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Communication

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Gold-Catalyzed Cycloisomerization of 1,7-Diyne Benzoates to Indeno[1,2-*c*]azepines and Azabicyclo[4.2.0]octa-1(8),5-dines

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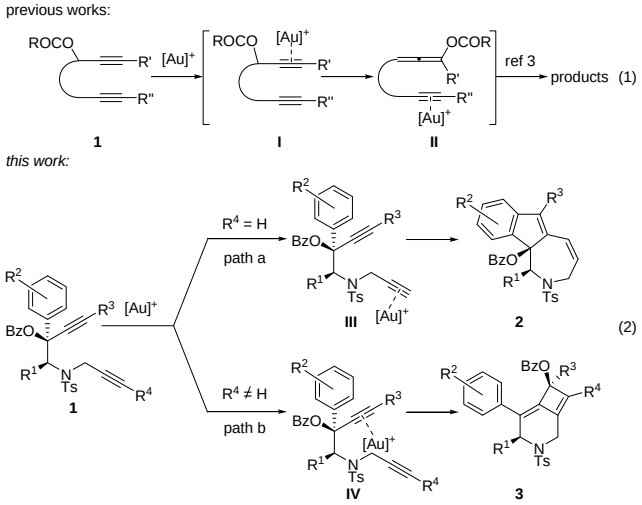
Supporting Information Placeholder

ABSTRACT: A synthetic method that relies on Au(I)-catalyzed cycloisomerization reactions of 1,7-diyne benzoates to prepare indeno[1,2-*c*]azepines and azabicyclo[4.2.0]octa-1(8),5-dines is described. By taking advantage of the orthogonal modes of coordination between the π-bonds of the mono- and disubstituted substrate with the metal catalyst, a divergence in product selectivity was observed.

Gold-catalyzed cycloisomerizations of 1,*n*-diynes provide one of the most powerful and versatile synthetic strategies for the efficient and atom-economical assembly of complex molecules.[1-3] In recent years, this has hitherto included a handful of impressive methods to synthetically useful cyclic compounds from 1,*n*-diynes **1** containing a carboxylic ester moiety at one of the propargylic positions (Scheme 1, eq 1).[3] From a mechanistic viewpoint, the reaction relies on the proclivity of the acyloxy moiety of the gold-activated substrate **I** to undergo 1,3-migration. This is followed by further functionalization by a remaining pendant group of the corresponding allenyl ester intermediate **II**. A tandem process that allows for the selective activation of either alkyne moiety of a 1,*n*-diyne ester and access to a potentially wider scope of cycloisomerization products, by contrast, has not been investigated. In this context and as part of an ongoing program examining the utility of gold catalysis in heterocyclic synthesis,[4] we became interested in the potential cycloisomerization chemistry of 1,7-diyne benzoates **1** (Scheme 1, eq 2). We reasoned that when R^4 = H in this class of compounds, the gold catalyst might selectivity coordinate at the sterically less hindered propargyl moiety of the substrate (path a in Scheme 1, eq 2). In doing so, we discovered that the resultant putative Au(I)-coordinated species **III** generated in situ was susceptible to a concerted 5-*endo*-*dig* followed by a 7-*endo*-*dig* cyclization process triggered by nucleophilic attack by an appropriately placed aryl moiety and provide the indeno[1,2-*c*]azepine ring system. To our knowledge, this mode of reactivity has not observed in 1,*n*-diyne cycloisomerizations because of other more facile and generally favored rearrangements.[1-3] On the other hand, in substrates where $R^4 \neq$ H, we reasoned activation of the estereal alkyne moiety of the 1,7-diyne benzoate might occur (path b in Scheme 1, eq 2). Subsequent tandem 1,3-migration/Prins-type [2+2] cycloaddition of the ensuing gold-activated intermediate **IV** would then be expected to deliver azabicyclo[4.2.0]octa-1(8),5-dine derivatives. This contrasts to a recent work that showed allenyl esters derived from Au(I)-catalyzed 1,3-migration of 1,6-diyne acetates to undergo a 5-*endo*-*dig* cyclization process to give 3-pyrrolines.[3b] Herein, we disclose the details of this chemistry, which offers an expedient and chemoselective approach to these two potentially useful classes of nitrogen heterocycles in good to excellent yields and as single regio- and diastereomers. The N-heterocycles were additionally obtained as a single enantiomer that demonstrated the nitrogen ring forming process occurred with efficient transfer of chirality from the enantiopure starting material to the product.

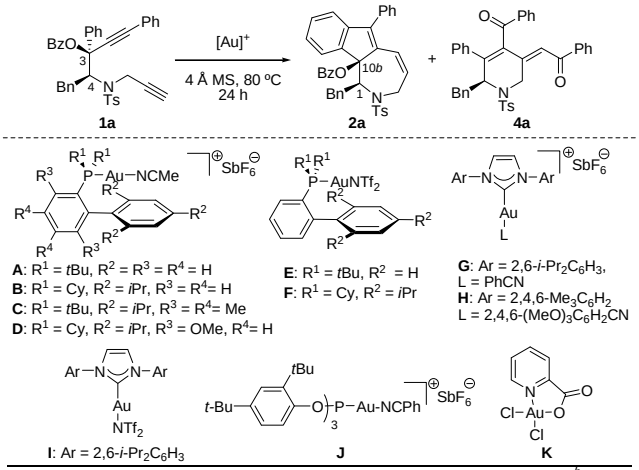
Scheme 1. Gold-Catalyzed Reactions of 1,*n*-Diyne Esters



We began by examining the gold-catalyzed cycloisomerizations of the enantiopure monosubstituted *syn*-1,7-diyne benzoate **1a**, prepared from L-phenylalanine following literature procedures,[5] to establish the reaction conditions (Table 1). The (3*S*,4*S*) absolute configuration of the starting material was determined by X-ray single crystal structure analysis of a closely related adduct (*vide infra*).[6] This study revealed that treating **1a** with 5 mol % of gold(I) catalyst **A** and 4Å molecular sieves (MS) in toluene at 80 °C for 24 h gave the best result, affording **2a** in 70% yield as a single regio-, diastereo- and enantiomer (entry 1).[7] The (1*S*,10*bS*) absolute configuration of the indeno[1,2-*c*]azepine product was ascertained by X-ray crystallography.[6] Lower product yields were obtained when the reaction was conducted at room temperature or in the absence of 4Å MS; in the case of the former, the substrate was also recovered in 70% yield (entries 2 and 3). A similar outcome was found when the reaction was repeated with Au(I) complexes **B-F** in place of **A** or changing the solvent from toluene to benzene or 1,2-dichloroethane (entries 4-5 and 8-12).[7] In contrast, the analogous reactions with gold(I) carbene complexes **G-I**, $Ph_3PAuNTf_2$, gold(I) phosphite complex **J** and gold(III) complex **K** as the catalyst gave a mixture of **2a**

and/or the δ-diketone byproduct **4a** in low yields (entries 13-17 and 20).[7-9] No reaction was detected when PPhAuCl, AuCl or $PtCl_2$ was used as the catalyst, or when polar solvents such as THF and CH_3CN were used as the reaction medium (entries 6 and 7, 18 and 19, and 21).

Table 1. Optimization of the Reaction Conditions[a]

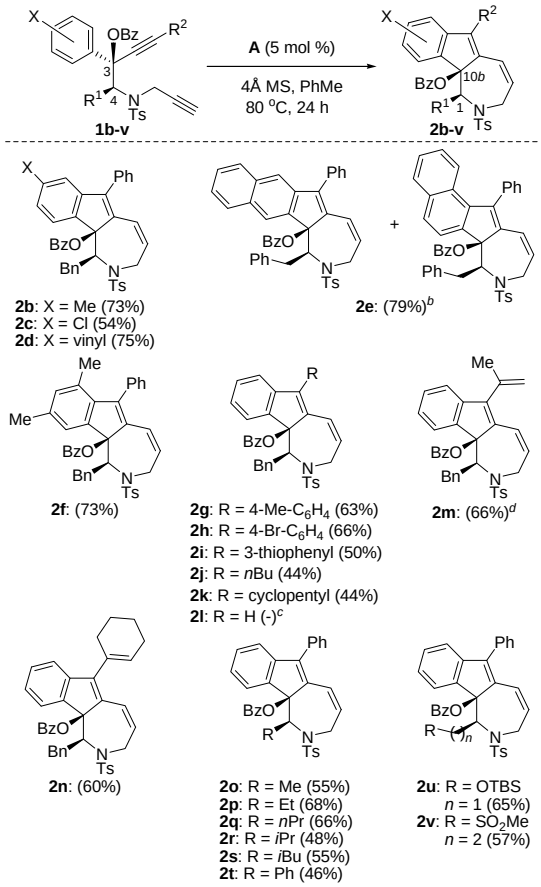


Entry	Catalyst	Solvent	Yield (%)[b]	
			2a	**4a**
1	**A**	PhMe	70	-
2[c]	**A**	PhMe	23	-
3[d]	**A**	PhMe	59	-
4	**A**	C_6H_6	65	-
5	**A**	$(CH_2Cl)_2$	42	-
6	**A**	MeCN	-[e]	-
7	**A**	THF	-[e]	-
8	**B**	PhMe	39	-
9	**C**	PhMe	52	-
10	**D**	PhMe	43	-
11	**E**	PhMe	42	-
12	**F**	PhMe	37	-
13	**G**	PhMe	22	16
14	**H**	PhMe	-	27
15	**I**	PhMe	12	18
16	**J**	PhMe	-	12
17	$Ph_3PAuNTf_2$	PhMe	13	21
18	Ph_3PAuCl	PhMe	-[e]	-
19	AuCl	PhMe	-[e]	-
20	**K**	PhMe	-	8
21	$PtCl_2$	PhMe	-[e]	-

[a] All reactions were performed at the 0.15 mmol scale with catalyst:**1a** ratio = 1:20 and 4Å MS (150 mg) at 80 °C for 24 h. [b] Isolated yield. [c] Reaction carried out at room temperature and **1a** was recovered in 70% yield. [d] Reaction carried out in the absence of 4Å MS. [e] No reaction based on TLC and ^{1}H NMR analysis of the crude mixture.

To define the scope of these conditions, we next proceeded on to assess their generality for a series of monosubstituted 1,7-diyne benzoates prepared from the corresponding L-α-amino acids, and the results are summarized in Table 2. Overall, we were pleased to find the reaction conditions to be broad, delivering a variety of substituted indeno[1,2-*c*]azepines in 44-79% yield from the corresponding substrates **1b**-**v**. Starting 1,7-diyne benzoates with a pendant alkyl, aryl or thiophene group at the benzoate or alkyne carbon center (**1b**-**k**) were found to react well, affording the corresponding tricyclic adducts in 44-79% yield. The presence of a *p*-styrenyl at the C3 position or vinyl moiety on the alkyne carbon center of the substrate was found to have no influence on the course of the reaction with **2d** and **2m**-**n** furnished in 60-75% yield. A 1,7-diyne benzoate with two terminal alkyne moieties was also examined under the standard conditions at room temperature and 80 °C but was found to give a mixture of decomposition products that could not be identified by ^{1}H NMR analysis of the crude mixture. On the other hand, the indeno[1,2-*c*]azepines **2o**-**t** containing an alkyl or phenyl group on the amino carbon center, were obtained in good yield from the corresponding 1,7-diyne benzoates **1o**-**t**. Likewise, substrates containing a OTBS (**1u**) or SO_2Me moiety (**1v**) were found to be well-tolerated under the reaction conditions and gave the corresponding N-heterocyclic products **2u** and **2v** in 65 and 57% yield, respectively. More notably, these cycloisomerizations also demonstrated that the ring-forming process occurs in a highly selective manner. In contrast to recent reports showing the propensity of Au-catalyzed 1,*n*-diyne ester cyclizations to undergo an initial 1,3-migration step,[3] other than a number of unidentifiable decomposition products, no other cyclic products that could be formed from such a pathway were detected by ^{1}H NMR analysis of the crude mixtures. Additionally, the [1,2-*c*]-tricyclic ring adducts were afforded as a single diastereo- and enantiomer with the (1*S*,10*bS*) absolute configurations for **2h** and **2t** established by X-ray crystallography.[6]

Table 2. Cycloisomerization of Monosubstituted 1,7-Diyne Benzoates 1b-v Catalyzed by A[a]

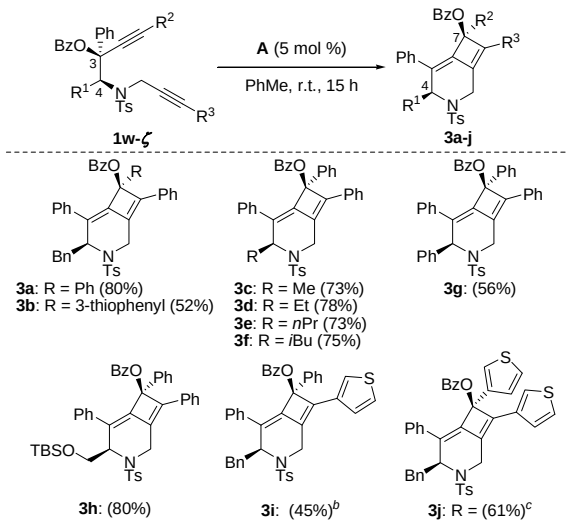


[a] All reactions were performed at the 0.15 mmol scale with **A**:**1** ratio = 1:20 and 4Å MS (150 mg) in toluene at 80 °C for 24 h. Values in parenthesis denote isolated product yields. [b] Isolated as an inseparable mixture of regioisomers in a ratio = 1.2:1. [c] Mixture of unknown decomposition products afforded based on ^{1}H NMR analysis of the crude mixture. [d] Reaction carried out at 120 °C for 20 h.

The only exception was the cycloisomerization of **1e**, which was found to give **2e** as a mixture of regioisomers in a ratio of 1.2:1.

With the reaction conditions for indeno[1,2-*c*]azepines established, we next examined the applicability of this new methodology for the synthesis of azabicyclo[4.2.0]octa-1(8),5-dines. As shown in Scheme 1, we anticipated that a change in mode of reactivity should be achievable by switching from a monosubstituted to a disubstituted 1,7-diyne benzoate substrate. With this in mind, we first tested the reaction of enantiopure disubstituted 1,7-diyne benzoate **1w**, prepared again from L-phenylalanine following literature procedures,[5] with 5 mol % of **A** under the standard conditions (Table 3). This revealed that the cyclobutene fused piperidine **3a** could be obtained in 80% yield and as a single diastereo- and enantiomer. Under similar conditions at room temperature, repetition of the reaction with the disubstituted 1,7-diyne benozates **1x-ζ**,[5] variably containing alkyl, phenyl, thiophene and OTBS groups, gave the corresponding bicyclic N-heterocyclic products **3b-j** in 45-80% yield. The (4*S*,7*S*) absolute configurations for **3d** and **3g** were determined by X-ray crystallographic analysis.[6]

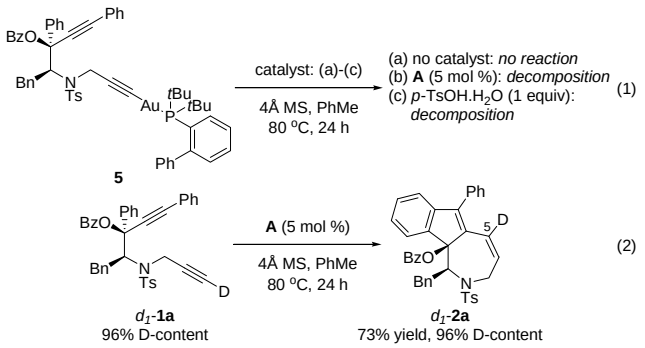
Table 3. Tandem 1,3-Migration/[2+2] Cycloaddition of Disubstituted 1,7-Diyne Benzoates 1w-ζ Catalyzed by A[a]



[a] All reactions were performed at the 0.15 mmol scale with **A**:**1** ratio = 1:20 in toluene at room temperature for 15 h. Values in parenthesis denote isolated product yields. [b] Reaction conducted at 80 °C for 15 h. [c] Reaction conducted for 48 h.

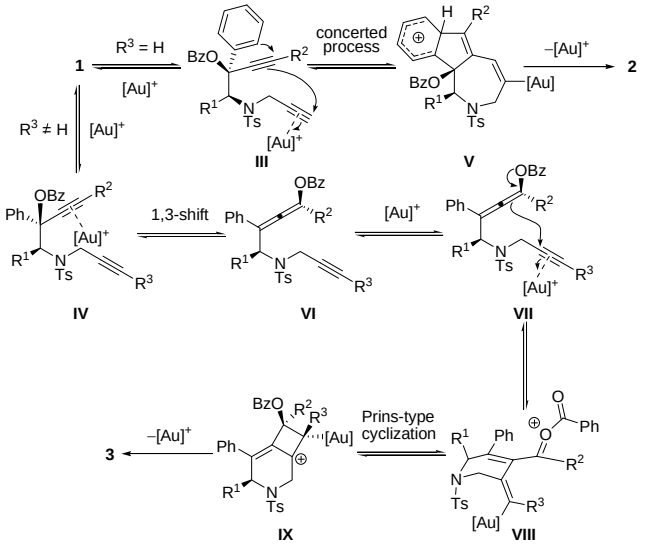
While the above results corroborate the mechanism premise outlined in Scheme 1, other possible pathways were considered but then discounted based on the following control experiments (Scheme 2). As gold(I)-activated alkynylgold(I) species have been proposed in alkyne cycloisomerizations mediated by the metal catalyst,[2a-c,10] the reactions of alkynylgold(I) complex **5** under the various conditions described in Scheme 2, eq 1 were first examined.[5,6] This revealed the organogold(I) complex was recovered in near quantitative yield in the absence of a catalyst but decomposed on introducing 5 mol % of **A** or 1 equiv of *p*-TsOH·H_2O, as a proton source, to the reaction conditions. These tests led us to rule out the possible involvement of a dual activation pathway in which the alkyne terminus of monosubstituted **1** was activated by two molecules of the Au(I) catalyst. This was further supported by the outcome found when a solution of d_1-**1a** in toluene was treated with 5 mol % of **A** under the conditions shown in Scheme 2, eq 2. This revealed the expected deuterated indeno[1,2-*c*]azepine product d_1-**2a** was obtained in 73% yield with deuterium incorporation solely at the C5 position of the adduct, as determined by ^{1}H NMR and LCMS measurements as well as X-ray crystal structure analysis.[6] Our findings that showed no intermediates could be trapped when the reaction of **1a** was repeated in the presence of excess amounts of either 1*H*-indole or H_2O also led us to surmise that a stepwise double cyclization pathway was unlikely.[11] On the other hand, our results showing the reaction of **1l** providing only a mixture of byproducts in Table 2 suggests that it is more likely steric factors between the alkyne groups in the substrate with the Au(I) catalyst which play a critical role in controlling the mode of reactivity.

Scheme 2. Control Experiments with Alkynylgold(I) Complex 5 and d_1-1a Catalyzed by A



A plausible mechanism for the present Au(I)-catalyzed cycloisomerization reactions is outlined in Scheme 3. For monosubstituted 1,7-diyne benzoates, this could involve selective activation of the alkyne terminus of the substrate by the gold(I) catalyst. This gives the gold-coordinated species **III**, which undergoes a concerted double cyclization upon nucleophilic attack by the aryl moiety situated on the carbinol carbon center of the substrate.[12] Re-aromatization of the resultant Wheland-type intermediate **V** followed by protodeauration would then deliver **2**. In the case of the disubstituted substrate, it is thought that coordination of the gold(I) catalyst at the estereal triple bond of the 1,7-diyne benzoate preferentially occurs to give the gold-coordinated species **IV**. This results in

Scheme 3. Proposed Mechanism for the Cycloisomerizations of 1,7-Diyne Benzoates Catalyzed by A



syn 1,3-migration of the benzoate group and formation of the corresponding allenyne intermediate **VI**. Further coordination by the gold(I) catalyst to the remaining alkyne moiety of this adduct would give **VII**, the active species that undergoes the stepwise [2+2] cycloaddition process involving addition of the allenic group to the C≡C bond and formation of the piperidine adduct **VIII**. In a manner similar to the analogous Au(I)-catalyzed reactions of 1,6-enynes bearing a carbonyl group,[13] subsequent Prins-type cyclization of the vinyl gold moiety to the carbonyl carbon center in **VIII** would give the bicyclic carbocationic species **IX**. On release of the metal catalyst, this bicyclic adduct would then provide **3**. The diketone **4a** could originate from **1a** undergoing a tandem 1,3-migration/6-*exo*-*dig* cyclization/1,5-acyl migration process in a manner similar to that recently reported for gold(I)-catalyzed cycloisomerizations of 1,6-diyne acetates.[3a] The formation of both N-heterocycles as a single enantiomer from an enantiopure substrate also implies that neither the starting material nor any of the putative intermediates are prone to racemization. As a consequence, this provides efficient transfer of the retained chirality at the C4 position that leads to the enantioselectivities observed at the newly formed stereogenic centers.

In summary, we have developed a gold(I)-catalyzed strategy for the construction of highly functionalized indeno[1,2-*c*]azepines and azabicyclo[4.2.0]octa-1(8),5-dines from the respective mono- and disubstituted 1,7-diyne benzoates. Our studies suggest that complete control of product selectivity was found to be possible by exploiting the steric interactions between the alkyne moieties in the substrate with the gold(I) catalyst. Efforts to explore the scope and synthetic applications of the present reactions are currently underway and will be reported in due course.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures, characterization data, crystal structure data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) See the Supporting Information (SI) for details.

(6) See Figures S128-S135 in the SI for ORTEP drawings of the crystal structures reported in this work.

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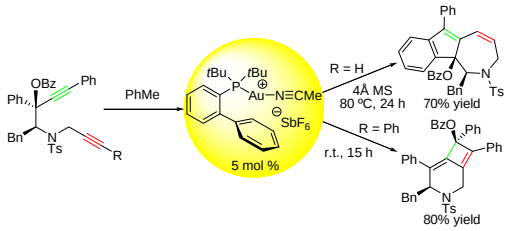
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