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Design and Synthesis of Alanine Triazole Ligands and Application in Promotion of Hydration, Allene Synthesis and Borrowing Hydrogen Reactions

Yongchun Yang,[a] Anni Qin,[a] Keyan Zhao,[a] Dawei Wang,[a,*] and Xiaodong Shi[b,*]

[a] The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, Jiangsu Province, People's Republic of China
E-mail: wangdw@jiangnan.edu.cn
[b] Department of Chemistry, University of South Florida, 4202 E Fowler Ave, Tampa, Florida, USA
E-mail: xmshi@usf.edu

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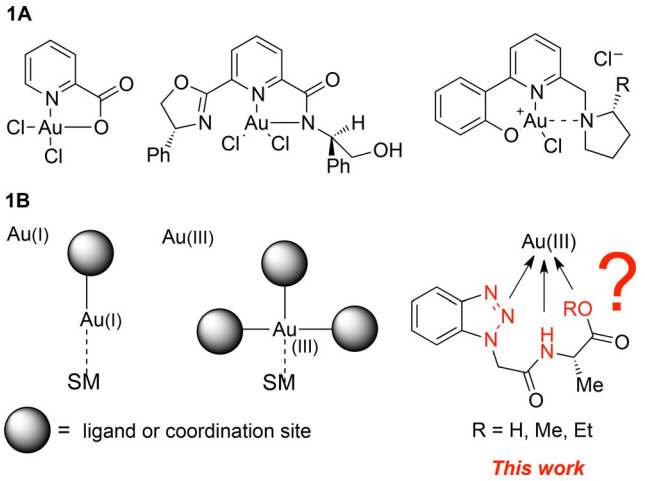
Abstract: A new type of alanine triazole (ATA) ligand was found to be an efficient partner for the stabilization of gold(III), thus rendering improved stability and high catalytic activities in allene synthesis and hydration reactions through the 3,3′-arrangement of propargyl esters and propargyl alcohols. In addition to Au(I), ATA-gold(III) was also proven to be an effective catalyst in promoting the formation of allenes with high yields. Furthermore, alanine triazole ruthenium has exhibited excellent potential as a means to catalyze borrowing hydrogen of alcohols and amines, ketones and alcohols.

Keywords: alanine; allenes; gold; rearrangement; triazoles

The use of ligands represents one of the most powerful and versatile methods to build organic molecular and functional groups, and has attracted a great deal of attention from the chemical community.[1] The development of new ligands promotes lots of new reactions and methodologies and has played a great role in modern synthetic chemistry. Notably, the role of ligands in gold chemistry is more prominent and significant because of the easy decomposition of gold catalysts.[2] The reactivity and stability of gold complexes largely depends on ligands coordinating with gold cations, stabilizing the catalytically active species and not on accelerating the catalysis.[3] Therefore, the development of new skeleton ligands is an effective and important method to solve the stability problems of gold catalysts, especially for gold(III) catalysts.[4] However, the design the synthesis of effective ligands to stabilize gold(III) is rarely reported and remains a challenging scientific issue.[5]

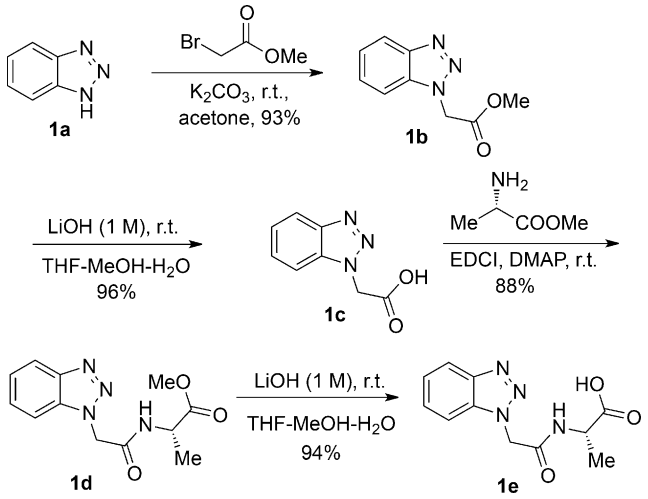
It is widely accepted that there are two main states of gold catalyst: gold(I) and gold(III). Among the two typical oxidation states of gold catalyst, gold(I) complexes are considered as having two coordination sites with linear geometry, while those of gold(III) are accepted as having a square planar geometry with four coordination sites, which should be conveniently fine-tuned by ligand changes (Scheme 1).[6] For gold(I), excellent examples are the development of PR_3 derivatives[7] and N-heterocyclic carbene (NHC) ligands,[8] which greatly enhanced the catalyst stability and enriched the catalytic applications of gold catalysts through metal-ligand back-bonding. Meanwhile, gold(III) complexes have usually been stabilized by bidentate and tridentate ligands.[9–11] Typical examples are $PicAuCl_2$ and its derivatives,[10] which exhibit high stability in gold(III)-catalyzed transformations (Scheme 1).



Scheme 1. Alanine triazole ligands.

Natural amino acid derivatives are universal and common organic compounds, which are very cheap and conveniently obtained and achieved huge applications in hot research areas, like the catalytic area, life science, pharmaceutical chemistry, biochemistry, agriculture and so on. Now, we have a proposal about this: if the triazole ligand[12,13] was introduced into amino acid derivatives, the designed new ligands could improve the reactivity and stability of gold(III) through three kinds of functional groups or coordination sites: ester group, amino group and triazole part (Scheme 1B). Based on the easy decomposition of gold(III) with the strong coordination ability of triazole, the alanine triazole ligand may be a good choice to stabilize gold(III) serving as a tridentate or a bidentate ligand with three possible coordination sites. Herein, we have synthesized the alanine triazole ligands (ATA) and explored their coordination function with gold(III). It was found that ATA-Au(III)Cl exhibited improved stability and good catalytic activities in allene synthesis and hydration reactions through the 3,3′-arrangement of propargyl esters and alcohols. Besides, alanine triazole ruthenium has been proved to be excellent as a means to promote borrowing hydrogen of alcohols and amines, ketones and alcohols.

Initially, the alanine triazole ligand (**1e**) was prepared conveniently in totally 74% yield for four steps through alkylation, hydration and condensation reactions (Scheme 2). It was found that ATA was easily coordinated with gold(III), and a yellow solid ATA-gold(III)Cl was obtained with 83% yield, but it failed to cultivate crystals even though many solvents were tried. In order to test the thermal stability of this ATA-gold(III) complex, a TG experiment was carried on and the thermal curves are shown in Figure 1. The stability experiment indicated that the ATA-Au(III)Cl complex is stable up to 170 °C and the results showed



Scheme 2. The synthesis of alanine triazole ligand.

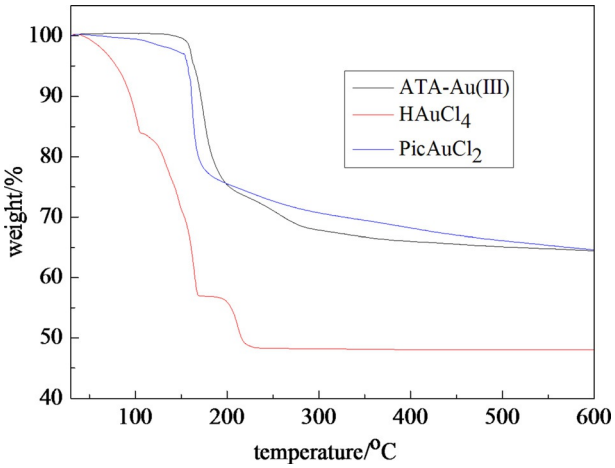


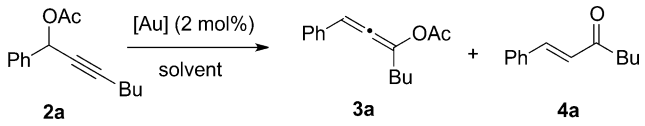
Figure 1. Thermogravimetric curves of ATA-Au(III).

that ATA-Au(III)Cl exhibited much greater stability than the simple gold salt.

Next, the classical substrate propargyl ester (**2a**) was selected to test the catalytic activity of ATA-gold(III). The 3,3′-arrangement of the propargyl ester[14,15] was carried out under KAu(III)Cl_4/**1d** or KAu(III)Cl_4/**1e** conditions and the results are summarized in Table 1. According to the literature, the simple Au(I) promotes allene synthesis from propargyl esters through a 3,3′-rearrangement. Nolan reported that [(IPr)AuOH](I) and [(IPr)Au(pyr)][BF_4](I) could catalyze this transformation.[15b] We found that TA-Au(I) could promote allene synthesis with high yields and this was verified by Hashmi.[14c,15c] A concern is that Au(III) can realize allene synthesis from propargyl esters? Here, it was found that the simple Au(III) salts could not catalyze the formation of allenes, even when several common solvents were tried (entries 1–6, Table 1). Interestingly, a much higher yield of allene was achieved when the ligand **1d** or **1e** was added in order to adjust the gold(III) catalyst under the same conditions (entries 5–7, Table 1). It was found that allenes could not be achieved in the absence of ligands with this methodology (entries 5 and 6, Table 1). The best result was achieved in DCM with **1e** as a ligand (entry 9, Table 1), while a slightly lower yield was achieved with **1d** as a ligand. Notably, the simple gold salt ($AuCl_3$) could not catalyze the reaction, but this was consistent with the published results (entry 11, Table 1).[15a] The reaction solution began to gradually become dark in 0.5 h for allene synthesis from propargyl ester with $AuCl_3$ as a catalyst (entry 10, Table 1), meaning that the gold salt began to partly decompose even after half an hour.[12] This is further evidence to explain the importance of the ligand in the stabilization of gold(III).

Encouraged by the promising results, we further examined the reaction scope of gold-catalyzed 3,3-rear-

Table 1. Screening of the reaction conditions.[a]



2a 3a 4a

Entry	Au	Solvent	Conv. [%][b]	3a [%][c]	4a [%][c]
1	$KAuCl_4$	THF	23	<5	<5
2	$KAuCl_4$	CH_3CN	14	<5	<5
3	$KAuCl_4$	MeOH	20	<5	12
4	$KAuCl_4$	acetone	<5	<5	<5
5	$KAuCl_4$	toluene	28	<5	8
6	$KAuCl_4$/**1e**	toluene	66	51	6
7	$KAuCl_4$/**1d**	toluene	57	43	13
8	$KAuCl_4$/**1d**	DCM	86	73	8
9	$KAuCl_4$/**1e**	DCM	>95	81	8
10	$AuCl_3$	DCM	<5	<5[d]	<5
11	$AuCl_3$	DCE	<15	-[e]	-[15a]
12	$AuPPh_3Cl(I)$	DCM	<15	-	-
13	$AuPPh_3Cl(I)$/$AgBF_4$	DCM	>95	8[f]	<5
14	IPrAuCl(I)/$AgBF_4$	DCM	>95	<5[g]	<5
15	IPrAuCl(I)	DCM	<5	<5	<5

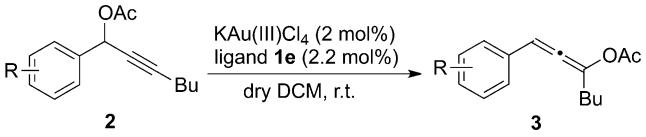
[a] *Conditions:* **2a** (1 mmol), [Au(III)] (2 mol%), ligand **1d** or **1e** (2.2 mol%), dry solvent (5 mL), 3-12 h, room temperature.
[b] Determined by ^1H NMR.
[c] Isolated yields based on **2a**.
[d] The reaction solution began to gradually become dark for 0.5 h.
[e] Similar reference reaction: another alkynyl acetate 1-(2-acetyl-phenyl)hept-2-yn-1-yl acetate was used as a substrate, ref.[15a]
[f] 51% of indene instead, ref.[14k]
[g] 92% of indene instead, ref.[14k]

rangement of propargyl esters (Table 2). Generally, various propargyl esters could be smoothly turned into the corresponding allene products with moderate to good yields. When the substrate containing a terminal alkyne was used to test this reaction, the reaction did not occur.

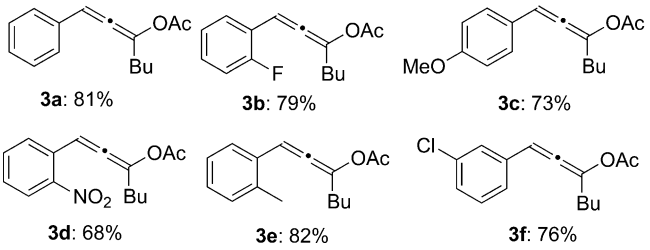
The Meyer–Schuster rearrangement of propargyl alcohols[16] was conducted with $KAuCl_4$/**1e** as a catalyst under wet MeOH conditions. We were pleased to find that the enones were obtained with overall moderate to high yields, and the substrate experiments are listed in Table 3. Nearly all the propargyl alcohols reacted smoothly to give the enones with only 2.2% of **1e** added in the catalytic system. These experiments revealed that alanine triazole ligands (ATA) greatly improved the stability of Au(III), and therefore enhanced the catalytic activity of these catalysts.

Compared to the Meyer–Schuster arrangement of propargyl alcohols, the hydration of alkynes was much more difficult. Here, we found that the $KAuCl_4$/

Table 2. Substrate scope of propargyl esters.[a,b]

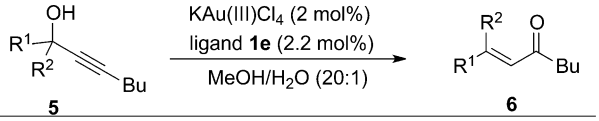


2 3

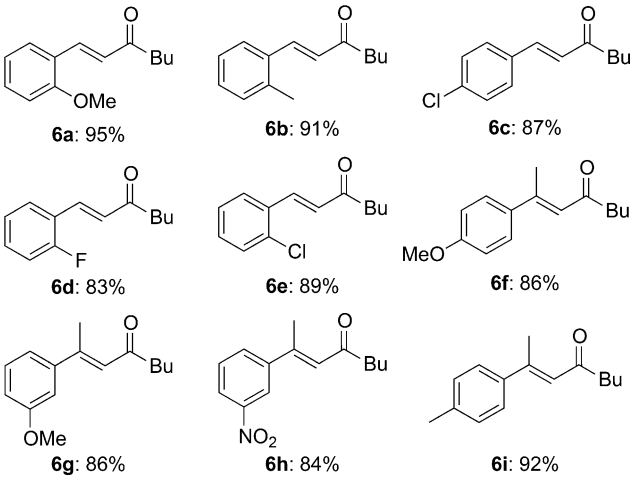


[a] *Conditions:* $KAu(III)Cl_4$ (2 mol%), ligand **1e** (2.2 mol%), **2** (1 mmol), dry DCM (5 mL), 6–12 h, room temperature.
[b] Isolated yields based on **2**.

Table 3. Substrate scope of propargyl alcohols.[a,b]



5 6

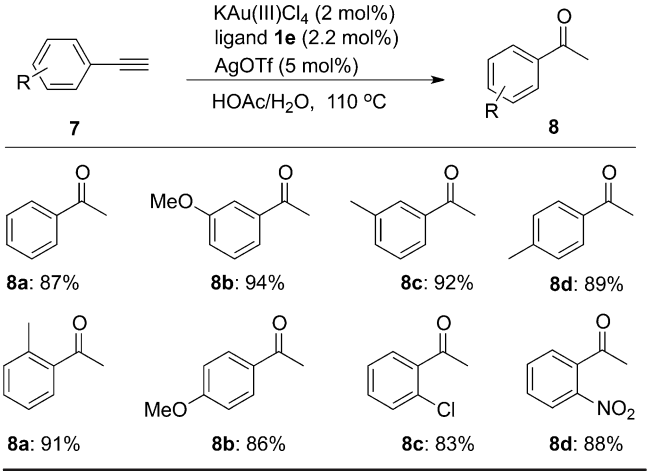


[a] *Conditions:* **5** (1 mmol), $KAu(III)Cl_4$ (2 mol%), ligand **1e** (2.2 mol%), MeOH/H_2O (20:1), 8 h, 50 °C.
[b] Isolated yields based on **5.**

1e was an effective catalyst for the hydration of alkynes. A series of ketones was obtained with good yields, as the data in Table 4 show. All three reactions (allene synthesis, 3,3′-rearrangement of propargyl esters and hydration reaction) indicated that the alanine triazole ligand (ATA) is an excellent partner in the stabilization of gold(III).

The concept of borrowing hydrogen reaction also known as hydrogen autotransfer (BH/HA) has attracted considerable attention over the past ten years, mainly because it offers an alternative to the alkyla-

Table 4. Gold-catalyzed hydration of alkynes.[a,b]



[a] *Conditions:* KAu(III)Cl_4 (2 mol%), ligand **1e** (2.2 mol%), **7** (1.0 mmol), HOAc/H_2O, 12 h, room temperature.
[b] Isolated yields based on **7**.

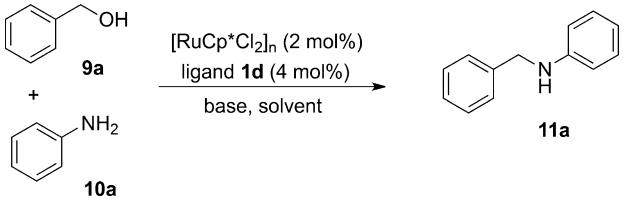
tion of amines with a more greener and atom-efficient process, in which water is the only by-product.[17] The process usually involves the dehydrogenation of alcohols and reduction of imines to obtain N-alkylated or C-alkylated products. However, an often overlooked fact is that transfer hydrogenation is an important competitive reaction. Here, we found that the alanine triazole ligand was effective as a means to promote the iridium-catalyzed N-alkylation reactions of arylamines and various alcohols.

In order to show the excellent catalytic activity of these ATA ligands, we explored their application in borrowing hydrogen reactions. According to our previous efforts,[18] the classical aniline and benzyl alcohol were selected as the model substrates to test the N-alkylation reaction. All screening experiments for the reaction conditions are shown in Table 5. They revealed that the ATA ligand (**1d**) greatly enhanced this transformation (entries 1 and 2, Table 5), which is consistent with the reported results.[19]

Subsequently, we examined the N-alkylation reactions of other arylamines with benzyl alcohols through the use of the catalyst [Ru]/**1d**. The experiments showed that different N-alkylated anilines were achieved with moderate to high yields (Table 6). Generally, the reaction had a better substituent tolerance scope. The substituents with different electronic properties on the aryl rings of aromatic amines significantly affected the reaction yields. Most often, those aromatic amines possessing electron-donating groups gave the corresponding products in higher yields as compared to those with electron-poor ones.

The borrowing hydrogen reaction of ketones with alcohols is a very important method to build functional ketones. However, an often overlooked fact is that transfer hydrogenation is an unavoidable competitive

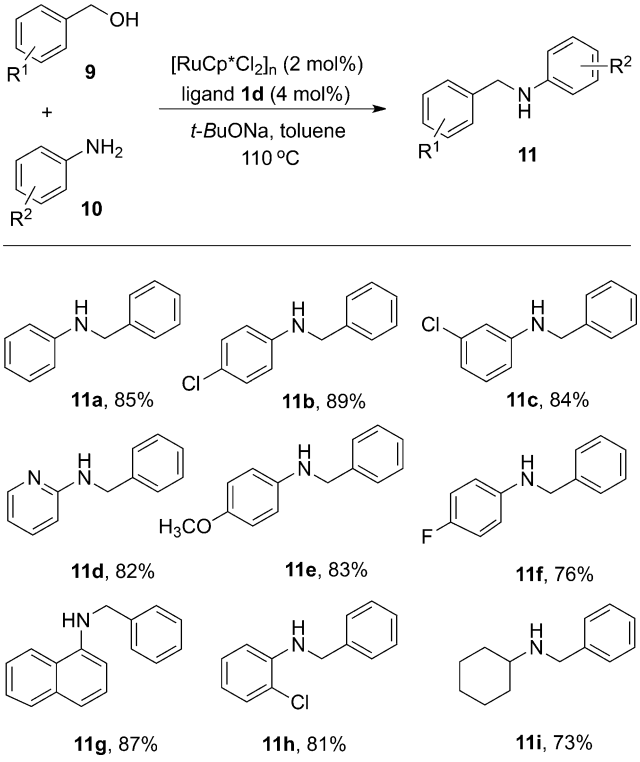
Table 5. Screening of the reaction conditions.[a,b]



Entry	Ligand	Solvent	Base	**3a** [%]
1	none	toluene	*t*-BuONa	35
2	**1d**	toluene	*t*-BuONa	88
3	**1e**	toluene	*t*-BuONa	63
4	**1d**	toluene	Na_2CO_3	41
5	**1d**	toluene	KOH	76
6	**1d**	CH_2Cl_2	*t*-BuONa	21
7	**1d**	THF	*t*-BuONa	45
8	**1d**	DMF	*t*-BuONa	<5

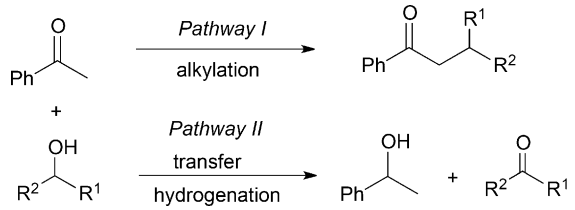
[a] *Conditions:* **9a** (1 mmol), **10a** (1.1 mmol), [RuCp*Cl_2]$_n$ (2 mol%), ligand (4 mol%), base (1.2 mmol), dry solvent (5 mL), 48 h, reflux.
[b] Isolated yields based on **9a**.

Table 6. Ru-catalyzed N-alkylation of anilines.[a,b]



[a] *Conditions:* **9** (1 mmol), **10** (1.1 mmol), [RuCp*Cl_2]$_n$ (2 mol%), **1d** (4 mol%), *t*-BuONa (1.2 mmol), dry toluene (5 mL), 48 h, reflux.
[b] Isolated yields based on **9**.

reaction. In some cases, the competition of the two transformations greatly reduces the application of useful functional ketones (Scheme 3). When the

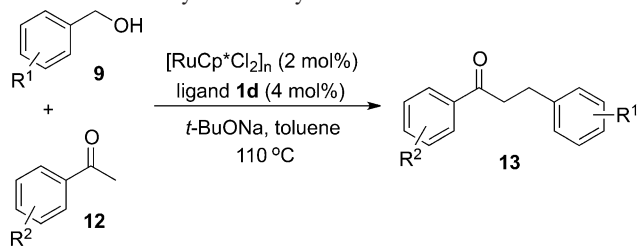


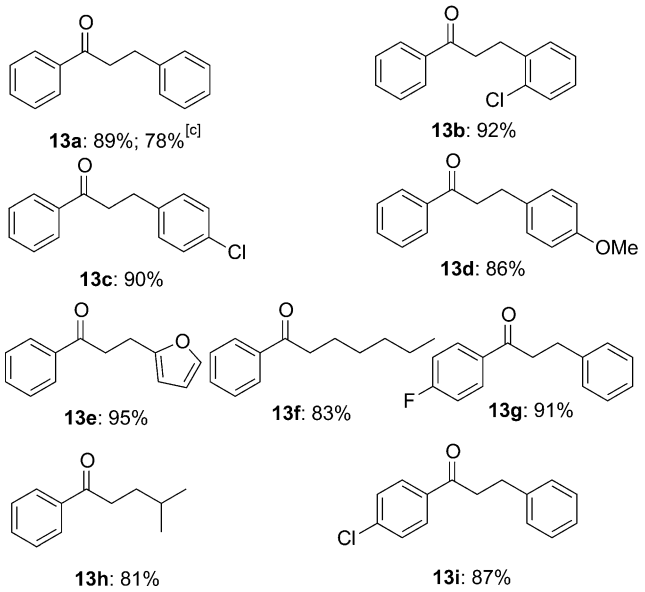
Scheme 3. The competition of transfer hydrogenation and alkylation reactions.

upper catalytic system was used for this transformation, it was found that only the C-alkylated product was obtained.

Next, we further employed the above methods to the borrowing reaction of alcohols with ketones. The results were summarized in Table 7. All the substrates with electron-neutral, electron-rich, and electron-deficient functional groups at the arene moiety were well tolerated, giving **13a–13i** with generally good yields. The furan group in the substrate could also be incorporated into the product **13e** with a high yield.

Table 7. Ru-catalyzed C-alkylation of ketones.[a,b]





[a] *Conditions:* **9** (1.2 mmol), **12** (1.0 mmol), $[RuCp^*Cl_2]_n$ (2 mol%), **1d** (4 mol%), *t*-BuONa (1.5 mmol), dry toluene (5 mL), 48 h, reflux.
[b] Isolated yields based on **9**.
[c] The ligand **1d** was not added.

In summary, the new type of alanine triazole (ATA) ligand has been developed with good yield. The ATA-gold(III)Cl revealed improved stability and good catalytic activities in hydration reactions and allene synthesis through the rearrangement of propargyl esters and alcohols. Additionally, the alanine triazole Ru catalyst has proved to be excellent as a means to promote borrowing hydrogen of alcohols and amines, ketones and alcohols. Further investigations on the extension of this kind of ligand to other transformations are currently undergoing in our group.

Experimental Section

The Synthesis of Alanine Triazole Ligand

To the solution of **1c** (1.772 g, 10 mmol) in dry DCM was added methyl 2-aminopropanoate (2.094 g, 15 mmol), 4-dimethylaminopyridine (DMAP, 1.222 g, 10 mmol), EDCI (3.834 g, 20 mmol), and NEt_3 (2.530 g, 25 mmol) under N_2. The reaction mixture was stirred overnight at room temperature and monitored by TLC, and then the solvent was removed under reduced pressure and purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate = 2:1) afforded compound **1d** as a white solid; yield: 88%.

To a mixed solution of THF/MeOH(1:1) (20 mL) and LiOH (1 M, 20 mL, in H_2O) was successively added the solution of **1d** (20 mmol) in THF/MeOH (1:1) (20 mL) at room temperature. After one hour, the reaction mixture was acidified to pH 2 by adding an aqueous solution of 1 N HCl, the acid product (**1e**) was washed with EtOH, then evaporated to dryness to give **1e**; yield: 94%.

Typical Procedure for Synthesis of Allenes

To a 20-mL Schlenk tube were added $KAuCl_4$ (2 mol%), ligand **1e** (2.2 mol%), dry CH_2Cl_2 (1.0 mL), after the mixture was stirred for 30 min, **2a** (1 mmol) in CH_2Cl_2 (4.0 mL) was added to the reaction mixture at room temperature. After stirring for 3–4 h and monitored by TLC, the solvent was removed under reduced pressure and purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate = 80:1) afforded the title compound **3a** as a colorless oil; yield: 81%.

Acknowledgements

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