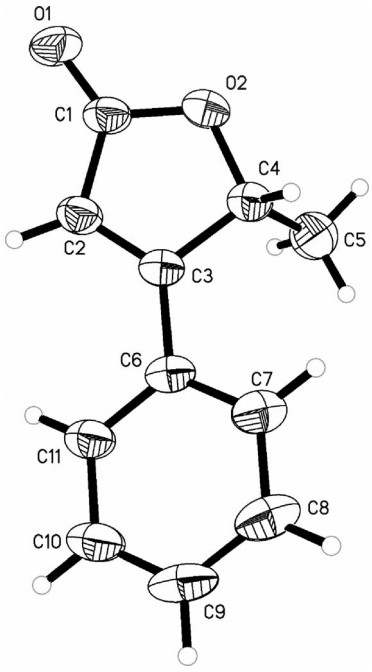
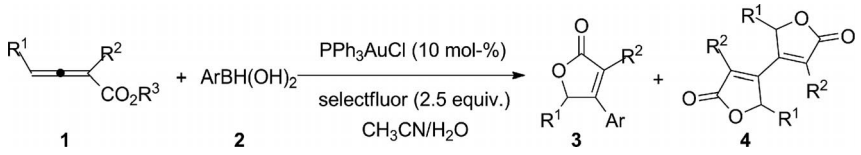


Figure 2. ORTEP drawing of butenolide **3a**.

(Table 1, entries 17–19). It was clear that 10 equiv. **2a** is required in this oxidative cyclization and arylation process because when 2.0 equiv. **2a** was used **3a** was afforded in lower yields (Table 1, entries 20–21). Furthermore, the yield of **3a** decreased to 41% when $[PPh_3AuCl]/[AgNTf_2]$ was used as the catalyst (Table 1, entry 23). In the presence of $[PPh_3AuCl]/[Pd_2(dba)_3]$, complex product mixtures were obtained under otherwise identical conditions (Table 1, entry 24). More detailed reaction conditions are summarized in the Supporting Information as Table SI-1. The structure of butenolide **3a** was unambiguously determined by X-ray diffraction analysis; its crystal structure is shown in Figure 2 and the CIF data are presented in the Supporting Information.

Having established the optimal reaction conditions, the substrate scope of this oxidative arylation and cyclization reaction with various allenoates and diverse arylboronic acids was evaluated; the results are summarized in Table 2. This oxidative transformation was compatible with a wide range of arylboronic acids including *para*-, *meta*-, and *ortho*-substituted derivatives. Arylboronic acids bearing a methyl group at the *ortho*-position gave the desired product in lower yields, perhaps due to steric effects (Table 2, entries 1–9 and 16–20). It was clear that, regardless of whether electron-poor or -rich arylboronic acids were used in this reaction, all reactions proceeded smoothly, affording the de-

Table 2. Cascade oxidative cyclization and arylation of allenoates.[a]



1 2 3 4

Entry	**1**				**2**		Yield (%)[b]	
	R^1	R^2	R^3		Ar		**3**	**4**
1	Me	H	*t*Bu	**1a**	2-MeC_6H_4	**2b**	32 (**3b**)	26 (**4a**)
2	Me	H	*t*Bu	**1a**	3-MeC_6H_4	**2c**	46 (**3c**)	40 (**4a**)[c]
3	Me	H	*t*Bu	**1a**	4-MeC_6H_4	**2d**	63 (**3d**)	26 (**4a**)[c]
4	Me	H	*t*Bu	**1a**	3,5-$Me_2C_6H_3$	**2e**	55 (**3e**)	21 (**4a**)[c]
5	Me	H	*t*Bu	**1a**	4,4′-biphenyl	**2f**	30 (**3f**)	35 (**4a**)[c]
6	Me	H	*t*Bu	**1a**	4-*t*BuC_6H_3	**2g**	60 (**3g**)	27 (**4a**)[c]
7	Me	H	*t*Bu	**1a**	3-FC_6H_4	**2h**	65 (**3h**)	21 (**4a**)[c]
8	Me	H	*t*Bu	**1a**	3,5-$F_2C_6H_3$	**2i**	30 (**3i**)	50 (**4a**)[c]
9	Me	H	*t*Bu	**1a**	3,5-$Cl_2C_6H_3$	**2j**	50 (**3j**)	16 (**4a**)[c]
10	Me	H	*t*Bu	**1a**	4-ClC_6H_4	**2k**	29 (**3k**)	55 (**4a**)[c]
11	Me	H	*t*Bu	**1a**	4-FC_6H_4	**2l**	42 (**3l**)	32 (**4a**)
12	Me	H	*t*Bu	**1a**	2-FC_6H_4	**2m**	42 (**3m**)	50 (**4a**)[c]
13	Me	H	*t*Bu	**1a**	4-$CHOC_6H_4$	**2n**	complex	–
14	Me	H	*t*Bu	**1a**	4-OHC_6H_4	**2o**	complex	–
15	H	H	*t*Bu	**1b**	Ph	**2a**	64 (**3n**)	–
16	H	H	*t*Bu	**1b**	4-MeC_6H_4	**2d**	65 (**3o**)	–
17	H	H	*t*Bu	**1b**	3-FC_6H_4	**2h**	60 (**3p**)	–
18	H	H	*t*Bu	**1b**	3,5-$Cl_2C_6H_3$	**2j**	38 (**3q**)	–
19	H	H	*t*Bu	**1b**	3-MeC_6H_4	**2c**	51 (**3r**)	–
20	H	H	*t*Bu	**1b**	2-MeC_6H_4	**2b**	30 (**3s**)	–
21	H	Me	*t*Bu	**1c**	Ph	**2a**	50 (**3t**)	24 (**4b**)
22	H	H	Et	**1d**	Ph	**2a**	complex	
23[d]	H	H	Bn	**1e**	Ph	**2a**	21 (**3n**)	–

[a] Reaction conditions: to a mixture of arylboronic acid **2** (2.0 mmol), $[PPh_3AuCl]$ (10 mol-%), Selectfluor (0.5 mmol) and CH_3CN/H_2O (1.0 mL/10.0 equiv.) was added allenoate **1** (0.2 mmol) in CH_3CN (1.0 mL) at 40 °C over 2 h. [b] Isolated yield. [c] The dimer was mixed with $ArB(OH)_2$. [d] The reaction mixture was stirred at 60 °C for 48 h.

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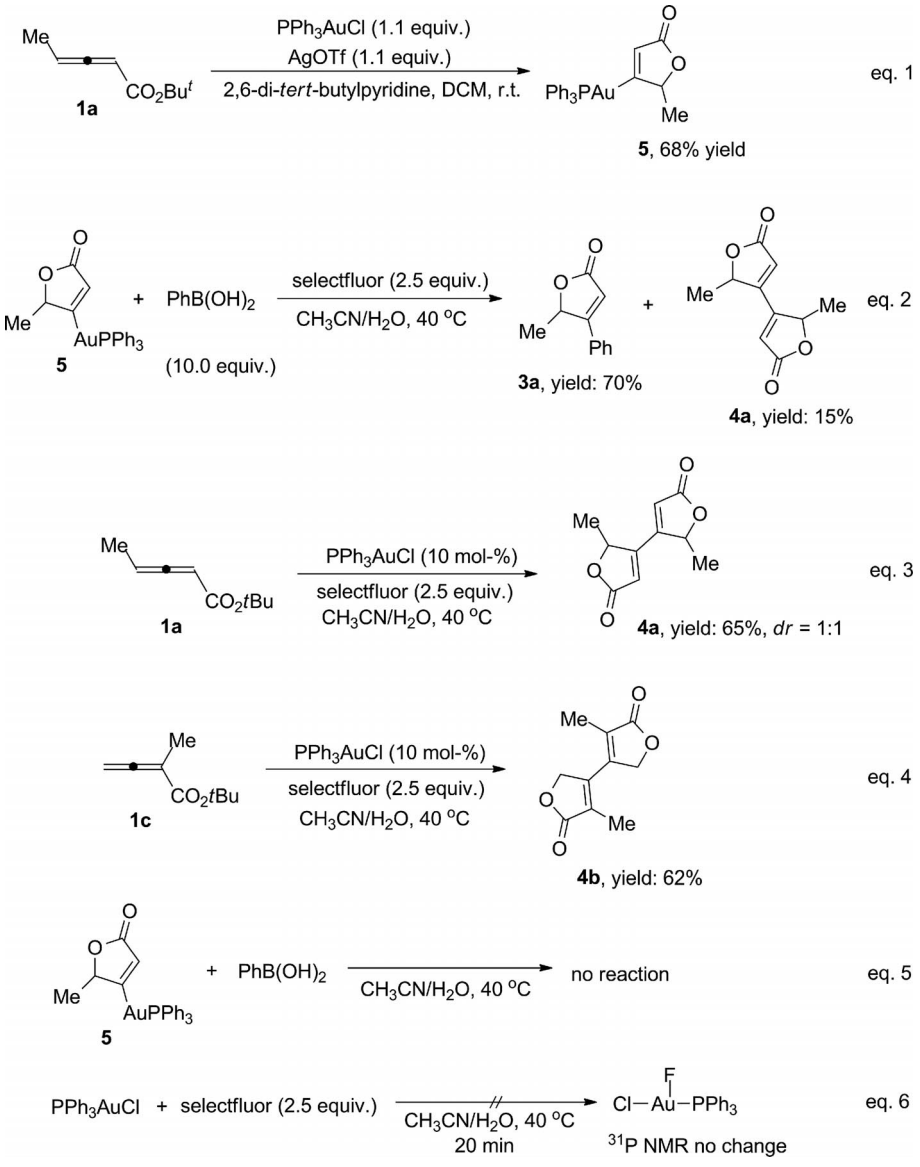
sire products in moderate yields (Table 2, entries 1–12). Unfortunately, when arylboronic acids having OH or CHO functional groups were employed in this reaction, complex product mixtures were formed (Table 2, entries 13 and 14).

The generality of the reaction with respect to allenoates was also examined by using **1b**–**e** as substrates under the standard conditions.[14] Allenoate **1b** also afforded the desired oxidative cyclization and arylation products in moderate yields (30–65%) with various arylboronic acids, but without formation of the corresponding homocoupling product derived from **1b** (Table 2, entries 15–20). By using allenoate **1c** as the substrate, in which R^1 = H, R^2 = Me, R^3 = *t*Bu, the reaction also proceeded efficiently, giving **3t** in 50% yield, albeit along with 24% yield of the homocoupling product bibutenolide **4b** (Table 2, entry 21). Ethyl allenoate **1d** was not tolerated in this catalytic system, providing complex product mixtures (Table 2, entry 22). The cyclization oxidative cross-coupling was also successful with benzyl allenoate **1e**. When the reaction was stirred at 60 °C for 48 h, the desired product **3n** was afforded in 21% yield, presumably because release of a benzyl group is more difficult than a *tert*-butyl group under identical conditions.

To establish a plausible reaction mechanism, several control reactions were performed (Scheme 1). The related intermediate gold(I) complex **5** was synthesized in 68% yield according to a reported procedure[15] and its structure was confirmed by X-ray diffraction analysis [see Figure 3 and Scheme 1, Equation (1)]. Treatment of intermediate **5** afforded the desired oxidative cyclization and arylation cross-coupling product **3a** in 70% yield, together with bibutenolide **4a** (15% yield), which is consistent with above reaction outcome, suggesting that gold(I) complex **5** was indeed formed in the above reaction and it is the real intermediate in this cross-coupling reaction [Scheme 1, Equation (2)].



Scheme 1. Control experiments.

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Treatment of **1a** and **1c** without any arylboronic acid under the optimized conditions delivered the corresponding bibutenolide **4a** and **4b** in 65 and 62% yield, respectively [Scheme 1, Equation (3) and Equation (4)]. No reaction occurred in the absence of Selectfluor [Scheme 1, Equation (5)] and the ^{31}P NMR spectroscopy indicated that no change took place when a mixture of [PPh_3AuCl] and Selectfluor was stirred at 40 °C for 20 min, which is consistent with the observations reported by Hammond's group.[9a] Moreover, BnOH was detected by GC–MS analysis of the crude reaction mixture when allenoate **1e** was used as the substrate under the standard conditions, indicating that the gold-catalyzed cyclization of **1** combined with the hydrolysis of the ester moiety (see the Supporting Information).

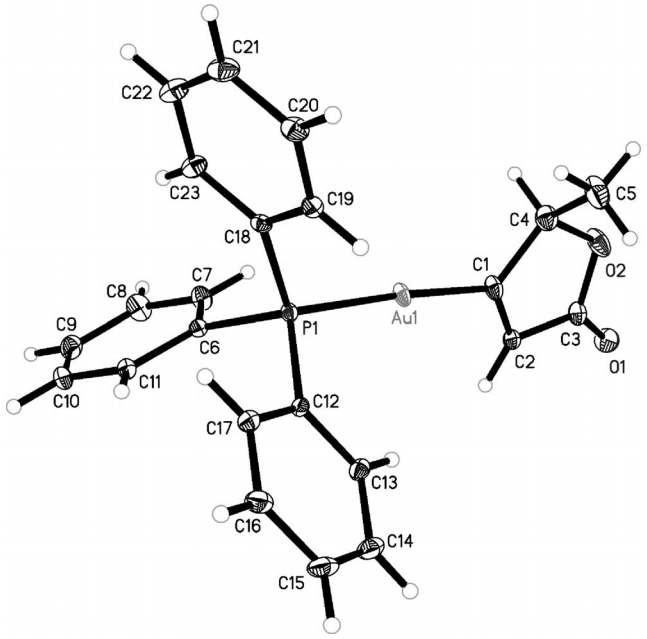
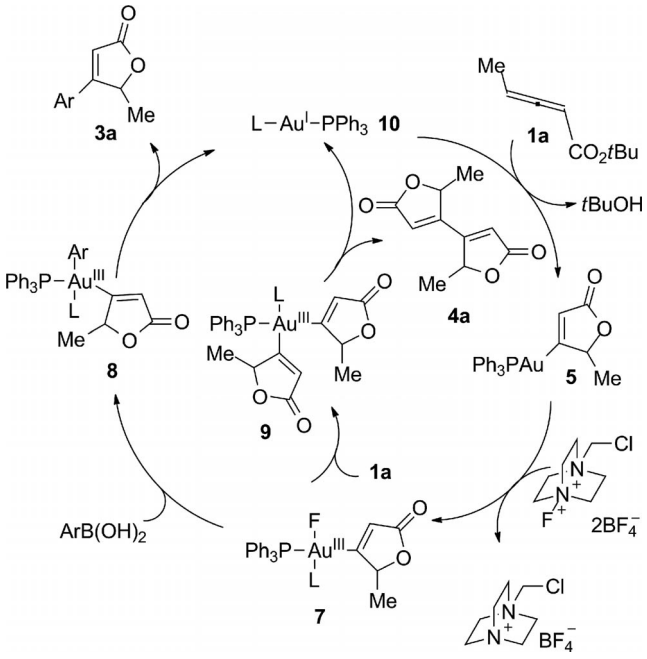


Figure 3. ORTEP drawing of gold(I) complex **5**.

On the basis of above investigation and on the results of previous mechanistic studies conducted by Hashmi,[7a] Toste,[8c] Hammond,[11] Zhang,[8a] and Gouverneur,[10b] a plausible catalytic cycle has been outlined in Scheme 2. The reaction of gold(I) complex **10** with **1a** gives intermediate vinyl-gold complex **5** through a cyclization process. Subsequently, the gold(III) complex **7** is formed through oxidation of **5** with Selectfluor, which reacts with arylboronic acid through a transmetalation process to give intermediate **8**. This process is favored by the strong B–F bond and weak Au–F bond.[16] Reductive elimination of intermediate **8** gives the desired product **3a** and regenerates the gold catalyst **10**. Furthermore, the gold(III) complex **7** can react with a second molecule of **1a** to produce intermediate **9**, which undergoes reductive elimination to give the homocoupling product bibutenolide **4a**, also along with the regeneration of the gold catalyst **10**.



Scheme 2. Proposed reaction mechanism.

Conclusions

We have found an interesting Au^I/Au^{III} redox catalytic system for the cascade oxidative arylation and cyclization of allenoates in CH_3CN/H_2O with various arylboronic acids, giving β-aryl-γ-butenolides derivatives in moderate yields under mild conditions. This catalytic system is applicable to both electron-poor and electron-rich arylboronic acids. We believe that this is a significant step towards the development of cascade reactions combining traditional gold catalysis. Further studies to find more efficient catalytic systems based on gold catalysis or other metal catalytic systems are underway.

Experimental Section

General Procedure: [PPh_3AuCl] (10 mol-%, 0.02 mmol) was dissolved in CH_3CN/H_2O (1.0 mL/36 μL) in a flame-dried Schlenk tube equipped with a septum cap and stirring bar. Arylboronic acid (2.0 mmol) and Selectfluor (0.5 mmol) were added under argon, then a solution of allenoate (0.2 mmol) in CH_3CN (1.0 mL) was slowly added over 2 h by using a syringe pump, and the reaction mixture was stirred at 40 °C for another 10 min. H_2O (5 mL) was added, the mixture was extracted with EtOAc and the combined organic phases were filtered through a thin layer of Celite. The filtrate was washed with brine (5 mL), dried with anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography on silica gel (EtOAc/petroleum ether, 1:6) to give the pure product.

5-Methyl-4-phenylfuran-2(5*H*)-one (3a): Yield: 65% (23 mg); white solid.[17] IR (CH_2Cl_2): $\tilde{\nu}$ = 2960, 2925, 2864, 1751, 1621, 1450, 1376, 1259, 1080, 1015, 934, 860, 796, 690 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.51–7.47 (m, 5 H), 6.28 (d, J = 1.2 Hz, 1 H), 5.57 (qd, J = 1.2, 6.8 Hz, 1 H), 1.54 (d, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 172.6, 168.9, 131.3, 129.9,

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129.2, 127.2, 113.7, 78.6, 19.8 ppm. MS (%): *m*/*z* (%) = 174.1 (24) [M^+], 131.0 (100), 103.1 (27), 77.0 (6). HRMS (EI): Calcd. for $C_{11}H_{10}O_2$ 174.0681; found 174.0682.

CCDC-930411 (for **3a**) and CCDC-909123 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Spectroscopic data of compounds and detailed descriptions of experimental procedures.

Acknowledgments

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