Unprecedented C,O-Chelated BINOL-Gold(III) Complexes: Synthesis and Catalysis with Tunable Product Profiles

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Abstract: *Unprecedented stable BINOL-gold(III) complexes adopting a novel C,O-chelation mode were synthesized via a modular approach by combination of 1,1'-binaphthalene-2,2'-diols (BINOLs) and cyclometallated gold(III) dichloride complexes [(C^N)AuCl$_2$]. X-ray crystallographic analysis revealed that the bidentate BINOL ligands tautomerized and bonded to the Au^{III} atom via C,O-chelation to form a five-membered ring instead of conventional O,O'-chelation giving a seven-membered ring. These gold(III) complexes were able to catalyze acetalization/cycloisomerization and carboalkoxylation of ortho-alkynylbenzaldehydes with trialkyl orthoformates.*

Gold catalysis has contributed to a diversity of novel organic transformation reactions streamlining organic synthesis with excellent atom-economy and operational simplicity owing to its superior reactivity, excellent selectivity and high functional group tolerance.[1] Meticulous choices of ligands in gold catalysis is of significance to prevent the decomposition of simple gold salts in catalytic cycles and fine-tune the catalytic activity and product enantioselectivity.[1i, 2] In particular, a variety of phosphine-gold(I) and *N*-heterocyclic carbene-gold(I) complexes have been developed as efficient catalysts for novel synthetic transformations. However, gold(I) complexes have two coordination sites with a linear geometry leading to a great challenge to arrange ligands around the gold(I) center for tuning catalytic activity and introducing chiral environment.[1e, 1i, 2a]

Gold(III) complexes have a square planar geometry with four coordination sites, allowing easy fine-tuning through diverse ligand design in a modular approach. However, the development of gold(III) complexes for catalysis remains largely unexplored due to difficult access to the high oxidation state under mild reaction conditions and a lack of suitable non-redox ligands.[3] The great challenge in synthesizing stable gold(III) complexes comes from the facile reduction of gold(III) complexes to gold(I) or gold(0) species.[4] For example, electron-rich tertiary phosphine and amine ligands[3h] are not compatible with gold(III) ion owing to the possible gold(III) reduction. Thus, neutral or electron-deficient nitrogen-containing compounds, such as pyridines,[3a, 3b, 3f] Schiff bases,[3c], *N*-heterocyclic carbenes,[5] and triazole derivatives[3g, 3h] have been used as ligands for gold(III) complexes (Figure 1, a). In principle, the stability of gold(III) ions significantly increases upon complexation with ligands. However, stable gold(III) complexes generally exhibit poor catalytic activity. Thus, a significant challenge in the successful development of gold(III) complexes as efficient catalysts is to strike a balance between stability and catalytic activity.[5-6]

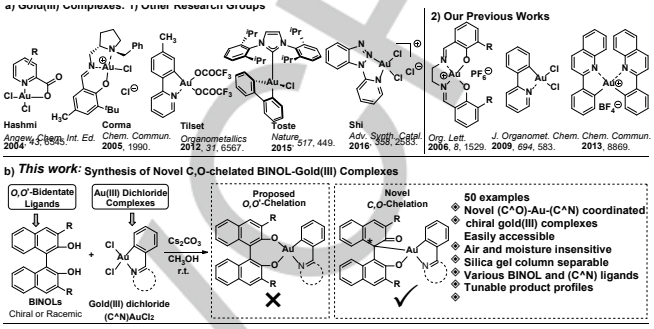

Figure 1. a) Gold(III) complexes previously reported by other research groups and our group; b) Synthesis of unprecedented stable BINOL-gold(III) complexes adopting a novel C,O-chelation mode.

Over the years, we have been developing gold(III) complexes, including Salen-based gold(III) complexes[7] and cyclometallated gold(III) dichloride complexes [(C^N)AuCl$_2$, C^N = 2-arylpyridyl],[8] as efficient catalysts for organic synthesis. In addition, we reported that bis-cyclometallated gold(III) complex [(C^N)$_2$AuBF$_4$] is able to enhance the stability of Au(III) cation with good catalytic activity.[6] To further explore the potential of gold(III) catalysis, it is important to develop easily assessable, stable, and tunable gold(III) complexes.

1,1'-Binaphthalene-2,2'-diols (BINOLs), which are readily bound to transition metals through both oxygen atoms to form a seven-membered ring[9], are privileged ligands in asymmetric transition metal catalysis.[10] The reported stabilization of cationic gold(III) complexes by catechol derivatives inspired us to examine BINOLs as the supporting ligands.[11] The two consecutive O-anionic centers on the BINOL ligands were able to donate sufficient electron density to stabilize a highly electrophilic Au^{III} center. However, such phenolate ligands are strong reductants, and even the preparation of gold(I) phenolate complexes was highly challenging and the compounds were very sensitive.[12] To fully utilize the four coordination sites of gold(III) complexes, we hypothesized that incorporating a BINOL ligand into a cyclometallated Au(III) dichloride complex [(C^N)AuCl$_2$] *via* O,O'-chelation with the Au^{III} center by replacing the two chloride atoms would give a stable, neutral, and tetracoordinated gold(III) complex while maintaining tunable catalytic activity in organic synthesis. *To our surprise, unprecedented gold(III) complexes in which the BINOL moiety adopted an unusual C,O-chelation mode with the Au^{III} center were obtained instead of the expected O,O'-chelation (Figure 1, b).*

Initially, an oxazoline-based gold(III) dichloride complex **S1** was prepared by literature method.[13] Treatment of **S1** with commercially available (*S*)-BINOL in the presence of Cs_2CO_3 in methanol at room temperature afforded an orange red solid (*R*)-**1** in 85% yield (Scheme 1, a), which was characterized by ^{1}H NMR, ^{13}C NMR, and high resolution ESI-MS. However, the unsymmetrical proton signal in the ^{1}H NMR spectra and the carbonyl signal (~ 200 ppm) appearing in the ^{13}C NMR spectra indicated that the structure of this Au(III) complex is not the proposed O,O'-chelated Au(III) complex. Notably, X-ray crystallographic analysis revealed that the structure of (*R*)-**1**[14] in which the BINOL moiety adopted an unprecedented C,O-chelation mode with the Au^{III} center (Scheme 1, a).[15] The O,O'-bidentate (*S*)-BINOL ligand tautomerized and bonded to the Au atom *via* C,O-

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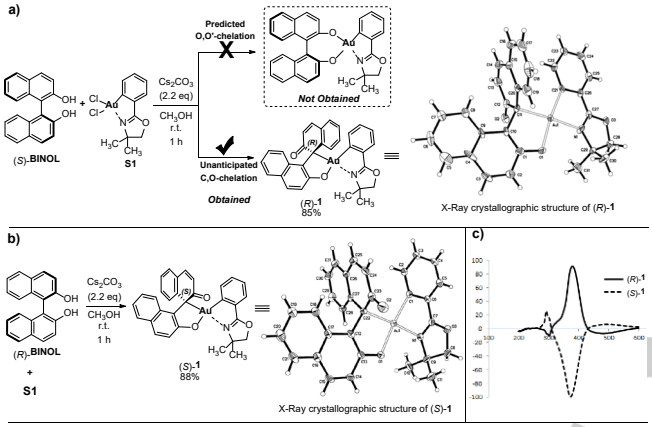
chelation to form a five-membered ring instead of O,O'-chelation giving a seven-membered ring. The crystal structure reveals that the gold(III) atom in (*R*)-**1** adopts a square planar geometry surrounded by *cis*-oxygen-nitrogen and *cis*-carbon-carbon atoms. Complex (*R*)-**1** was light, air, and moisture insensitive that could be isolated and stored at ambient conditions and was found to be stable upon exposure to air for months. Remarkably, an axial-to-central chirality transfer occurred during the complex formation between (*S*)-BINOL and [(C^N)AuCl$_2$]; the (*S*)-BINOL exclusively afforded the gold(III) complex (*R*)-**1** with the quaternary stereogenic carbon center in *R* configuration. Moreover, **S1** reacted with (*R*)-BINOL under the same reaction conditions to afford the enantiomer (*S*)-**1** in 88% yield which was also well-characterized by ^{1}H NMR, ^{13}C NMR, high resolution ESI-MS, and X-ray crystallographic analysis (Scheme 1, b) Circular dichroism (CD) indicated the stereochemical properties of the enantiomers (*R*)-**1** and (*S*)-**1** (Scheme 1, c).

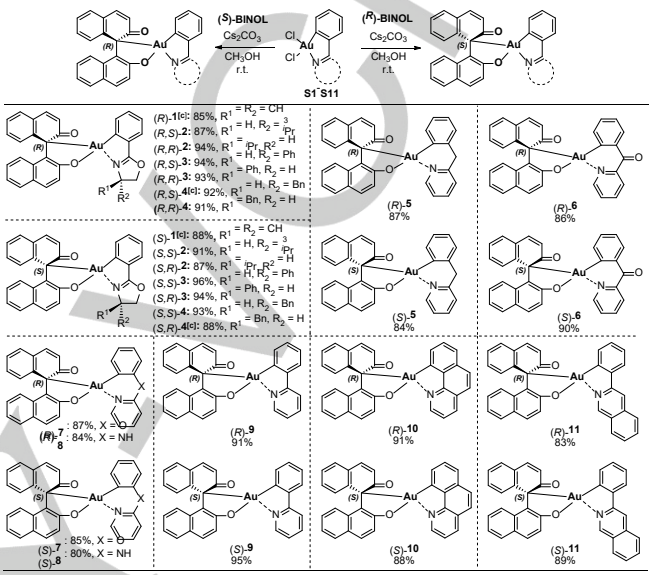


Scheme 1. a) Formation of stable gold(III) complex (*R*)-**1** derived from (*S*)-BINOL and cyclometallated gold(III) dichloride **S1** in an unusual C,O-chelation manner, and the X-ray crystal structure of (*R*)-**1**; b) Formation of stable gold(III) complex (*S*)-**1**, and the X-ray crystal structure of (*S*)-**1**; c) Circular dichroism (CD) spectrum of (*R*)-**1** and (*S*)-**1**, 0.1 mg/mL in $CHCl_3$.

A search of literatures revealed that this kind of peculiar C,O-chelation mode for BINOL derivatives with Pd(II) and Pt(II) have rarely been reported.[16] To our knowledge, we are the first to synthesize chiral BINOL-oxazoline hybrid gold(III) complexes (*R*)-**1** and (*S*)-**1** with unusual C,O-chelation mode. The possible reasons for (*R*)-**1** and (*S*)-**1** accommodating the peculiar C,O binding mode would be enol-keto tautomerization of BINOL in the presence of Cs_2CO_3 and the higher tendency of the gold center coordinating to carbanion than phenoxide.[16] This unprecedented C,O-chelation rather than O,O'-chelation mode of BINOL towards the Au^{III} center of complex [Au(C^N)Cl$_2$] represents a facile approach for generating strong Au–C and Au-O bonds paving the way to stable gold(III) complexes. In this work, we are the first to develop a modular approach for synthesizing a series of novel chiral C,O-chelated BINOL-gold(III) complexes by combination of diverse chiral (*S*)-BINOL and (*R*)-BINOL derivatives with various oxazoline- and pyridine-based cyclometallated gold(III) complexes.

The scope of using various oxazoline- and pyridine-based cyclometallated gold(III) dichloride complexes [(C^N)AuCl$_2$] for synthesizing chiral C,O-chelated BINOL-gold(III) complexes were studied (Table 1). Chiral oxazoline-based gold(III) dichloride complexes **S2-S4** were prepared by a literature method with modifications (see Supporting Information, Scheme S2-S3).[13a, 17] Treatment of (*S*)-BINOL and (*R*)-BINOL with these chiral oxazoline-based gold(III) dichloride complexes under the optimized reaction conditions, respectively, gave the four stereoisomers of chiral BINOL-oxazoline hybrid cyclometallated gold(III) complexes **2-4** (with (*R,S*)-, (*R,R*)-, (*S,S*)-, and (*S,R*)-configurations, respectively) in 87-96% yield. Reactions of (*S*)-BINOL and (*R*)-BINOL with *ortho*-substituted pyridine-based complexes **S5-S11**, respectively, afforded chiral gold(III) complexes **5-11** with (*R*)- and (*S*)-configuration in 80-95% yield.

Table 1. Scope of using oxazoline- and pyridine-based cyclometallated gold(III) dichloride complexes for the synthesis of **1-11**.[a][b]

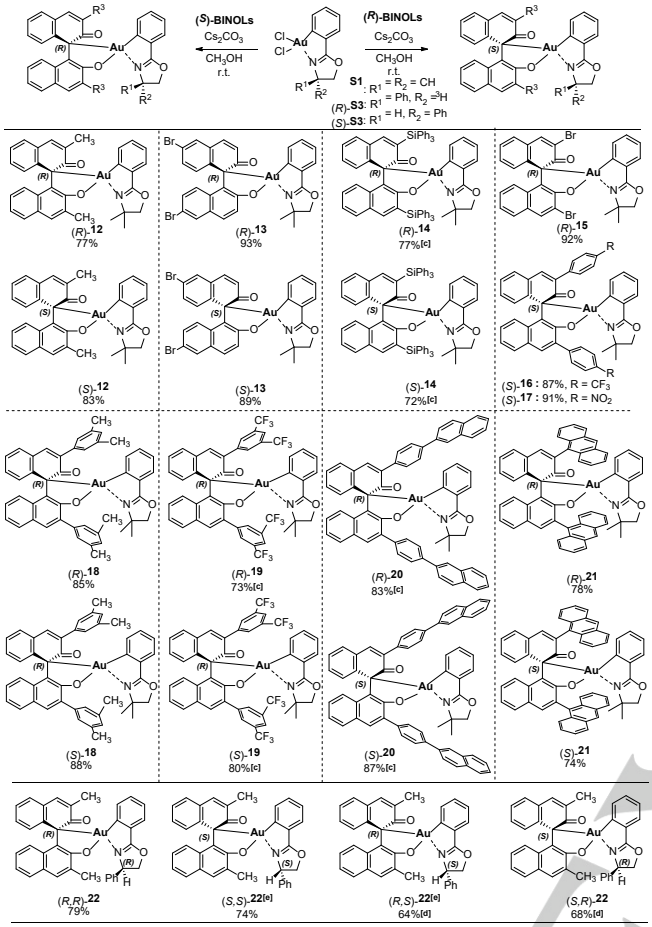


[a] Reaction conditions: gold(III) dichloride complex (0.2 mmol), (*S*)-BINOL or (*R*)-BINOL (1.1 equiv.), Cs_2CO_3 (2.2 equiv.), methanol (10 mL), room temperature, reaction time: 1 h. [b] Yield of isolated product. [d] Configuration validated by X-ray crystallographic analysis.

As literature reported that the coordination mode of Pd(II) and Pt(II) with BINOL and VANOL exclusively adopted the O,O'-chelation, while the apparently more bulky ligands 3,3'-Me$_2$BINOL and VAPOL prefered the C,O-chelation.[16d]. We proceeded to employ 3,3'-disubstituted BINOLs for the formation of the C,O-chelated BINOL-gold(III) complexes (Table 2). (*S*)-3,3'-Me$_2$BINOL and (*R*)-3,3'-Me$_2$BINOL were used to react with oxazoline-based cyclometallated gold(III) dichloride **S1**, giving C,O-chelation products (*R*)-**12** and (*S*)-**12** in 77% and 83% yield, respectively. Similarly, reaction of (*S*)-6,6'-dibromo-BINOL and (*R*)-6,6'-dibromo-BINOL with **S1** also afforded the enantiomers (*R*)-**13** and (*S*)-**13** in excellent yield (93% and 89%), respectively. Next, the scope of various sterically bulky 3,3'-disubstituted BINOLs were investigated. BINOLs with SiPh$_3$, Br, aryl groups on 3,3'-positions were well-compatible with **S1** to form the cyclometallated gold(III) complexes **14-21** (72-92% yield) with the C,O-chelation (Table 2). Furthermore, (*S*)-3,3'-Me$_2$BINOL and (*R*)-3,3'-Me$_2$BINOL reacted with chiral oxazoline-based gold(III) dichloride complexes (*S*)-**S3** and (*R*)-**S3**, respectively, afforded the four stereoisomers (*R,S*)-**22**, (*R,R*)-**22**, (*S,S*)-**22**, and (*S,R*)-**22** in 64-79% yield.

The axial-to-central chirality transfer from the chiral BINOL to the resulting gold(III) complexes was again confirmed by X-ray crystallographic analysis (Figure 2).[14] Reaction of (*R*)-BINOL with (*S*)-**S4**, and reaction of with (*S*)-BINOL with (*R*)-**S4** afforded the corresponding (*R,S*)-**4** and (*S,R*)-**4**, respectively, indicating that the axial chirality on the chiral BINOL exclusively transferred to the resulting optically pure gold(III) complexes. This kind of efficient axial-to-central chirality transfer was also applicable on the synthesis of (*R,S*)-**22** and (*S,S*)-**22**.

Table 2. Scope of using chiral 3,3′-disubstituted BINOL ligands for the synthesis of **12-22**.[a][b]



[a] Reaction conditions: gold(III) dichloride complex (0.1 mmol), (*S*)-3,3′-disubstituted BINOL or (*R*)-3,3′-disubstituted BINOL (1.1 equiv.), Cs_2CO_3 (2.2 equiv.), methanol (5 mL), room temperature, reaction time: 1 h. [b] Yield of isolated product. [c] 0.05 mmol. [d] 24 h. [e] Configuration validated by X-ray crystallographic analysis.

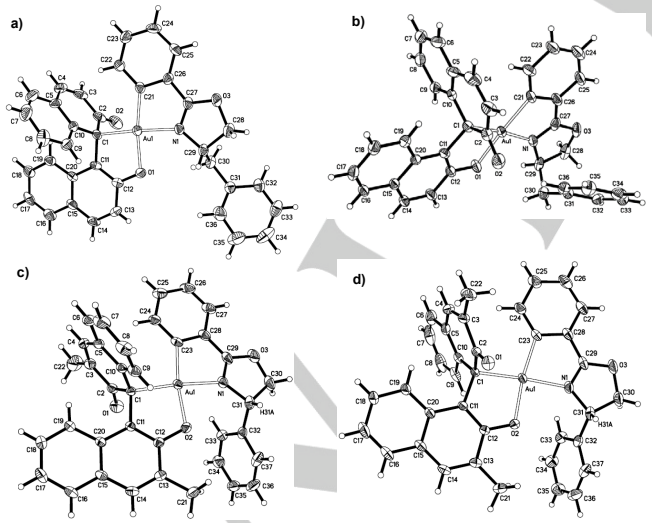
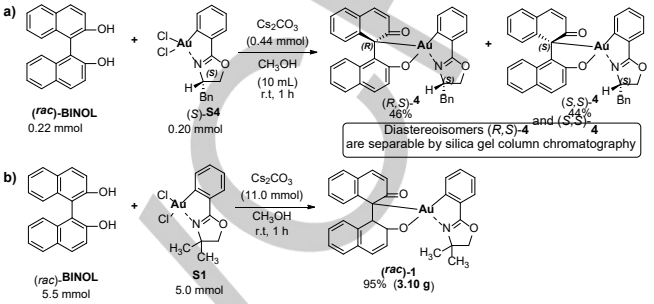


Figure 2. X-ray crystal structures of a) (*R,S*)-**4**, b) (*S,R*)-**4**, c) (*R,S*)-**22**, and d) (*S,S*)-**22**. Displacement ellipsoids are drawn at the 50% probability level. Solvent molecules are omitted for clarity.

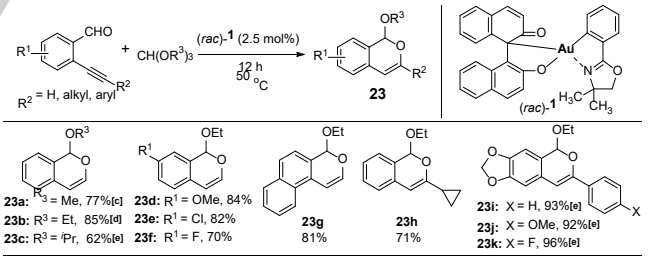
Reaction of (*rac*)-BINOL with chiral oxazoline-based gold(III) dichloride complex (*S*)-**S4** was conducted under the standard reaction conditions. Diastereoisomers (*R,S*)-**4** and (*S,S*)-**4** were well-separated by column chromatography on silica gel in 46% and 44% yield, respectively (Scheme 2, a). These results indicated that chiral BINOL-gold(III) complexes could be synthesized from chiral oxazoline-based gold(III) dichloride complexes and inexpensive racemic BINOL. A gram-scale reaction of (*rac*)-BINOL with oxazoline-based gold(III) dichloride complex **S1** was conducted (Scheme 2, b). (*rac*)-BINOL (1.58 g, 5.5 mmol) reacted with **S1** (2.21 g, 5.0 mmol) in the presence of Cs_2CO_3 in methanol at room temperature for 1 h to afford (*rac*)-**1** in 95% yield (3.10 g).



Scheme 2. a) Access to chiral diastereoisomers (*R,S*)-**4** and (*S,S*)-**4** from reaction of racemic BINOL and (*S*)-**S4**; b) A gram-scale synthesis of gold(III) complex (*rac*)-**1** from racemic BINOL and oxazoline-based gold(III) dichloride **S1.**

With (*rac*)-**1** in hand, we proceeded to examine the catalytic activity of the newly developed C,O-chelated BINOL-gold(III) complexes in organic transformation reactions of *ortho*-alkynylbenzaldehydes.[18] Treatment of various *ortho*-alkynylbenzaldehydes with trialkyl orthoformates in the presence of 2.5 mol% of Au(III) complex (*rac*)-**1** gave six-membered acetal products **23a-23k** in 62-96% yield without the five-membered counterpart reported in literature[18d] (Table 3). These findings showed that the catalysis of complex (*rac*)-**1** towards tandem acetalization/cyclo-isomerization of *ortho*-alkynylbenzaldehydes with trialkyl orthoformates has excellent regioselectivity.

Table 3. Gold(III) complex (*rac*)-**1** catalyzed tandem acetalization/cyclo-isomerization of *ortho*-alkynylbenzaldehydes with trialkyl orthoformates.[a][b]



[a] Reaction conditions: *ortho*-alkynylbenzaldehyde (0.5 mmol), $CH(OR^3)_3$ (3.0 mmol, 6.0 equiv.), DCE (3.0 mL), 50 °C, 12 h. [b] Yield of isolated product. [c] At room temperature. [d] 8 h. [e] 24 h. DCE = dichloroethane.

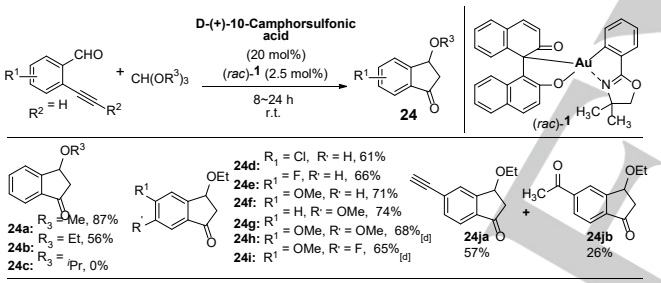
Interestingly, when sulfonic acid (20 mol%) was added to the reaction mixture with 2.5 mol% gold(III) catalyst (*rac*)-**1**, a carboalkoxylation product **24a**[19] was exclusively formed in 72% yield, but the tandem acetalization/cycloisomerization product **23a** was not obtained. The drastic change in product distribution indicated that the product selectivity of gold(III) complex (*rac*)-**1** towards *ortho*-alkynylbenzaldehyde would be adjusted by addition of acid. Encouraged by these findings, we set out to optimize the reaction conditions by screening various gold(I), gold(III) catalysts, Brφnsted acids, loading of catalysts and sulfonic acid, amount of trimethyl orthoformate, as well as solvents (see Supporting Information, Table S1-S4). As summarized in the Supporting Information, no carboalkoxylation product was obtained when simple gold(I) salt

(AuCl), phosphine-gold(I) complexes LAuCl (L = PPh_3 and JohnPhos), and mono- and bis-cyclometallated gold(III) complexes [(C^N)$AuCl_2$ and (C^N)$_2AuBF_4$] were used. We found that using 2.5 mol% (*rac*)-**1**, 20 mol% camphorsulfonic acid and 6.0 equivalent of $CH(OEt)_3$ in DCE gave the best yield (87%).

With the optimized reaction conditions, we investigated the scope of this gold(III)-catalyzed carboalkoxylation reaction of *ortho*-ethynylbenzaldehydes (Table 4). Using trimethyl orthoformate, the corresponding indanone **24b** was obtainied with lower yield (56%). Yet, no carboalkoxylation product was found when triisopropyl orthoformate was used. Substrates with electron-withdrawing group (Cl, F), electron-donating group (OMe), as well as two substituents on the aryl ring were well-tolerated (products **24d-24i** in 61-74% yield). The reaction of an ethynyl-substituted substrate proceeded smoothly under the standard conditions, giving the corresponding indanone **24ja** in 57% yield together with **24jb (**hydration product of **24ja)** in 26% yield.

As shown in Table 3, reaction of *ortho*-alkynylbenzaldehydes with trialkyl orthoformates catalyzed by (*rac*)-**1** gave six-membered acetal products **23**. On the other hand, addition of camphorsulfonic acid switched to carboalkoxylation product **24** (Table 4). One possibility might be the acid-promoted formation of acetals from 2-alkynylbenzaldehydes followed by subsequent carboalkoxylation reaction pathway[19] to give the product **24** (mechanistic studies of these reaction pathways are ongoing in our laboratory).

Table 4. Gold(III) complex (*rac*)-**1** catalyzed carboalkoxylation of *ortho*-alkynylbenzaldehydes with trialkyl orthoformates.[a][b]



[a] Reaction conditions: *ortho*-ethynylbenzaldehyde (0.5 mmol), $CH(OR^3)_3$ (3.0 mmol, 6.0 equiv.), D-(+)-10-Camphorsulfonic acid (20 mmol%), DCE (3.0 mL), room temperature, 24 h. [b] Yield of isolated product. [c] 8 h. [d] At 60 °C. DCE = dichloroethane.

In this work, the new approach of synthesizing novel C,O-chelated BINOL-gold(III) complexes has opened up a new research direction for gold catalysis based on high valent gold(III) chemistry. It is envisioned that further development of gold(III) catalysis would lead to the discovery of novel organic transformation reactions that would have significant different reactivity, selectivity, and substrate scope compared with gold(I) catalysis. Moreover, it is worthy of exploring the unique chiral environment around the Au(III) center in asymmetric catalysis. Our preliminary studies showed that using chiral BINOL-gold(III) complex (*R,R*)-**2** (2.5 mol%) as catalyst, carboalkoxylation of *ortho*-alkynylbenzaldehyde with CH_3OH gave **24b** in 52% yield with 41% ee (see Supporting Information, Figure S1).

Acknowledgements

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Keywords: gold(III) complexes • BINOL • cyclometallated • cycloisomerization • carboalkoxylation

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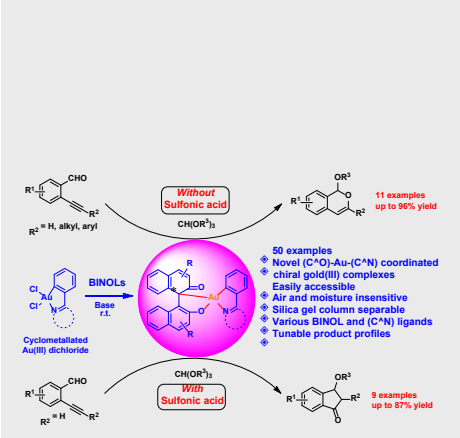
Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Novel gold(III) complexes: stable BINOL-gold(III) complexes adopting an unusual C,O-chelation mode were synthesized *via* a modular approach by combination of BINOLs and cyclometallated gold(III) dichloride complexes. These gold(III) complexes catalyzed acetalization/cyclo-isomerization and carboalkoxylation of ortho-alkynylbenzaldehydes with trialkyl orthoformates.



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Unprecedented C,O-Chelated BINOL-Gold(III) Complexes: Synthesis and Catalysis with Tunable Product Profiles