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Gold(I)-Catalyzed Intramolecular Dehydrative Amination of Sulfamate Esters Tethered to Allylic Alcohols: A Strategy for the Synthesis of Cyclic Sulfamidates

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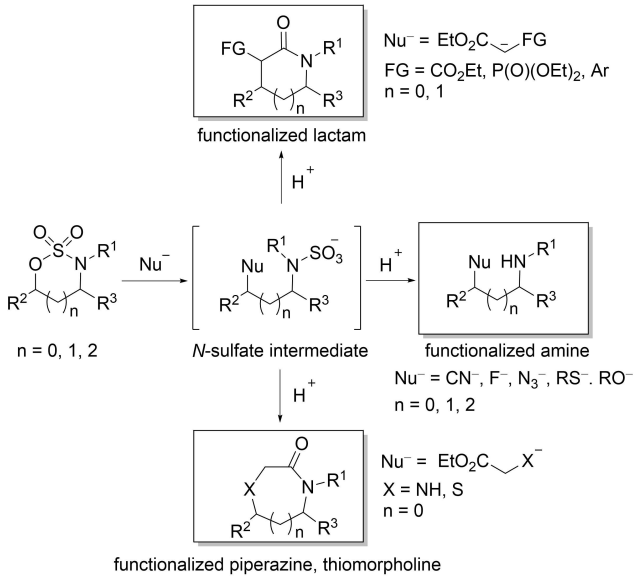
Abstract: An efficient synthesis protocol for cyclic sulfamidates has been developed via catalytic intramolecular cyclizations of sulfamate esters tethered to allylic alcohols. The reactions proceed smoothly at room temperature in the presence of (IPr)AuCl (5 mol%) and $AgBF_4$ (5 mol%). This protocol features good to excellent yields, high selectivity, broad substrate scope, and mild reaction conditions. This method is also applicable to the synthesis of a seven-membered sulfamidate.

Keywords: Homogeneous catalysis; Gold; Silver; Amination; Cyclic sulfamidate

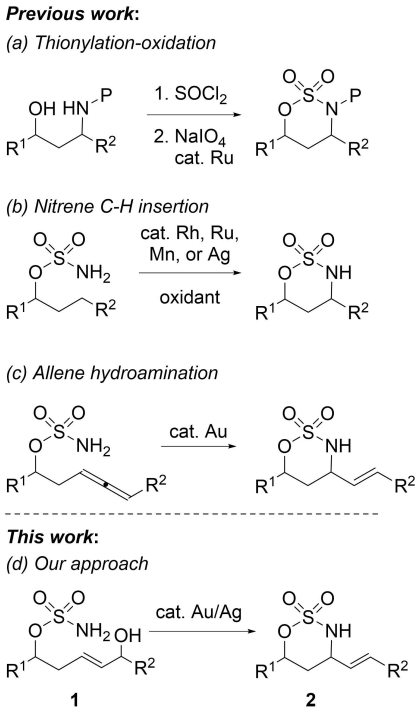
Cyclic sulfamidates[1] are flexible synthetic intermediates widely used for the synthesis of various functionalized amines. Notably, the reactivity of 1,2- and 1,3-cyclic sulfamidates is comparable to that of activated aziridines and azetidines, respectively.[2] Thus, various nucleophiles readily attack exclusively at the *O*-bearing carbon center in a stereospecific (S_N2) manner to deliver an *N*-sulfate intermediate[3] further hydrolyzed under acidic conditions to the final functionalized amine ($Nu^- = CN^-$, F^-, N_3^-, RS^-, RO^-),[4] functionalized lactam ($Nu^- = EtO_2CHC^-FG$),[2] or functionalized piperazine/thiomorpholine ($Nu^- = EtO_2CCH_2X^-$)[5] (Scheme 1).

Conventionally, cyclic sulfamidates are prepared from the thionylation of amino alcohol followed by oxidation (Scheme 2a).[6] Alternatively, transition metal (Rh, Ru, Mn, or Ag)-catalyzed intramolecular oxidative nitrene insertion into the C(sp^3)–H bond has been extensively studied (Scheme 2b),[7] and gold(I)-catalyzed allene hydroamination has also been recently reported (Scheme 2c).[8] However, the use of strong oxidants and the preparation of complex allene substrates remain critical issues associated with these strategies. Despite the aforementioned elegant works, there is still an increasing demand to develop a general and mild method to synthesize various cyclic sulfamidates, which must be devoid of oxidant and harsh reaction conditions. To meet such a demanding goal, we have addressed this issue by using cyclization of sulfamate esters tethered to allylic alcohols (Scheme 2d).

We selected the Au/Ag catalyst combination system for the development of new catalytic methods to synthesize cyclic sulfamidates. Over the past decades, homogeneous gold and silver catalysis has proved to be a versatile tool for the construction of complex



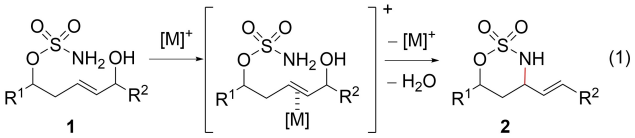
Scheme 1. Cyclic sulfamidate as a synthetic intermediate.



Scheme 2. Strategies for the synthesis of cyclic sulfamidates.

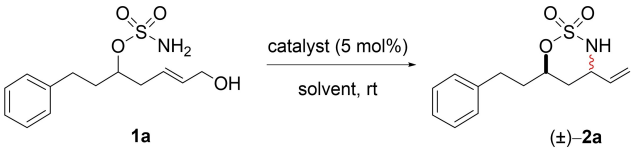
molecular architecture.[9] Gold and silver act as soft and carbophilic Lewis acids,[10] and hence can make the C–C π bond more susceptible to a nucleophilic attack. However, despite much success in alkyne, allene, and terminal alkene activation, the activation of internal olefins by gold and silver catalysts has been elusive and remained relatively unexplored.

Related to this topic, allylic alcohols have been used as important substrates. Especially, the gold-catalyzed intramolecular dehydrative functionalizations of allylic alcohols have been widely studied and well documented for a range of nucleophiles. Bandini and co-workers reported gold-catalyzed cyclization of indoles tethered to allylic alcohols.[11] In addition, Aponick, Bandini, and Widenhoefer independently developed gold-catalyzed intramolecular functionalization of allylic alcohols using *O*-nucleophiles[12] and *N*-nucleophiles.[13] In these reactions, allylic alcohols served as valuable synthetic equivalents of non-activated alkenes and/or allenes. As part of a program to develop new catalytic synthetic methods for cyclic sulfamidates, we herein report gold/silver-catalyzed intramolecular dehydrative amination of sulfamate esters tethered to more easily accessible allylic alcohols.



We envisaged a process in which a π-acidic cationic gold/silver species would react with the alkene moiety of allylic alcohol, and subsequent elimination of water molecule would drive the cyclization to completion (eq. 1). To validate our hypothesis, we began our study by examining the cyclization of allylic alcohol-tethered sulfamate ester **1** using a variety of gold and silver salts as catalysts (Table 1). At the outset of this project, various gold chloride salts including $AuCl_3$, $NaAuCl_4{\cdot}2H_2O$, AuCl, (IPr)AuCl, $(PMe_3)AuCl$, $(PCy_3)AuCl$, and $(PPh_3)AuCl$ were tested for cyclization at room temperature in CH_2Cl_2 solvent (entries 1–7). Gold(III) and gold(I) salts having Cl^- ion were not effective, and only a trace amount of cyclized product **2a** was observed even after 48 h. However, $(PPh_3)Au$-catalyst carrying $^-NTf_2$ increased the yield up to 35% (entry 8). To our delight, treatment of **1a** with the catalyst combination $(PPh_3)AuCl/AgOTf$ gave the cyclic sulfamidate **2a** in much improved yields after 22 h (91%, entry 9).

Table 1. Catalyst screening and optimization of reaction conditions.[a]



entry	catalyst	time (h)	solvent	yield (%) [b] (*cis*:*trans*) [c]
1	$AuCl_3$	48	CH_2Cl_2	trace[d]
2	$NaAuCl_4{\cdot}2H_2O$	48	CH_2Cl_2	trace[d]
3	AuCl	48	CH_2Cl_2	trace[d]
4	(IPr)AuCl	48	CH_2Cl_2	0[d]
5	$(PMe_3)AuCl$	48	CH_2Cl_2	0[d]
6	$(PCy_3)AuCl$	48	CH_2Cl_2	trace[d]
7	$(PPh_3)AuCl$	48	CH_2Cl_2	0[d]
8	$(PPh_3)AuNTf_2$	48	CH_2Cl_2	35 (3.7:1)
9	**$(PPh_3)AuCl/AgOTf$**	**22**	**CH_2Cl_2**	**91 (4.1:1)**
10	$(PPh_3)AuCl/AgOTf$[e]	26	toluene	38 (2.5:1)[e]
11	$(PPh_3)AuCl/AgOTf$	48	THF	trace[d]
12	$(PPh_3)AuCl/AgOTf$	24	dioxane	16 (2.9:1)[d]
13	$(PPh_3)AuCl/AgOTf$	48	CH_3CN	trace[d]

[a] Reaction conditions: **1a** (300 μmol), gold catalyst (15.0 μmol), silver catalyst (15.0 μmol), solvent (3.0 mL).
[b] Isolated yields after column chromatography.
[c] Diastereomeric ratio is based on ^1H NMR.
[d] Starting material was recovered.
[e] Carried out at 60 °C.

At this stage, we investigated the solvent effect on the yield of gold(I)-catalyzed intramolecular dehydrative amination of sulfamate ester **1a** in the presence of silver salt to choose the best solvent condition for further catalyst screening. The yields were varied based on the used solvents. The reaction was only effective in CH_2Cl_2, and a small amount of the product was observed or isolated in the other solvents, such as toluene, THF, dioxane, and CH_3CN (Table 1, entries 10–13). Considering the yield of the product, CH_2Cl_2 was the best solvent for the reaction (Table 1, entry 9), and thus chosen for further study.

Interestingly, changing the PPh_3 ligand to IPr dramatically accelerated the reaction: the reaction using (IPr)AuCl/AgOTf combination rapidly completed in 3 hours, and afforded the desired product **2a** in a better yield and selectivity compared with the reaction of (PPh_3)AuCl/AgOTf (3 h, 97%, Table 2, entry 1, vs. 22 h, 91%, Table 1, entry 9). Since IPr turned out to be the best ligand for gold catalysts, we decided to screen a variety of silver salts combined with (IPr)AuCl (Table 2, entries 1–6). The reactions were efficiently catalyzed by a 1:1 mixture of (IPr)AuCl and a range of silver salts. Among the silver salts screened, $AgBF_4$ was particularly rapid and effective, and provided **2a** in the best yield (99%) in 2 h (Table 2, entry 6). However, the best selectivity was obtained with AgOTs (dr = 24:1, Table 2, entry 2), although the reaction was slower than the $AgBF_4$ reaction.

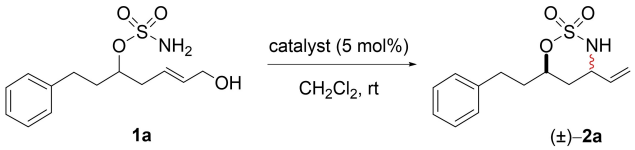
The addition of silver salt significantly enhanced the reactivity of the gold catalyst, which encouraged us to further investigate the effect of counterion and silver on the cyclization reaction. As shown in entry 7 in Table 2, AgOTf alone was not an effective catalyst. When used as a sole catalyst, only a trace of the product was observed after 48 h. However, the (PPh_3)AuCl/AgOTf combination showed a better activity over (PPh_3)AuCl or AgOTf alone (Table 1, entry 9, vs. Table 1, entry 7, and Table 2, entry 7). Likewise, the (IPr)AuCl/$AgBF_4$ combination demonstrated a better activity over (IPr)AuCl or $AgBF_4$ alone (Table 2, entry 6, vs. Table 1, entry 4, and Table 2, entry 8), which could originate from the silver[14] or/and counterion[15] effect. To assess the silver and counterion effect, we performed the control reaction catalyzed by (IPr)AuOTs, prepared by premixing (IPr)$AuCH_3$ and TsOH in the absence of silver salts, which gave **2a** in 80% yield after 48 h (Table 2, entry 9). The reaction was clean and comparable to the reaction of (IPr)-AuCl/AgOTs. Compared with the poor reactivity of (IPr)AuCl (Table 1, entry 4) or AgOTs alone (Table 2, entry 10), the improved reactivity of the (IPr)AuCl/AgOTs combination might derive from the counterion and the intrinsic activity of the gold(I) catalyst rather than from the silver(I) catalyst. Meanwhile, TsOH did not catalyze the cyclization (Table 2, entry 11). According to our observation, the counterion effect[15] is unambiguously more significant than silver effect.[14]

Therefore, it cannot be excluded that the apparent silver salt effect may originate from the counterion effect. Our observation is well consistent with recent report about counterion effect: weakly coordinating anions generate more-electrophilic gold centers with consequent stronger metal-π system interactions.[15] Currently, further investigation of the silver and counterion effect on the yield and selectivity of cyclization reaction is in progress.

After establishing the optimal conditions, we demonstrated the scope of gold(I)-catalyzed intramolecular dehydrative amination of allylic alcohol-tethered sulfamate esters **1b–p** using (IPr)AuCl and silver salts including $AgBF_4$, AgOTs, $AgSbF_6$, or AgOTf (Scheme 3). In most cases, $AgBF_4$ showed the best performance in terms of yield and reaction times, whereas in cases of **2g** and **2l**, AgOTf and $AgSbF_6$ provided respective desired cyclized products in better yields than $AgBF_4$. Notably, improved dr's were observed with AgOTs (except in cases of **2o** and **2p**), although the reaction time was prolonged, and the yield decreased.

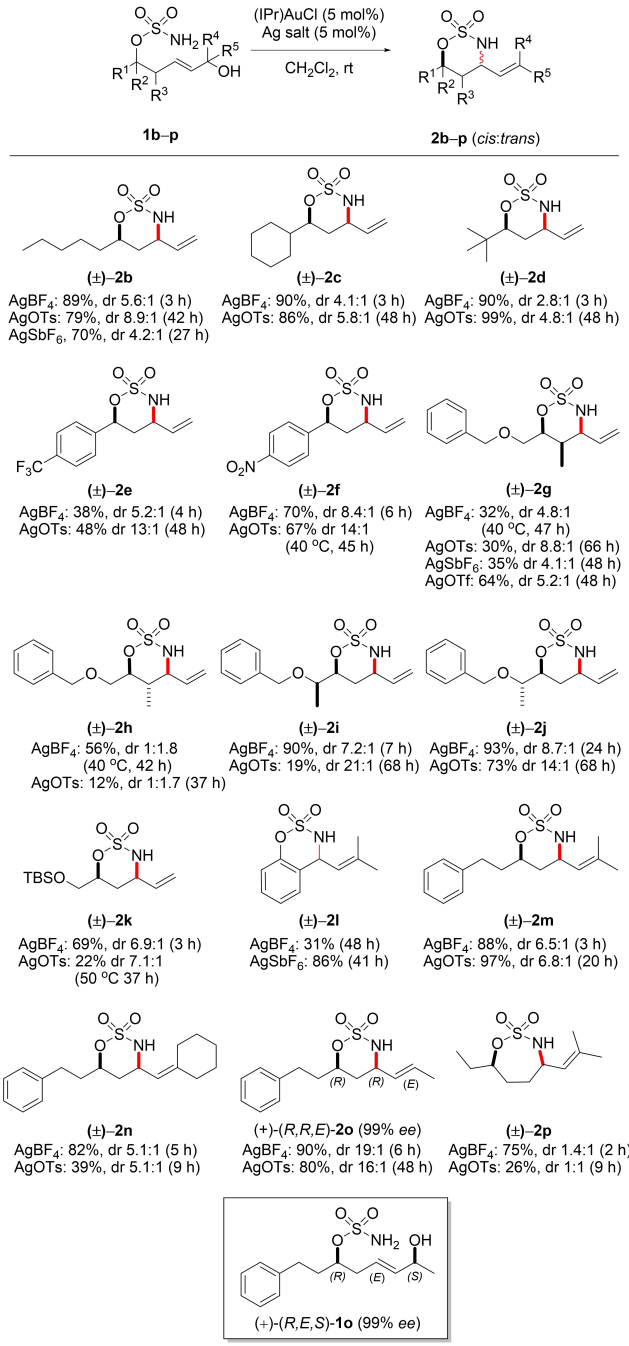
When $AgBF_4$ was used, the substrates containing aliphatic substituents such as *n*-pentyl, *c*-hexyl, and *t*-butyl groups smoothly provided the cyclized products **2b–d** in 3 h in excellent yields (89–90%). The

Table 2. Silver salt and counterion effect on the cyclization of allylic alcohol-tethered sulfamate ester.[a]



entry	catalyst	time (h)	yield (%) [b] (*cis*:*trans*) [c]
1	(IPr)AuCl/AgOTf	3	97 (7.0:1)
2	**(IPr)AuCl/AgOTs**	**48**	**93 (24:1)**
3	(IPr)AuCl/$AgNO_3$	48	84 (19:1)
4	(IPr)AuCl/$AgSbF_6$	3	97 (3.5:1)
5	(IPr)AuCl/$AgNTf_2$	48	73 (22:1)
6	**(IPr)AuCl/$AgBF_4$**	**2**	**99 (11:1)**
7	AgOTf	48	trace[d]
8	$AgBF_4$	48	trace[d]
9	(IPr)$AuCH_3$/TsOH	48	80 (16:1)
10	AgOTs	48	0[d]
11	TsOH	48	trace[d]

[a] Reaction conditions: **1a** (300 μmol), gold catalyst (15.0 μmol), silver catalyst (15.0 μmol), CH_2Cl_2 (3.0 mL).
[b] Isolated yields after column chromatography.
[c] Diastereomeric ratio is based on ^1H NMR.
[d] Starting material was recovered.



[a] Reaction conditions: **1a–p** (300 μmol), (IPr) AuCl (9.3 mg, 15.0 μmol), Ag salts (15.0 μmol), CH_2Cl_2 (3.0 mL). Diastereomeric ratio based on ^1H NMR.

Scheme 3. Synthesis of cyclic sulfamidates via gold(I)-catalyzed intramolecular cyclization reaction.[a]

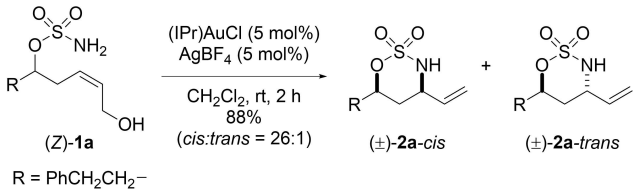
substrates containing aromatic substituents such as *p*-trifluoromethylphenyl and *p*-nitrophenyl groups also afforded the corresponding cyclized product **2e** and **2f** in 38% and 70% yield, respectively. Benzyl and TBS protecting groups for the hydroxyl group were compatible with the (IPr)AuCl/$AgBF_4$ conditions (**2g–k**). The methyl substituent on the sulfamidate ring significantly affected the dr (*cis/trans* 4.8:1 for **2g** vs. *cis/trans* 1:1.8 for **2h**) due to the large energy difference between the transition states during cyclization, while the methyl substituent on the side chain showed a negligible effect on the dr (*cis/trans* 7.2:1 for **2i** vs. *cis/trans* 8.7:1 for **2j**). The reaction was also effective for the synthesis of benzo-fused cyclic sulfamidate[16] heterocycle: **2l** was obtained in 86% yield at room temperature after 41 h in the presence of $AgSbF_6$ under standard conditions.

The power of this method was well-demonstrated by the synthesis of cyclic sulfamidates variously substituted on alkene residue. The reaction was tolerant of various types of substituents on allylic moiety: treatment of **1m**, **1n**, and **1o** with (IPr)AuCl/$AgBF_4$ led to the clean formation of *gem*-dimethyl, *c*-hexyl, and methyl-substituted products **2m**, **2n**, and **2o**.

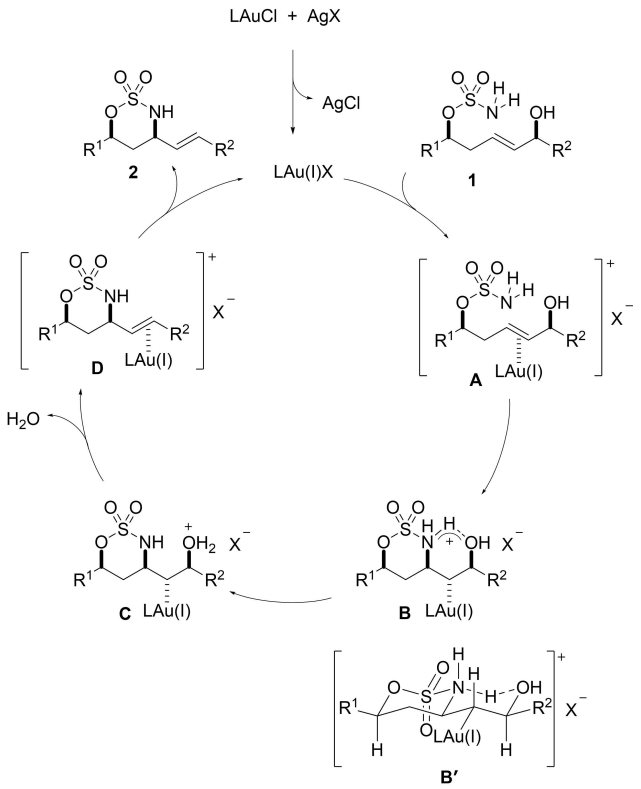
Another feature of note is a seven-membered ring formation. Even though transition metal-catalyzed intramolecular hydroaminations show remarkable efficiency, unfortunately, seven-membered ring cyclization is hampered by both unfavorable enthalpic and entropic factors.[17] Despite extensive studies on the gold-catalyzed intramolecular hydroamination of alkene, allene, and alkyne, seven-membered ring formation is rare and limited to the alkyne substrate preorganized for cyclization.[18] Surprisingly, our method was well applicable to the synthesis of seven-membered sulfamidate **2p**, which was obtained in 75% yield in the presence of (IPr)AuCl/$AgBF_4$ at room temperature rapidly in 2 h.

The effect of the double-bond configuration of the substrate on this gold(I)-catalyzed dehydrative amination was also evaluated employing *Z*-allylic alcohol substrate (*Z*)-**1a**, which can be considered as an alternative substrate (Scheme 4). When *Z*-allylic alcohol substrate (*Z*)-**1a** was subjected to the standard catalytic conditions, (±)-**2a** was isolated in a somewhat decreased yield with improved selectivity (88%, *cis/trans* = 26:1), compared to the reaction of (*E*)-**1a** (Table 2, entry 6).

A plausible brief mechanistic pathway is proposed in Scheme 5, based on previous studies[12c,13,19] and our observation. The initial coordination of π-acidic cationic gold(I) species[20] to the olefin of **1** would form



Scheme 4. The cyclization of *Z*-allylic alcohol-tethered sulfamate ester.



Scheme 5. Plausible mechanism.

metal-π-alkene complex **A**, the intramolecular cyclization of which would proceed via an *anti*-addition and lead to the hydrogen-bonded metal-alkyl complex **B**. Proton transfer to the hydroxyl group would generate intermediate **C**, and the subsequent *anti*-elimination of water would yield the cyclic sulfamidate **2** through the metal-π-alkene complex **D**. This proposed mechanism is well-supported by previous studies[12c,13,19] for an *anti*-addition/*anti*-elimination sequence for the gold(I)-catalyzed intramolecular functionalization of allylic alcohols. However, a detailed mechanism and the participation of silver is still unclear.

Scheme 3 shows the formation of *cis*-cyclic sulfamidate (+)-(*R*,*R*,*E*)-**2 o** as a major product in good yields with good diastereoselectivity from configurationally defined and enantiomerically enriched allylic alcohol substrate (+)-(*R*,*E*,*S*)-**1 o**. The effect of a chiral secondary allylic alcohol moiety on the efficiency and stereoselectivity of gold-catalyzed allylic amination/alkoxylation was well-documented by Aponick[12c] and Widenhoefer.[13c] In our case, the similar net *syn* addition of $-NH_2$ relative to –OH was also observed. Regarding the stereoselective intramolecular dehydrative amination of chiral secondary allylic alcohols, Widenhoefer and co-workers proposed hydrogen-bonded decalin-type conformation.[13c] Likewise, the selective formation of (+)-(*R*,*R*,*E*)-**2 o** can be rationalized by the potential *trans*-decalin-type chair-like conformation **B′** (Scheme 5). The structure of (+)-(*R*,*R*,*E*)-**2 o** and dr of the reaction were unambiguously confirmed by NMR experiments (Supporting Information).

In summary, we have successfully developed an efficient gold/silver-catalyzed intramolecular dehydrative amination of sulfamate esters tethered to allylic alcohols to furnish cyclic sulfamidates under mild conditions. This is the first report on the construction of synthetically valuable cyclic sulfamidates using sulfamate esters tethered to allylic alcohols, which are easily accessible. This methodology is useful in medicinal chemistry, and its application to the synthesis of bioactive natural products is currently underway in our laboratory.

Experimental Section

Synthesis of Cyclic Sulfamidates 2 a; Typical Procedure

To a 5 mL oven-dried round-bottom flask with a side arm were added (IPr)AuCl (9.3 mg, 15.0 μmol, 5 mol%.) and $AgBF_4$ (2.9 mg, 15.0 μmol, 5 mol%). A solution of (*E*)-7-hydroxy-1-phenylhept-5-en-3-yl sulfamate (**1 a**, 85.6 mg, 300 μmol) in anhydrous CH_2Cl_2 (3 mL) was added. The reaction mixture was stirred at room temperature for 2 h. Upon completion of the reaction, the reaction mixture was filtered through a plug of Celite® and rinsed with EtOAc (30 mL). The filtrate was concentrated *in vacuo* and purified by column chromatography hexanes/EtOAc, (4:1→2:1) to afford *cis* and *trans* sulfamidates **2 a**.

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