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Catalysis

Insights into the Gold-Catalyzed Propargyl Ester Rearrangement/Tandem Cyclization Sequence: Radical versus Gold Catalysis—Myers–Saito- versus Schmittel-Type Cyclization

Eva Rettenmeier,[a] Max M. Hansmann,[a] Alexander Ahrens,[a] Katharina Rübenacker,[a] Tapish Saboo,[a] Joy Massholder,[a] Christian Meier,[a] Matthias Rudolph,[a] Frank Rominger,[a] and A. Stephen K. Hashmi*[a, b]

Abstract: A detailed study of the gold-catalyzed tandem 1,3-carboxy migration/allene–enyne cycloisomerization was undertaken. It was found that after the initial allene formation the selectivity of the reaction is strongly influenced by the polarization of the remaining alkyne. Depending on the substitution pattern of the starting diynes, either a Schmittel- or a Myers–Saito-type cyclization was triggered. The 6-*endo-dig* Myers–Saito-type cyclization gave access to benzo[b]-fluorenes, while the Schmittel pathway (5-*exo-dig*) delivered benzofulvenes as final products. In special cases a yet unknown pathway was opened by the ambiphilic nature of the allene moiety. In these cases completely different products were obtained by the nucleophilic attack of the alkyne moiety onto the allene that can also act as an electrophile. Mechanistic studies revealed that diradical pathways can be ruled out for this type of tandem cyclization reactions and it is shown that both steps of the reaction cascade are catalyzed by the gold complex.

Introduction

Cycloisomerization reactions are a powerful and efficient method for atom economic[1]C–C bond formations. Among the many investigated reactions the diyne and yne-allene cyclization reactions play a significant role in organic synthesis.[2] Several strategies exist for which in a tandem process highly reactive enyne-allene intermediates are initially formed that can then undergo subsequent cycloisomerization reactions to valuable products.[3] Yne-allenes have been demonstrated to undergo two main thermal diradical cyclization pathways: 1) Myers–Saito cyclization[4] and 2) Schmittel cyclization.[5] As mentioned above, such substrates can be prepared in a stoichiometric fashion[6] or by thermal rearrangement reactions.[7] In addition there exist several reports on the transition-metal-catalyzed formation of such yne-allene intermediates. One of these strategies is the generation of the allene fragment by a transition-metal-catalyzed 1,3-acyl migration of propargyl esters.[8] In the case of a gold-catalyzed 1,3-acyl shift, carboxyallenes are generated that can act as a nucleophile[9] or electrophile[10] for further applications in tandem reactions.[11,12]

Toste et al. and Oh and Kim et al. combined a silver or gold-catalyzed allene formation by 1,3-acyl migration of nonterminal propargylic esters with a Myers–Saito-type enyne–allene cyclization to form highly functionalized aromatic compounds (Scheme 1a).[9e,11p] Liu et al. published a similar reaction using propargyl carbonates instead of the corresponding esters.[13] Here the resulting oxocarbenium ion formed in the gold-catalyzed 6-*endo-dig* cyclization step could be further attacked by the aryl moiety, giving rise to a second cyclization reaction (Scheme 1b). In the case of an aliphatic backbone, Malacria, Gandon, and Fensterbank et al. showed that a Schmittel-type 5-*exo-dig* enyne–allene cyclization proceeds (Scheme 1c).[14] Just recently Chen et al. published a platinum-catalyzed reaction using a similar 1,3-acyl migration strategy to obtain benzofulvenes also through a Schmittel-type enyne–allene cyclization (Scheme 1d).[15]

Compared to the previously described reactions, which proceed through a tandem cyclization cascade in which both independent steps are postulated to be transition-metal-catalyzed, Shi et al. reported a tandem reaction in which the second step is an uncatalyzed radical Schmittel cyclization (Scheme 2a).[16] In this case the pivotal intermediate, the enyne-allene, is generated by a gold-catalyzed propargyl vinyl rearrangement with a triazole gold catalyst. While most of the starting materials are derived upon addition of a terminal alkyne to benzaldehyde, propargyl esters containing the ester

[a] Dipl.-Chem. E. Rettenmeier, Dr. M. M. Hansmann, A. Ahrens, K. Rübenacker, T. Saboo, J. Massholder, C. Meier, Dr. M. Rudolph, Dr. F. Rominger,[+] Prof. Dr. A. S. K. Hashmi
Organisch-Chemisches Institut
Ruprecht-Karls-Universität Heidelberg
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)
E-mail: hashmi@hashmi.de
Homepage: http://www.hashmi.de

[b] Prof. Dr. A. S. K. Hashmi
Chemistry Department, Faculty of Science, King Abdulaziz University
Jeddah 21589 (Saudi Arabia)

[+] Crystallographic investigation

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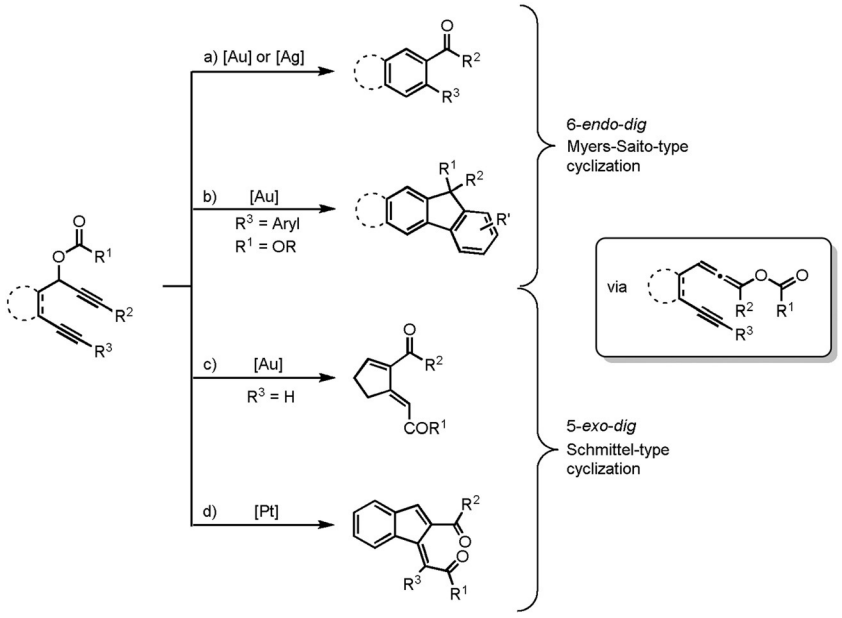


Scheme 1. Transition-metal-catalyzed tandem cyclization reactions of diyne acetates/carbonates.

functionality on the nonaromatic terminus, as depicted in Scheme 2, are far less studied.

Herein we report a detailed study of such substituted propargyl esters to form benzo[b]fluorenes and benzofulvenes by a gold-catalyzed rearrangement/cyclization cascade. Compared to the previous literature, one major focus is the electronic influence on the product distribution of Myers–Saito- and Schmittel-type cyclization products as well as novel side pathways. Furthermore, the question if this transformation contains two gold-catalyzed or a gold-catalyzed and a radical cyclization step is addressed.

Results and Discussion

We started our investigation by reacting propargyl acetate **1a** with 5 mol% of [IPrAuNTf$_2$] in CH_2Cl_2. In a fast reaction at room temperature in less than 1 h we could isolate a new product as yellow solid. To our delight, we were able to obtain single crystals suitable for X-ray diffraction.[17] The solid-state structure obtained by X-ray diffraction analysis revealed a statistically disordered isomer superposition of 80% benzo[b]fluorene (**2a**) and 20% benzofulvene (**3a**) (for the visualization of the solid-state structure of compound **2a**, see Figure 1). Based on 2D NMR spectroscopic analysis we could

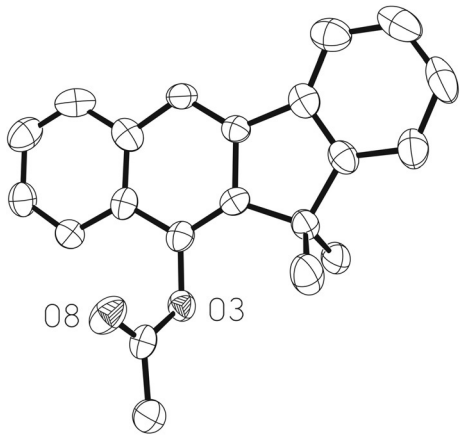
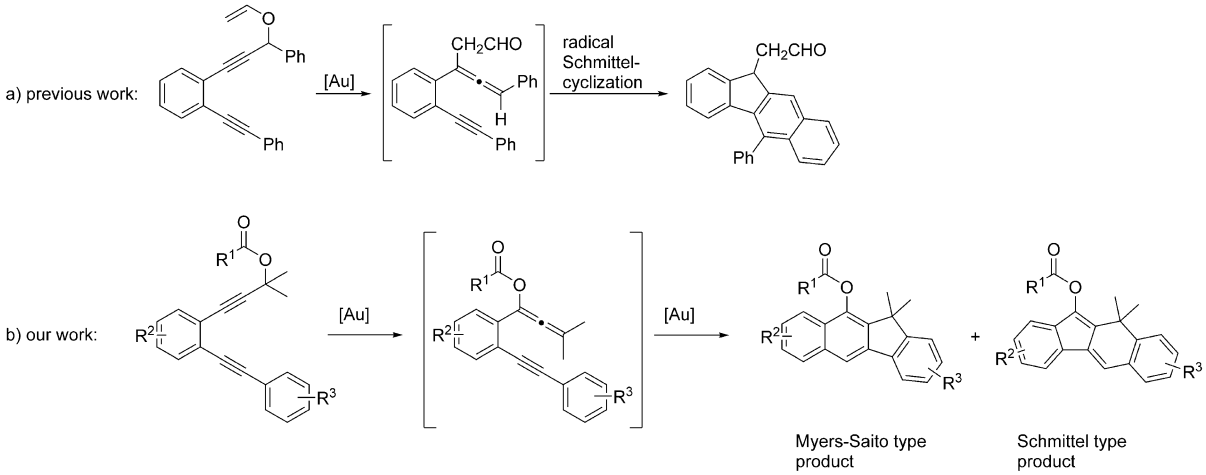
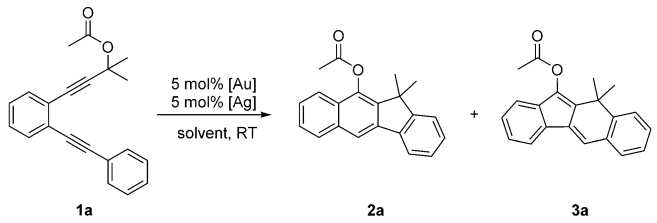


Figure 1. Solid-state molecular structure of compound **2a**.

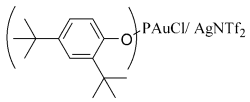


Scheme 2. Gold-catalyzed tandem cyclization reactions.

Table 1. Catalyst and solvent screening. Yields and isomeric ratio were determined by ^{1}H NMR spectroscopic integration using 1,4-dioxane as an internal standard.



1a 2a 3a

Entry	Solvent	Catalyst	Yield [%]	Isomeric ratio
1	CD_2Cl_2	[IPrAuCl]/$AgNTf_2$	87	80:20
2	CD_2Cl_2	[IPrAuCl]/$AgSbF_6$	70	79:21
3	CD_2Cl_2	[IPrAuCl]/AgOTf	83	77:23
4	CD_2Cl_2	[IPrAuCl]/$AgPF_6$	81	76:24
5	CD_2Cl_2	[PPh_3AuCl]/$AgNTf_2$	5	76:24
6	CD_2Cl_2	[PPh_3AuCl]/$AgSbF_6$	21	80:20
7	CD_2Cl_2	 A	traces	–
8	CD_2Cl_2	**A**/$AgSbF_6$	11	81:19
9	CD_2Cl_2	[SPhosAuCl]/$AgNTf_2$	47	57:43
10	CD_2Cl_2	[SPhosAuCl]/$AgSbF_6$	54	58:42
11	CD_2Cl_2	$AuCl_3$	17	74:26
12	[D_8]toluene	[IPrAuCl]/$AgNTf_2$	–	–
13	[D_8]toluene	[IPrAuCl]/$AgSbF_6$	42	86:14
14	CD_3CN	[IPrAuCl]/$AgNTf_2$	5	74:26
15	CD_3CN	[IPrAuCl]/$AgSbF_6$	8	69:31
16	CD_2Cl_2	$AgNTf_2$	–	–

clearly assign this product to be an 80:20 mixture of 6-*endo-dig* (Myers–Saito-type, **2a**) and 5-*exo-dig* (Schmittel-type, **3a**) cyclization compounds.

We next performed a catalyst and solvent screening (Table 1). Different silver salts in the presence of [IPrAuCl] were used for the pre-activation and tested in the cycloisomerization reaction (Table 1, entries 1–4). Among the different counter ions tested, $AgNTf_2$ performed extraordinarily well to give an 80:20 (**2a**/**3a**) isomer mixture in 87% yield. Next we studied the effect of different ligands on the reaction outcome (entries 5–10). Except the SPhos-ligand (47, 54%; entries 9 and 10) all other ligands tested performed poorly (entries 5–8). Gold(III) was also able to catalyze the reaction in a similar isomeric ratio as [IPrAuNTf$_2$] but only in low yields (entry 11). As a next step, different solvents were tested (entries 12–15). Even though in toluene we could observe an increase in the isomeric ratio towards the 6-*endo-dig* cyclization product (entry 13), the overall obtained yield was not satisfying. In a control experiment just $AgNTf_2$ showed no desired product (entry 16). The optimized conditions proved to be 5 mol% [IPrAuNTf$_2$] in CH_2Cl_2. The in situ generation of [IPrAuNTf$_2$] with $AgNTf_2$ and [IPrAuCl] gave nearly identical results as employing the isolated, pre-activated silver-free complex.

With the optimized conditions in hand, we investigated the scope of the reaction. First, we varied the substituents on the phenyl moiety (Table 2). Depending on the electronic properties of the phenyl group we observed varying product selectivities. Using electron-donating substituents in the *para* or *ortho*-position to the alkyne fragment shifted the ratio between the two resulting isomers towards the Myers–Saito-type product (isomer **2**).

Strong electron-donating substituents (OMe, **1c** and **1d**) as well as weaker donating substituents (Me, **1e**) induced a significant shift towards the 6-*endo-dig* products **2c**–**e** (Table 2, entries 3–5). Importantly, the electron-rich substrate containing three methyl groups on the phenyl moiety gave rise to a single isomer **2f** (entry 6), which also could be characterized by an X-ray single-crystal structure analysis (Figure 2).[17] A methoxy group located at the *ortho*-

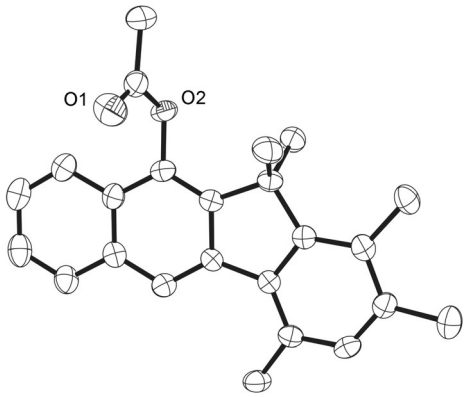
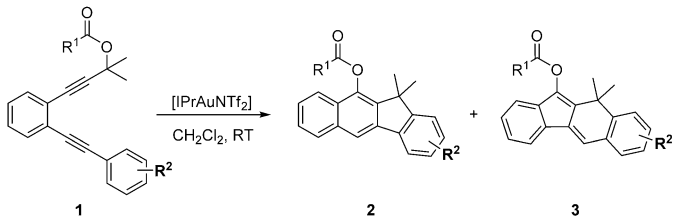


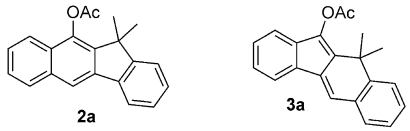
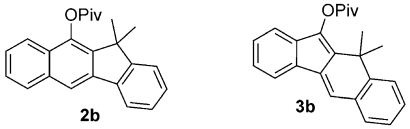
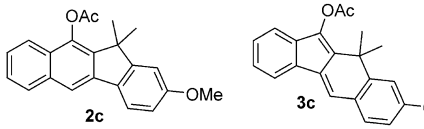
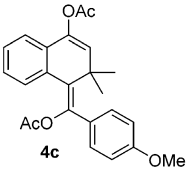
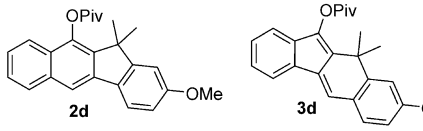
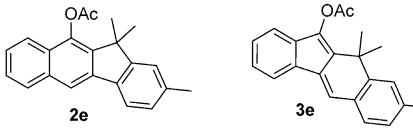
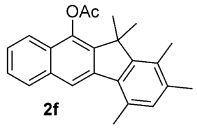
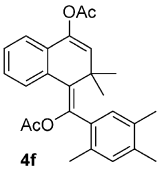
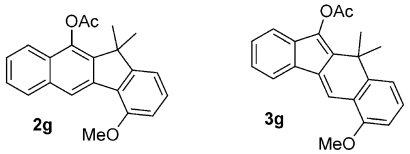
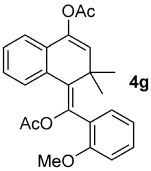
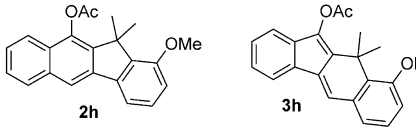
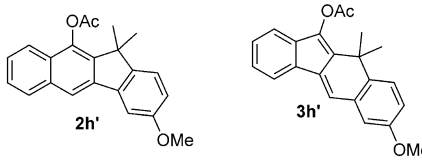
Figure 2. Solid-state molecular structure of compound **2f**. Hydrogen atoms are omitted for clarity.

position showed only little influence on the **2**/**3** isomeric ratio (entry 7). A methoxy group in *meta*-position led to a mixture of two sets of regioisomers in 48 and 43% yield—one pair leading to 1,2,3-substitution on the aryl moiety in lower **2**/**3** selectivity (**2h**, **3h**), whereas the regioisomer with 1,3,4-substitution showed a high selectivity towards Myers–Saito-type cyclization product **2h'** (entry 8). Similarly, we also obtained a high selectivity of 91:9 towards 6-*endo-dig* cyclization product **2i** in the case of an electron-rich dimethoxy substitution (entry 9). Switching to a bromide substituent in *para*-position showed no significant influence on the selectivity of 81:19 (entry 10). However, installing a methyl group at the *ortho*-position resulted in a clean formation of a single isomer (entry 11). Comparing *meta* versus *para*-bromide substitution (**1j** vs. **1l**) delivered a similar high yield of 89% and a drop in selectivity that might arise from the missing electron-donating mesomeric effect (entry 12). Finally, installation of an electron-withdrawing group (CF_3, **1m**) resulted in an increase of the Schmittel-type cyclization product **3m** (entry 13). Most of the reactions gave moderate to excellent yields (60–91%, entries 1–2, 4–5, and 8–13). In the case of a very strong electron-donating substituent, the yield of the isomeric mixture decreased (13, 39, and 5%; entries 3, 6, and 7) and a new byproduct was observed, which in some cases could be isolated as the main product (entries 3 and 7; for a detailed discussion on this byproduct see below). When switching from the acetyl to the pivaloyl ester, this side

Table 2. Synthesis of benzo[b]fluorene **2** and benzofulvene **3** under optimized reaction conditions. Reactions were performed on a 0.25 mmol scale (0.13 M in CH_2Cl_2). Isolated yields are indicated.



1 2 3

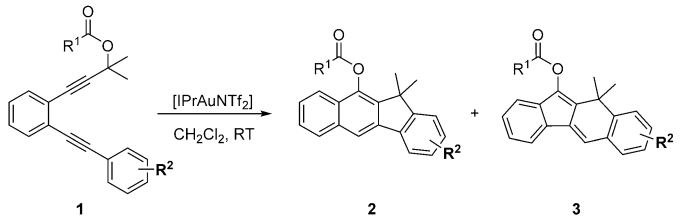
Entry	Product	Yield [%]	Side product	Yield [%]
1	 **2a** **3a**	85, 80:20		
2	 **2b** **3b**	91, 76:24		
3	 **2c** **3c**	13, 92:8	 **4c**	26
4	 **2d** **3d**	79, 90:10		
5	 **2e** **3e**	63, 89:11		
6	 **2f**	39	 **4f**	32
7	 **2g** **3g**	5, 83:17	 **4g**	31
8	 **2h** **3h**	48, 76:24		
	 **2h'** **3h'**	43, 90:10		

pathway could be completely suppressed and a good yield of 79% was restored (entry 4).

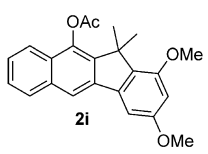
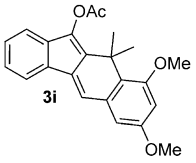
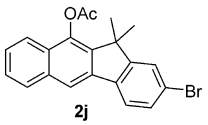
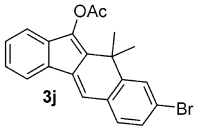
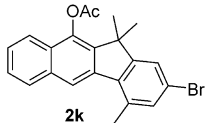
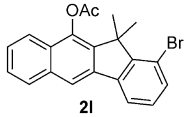
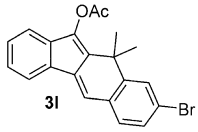
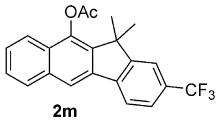
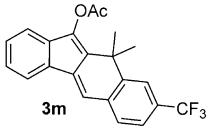
Next, we investigated the influence of different substituents at the backbone of the propargyl ester (R^3; Table 3). Here, the electron-donating methoxy group shifted the reaction towards the 5-*exo-dig* cyclization product and we obtained a 1:1 ratio of the two isomers (Table 3, entry 1). Increasing the electron density by adding another methoxy group resulted in a favored Schmittel-type cyclization and for the first time we isolated isomer **3** as our major product (entry 2). As expected, changing to electron-withdrawing groups the 6-*endo-dig* cyclization product was again favored and obtained with an isomeric ratio of up to 93:7 (entries 3–6). Taking into account the high selectivity of the favored 6-*endo-dig* cyclization with electron-rich aryl groups (R^2) and electron-deficient backbones (R^3), we combined these trends in synthesizing compounds **1t–w**. The cyclization of propargyl esters containing an acetyl group resulted mainly (**4t**) and in two cases even exclusively (**4v**, **4w**) in the formation of the byproduct as mentioned earlier (entries 7, 9, and 10). We were able to fully characterize this side product and to obtain crystals suitable for X-ray diffraction proving the exact connectivity (Figure 3).[17]

This side product arises from the formal addition of acetic acid, which is generated by elimination of another molecule of starting material. In the case of the original cyclization reaction we observed a high selectivity for the Myers–Saito-type cyclization reaction isolating **2t** as the single isomer (Table 3, entry 7). However, changing the acetyl group by a pivaloyl group again suppressed the side-product formation and increased the yield of **2u** to 83% (entry 8).

Table 2. (Continued)



1 2 3

Entry	Product	Yield [%]	Side product	Yield [%]
9	 **2i**	78, 91:9	 **3i**	
10	 **2j**	84, 81:19	 **3j**	
11	 **2k**	60		
12	 **2l**	89, 67:33	 **3l**	
13	 **2m**	60, 62:38	 **3m**	

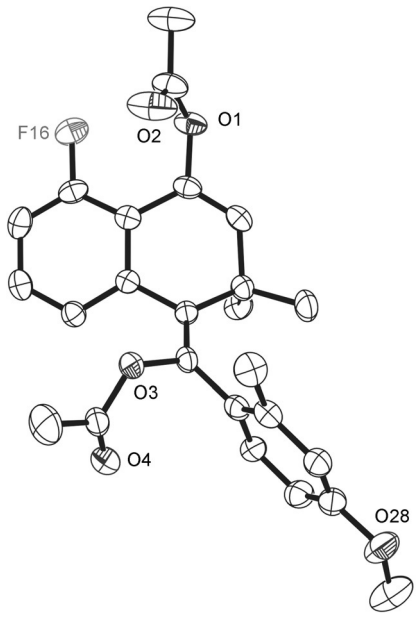
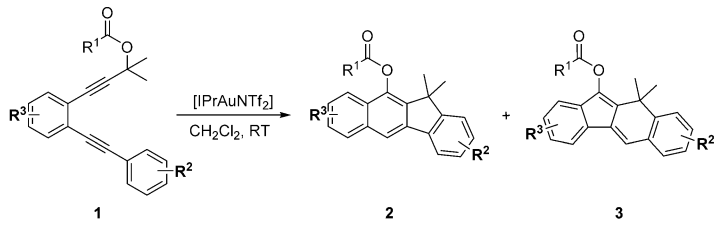


Figure 3. Solid-state molecular structure of compound **4w**. Hydrogen atoms are omitted for clarity.

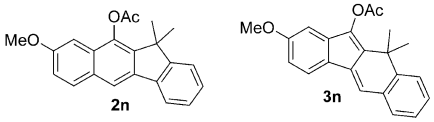
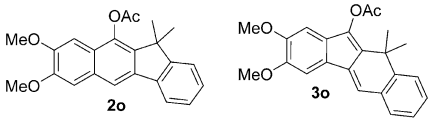
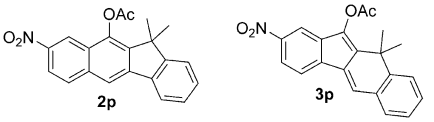
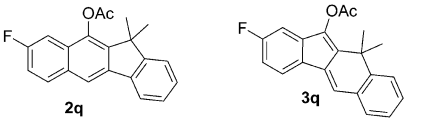
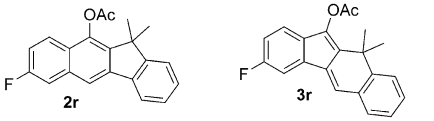
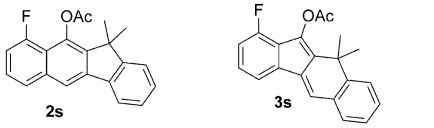
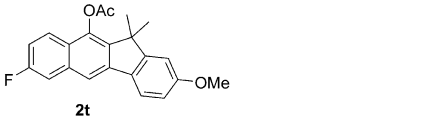
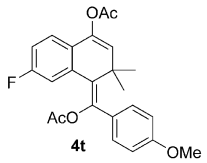
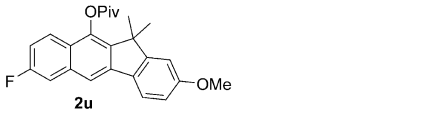
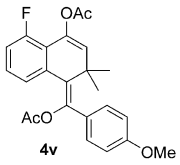
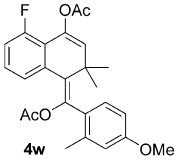
Our proposed mechanism for the reaction starts with the gold-catalyzed 1,3-acyl shift forming the enyne-allene **I**. Activation of the lower alkyne unit by gold coordination initiates two potential cyclization pathways: 1) 6-*endo-dig* cyclization to form naphthyl intermediate **III** (path a) or 2) 5-*exo-dig* cyclization to generate fulvene intermediate **IV** (path b). In both cases, electrophilic aromatic substitution generates the benzo[b]fluorene and benzofulvene core **V** and **VI** followed by aromatization and protodeauration to close the catalytic cycle (Scheme 3). Interestingly, after the 1,3-acyl shift gold can also activate the electron-rich allene moiety rather than the alkyne fragment. In this case the alkyne acts as the nucleophile to attack the gold-activated allenyl acetate to form intermediate **VII** (path c). This species is trapped by acetate presumably generated by the elimination of HOAc from another molecule of starting material to give rise to the byproduct **4**. The attack of acetate proceeds exclusively from the sterically less hindered and not from the *gem*-dimethyl side to give rise to a single isomer. This mechanism is in accordance with the generation of diacetate **4** in the case of electron-rich aryl groups as these represent stronger nucleophiles and are superior in stabilizing the vinyl cation **VII**. In addition, this pathway could be suppressed by the installation of a sterically more demanding pivaloyl moiety that prevents the nucleophilic attack onto the vinyl cation. Furthermore, the selectivity for the two cyclization pathways (a and b) can be explained by the polarization of the alkyne fragment. In the case of an electron-rich aryl group and an electron-deficient backbone gold preferentially coordinates towards the backbone controlling the selectivity for the 6-*endo* cyclization pathway (path a) and vice versa.

To support our mechanism we synthesized propargyl esters **1x–z**. Under optimized conditions, we isolated the elimination products **5x–z** (Scheme 4). In these cases, the addition to the carbenium ion **III** is inhibited as either both *ortho*-positions are substituted (**1x**, **1y**) or the aryl moiety is substituted by an alkyl chain (**1z**) giving rise to the elimination products **5x–z**. In case of **1x**, the diacetate byproduct (**4x**) was obtained as the major product and could also be isolated in trace amounts in the case of the pivaloate **1y**.

Table 3. Synthesis of benzo[b]fluorene **2** and benzofulvene **3** under optimized conditions. Reactions were performed on a 0.25 mmol scale (0.13 M in CH_2Cl_2). Isolated yields are indicated.

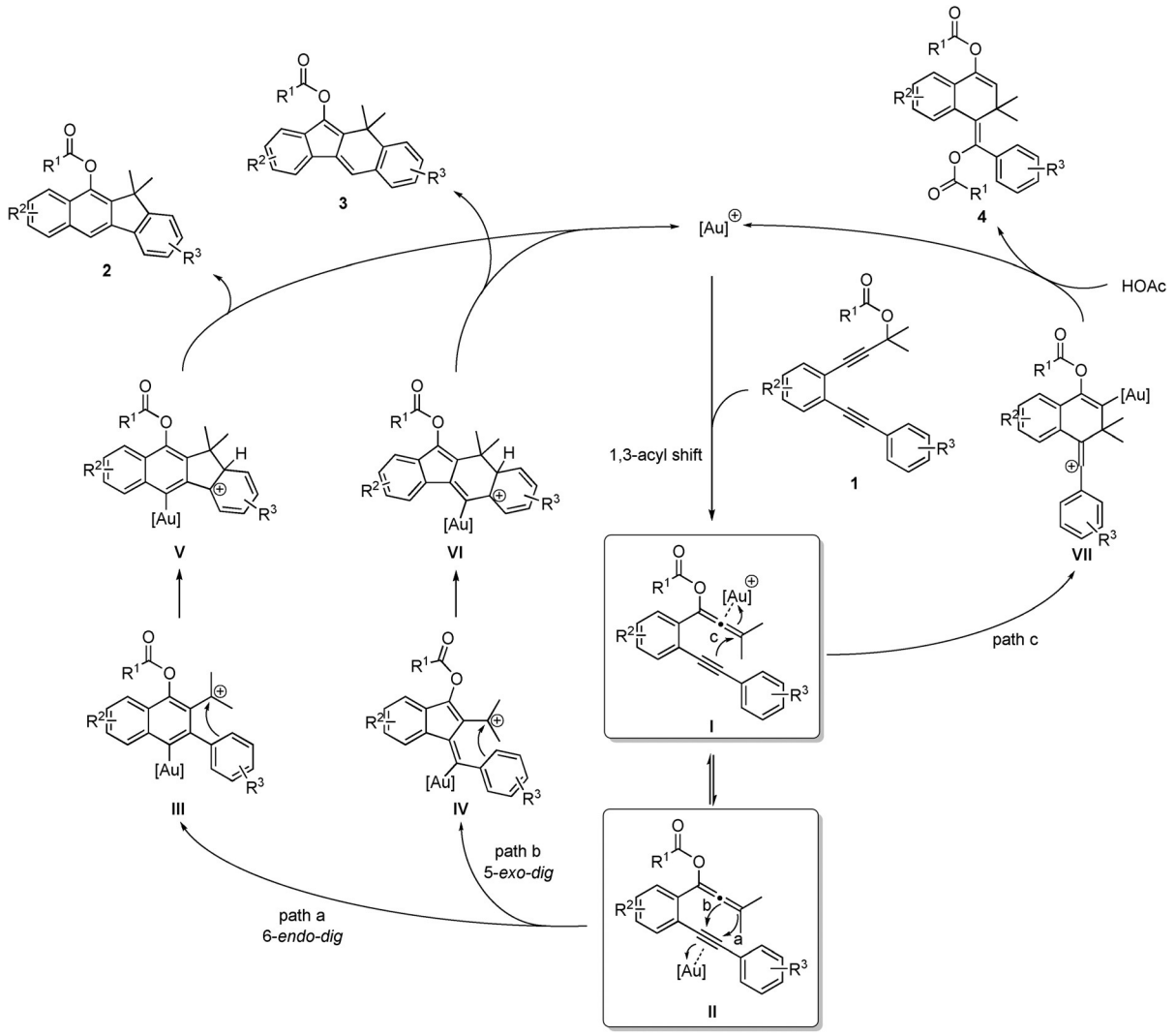


1 2 3

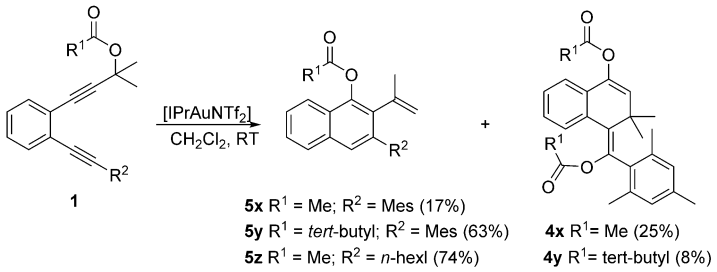
Entry	Product	Yield [%]	Side product	Yield [%]
1	 **2n** + **3n**	88, 50:50		
2	 **2o** + **3o**	68, 12:88		
3	 **2p** + **3p**	83, 93:7		
4	 **2q** + **3q**	96, 86:14		
5	 **2r** + **3r**	87, 93:7		
6	 **2s** + **3s**	80, 85:15		
7	 **2t**	18	 **4t**	32
8	 **2u**	83		
9			 **4v**	47
10			 **4w**	44

At this stage we could not rule out a mechanism, which proceeds through a domino gold-catalyzed 1,3-acyl shift followed by a radical Schmittel cyclization as demonstrated by Shi et al.[16] To prove our hypothesis of a tandem gold-catalyzed reaction rather than a gold-catalyzed transformation followed by a radical cyclization, we independently synthesized allenyl acetate **6a** and **6x** by copper-mediated conjugate addition to the corresponding yne-one.[18] Interestingly, these compounds undergo a very clean and selective radical Schmittel cyclization to afford the fulvenes **7a** and **7x** as single isomers in quantitative yield (Scheme 5). Remarkably, in the case of yne-allene **6a**, the generated diradical intermediate does not undergo a further radical cyclization but undergoes elimination to give the five-membered ring compound **7a**. In the case of compound **7x**, we were able to obtain single crystals for X-ray diffraction clearly proving the connectivity (Figure 4).[17] The formation of the C^2–C^6 Schmittel products and not the corresponding Myers–Saito products is in agreement with similar substrates bearing aryl substitution on the alkyne fragment.[5a,b,18,19]

However, reacting allenyl acetate **6a** under our optimized gold catalysis conditions gave in a very fast reaction rise to the same product mixture of benzo[b]fluorene **2a** and benzofulvene **3a** as previously observed (Scheme 5a). In the case of allenyl acetate **6x** under gold catalysis we detected the formation of the 6-*endo* cyclization/elimination product **5x** (Scheme 5b). As the thermal/radical reactions give rise to different cyclization products, these experiments clearly demonstrate a domino gold-catalyzed reaction and not a domino gold/radical cyclization with an allenyl acetate inter-



Scheme 3. Proposed reaction mechanism.

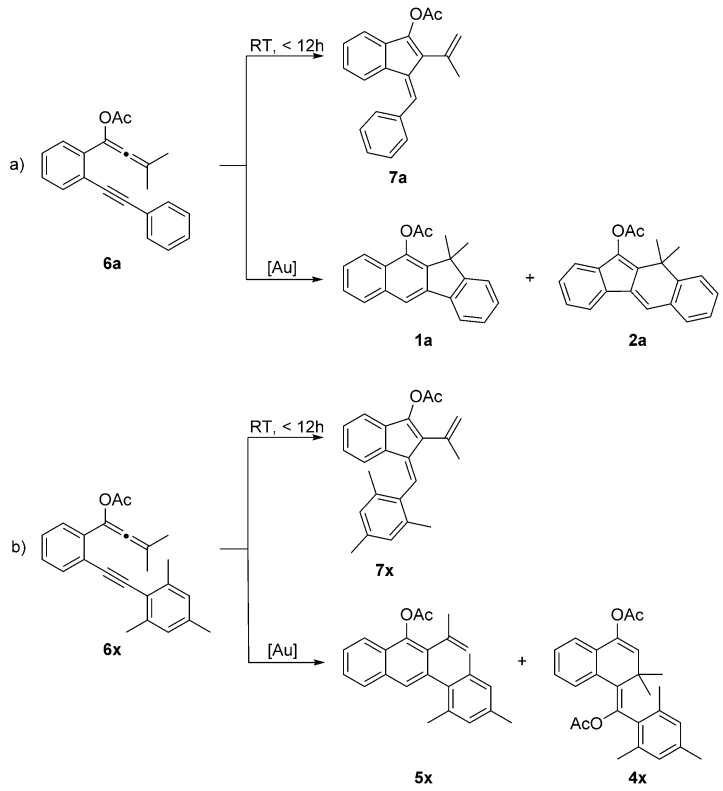


Scheme 4. Synthesis of cyclization/elimination products **5x**–**z**.

mediate being involved. However, we were interested in using triazole catalyst [Ph_3PAu(triazole)OTf], which is known for generating the allene intermediate from propargylic esters without catalyzing following cyclization reactions.[20] Unfortunately, this reaction was unselective and based on in situ NMR spectra we could identify small amounts of a twofold gold-catalyzed domino transformation as well as the gold/radical cyclization product.

Conclusion

We demonstrated a domino gold-catalyzed formation of benzo[b]fluorenes and benzofulvenes from propargyl esters. This involves the generation of allenyl acetates by an 1,3-acyl shift followed by a gold-catalyzed cyclization reaction. We studied the influence of substitution on the aryl as well as on the backbone and could control Schmittel- and Myers–Saito-type cyclization pathways by different polarizations of the alkyne fragment. In specific cases, we were able to change the selectivity towards the exclusive formation of one cyclization product. Furthermore, new side products, which arise from activation of the allene by gold coordination could be isolated and fully characterized. This switch in nucleophilic/electrophilc nature of the allene could be controlled by substitution of the starting material and by the choice of the migrating ester moiety. Mechanistically, a radical cyclization pathway could be ruled out by synthesizing independently the corresponding allene intermediates.



Scheme 5. Thermal and gold-catalyzed cyclization reactions of allenyl acetates **6a** and **6x**.

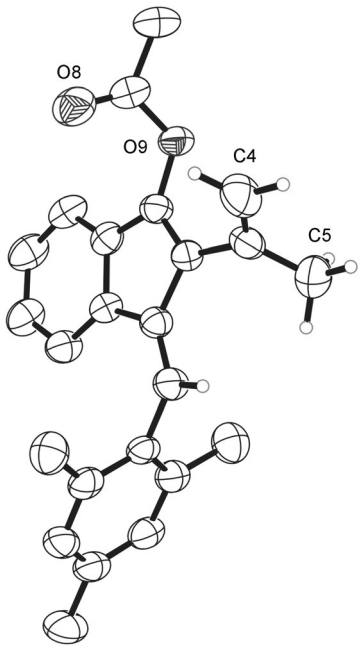


Figure 4. Solid-state molecular structure of compound **7x**.

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Keywords: alkynes · allenes · benzo[b]fluorenes · gold · propargylic carboxylates

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[17] CCDC-1059723 (**2a**), 1059724 (**2f**), 1059725 (**4w**), and 1059726 (**7x**) 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.

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