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Axially Chiral N-Heterocyclic Carbene Gold(I) Complex Catalyzed Asymmetric Cycloisomerization of 1,6-Enynes

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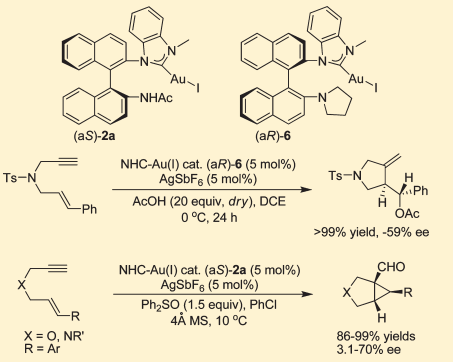
Supporting Information

ABSTRACT: A new class of axially chiral NHC-Au(I) complexes (**1**−**11**) has been developed from optically active BINAM and fully characterized by NMR, ESI-MS, and IR spectroscopic data, where structures of complexes **1**, **2a**, and **6** have been further determined by X-ray diffraction studies of their single crystals, exhibiting a nearly linear coordination geometry around the gold(I) center. Within the carried out investigations herein, the sterically less hindered gold(I) complex (a*R*)-**6**, having a pyrrolidin-1-yl group, has been realized to be the best catalyst in gold(I)-catalyzed asymmetric acetoxycyclization of 1,6-enyne **52a**, giving product **53a** in >99% yield with −59% ee at 0 °C, and the sterically less hindered gold(I) catalyst (a*S*)-**2a** is the best catalyst in the asymmetric oxidative rearrangement of 1,6-enynes, affording the corresponding aldehydes **56a**,**c**−**h** in excellent yields (up to >99%) and modest enantioselectivities (3.1−70% ee) using PhCl as the solvent at 10 °C.



INTRODUCTION

During the past decade homogeneous gold catalysis has been achieved, with an explosive growth in C−C, C−O, or C−N bond formations being mainly attributed to the soft carbophilic Lewis acid properties of gold complexes toward C−C multiple bonds.[1] In comparison with other transition metal catalysts, gold complexes could efficiently catalyze reactions under very mild conditions tolerant of air or moisture to give excellent chemoselectivity and wide functional group compatibility. Although the first example of a gold-catalyzed enantioselective reaction was reported by Hayashi and Ito in 1986 for the aldol condensation between isocyanates and aldehydes,[2] gold-catalyzed asymmetric transformations are still challenging topics with scarce investigations even at the present stage[3] despite the rapid development of several synthetic applications.[4] To the best of our knowledge, most studies on this topic have been focused on the gold activation of allenes toward nucleophilic attack, such as asymmetric hydrofunctionalization of allenes[4b−f] and [2+2] cycloaddition and cycloisomerization of enallenes.[5] Only a few reports addressed the asymmetric activation of substrates containing an alkyne functional group.[4a,6] The difficulty of enantioselective gold(I)-catalyzed transformations is probably due to the linear coordination geometry of the Au(I) center with the reaction site far away from the chiral environment; thus special strategies or chiral ligands were needed to provide spatial arrangements of the opposite site of the metal cation.[3,7]

N-Heterocyclic carbenes (NHCs) represent a growing class of ligands in transition metal catalysis[8] and have several typical features such as stability to air and moisture, low toxicity, and strong σ-donor and poor π-acceptor properties.[9] Thus far, in almost all successful systems for asymmetric gold catalysis, chiral phosphines were employed as ligands,[2−6] but chiral NHC-Au(I) complexes as catalysts were very scarcely reported,[6g,10] although NHCs have emerged as an effective alternative for a number of homogeneous gold catalyses.[8k,11] During our ongoing survey in the literature, there is only one unique relevant paper, reported by Tomioka and co-workers using C_2-symmetric NHC-Au(I) complexes in the cycloisomerization of 1,6-enynes, providing the corresponding cyclopentane products in high yields but with moderate enantioselectivities (up to 59% ee).[6g] On the basis of our previous successful examples in the NHC-metal complex catalyzed asymmetric transformations,[12] herein we wish to represent the first synthesis and characterization of a series of axially chiral NHC-Au(I) complexes and the subsequent investigation on their applications as catalysts in the asymmetric cycloisomerization of 1,6-enynes[1j,6a−6d,6g] to achieve the best results of stereochemical induction.

RESULTS AND DISCUSSION

Synthesis of Axially Chiral NHC-Au(I) Complexes. As summarized in Figure 1, a series of axially chiral NHC-Au(I)

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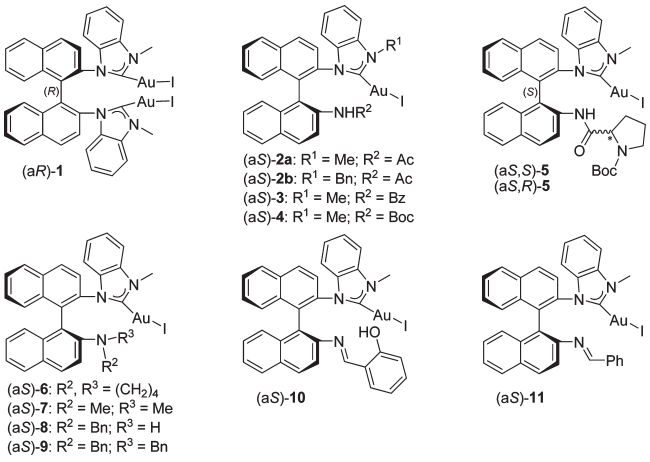


Figure 1. Axially chiral NHC-Au(I) complexes **1**, **2a,b**, and **3**−**11**.

complexes have been synthesized from optically active binaphthyl-2,2′-diamine (BINAM) during this whole work.

At first, we found that when benzimidazolium salt **13** derived from (a*R*)-**12** was treated with [(Me_2S)AuCl] at 85 °C in CH_3CN for 9 h in the presence of NaOAc, the corresponding NHC-gold complex **1** could be produced as a white solid in 52% yield after purification by silica gel flash column chromatography (Scheme 1).[11a] This complex is air and moisture stable in the solid or solution state and even under the heating conditions. Its characteristic structure was determined by NMR, ESI-MS, and IR spectroscopic data. Single crystals of complex **1** suitable for an X-ray diffraction study were grown from a solution of **1** in mixed petroleum ether/CH_3CN/CH_2Cl_2 (1:2:2) (Figure 2). The molecular structure and selected crystal data are shown in Figure 2,[13] which reveals actually a two-metal-center structure, similar to bis-gold(I) biarylphosphine complexes.[2−6] The crystal data of Au(1)−C(1) (2.005(7) Å) and Au(2)−C(29) (2.000(7) Å) are both typical Au−C^{NHC} bond lengths, in line with those of other reported examples.[11] Furthermore, angles of C(1)−Au(1)−I(1) = 178.3(2)° and C(29)−Au(2)−I(2) = 178.1(2)° suggested a nearly linear coordination geometry around the gold(I) center, which was also a typical feature for known gold(I) complexes.[11]

Aiming at conveniently modifying the structures of NHC-Au(I) complexes, a type of mono-NHC ligands was next designed by the introduction of various substituents on the 2′-amino moiety of the binaphthyl scaffold (Figure 1).

As a representative complex of NHC-amide ligands, NHC-Au(I) complex (a*S*)-**2a**, with an acetyl amide substituent on the binaphthyl scaffold, was synthesized according to the procedures shown in Scheme 2. In one word, monobenzimidazole compound (a*S*)-**17** was initially prepared from (a*S*)-BINAM via a sequence of palladium-catalyzed coupling, acetylation of primary amine, palladium-catalyzed hydrogenation of the nitro group, and ring closing with triethyl orthoformate.[14] While imidazolium salt (a*S*)-**18** was obtained upon refluxing (a*S*)-**17** and CH_3I in CH_3CN, the treatment of NHC precursor **18** with [(Me_2S)AuCl] and NaOAc at 85 °C in CH_3CN smoothly afforded NHC-gold(I) complex (a*S*)-**2a** as a white solid in 54% yield (Scheme 2). The gold(I) complexes **2b** and **3**−**5** of NHC-amide ligands were also successfully prepared from nitro-group-containing compound **14** according to the slightly modified procedures similar to that of complex **2a** (see the Supporting Information).

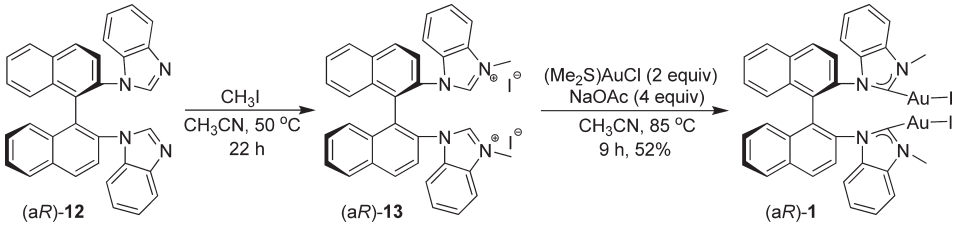
Complexes **2**−**5** are also air and moisture stable in the solid or solution state and even under the heating conditions, and their structures were all confirmed by NMR, ESI-MS, and IR spectroscopic data. Notably, the structure of complex **2a** was further determined by an X-ray diffraction study of single crystals grown from a solution of **2a** in mixed ethyl ether/CH_2Cl_2 (1:1) (Figure 3). The molecular structure and selected crystal data are shown in Figure 3,[15] which reveals that the acetyl amide moiety still does not participate in the coordination on the gold center. While the bond length of Au(1)−C(1) (2.038(14) Å) is consistent with the data of Au−C^{NHC} bonds in the previous literature, the angle of C(1)−Au(1)−I(1) = 179.1(4)° also typically indicates a nearly linear coordination geometry around the gold(I) center (Figure 3).[11]

Moreover, if nitro-group-containing compound **14** was reacted with $Br(CH_2)_4Br$ in the presence of $^iPr_2NEt$, the compound **32**, having a pyrrolidin-1-yl group, could be obtained in 66% yield, which was followed by a sequence of palladium-catalyzed hydrogenation of the nitro group, ring closing of the *o*-phenylenediamine moiety in triethyl orthoformate, and N-methylation to easily give imidazolium salt **35** in a reasonable yield (see the Supporting Information). Then the reaction of NHC precursor **35** with [(Me_2S)AuCl] and NaOAc at 85 °C in CH_3CN successfully afforded NHC-gold(I) complex (a*S*)-**6** as a white solid in 64% yield (Scheme 3). According to the slightly modified procedures similar to that of gold(I) complex **6**, bearing a pyrrolidin-1-yl group, the gold(I) complexes **7**−**9**, with *N*(H)-alkyl or *N*,*N*-dialkyl substituents on the binaphthyl scaffold, were also successfully synthesized from compound **14** (see the Supporting Information). While complexes **6**−**9** were all fully characterized by NMR, ESI-MS, and IR spectroscopic data, the structure of complex **6** was further confirmed by an X-ray diffraction study of single crystals grown from a solution of **6** in mixed petroleum ether/CH_3CN/CH_2Cl_2 (1:1:1) (Figure 4). The molecular structure and selected crystal data are shown in Figure 4[16] and exhibit similar features to those of complexes **1** and **2a**. For example, our determined Au(1)−C(1) bond length of 1.988(6) Å is consistent with the previously reported data, and the angle of C(1)−Au(1)−I(1) = 177.1(3)° also indicates a nearly linear coordination geometry around the gold(I) center (Figure 4).[11]

In addition, upon treatment of the corresponding imidazolium salts with [(Me_2S)AuCl] and NaOAc, we have also synthesized NHC-gold(I) complexes **10** and **11**, containing an imino moiety, in 66% and 41% yield, respectively.[14b] The imino moiety was perfectly preserved during the reaction and even through purification by silica gel flash column chromatography. Particularly, a signal at δ 11.82 ppm in the ^{1}H NMR spectra for complex **10** indicated the intramolecular hydrogen bonding between the OH and imine nitrogen atom without cleavage even in the presence of NaOAc as the base (see the Supporting Information).[14b]

NHC-Au(I) Complex Catalyzed Asymmetric Acetoxycyclization of 1,6-Enyne. An initial experiment was performed to examine the gold(I)-catalyzed asymmetric cyclization of 1,6-enyne **52a** in the presence of these NHC-Au(I) complexes (5 mol %) and $AgSbF_6$ (5 mol %) using anhydrous acetic acid as the solvent at room temperature.[1j,6a−6d,6g] After the reaction was conducted for 50 h, the expected acetoxycyclization product **53a** was obtained as a single diastereoisomer in >99% yield and 40% ee using bis[NHC-Au(I)] complex (a*R*)-**1** as the catalyst (Table 1, entry 1).[17] The use of NHC-Au(I) complex (a*S*)-**2a** resulted in product **53a** in 73% yield and a slightly decreased enantioselectivity of 35% ee, but its absolute configuration was

Scheme 1. Synthesis of Bis[NHC-Au(I)] Complex (a*R*)-1



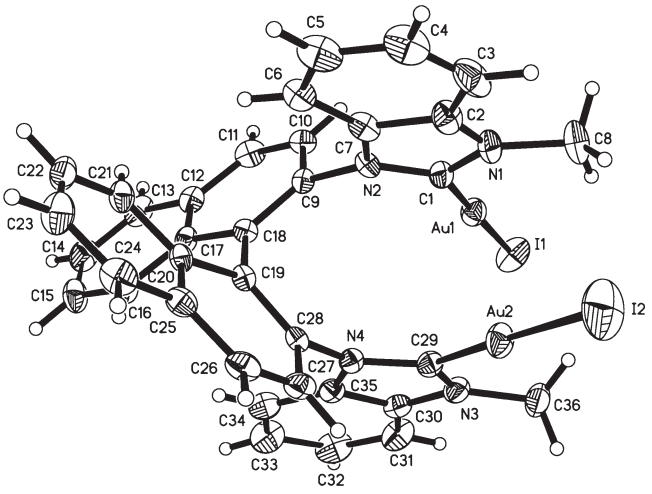


Figure 2. ORTEP drawing of bis[NHC-Au(I)] complex **1** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): Au(1)−C(1) = 2.005(7), Au(1)−I(1) = 2.5376(7), Au(2)−C(29) = 2.000(7), Au(2)−I(2) = 2.5189(8), C(1)−Au(1)−I(1) = 178.3(2), C(29)−Au(2)−I(2) = 178.1(2), N(1)−C(1)−N(2) = 106.5(6), N(3)−C(29)−N(4) = 107.8(6).

identical with that induced by gold(I) complex (a*R*)-**1** (Table 1, entry 2). Furthermore, the transformation of 1,6-enyne **52b** also proceeded smoothly to give the corresponding product **53b** in moderate yields along with 30% and 20% ee,[17] respectively, using complexes (a*R*)-**1** and (a*S*)-**2a** as catalysts under the standard conditions (Table 1, entries 3 and 4).

The use of 1,2-dichloroethane (DCE) as the solvent also led to acetoxycyclization product **53a** in 58% yield and 48% ee with 20 equiv of AcOH as the additive (Scheme 4, eq 1). Because of a trace of H_2O occurring in the commercially available AcOH, hydroxycyclization product **54** was simultaneously isolated in 40% yield and 48% ee. The same 48% ee value for **53a** and **54** indicated that the enantioselectivity was possibly not influenced by nucleophiles such as AcOH and H_2O, which was further supported by the similar result of a control experiment with H_2O as the only additive (Scheme 4, eq 2). The absolute configurations of the products **53a** and **54** were assigned by comparison of the sign of the optical rotation of **54** with that in the previous literature.[6b,17]

The reaction conditions were next investigated to achieve better catalytic results by using anhydrous AcOH (20 equiv) as the nucleophile in the solvent of DCE (Table 2). The system of complex (a*S*)-**2a** (5 mol %) and $AgSbF_6$ (5 mol %) exclusively gave the acetoxycyclization product **53a** in 93% yield and 43% ee (Table 2, entry 1). Using another silver salt (AgX) instead could significantly change the yields but slightly decrease the enantioselectivities (Table 2, entries 3−5), which may be attributed to AgX being directly involved in the formation of active cationic NHC-Au^+ species.[1,3,4] Notably, the control experiments suggested that a potential Ag-catalyzed process was almost negligible during this transformation (Table 2, entry 6).[18] Reducing the reaction temperature could offer better results, with the formation of **53a** in 88% yield and 55% ee at −20 °C as an example (Table 2, entries 7 and 8). The 80% yield and 25% ee of product **53a** obtained by using bis[NHC-Au(I)] complex (a*R*)-**1** as the catalyst have both been decreased in DCE in comparison with those in AcOH (Table 2, entry 9). While introducing bulky substituents on the N-heterocycle or the binaphthyl scaffold was detrimental to the chiral induction (Table 2, entries 10−13), gold(I) complex (a*R*)-**6**, bearing a pyrrolidin-1-yl group, was realized as the best catalyst in this reaction, giving **53a** in 91% yield and −53% ee at room temperature (Table 2, entry 14). Furthermore, properly lowering the reaction temperature gave a better reaction outcome, where complex (a*R*)-**6** afforded **53a** in >99% yield and −59% ee at 0 °C, although a trace of product was formed at −20 °C (Table 2, entries 15 and 16).

It is worth noting that conjugate diene **55** was more or less detected as a concomitant product during the reaction, particularly that which was isolated in 22% yield for entry 12 of Table 2.[1j,19] On the basis of previous literature on the gold(I)-catalyzed transformations, a plausible reaction mechanism as shown in Figure 5 was proposed to explain the generation of products **53**, **54**, and **55**.[1j,6a−6d,19] An initial complexation of the carbophilic Lewis acid cationic gold catalyst to the alkyne π-bond was followed by a stereoselective attack of the alkene functional group on the alkyne to then form a transient cyclopropylcarbene species **B**.[20,21] When nucleophiles such as AcOH were present, the proposed gold(I)-carbenoid intermediate **B** could be attacked on the cyclopropyl group to release vinylaurate intermediate **C**, which underwent a protodemetalation process to afford the corresponding acetoxycyclization product **53a** (Figure 5, path 1). If any nucleophile was absent in the reaction system, a skeletal rearrangement of intermediate **B** could allow the formation of carbocation **D**, which then underwent metal elimination to give diene **55** (Figure 5, path 2).

NHC-Au(I) Complex Catalyzed Asymmetric Oxidative Rearrangement of 1,6-Enynes. During screening different silver salts in Table 2, we found that using $AgClO_4$ (30 mol %) instead of $AgSbF_6$ (5 mol %) exceptionally afforded another main product, **56a**, as a single diastereoisomer in 32% yield and 47% ee, rather than acetoxycyclization product **53a** (Table 3, entry 1). Additionally, a similar result with 47% yield and 41% ee for aldehyde **56a** was also obtained in the presence of $AgClO_4$, without the addition of AcOH, after 12 h (Table 3, entry 2). Aldehyde **56a** was seemingly generated by an oxygenation

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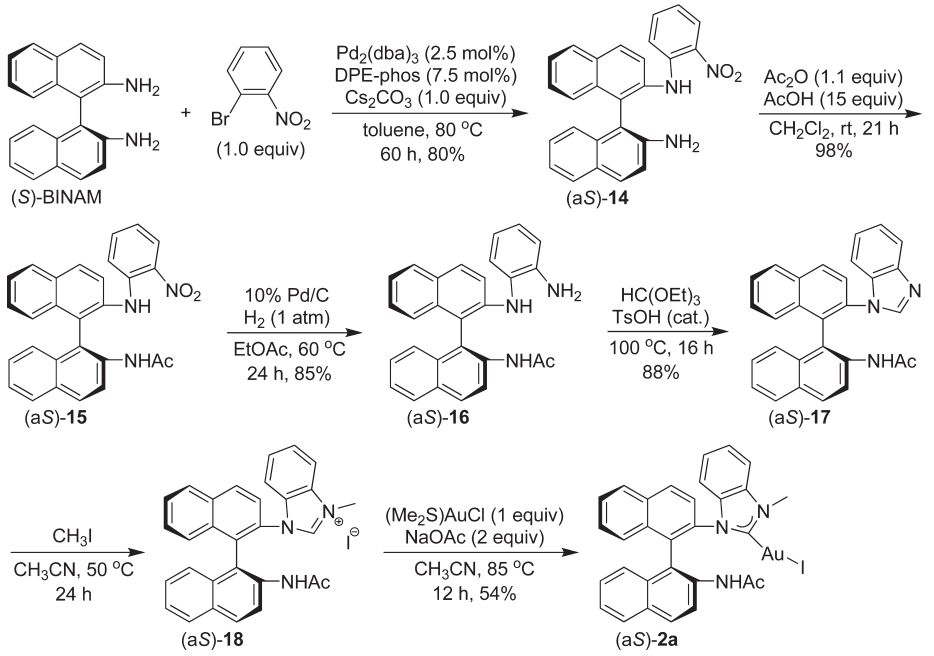
Scheme 2. Synthesis of NHC-Au(I) Complex (a*S*)-2a



process via the transfer of an oxygen atom from $AgClO_4$ to the gold(I)-carbenoid intermediate **B**, which was similar to the results reported by Toste et al., where an oxygen atom could transfer from various sulfoxides to the gold(I)-carbenoid intermediate.[20c]

Thus, we next attempted to use dimethylsulfoxide (2 equiv) as the oxidant in this reaction and found that the desired aldehyde **56a** was successfully obtained in 27% yield and 34% ee along with most of the unreacted starting material **52a** even after 6 days (Table 3, entry 3). Furthermore, replacing DMSO with diphenylsulfoxide could significantly improve the yield of aldehyde **56a** to >99% after only 8 h along with 43% ee (Table 3, entry 4). These preliminary experiments in Table 3 were in fact intercepting the proposed gold(I)-carbenoid intermediate **B** in the cycloisomerization of 1,6-enyne **52a** by using relevant oxidants (Figure 5, path 3).[20]

Reducing the employed amount of diphenylsulfoxide to 1.5 equiv did not significantly affect the reaction outcome because NHC-Au(I) complex (a*S*)-**2a** could still afford aldehyde **56a** in >99% yield and 43% ee after 2 h (Table 4, entry 2). Later on, various NHC-Au(I) complexes were investigated for this gold-(I)-catalyzed oxidative rearrangement of 1,6-enyne to seek out better catalytic activities and chiral inductions. For example, bis[NHC-Au(I)] complex (a*R*)-**1** could accomplish the transformation of **52a** efficiently, giving aldehyde **56a** in 91% yield and 29% ee within 3 h, although it had a different configuration of the chiral binaphthyl scaffold compared with (a*S*)-**2a** (Table 4, entry 1). While complex (a*S*)-**2b**, with the N-heterocycle substituted by a *N*-CH_2Ph moiety afforded **56a** in a similar yield (94%) but lower ee value (25%), the bulky amide substituents on the binaphthyl scaffold of NHC-Au(I) complexes were also detrimental to the enantioselectivities, and in some cases, the corresponding products were obtained with only 3% ee values despite being in high yields (Table 4, entries 3−7).

On the other hand, NHC-Au(I) complexes with various *N*(H)-alkyl substituents on the binaphthyl scaffold were also

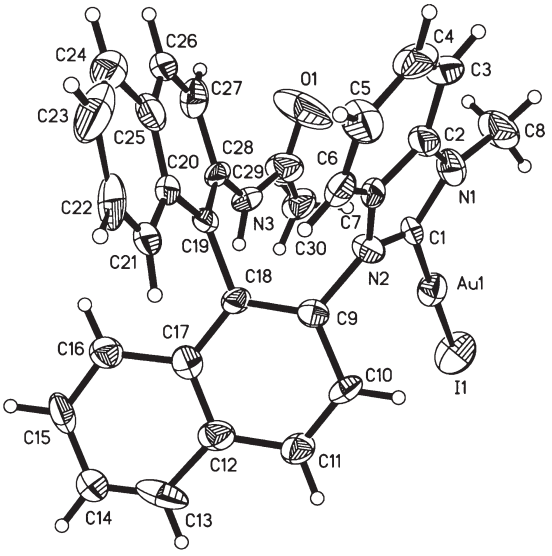


Figure 3. ORTEP drawing of NHC-Au(I) complex **2a** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): Au(1)−C(1) = 2.038(14), Au(1)−I(1) = 2.5005(14), C(1)−Au(1)−I(1) = 179.1(4), N(1)−C(1)−N(2) = 107.6(12).

tested during this transformation of 1,6-enyne **52a**. In contrast with the acetoxycyclization of **52a** (Table 2, entries 1 and 14), the results of >99% yields along with 36% ee and −32% ee obtained by using gold(I) complexes (a*S*)-**6** and (a*R*)-**6**, respectively, indicated that they were also effective catalysts in this reaction, but slightly less effective than gold(I) complex (a*S*)-**2a** (Table 4, entries 8 and 9). Furthermore, sterically less hindered *N*,*N*-dimethyl gold(I) complex (a*S*)-**7** was also effective herein, giving aldehyde **56a** in 97% yield and 44% ee, but complexes with sterically bulky substituents such as *N*(H)-benzyl (**8**) and

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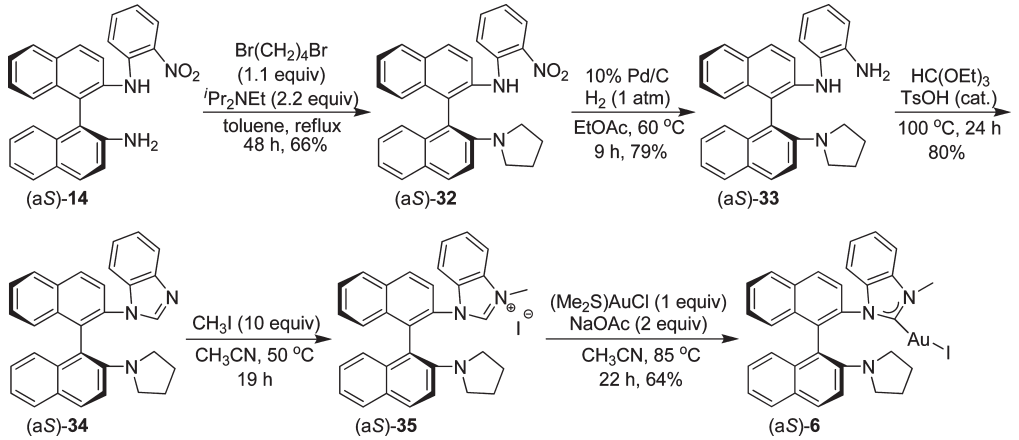
Scheme 3. Synthesis of NHC-Au(I) Complex (a*S*)-6



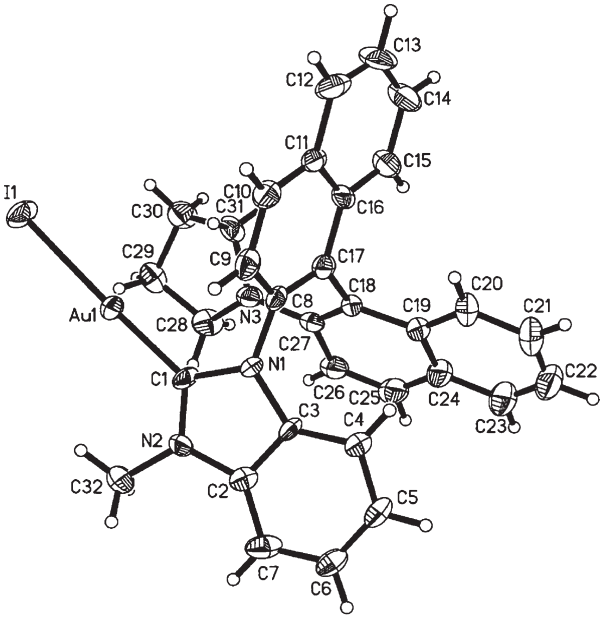
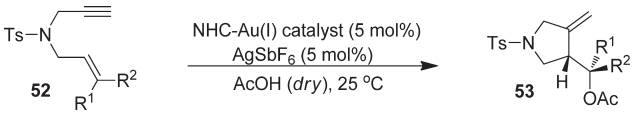


Figure 4. ORTEP drawing of NHC-Au(I) complex **6** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): Au(1)−C(1) = 1.988(6), Au(1)−I(1) = 2.5462(6), C(1)−Au(1)−I(1) = 177.1(3), N(1)−C(1)−N(2) = 106.2(5).

N,*N*-dibenzyl (**9**) both led to a significant decrease of enantioselectivities along with −12% ee and −4% ee, respectively (Table 4, entries 10−12). In addition, gold(I) complexes **10** and **11**, substituted with imine moieties, were successfully prepared, but unfortunately they all exhibited poor asymmetric induction abilities in this reaction under the standard conditions, affording aldehyde **56a** in −6% ee and −2% ee, respectively (Table 4, entries 13 and 14).

Under the standard conditions mentioned above and using gold(I) complex (a*S*)-**2a** as the best catalyst, the solvent effect was next investigated at room temperature. It was found that, besides DCE, toluene and CH_2Cl_2 were both suitable media in this reaction, affording product **56a** in excellent yields with 42% ee and 48% ee, respectively (Table 5, entries 1−3). However, coordinative solvents such as THF, DMF, and CH_3CN were

Table 1. Asymmetric Intramolecular Cyclization of 1,6-Enynes Catalyzed by NHC-Au(I) Complexes[a]



entry	substrate	catalyst	time (h)	yield (%)[b]	ee (%)[c]
1	**52a** (R^1 = Ph, R^2 = H)	(a*R*)-**1**	50	>99 (**53a**)	40
2	**52a** (R^1 = Ph, R^2 = H)	(a*S*)-**2a**	66	73 (**53a**)	35
3	**52b** (R^1 = R^2 = Me)	(a*R*)-**1**	50	74 (**53b**)	30
4	**52b** (R^1 = R^2 = Me)	(a*S*)-**2a**	50	66 (**53b**)	20

[a] Reaction conditions: 5 mol % of catalyst based on Au center; 5 mol % of $AgSbF_6$; 0.1 mmol of **52**; 1 mL of AcOH. [b] Isolated yields. [c] Determined by chiral HPLC using a Chiralpak AD-H column.

harmful to the catalytic activities of NHC-gold(I) complexes, presumably attributed to their coordination on the metal center of the gold(I) complex against the generation of free cationic NHC-Au^+ species (Table 5, entries 4−6). On the other hand, the reactions in EtOAc, CH_3NO_2, or acetone could proceed smoothly within a short reaction time, but providing the product **56a** in less than 24% ee (Table 5, entries 7−9). Notably, changing the solvent from CH_2Cl_2 to $CHCl_3$ allowed an increase of enantioselectivity from 48% ee to 55% ee despite a lower yield (80%) for the formation of **56a** (Table 5, entries 3 and 10). Furthermore, when PhCl was used as the solvent instead of toluene, it was found that aldehyde **56a** was obtained in 91% yield and 60% ee within 4 h, indicating a significant improvement for the asymmetric induction (Table 5, entries 2 and 11). However, 1,2-dichlorobenzene and PhF, which are more polar solvents than PhCl, did not bring about further increase of ee values for the formation of **56a** (Table 5, entries 12 and 13).

All of the above-mentioned results suggested that this NHC-Au(I) complex catalyzed transformation of 1,6-enyne was typically dependent upon the employed solvent with regard to the catalytic activity and selectivity. Later on, the influence of reaction temperature was also explored using PhCl as the solvent. Lowering the temperature would bring about a dramatic decrease

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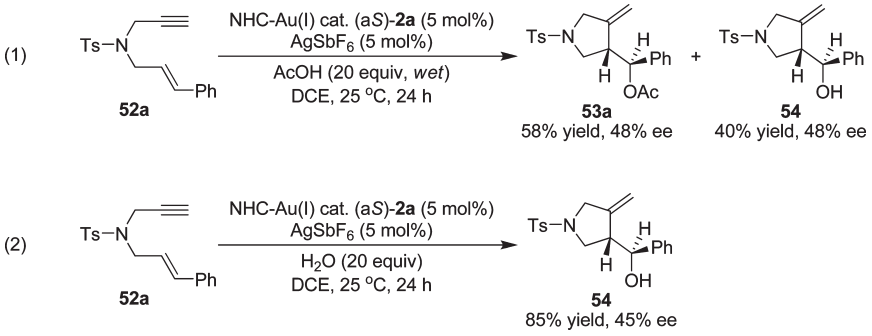
Scheme 4. Asymmetric Intramolecular Cyclization of 1,6-Enyne



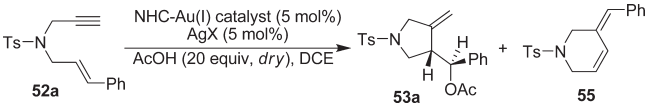
of the catalytic activity but have a minor effect on the enantioselectivity, such that product **56a** was obtained in >99% yield and 63% ee at 10 °C but in 25% yield and 66% ee within 90 h at 0 °C (Table 5, entries 14 and 15). Moreover, the addition of 4 Å MS allowed only a slight improvement of the results, in which **56a** was isolated in >99% yield and 65% ee at 10 °C (Table 5, entry 16).

In consideration of oxidants having some influence on this transformation (Table 3), other aryl sulfoxides were next synthesized and tested here to seek out better reaction outcomes (Figure 6).[20c] However, compared with the results using Ph_2SO as the oxidant at 10 °C, more sterically hindered sulfoxides **57b** and **57c** both slowed the reaction rate and gave the corresponding product in moderate asymmetric induction at 10 °C (Table 6, entries 1 and 2). However, when the reaction was carried out at 50 °C, the corresponding product **56a** was afforded in yields and enantioselectivities similar to those of **57a** (Table 6, entries 1 and 2).

Therefore, the optimized conditions were identified as using complex (a*S*)-**2a** and $AgSbF_6$ as the best catalyst system and Ph_2SO as the oxidant in a solvent of anhydrous PhCl at 10 °C with the addition of 4 Å MS (50 mg). Under these conditions, the substrate scope of 1,6-enynes was next investigated for their gold(I)-catalyzed oxidative rearrangements. The substrates with aryl substituents on the nonterminal alkenyl moiety were all tolerable in short times, such that mesityl **52c** was converted into **56c** in >99% yield and 58% ee, while naphthyl **52d** offered **56d** in >99% yield and 64% ee (Table 6, entries 3 and 4). On the other hand, the substituent on the nitrogen-tethered 1,6-enynes has significant influence on the enantioselectivities of the aldehyde products. For example, a 99% yield and the highest 70% ee were obtained for 4-bromobenzenesulfonyl product **56e** within 10 h, and 94% yield and 66% ee for 4-nitrobenzenesulfonyl product **56f** after 42 h (Table 6, entries 5 and 6). However, more sterically bulky and electron-rich substrate 2,4,6-triisopropylbenzenesulfonyl **52g** afforded the corresponding aldehyde **56g** only with 10.3% ee despite its >99% yield within 12.5 h (Table 6, entry 7). Similar results were delivered by the reaction of oxygen-tethered and sterically less hindered 1,6-enyne **52h**, giving the corresponding product **56h** in 86% yield with only 3.1% ee (Table 6, entry 8). All experiments mentioned above suggested that enantioselectivities for this oxidative rearrangement of 1,6-enynes were significantly dependent on the solvent as well as the substrate. On the other hand, as for substrate **52b** and other 1,6-enynes having a terminal alkenyl moiety or nonterminal alkynyl moiety, the reactions proceeded very sluggishly to afford the corresponding products in very poor yields.

In conclusion, we have developed a new class of gold(I) complexes **1**−**11** of axially chiral NHC ligands using optically active BINAM as the starting material. These NHC-Au(I) complexes have been conveniently isolated in satisfactory yields and fully characterized by NMR, ESI-MS, and IR spectroscopic data. Moreover, the structures of complexes **1**, **2a**, and **6** have been further determined by X-ray diffraction studies of single crystals, where they all exhibited a nearly linear coordination geometry around the gold(I) center.[11] The catalytic activity and chiral induction ability of these chiral NHC-Au(I) complexes were initially examined in the gold(I)-catalyzed asymmetric acetoxycyclization of 1,6-enynes. Within the carried out investigations herein, the sterically less hindered gold(I) complex

Table 2. NHC-Au(I) Complex Catalyzed Asymmetric Intramolecular Cyclization of 1,6-Enyne[a]



entry	catalyst	AgX	temperature (°C)	time (h)	yield (%)[b]	ee (%)[c]
1	(a*S*)-2a	$AgSbF_6$	25	24	93	43
2	none	$AgSbF_6$[d]	25	7 days	NR	–[e]
3	(a*S*)-**2a**	AgOTs	25	72	16	39
4	(a*S*)-**2a**	AgOTf	−20	75	73	42
5	(a*S*)-**2a**	$AgBF_4$	−20	75	73	29
6	(a*S*)-**2a**	$AgOC(O)CF_3$	25	6 days	trace	–[e]
7	(a*S*)-**2a**	$AgSbF_6$	0	24	83	50
8	(a*S*)-**2a**	$AgSbF_6$	−20	24	88	55
9	(a*R*)-**1**	$AgSbF_6$	25	36	80	25
10	(a*S*)-**2b**	$AgSbF_6$	25	12	76	21
11	(a*S*)-**3**	$AgSbF_6$	25	13	81	−1[f]
12	(a*S*)-**4**	$AgSbF_6$	25	36	60[g]	−2[f]
13	(a*S*,*S*)-5	$AgSbF_6$	25	9	84	−11[f]
14	(a*R*)-**6**	$AgSbF_6$	25	12	91	−53[f]
15	(a*R*)-**6**	$AgSbF_6$	−20	24	trace	–[e]
16	(a*R*)-**6**	$AgSbF_6$	0	24	>99	−59[f]

[a] Reaction conditions: 5 mol % of catalyst; 5 mol % of AgX; 0.1 mmol of **52a**; 1.0 mL of dry AcOH. [b] Isolated yields. [c] Determined by chiral HPLC using a Chiralpak AD-H column. [d] Only 20 mol % of $AgSbF_6$ was used. [e] Undetermined. [f] The negative sign of the ee value indicates an inversed absolute configuration compared with that of other entries. [g] Product **55** was also isolated in 22% yield.

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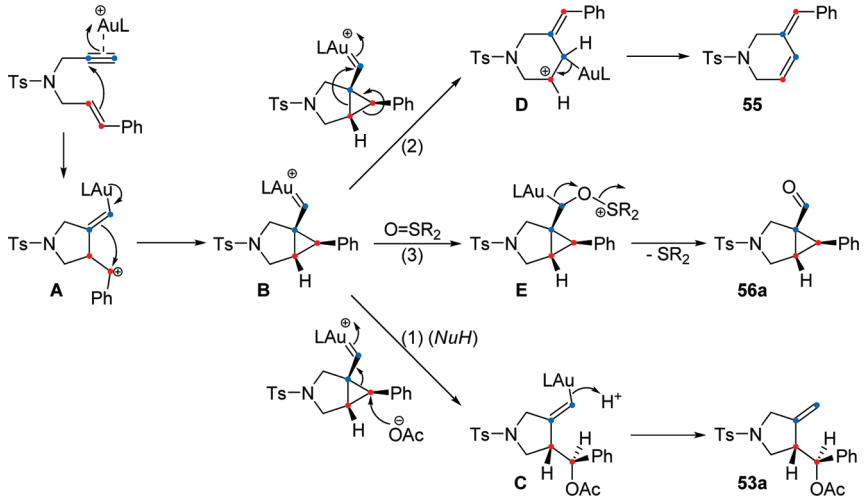


Figure 5. Proposed mechanism for the intramolecular rearrangements of 1,6-enyne.

(a*R*)-**6**, having a pyrrolidin-1-yl group, was realized to be the best catalyst in this reaction, giving product **53a** in >99% yield and −59% ee at 0 °C. On the basis of the understanding of a possible mechanism for gold(I)-catalyzed cycloisomerization of 1,6-enyne, we have in fact intercepted the proposed gold(I)-carbenoid intermediate **B** during the process by using $AgClO_4$ or sulfoxides as oxidants.[20] Furthermore, these axially chiral NHC-Au(I) complexes were successfully applied in the asymmetric oxidative rearrangement of 1,6-enynes, for the first time, to give the corresponding aldehyde products in good to high yields along with moderate ee values. Enantioselectivities for this transformation were significantly dependent on the solvent as well as substrate, where the reactions of 1,6-enynes **52a,c**−**h** all proceeded smoothly to give the corresponding aldehydes **56a,c**−**h** in excellent yields and 3.1−70% ee's using complex (a*S*)-**2a** as catalyst and PhCl as the solvent. To the best of our knowledge, the enantioselectivity of up to 70% ee was by far the best result for NHC-Au(I) complex catalyzed transformations.[3,6g,10] Although there are still many deficiencies, such as a limited scope of substrates, the work presented in this paper is beneficial to the future development of designing much more efficient chiral NHC-gold(I) complexes and exploring their asymmetric catalysis.[7] This work as well as detailed mechanistic investigations are currently underway in our laboratories to obtain more perspective results for gold(I)-catalyzed asymmetric cycloisomerization of 1,6-enynes and their potential utilization.

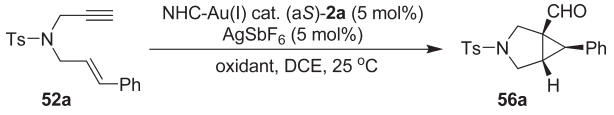
EXPERIMENTAL SECTION

Synthesis of NHC-Au(I) Complexes 1−11. As a representative complex, axially chiral NHC-Au(I) complex **2a** was synthesized via the following procedure from imidazolium salt **18**. Under an argon atmosphere, to a flame-dried Schlenk tube equipped with a septum and stirring bar were added NHC precursor **18** (57 mg, 0.1 mmol), NaOAc (17 mg, 0.2 mmol), and [(Me_2S)AuCl] (30 mg, 0.1 mmol) followed by the addition of dry CH_3CN (5.0 mL) as the solvent. After refluxing at 85 °C for about 12 h, the reaction mixture was cooled to room temperature and filtered through Celite. Then volatiles were removed under reduced pressure, and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 2.5:1) to give complex **2a** as a white solid in 54% yield. Single crystals of **2a** suitable for an X-ray diffraction study were grown from a solution of **2a** in mixed ethyl ether/CH_2Cl_2 (1:1). White solid: mp 259.5−260.6 °C (dec); $[\alpha]^{20}_D$ −52 (*c* 0.25, $CHCl_3$); IR (direct irradiation) ν 3324, 1702, 1507, 1482, 1465, 1391, 1354, 1306, 1245, 1150, 1133, 1013, 863, 828, 808, 763, 750, 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 2.07 (s, 3H), 3.94 (s, 3H), 6.82 (t, J = 8.0 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 7.12−7.22 (m, 5H), 7.25−7.29 (m, 1H), 7.39−7.46 (m, 2H), 7.64−7.69 (m, 3H), 7.80 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.8 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.25 (d, J = 9.2 Hz, 1H); LRMS (ESI) m/e 638.1 [M^+ − I]; HRMS (ESI) calcd for [$C_{30}H_{23}N_3IAu$ − I] requires 638.1507, found 638.1484 [M^+ − I].

The NHC-Au(I) complexes **1**, **2b**, and **3**−**11** were also successfully obtained from their corresponding imidazolium salts according to modified procedures, similar to that of complex **2a**.

Complex (a*R*)-**1**: white solid; mp 300.4−301.5 °C (dec); $[\alpha]^{20}_D$ +24 (*c* 0.25, $CHCl_3$); IR (direct irradiation) ν 3058, 2923, 2852, 1592, 1462, 1436, 1391, 1360, 1261, 1241, 1133, 1099, 1063, 1014, 862, 828, 806, 763, 738, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 4.24 (s, 6H), 6.54 (t, J = 8.0 Hz, 2H), 6.60 (d, J = 8.4 Hz, 2H), 7.14 (t, J = 7.6 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.55−7.70 (m, 8H), 7.95 (d, J = 9.2 Hz, 2H), 7.99 (d, J = 8.4 Hz, 2H); LRMS (ESI) m/e 1035.1 [M^+ − I]; HRMS (ESI) calcd for [$C_{36}H_{26}N_4I_2Au_2$ − I] requires 1035.0533, found 1035.0527 [M^+ − I].

Table 3. Asymmetric Oxidative Rearrangement of 1,6-Enyne 52a[a]



entry	oxidant	time (h)	yield (%)[b]	ee (%)[c]
1[d]	$AgClO_4$ (30 mol %)/AcOH (20 equiv)	72	32	47
2[d]	$AgClO_4$ (1 equiv)	12	47	41
3	Me_2SO (2 equiv)	6 days	27	34
4	Ph_2SO (2 equiv)	8	>99	43

[a] Reaction conditions: 5 mol % of (a*S*)-**2a**; 5 mol % of $AgSbF_e$; 0.1 mmol of **52a**; oxidant; 1.0 mL of DCE. [b] Isoated yields. [c] Determined by chiral HPLC using a Chiralpak AD-H column. [d] Without the addition of $AgSbF_e$ (5 mol %).

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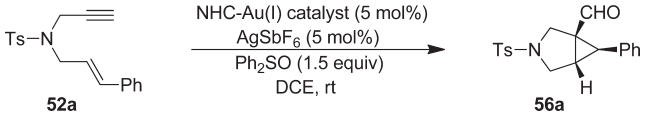
Table 4. NHC-Au(I) Complex Catalyzed Asymmetric Oxidative Rearrangement of 1,6-Enyne 52a[a]



entry	catalyst	time (h)	yield (%)[b]	ee (%)[c]
1	(a*R*)-**1**	3	91	29
2	(a*S*)-**2a**	2	>99	43
3	(a*S*)-**2b**	3	94	25
4	(a*S*)-**3**	3	>99	−3[d]
5	(a*S*)-**4**	5	>99	7
6	(a*S*,*S*)-**5**	4	99	−3[d]
7	(a*S*,*R*)-**5**	6	99	9
8	(a*S*)-**6**	3	>99	36
9	(a*R*)-**6**	3	>99	−32[d]
10	(a*S*)-**7**	4	97	44
11	(a*S*)-**8**	7	91	−12[d]
12	(a*S*)-**9**	4	94	−4[d]
13	(a*S*)-**10**	7	94	−6[d]
14	(a*S*)-**11**	6	>99	−2[d]

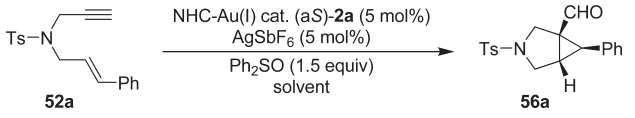
[a] Reaction conditions: 5 mol % of catalyst; 5 mol % of $AgSbF_6$; 0.1 mmol of **52a**; 1.5 equiv of Ph_2SO; 1 mL of DCE. [b] Isolated yields. [c] Determined by chiral HPLC using a Chiralpak AD-H column. [d] The negative sign of ee indicates an inversed absolute configuration compared with that of other entries.

Complex (a*S*)-**2b**: white solid; mp 291.9−293.0 °C (dec); $[\alpha]^{20}_D$ −31 (*c* 0.25, $CHCl_3$); IR (direct irradiation) ν 3428, 2923, 2853, 1701, 1618, 1595, 1568, 1495, 1423, 1402, 1346, 1306, 1278, 1252, 1223, 1192, 1013, 839, 823, 755, 731, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.99 (s, 3H), 5.37 (d, J = 15.6 Hz, 1H), 5.84 (d, J = 15.6 Hz, 1H), 6.82−6.84 (m, 2H), 6.89 (t, J = 7.2 Hz, 1H), 6.95−7.09 (m, 5H), 7.19 (t, J = 7.2 Hz, 1H), 7.28−7.29 (m, 4H), 7.48−7.49 (m, 2H), 7.66 (d, J = 8.4 Hz, 1H), 7.68−7.72 (m, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 8.10 (d, J = 8.8 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 8.29 (d, J = 8.4 Hz, 1H); LRMS (ESI) *m*/*e* 714.2 $[M^+ - I]$; HRMS (ESI) calcd for $[C_{36}H_{27}N_3IOAu - I]$ requires 714.1820, found 714.1821 $[M^+ - I]$.

Complex (a*S*)-**3**: white solid; mp 141.5−142.9 °C (dec); $[\alpha]^{20}_D$ −149 (*c* 0.25, $CHCl_3$); IR (direct irradiation) ν 3419, 3057, 2924, 2852, 1682, 1596, 1501, 1487, 1466, 1427, 1391, 1346, 1277, 1238, 1099, 1024, 860, 820, 744, 706 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 3.77 (s, 3H), 6.79 (d, J = 8.4 Hz, 1H), 7.02 (t, J = 7.2 Hz, 1H), 7.14 (d, J = 8.0 Hz, 1H), 7.20−7.30 (m, 5H), 7.36 (t, J = 7.2 Hz, 1H), 7.43−7.47 (m, 2H), 7.56−7.66 (m, 3H), 7.72 (d, J = 9.2 Hz, 2H), 7.76−7.81 (m, 3H), 8.21 (d, J = 8.4 Hz, 1H), 8.28 (d, J = 8.8 Hz, 1H), 8.40 (d, J = 9.2 Hz, 1H); LRMS (ESI) *m*/*e* 700.2 $[M^+ - I]$; HRMS (ESI) calcd for $[C_{35}H_{25}N_3IOAu - I]$ requires 700.1663, found 700.1661 $[M^+ - I]$.

Complex (a*S*)-**4**: white solid; mp 153.4−154.5 °C (dec); $[\alpha]^{20}_D$ −9.0 (*c* 0.25, $CHCl_3$); IR (direct irradiation) ν 3420, 2973, 2925, 1715, 1599, 1502, 1455, 1427, 1391, 1367, 1346, 1270, 1232, 1153, 1083, 1059, 871, 820, 804, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.53 (s, 9H), 3.99 (s, 3H), 6.27 (s, 1H), 6.56−6.61 (m, 2H), 7.04−7.10 (m, 2H), 7.19−7.23 (m, 2H), 7.29−7.32 (m, 1H), 7.37−7.45 (m, 2H), 7.59 (d, J = 8.8 Hz, 1H), 7.65−7.69 (m, 2H), 7.92 (d, J = 8.8 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 8.25 (d, J = 8.4 Hz, 1H); LRMS (ESI) *m*/*e* 696.2 $[M^+ - I]$; HRMS (ESI) calcd for $[C_{33}H_{29}N_3IO_2Au - I]$ requires 696.1925, found 696.1937 $[M^+ - I]$.

Table 5. Optimization for Asymmetric Oxidative Rearrangement of 1,6-Enyne 52a Catalyzed by (a*S*)-2a[a]



entry	solvent	temperature	time (h)	yield (%)[b]	ee (%)[c]
1	DCE	rt	2	>99	43
2	toluene	rt	5	94	42
3	CH_2Cl_2	rt	6	97	48
4	THF	rt	12 days	30[d]	20
5	DMF	rt	7 days	NR[d]	—[e]
6	CH_3CN	rt	7 days	64[d]	5
7	EtOAc	rt	5.5	89	24
8	CH_3NO_2	rt	3	91	11
9	acetone	rt	4	41	6
10	$CHCl_3$	rt	4	80	55
11	PhCI	rt	4	91	60
12	1,2-Cl,Cl-Ph	rt	3	>99	57
13	PhF	rt	3	94	56
14	PhCl	0 °C	90	25[d]	66
15	PhCl	10 °C	12	>99	63
16[f]	PhCl	10 °C	12	>99	65

[a] Reaction conditions: 5 mol % of (a*S*)-**2a;** 5 mol % of $AgSbF_6$; 0.1 mmol of **52a;** 1.5 equiv of Ph_2SO; 1 mL of solvent. [b] Isolated yields. [c] Determined by chiral HPLC using a Chiralpak AD-H column. [d] Determined by ^1H NMR integration of the crude product. [e] Undetermined. [f] 50 mg of 4 Å MS was used as additive.

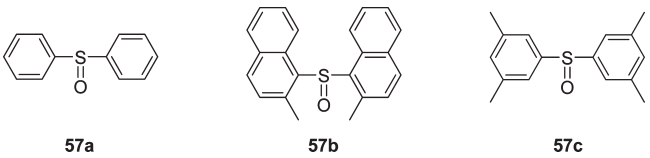
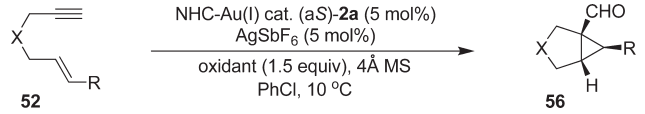


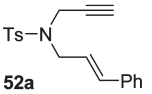
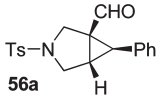
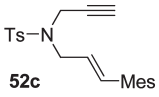
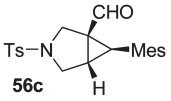
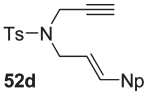
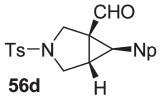
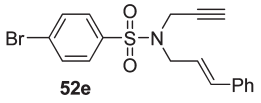
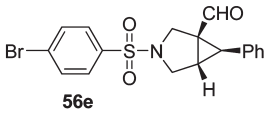
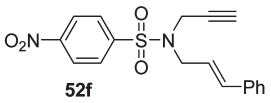
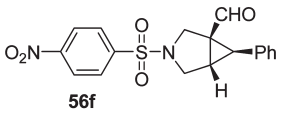
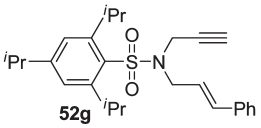
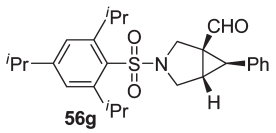
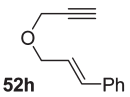
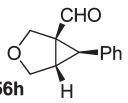
Figure 6. Aryl sulfoxides as the oxidants.

Complex (a*S*,*S*)-**5**: white solid; mp 224.9−225.8 °C (dec); $[\alpha]^{20}_D$ −102 (*c* 0.25, $CHCl_3$); IR (direct irradiation) ν 3360, 2924, 2853, 1691, 1596, 1501, 1467, 1451, 1425, 1391, 1362, 1305, 1274, 1254, 1156, 1114, 1089, 873, 831, 817, 745 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.20 (s, 9H), 1.62−2.10 (m, 6H), 2.86 (s, 1H), 3.77 (s, 3H), 4.31 (br, 1H), 7.10−7.13 (m, 1H), 7.21−7.32 (m, 3H), 7.38 (t, J = 7.6 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.50−7.54 (m, 1H), 7.59 (t, J = 7.2 Hz, 2H), 7.63 (d, J = 9.2 Hz, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 8.08 (s, 1H), 8.20 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 9.2 Hz, 1H), 8.53 (s, 1H); LRMS (ESI) *m*/*e* 793.2 $[M^+ - I]$; HRMS (ESI) calcd for $[C_{38}H_{36}N_4IO_3Au - I]$ requires 793.2453, found 793.2471 $[M^+ - I]$.

Complex (a*S*)-**6**: white solid; mp 286.0−287.5 °C (dec); $[\alpha]^{20}_D$ +172 (*c* 0.25, $CHCl_3$); IR (direct irradiation) ν 3061, 3035, 2957, 2922, 2899, 2853, 2831, 1614, 1595, 1504, 1468, 1440, 1426, 1393, 1377, 1345, 1244, 1150, 1133, 1010, 856, 822, 810, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.80−1.83 (m, 2H), 1.95−2.01 (m, 2H), 2.61 (t, J = 8.0 Hz, 2H), 2.99−3.05 (m, 2H), 4.06 (s, 3H), 6.19 (d, J = 8.4 Hz, 1H), 6.36 (t, J = 8.0 Hz, 1H), 6.71 (d, J = 8.8 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H), 7.12−7.17 (m, 3H), 7.19−7.23 (m, 1H), 7.27 (d, J = 9.2 Hz, 1H), 7.47−7.53 (m, 2H), 7.63−7.67 (m, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.92

Table 6. Asymmetric Oxidative Rearrangement of 1,6-Enynes Catalyzed by (aS)-2a[a,bcde]



entry	substrate	oxidant	time (h)	product	yield (%)[b]	ee (%)[c]
1	 **52a**	**57b**	168 (20)[d]	 **56a**	85 (94)[d]	61 (62)[d]
2		**57c**	168 (16)[d]		56 (> 99)[d]	64 (60)[d]
3	 **52c**	**57a**	12.5	 **56c**	> 99	58
4	 **52d**	**57a**	11	 **56d**	> 99	64
5	 **52e**	**57a**	10	 **56e**	99	70
6	 **52f**	**57a**	42	 **56f**	94	66[e]
7	 **52g**	**57a**	12.5	 **56g**	> 99	10.3
8	 **52h**	**57a**	29	 **56h**	86	3.1

[a] Reaction conditions: 5 mol % of (aS)-**2a**; 5 mol % of $AgSbF_6$; 0.1 mmol of **52**; 1.5 equiv of oxidant; 50 mg of 4 Å molecular sieves; 1 mL of dry PhCl at 10 °C. [b] Isolated yields. [c] Determined by chiral HPLC using a Chiralpak AD-H column. [d] The value in parentheses was that at 50 °C instead. [e] Determined by a chiral HPLC analysis of the alcohol derivative of product **56f**.

(d, J = 8.4 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 8.12 (d, J = 8.8 Hz, 1H); LRMS (ESI) m/e 650.2 [M^+ − I]; HRMS (ESI) calcd for [$C_{32}H_{27}N_3IAu$ − I] requires 650.1870, found 650.1880 [M^+ − I]. Anal. Calcd for $C_{32}H_{27}AuIN_3$: C 49.44, H 3.50, N 5.40. Found: C 49.24, H 3.69, N 5.25.

Complex (aS)-**7**: white solid; mp 259.0−260.7 °C (dec); $[\alpha]^{20}_D$ +48 (c 0.25, $CHCl_3$); IR (direct irradiation) ν 3061, 2923, 2899, 2852, 2776, 1712, 1593, 1505, 1464, 1397, 1360, 1245, 1126, 1097, 1081, 977, 859, 819, 804, 743, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 2.46 (s, 6H), 4.07 (s, 3H), 6.33 (d, J = 8.0 Hz, 1H), 6.41 (t, J = 7.2 Hz, 1H), 6.89 (d, J = 8.8 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H), 7.16−7.27 (m, 4H), 7.42−7.45 (m, 2H), 7.58−7.65 (m, 3H), 7.85 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 7.6 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H); LRMS (ESI) m/e 624.2 [M^+ − I]; HRMS (ESI) calcd for [$C_{30}H_{25}N_3IAu$ − I] requires 624.1714, found 624.1696 [M^+ − I].

Complex (aS)-**8**: pale yellow solid; mp 198.3−199.8 °C (dec); $[\alpha]^{20}_D$ +20 (c 0.25, $CHCl_3$); IR (direct irradiation) ν 3399, 2955, 2922, 2852, 1710, 1617, 1598, 1494, 1454, 1392, 1343, 1295, 1240, 1081, 827, 808, 740, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 3.95 (s, 3H), 4.38 (dd, J = 6.0, 16.0 Hz, 1H), 4.56 (t, J = 5.6 Hz, 1H), 4.62 (dd, J = 5.6, 16.0 Hz, 1H), 6.76 (d, J = 8.8 Hz, 1H), 6.85 (t, J = 7.6 Hz, 1H), 6.99 (d, J = 8.4 Hz, 1H), 7.02−7.05 (m, 4H), 7.08−7.17 (m, 5H), 7.23 (d, J = 8.4 Hz, 1H), 7.42−7.45 (m, 3H), 7.49 (d, J = 8.0 Hz, 1H), 7.67 (ddd, J = 2.8, 5.6, 8.0 Hz, 1H), 7.71 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 8.4 Hz, 1H); LRMS (ESI) m/e 686.2 [M^+ − I]; HRMS (ESI) calcd for [$C_{35}H_{27}N_3IAu$ − I] requires 686.1870, found 686.1844 [M^+ − I].

Complex (aS)-**9**: white solid; mp 240.8−241.8 °C (dec); $[\alpha]^{20}_D$ +51 (c 0.25, $CHCl_3$); IR (direct irradiation) ν 3059, 3023, 2923, 2852, 2814, 1618, 1596, 1505, 1450, 1392, 1353, 1216, 1150, 1124, 1098, 1070, 971, 942, 824, 807, 738, 699, 684 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 3.75 (s, 3H), 4.32 (s, 4H), 6.58 (d, J = 7.2 Hz, 4H), 6.67 (t, J = 8.4 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 6.82 (d, J = 9.2 Hz, 1H), 6.89 (t, J = 7.2 Hz, 4H), 7.00 (t, J = 7.2 Hz, 2H), 7.15−7.20 (m, 2H), 7.25−7.34 (m, 5H), 7.42 (d, J = 9.2 Hz, 1H), 7.51 (t, J = 7.2 Hz, 1H), 7.65−7.67 (m, 1H), 7.74 (d, J = 8.8 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 8.14 (d, J = 8.8 Hz, 1H); LRMS (ESI) m/e 776.2 [M^+ − I]; HRMS (ESI) calcd for [$C_{42}H_{33}N_3IAu$ − I] requires 776.2340, found 776.2352 [M^+ − I].

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Complex (a*S*)-**10**: yellow solid; mp 150.0−151.2 °C (dec); $[\alpha]^{20}_{D}$ −49 (*c* 0.25, $CHCl_3$); IR (direct irradiation) ν 3055, 2921, 2851, 2814, 1710, 1606, 1571, 1493, 1461, 1390, 1279, 1239, 1203, 1188, 1151, 1081, 964, 903, 859, 818, 744, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 3.76 (s, 3H), 6.68 (ddd, *J* = 2.8, 6.0, 8.4 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.90 (dt, *J* = 1.2, 8.0 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 7.16−7.17 (m, 2H), 7.25−7.40 (m, 5H), 7.43−7.47 (m, 1H), 7.55 (dt, *J* = 1.2, 8.0 Hz, 1H), 7.59−7.65 (m, 2H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 8.48 (s, 1H), 11.82 (s, 1H); LRMS (ESI) *m*/*e* 700.2 $[M^+ - I]$; HRMS (ESI) calcd for $[C_{35}H_{25}N_3IOAu - I]$ requires 700.1663, found 700.1666 $[M^+ - I]$.

Complex (a*S*)-**11**: pale yellow solid; mp 133.0−134.5 °C (dec); $[\alpha]^{20}_{D}$ −42 (*c* 0.25, $CHCl_3$); IR (direct irradiation) ν 3055, 2923, 2853, 1700, 1611, 1576, 1505, 1458, 1390, 1308, 1241, 1202, 1098, 964, 870, 815, 742, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 3.80 (s, 3H), 6.86 (ddd, *J* = 1.6, 6.0, 7.6 Hz, 1H), 7.15−7.26 (m, 4H), 7.29−7.34 (m, 3H), 7.36−7.41 (m, 2H), 7.46−7.55 (m, 4H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 8.39 (s, 1H); LRMS (ESI) *m*/*e* 684.2 $[M^+ - I]$; HRMS (ESI) calcd for $[C_{35}H_{25}N_3IAu - I]$ requires 684.1714, found 684.1713 $[M^+ - I]$.

General Procedure for NHC-Au(I) Complex Catalyzed Asymmetric Acetoxycyclization of 1,6-Enynes. A typical procedure is given below for the reactions shown in Table 2. To a solution of NHC-Au(I) complex (5 mol %), 1,6-enyne **52a** (33 mg, 0.1 mmol), and AgX (0.005 mmol) in dry DCE (1.0 mL) was added dry acetic acid (115 μL, 2.0 mmol) as the nucleophile under an argon atmosphere. The mixture was stirred at the proper temperature until **52a** was completely consumed by TLC monitoring. Then the reaction was quenched by filtering through Celite with a thin pad of silica gel, and volatiles were removed under reduced pressure. The residue was purified by silica gel flash column chromatography to give **53a** (eluent: petroleum ether/EtOAc, 8:1) as a white solid.

General Procedure for NHC-Au(I) Complex Catalyzed Enantioselective Oxidative Rearrangement of 1,6-Enynes. Under an argon atmosphere, to a flame-dried Schlenk tube equipped with a septum and stirring bar were added activated 4 Å MS (50 mg), NHC-Au(I) complex (5 mol %), 1,6-enyne **52** (0.1 mmol), Ph_2SO (30 mg, 0.15 mmol), and $AgSbF_6$ (2 mg, 0.005 mmol) followed by the injection of the corresponding dry solvent (1.0 mL). The mixture was stirred at the proper temperature until complete consumption of **52** by TLC monitoring before quenching by filtering with a thin pad of silica gel. Then volatiles were removed under reduced pressure, and the residue was purified by silica gel flash column chromatography to give the oxidative product **56**.

■ ASSOCIATED CONTENT

Supporting Information. Detailed descriptions of experimental procedures, spectral and analytical data for all new compounds shown in schemes, figures, and tables, CIF files and X-ray crystal data for **1**, **2a**, and **6**, and chiral HPLC traces of compounds **53**, **54**, and **56**. This material is available free of charge from the authors or via the Internet at http://pubs.acs.org.

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(13) The crystal data of **1** have been deposited with the CCDC with number 759948. Empirical formula: $C_{40}H_{32}Au_2I_2N_6$; formula weight: 1244.45; crystal color, habit: colorless, prismatic; crystal dimensions: 0.301 × 0.217 × 0.24 mm; crystal system: triclinic; lattice type: primitive; lattice parameters: a = 9.3794(9) Å, b = 10.4523(10) Å, c = 20.784(2) Å, α = 85.843(2)°, β = 77.783(2)°, γ = 80.838(2)°, V = 1964.5(3) Å^3; space group: $P\bar{1}$; Z = 2; D_{calc} = 2.104 g/cm^3; F_{000} = 1156; diffractometer: Bruker Smart CCD; residuals: R; R_w: 0.0448, 0.1129.

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(15) The crystal data of **2a** have been deposited with the CCDC with number 757529. Empirical formula: $C_{32}H_{27}AuCl_4IN_3O$; formula weight: 935.23; crystal color, habit: colorless, prismatic; crystal dimensions: 0.303 × 0.122 × 0.105 mm; crystal system: orthorhombic; lattice type: primitive; lattice parameters: a = 7.6150(13) Å, b = 14.252(2) Å, c = 30.775(5) Å, α = 90°, β = 90°, γ = 90°, V = 3340.1(10) Å^3; space group: $P2(1)2(1)2(1)$; Z = 4; D_{calc} = 1.860 g/cm^3; F_{000} = 1792; diffractometer: Bruker Smart CCD; residuals: R; R_w: 0.0635, 0.1464.

(16) The crystal data of **6** have been deposited with the CCDC with number 790740. Empirical formula: $C_{32}H_{27}AuIN_3$; formula weight: 777.43; crystal color, habit: colorless; crystal dimensions: 0.350 × 0.280 × 0.221 mm; crystal system: monoclinic; lattice parameters: a = 12.8532(14) Å, b = 7.4498(8) Å, c = 14.7707(17) Å, α = 90°, β = 90.459(2)°, γ = 90°, V = 1414.3(3) Å^3; space group: $P2(1)$; Z = 2; D_{calc} = 1.826 g/cm^3; F_{000} = 744; diffractometer: Bruker Smart CCD; residuals: R; R_w: 0.0406, 0.0790.

(17) The absolute stereochemistries of **53a** and **53b** were assigned by analogy to compound **54** followed by comparison of the sign of optical rotation of **54** with that in the literature: Charruault, L.; Michelet, V.; Taras, R.; Gladiali, S.; Genet, J. P. *Chem. Commun.* **2004**, 850–851.

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