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Gold-NHC-*N*-naphthamide complexes

Sondre Taugbøl Lomeland, Benedicte Øvrebø, Helgi Freyr Jónsson, and Anne Fiksdahl*

Department of Chemistry, Norwegian University of Science and Technology
Høgskoleringen 5, 7491 Trondheim, Norway
Email: anne.fiksdahl@ntnu.no

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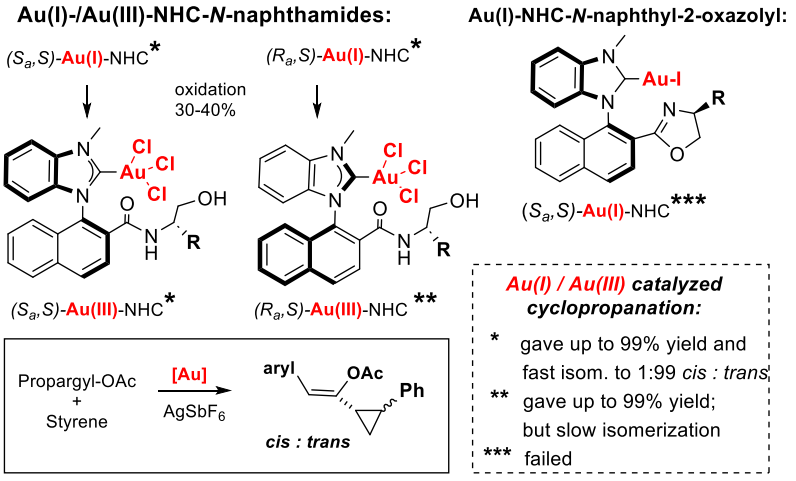
Abstract

Pure S_a,*S* and R_a,*S* atropoisomeric Au(I)- and Au(III)-NHC-complexes with benzimidazolyl *N*-(2-naphthamide) frameworks were prepared from appropriate axially chiral pre-ligands. The catalytic capacity of gold-NHC-*N*-naphthyl complexes was studied in cyclopropanation reactions. In contrast to corresponding unsuccessful Au(I)-NHC-*N*-naphthyl-oxazolyl complexes, all tested S_a,*S* and R_a,*S* diastereomers of Au(I) and Au(III)-NHC-*N*-naphthamide complexes were excellent catalysts to give both successful cyclopropanation (up to 99%, 15 min), as well as subsequent rapid *in situ cis*-to-*trans* isomerization. The results demonstrate that the new axially chiral Au(I)-/Au(III)-NHC-benzimidazolyl-*N*-naphthamide complexes represent an interesting group of gold catalysts with specific properties, affording fast cyclopropanation, excellent product yields and predictable *trans*-stereoselectivity (>99% yield; >99% *trans* in 15 min).



Keywords: Gold-NHC-naphthamide; Au(I)/Au(III) complexes; catalytic active, cyclopropanation

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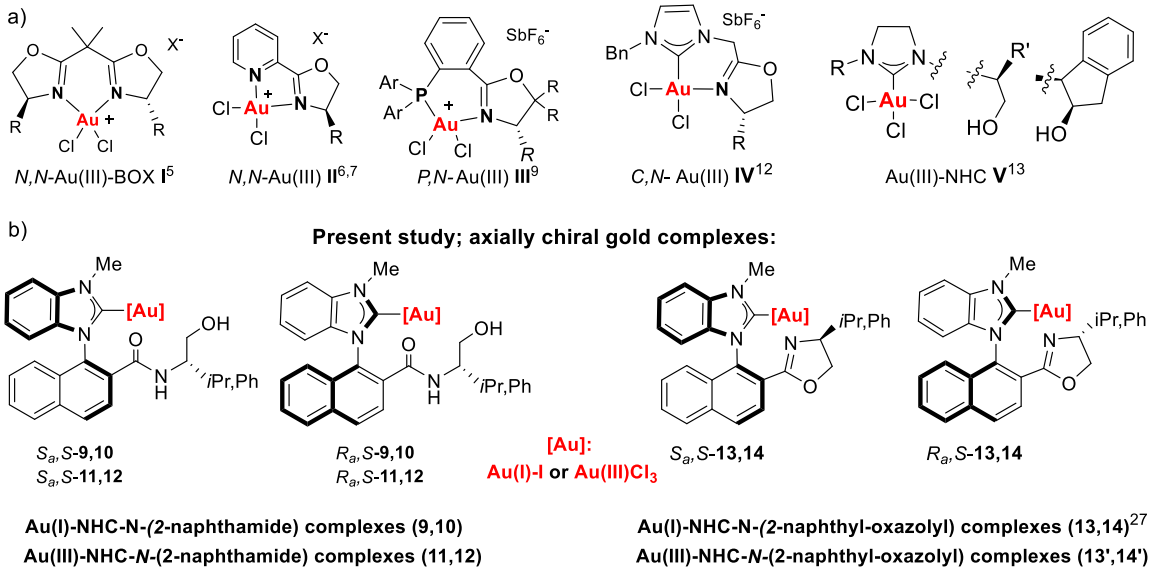
Introduction

Gold catalysis has been a rapidly emerging field within transition metal catalysis in the past two decades to promote a great variety of organic scaffolds from unsaturated substrates. Gold has a high affinity towards carbon-carbon multiple bonds, especially alkynes, which may be activated towards nucleophilic attack. Coupled with high functional group tolerance, usually mild reaction conditions allow for diverse gold catalyzed transformations to be achieved, also including enantioselective reactions.[1] A broad review on the status of gold chemistry has lately been published as a thematic issue edited by Hashmi.[2] Gold(I) catalysis is by far more developed and understood compared to gold(III) catalysis, as evidenced by the large number of reported ligated gold(I) complexes. The last years have witnessed a revival of gold(III) chemistry. The challenge of gold(III) complexes is the possible reduction to gold(I) or gold(0) species. While the stability of gold(III) ions increases upon ligand coordination, stable gold(III) complexes generally show poorer catalytic activity. Thus, the aim for successful development of gold(III) catalysts is to find the balance between stability and catalytic activity. The development of gold(III) complexes and the applications of gold(III) in synthesis and catalysis, including mechanistic aspects, have recently been reviewed.[3] The interest toward the synthesis of chiral gold(III) complexes is also steadily growing and the progress achieved in the synthesis of well-defined chiral gold(III) complexes has lately been summarized.[4]

We have previously reported studies on the gold(III) coordination ability of different ligands to give a variety of polydentate Au(III) complexes,[5-13] including oxazole and NHC based chiral Au(III) catalysts. The *N,N*-BOX-Au(III) complexes **I** (Scheme 1) based on bis-oxazoline ligands (BOX), were shown to represent an interesting group of Au(III) catalysts with specific catalytic properties.[5] Our experimental and theoretical studies on Au(III) bidentate coordination of a series of pyridine-oxazoline and quinoline-oxazoline **II** based ligands, concluded that the superior activity of the *N,N*-Au(III)-pyridine-oxazolyl complexes **II** is caused by de-coordination of the pyridine-*N* ligand as a crucial step for efficient generation of catalytic activity.[6] Further mechanistic studies (NMR, X-ray, DFT) of Au(III)-bidentate pyridine-oxazoline **II** mediated alkoxycyclization, also demonstrated that de-coordination of the pyridine nitrogen is involved as the rate-limiting step.[7] Based on our successful synthesis of *P,N*-Au(III)-phosphine-oxazoline complexes **III**,[9] as well as the efficient coordination affinity of oxazoline-nitrogen to generate *N,N*-Au(III)-bis-heterocyclic structures **II**, we synthesized oxazoline functionalized Au(III)-NHC complexes **IV**.[12] These Au(III) complexes were too unstable for proper isolation and spectroscopic characterization, but selective ^{15}N NMR techniques provided valuable proofs of *N*-coordination by formation of *N*-ligated Au(III) complexes. The changes in ^{15}N-shift values ($\Delta\delta^{15}$N), observed by ^{1}H,^{15}N-HMBC 2D NMR studies, going from Au(I)Cl, via Au(III)Cl$_3$ to the *C,N*-Au(III)-NHC-oxazolyl complexes, afforded important evidence that oxazoline-*N*-coordination to Au(III) took place. In particular, the huge up-field shift of the oxazoline-N ($\Delta\delta^{15}N_{oxaz}$) undoubtedly confirmed that the target six-membered bidentate *C,N*-Au(III)-NHC-oxazoline chelated complex **IV** was formed. Other studies showed that chiral alcohol functionalized Au(III)-NHC complexes **V** failed to generate bidentate *C,O*-Au(III)-NHC-alcohol complexes.[13]

Several axially chiral Au(I) complexes, based on a binaphthyl scaffold have been synthesized.[14,15] Such Au(I) complexes, formed as atropoisomeric diastereomers with an axis of chirality, have also been designed as binaphthyl ligands connected to various *N*-heterocyclic carbene ligands. These synthesized axially chiral Au(I)-NHC complexes were, in general, reported to provide moderate to high catalytic activities and modest chiral inductions in asymmetric intramolecular cyclizations.[16-25]



Scheme 1. Our a) previously reported *N*-oxazolyl or NHC Au(III) complexes **I-V**,[5-7,9,12,13] as well as b) the target Au(I)- and Au(III)-NHC-*N*-(2-naphthamide) (**9-12**), and Au(I)-NHC-*N*-(2-naphthyl-oxazolyl complexes (**13,14**),[27] which are compared in the present study.

No examples of axially chiral gold(III) complexes with binaphthyl based ligands have been reported. Likewise, the use of stabilizing NHC ligands in gold(III) chemistry is much less developed than the NHC-gold(I) complexes, which have proved to be powerful catalysts.[26] By replacing one naphthyl group in the binaphthyl scaffold with a benzimidazolium unit,[27] the NHC functionality becomes incorporated in the axially chiral bis-aryl structure (e.g. **9-14**, Schemes 1 and 2). The aim of this pro*J*ect was to synthesize new axially chiral atropoisomeric NHC pre-ligands to allow the formation of modified axially chiral Au(I)/(III)-NHC complexes based on an *N*-naphthyl structure.

We are presently reporting the synthesis of novel axially chiral Au(I) and Au(III) complexes (**9-12**) (Schemes 1 and 2) with a benzimidazolyl *N*-(2-naphthamide) framework. The corresponding Au(I) complexes with the *N-(*2-oxazolyl) moiety (**13**, **14**)[27] were attempted oxidized to provide Au(III)-NHC-(2-oxazolyl) complexes (**13'**, **14'**) (Scheme 2), with a *C,N*-bidentate Au(III)-NHC-(2-oxazolyl) metalacyclic structure, including both NHC and *N*-oxazoline Au(III)-coordination sites. The catalytic potential of the novel Au(I) and Au(III)-NHC-*N*-naphthamide complexes (**9-12**)**,** compared with the respective Au(I)-NHC-*N*-(2-oxazolyl) complexes (**13**, **14**)[27] in gold-catalyzed cyclopropanation was studied.

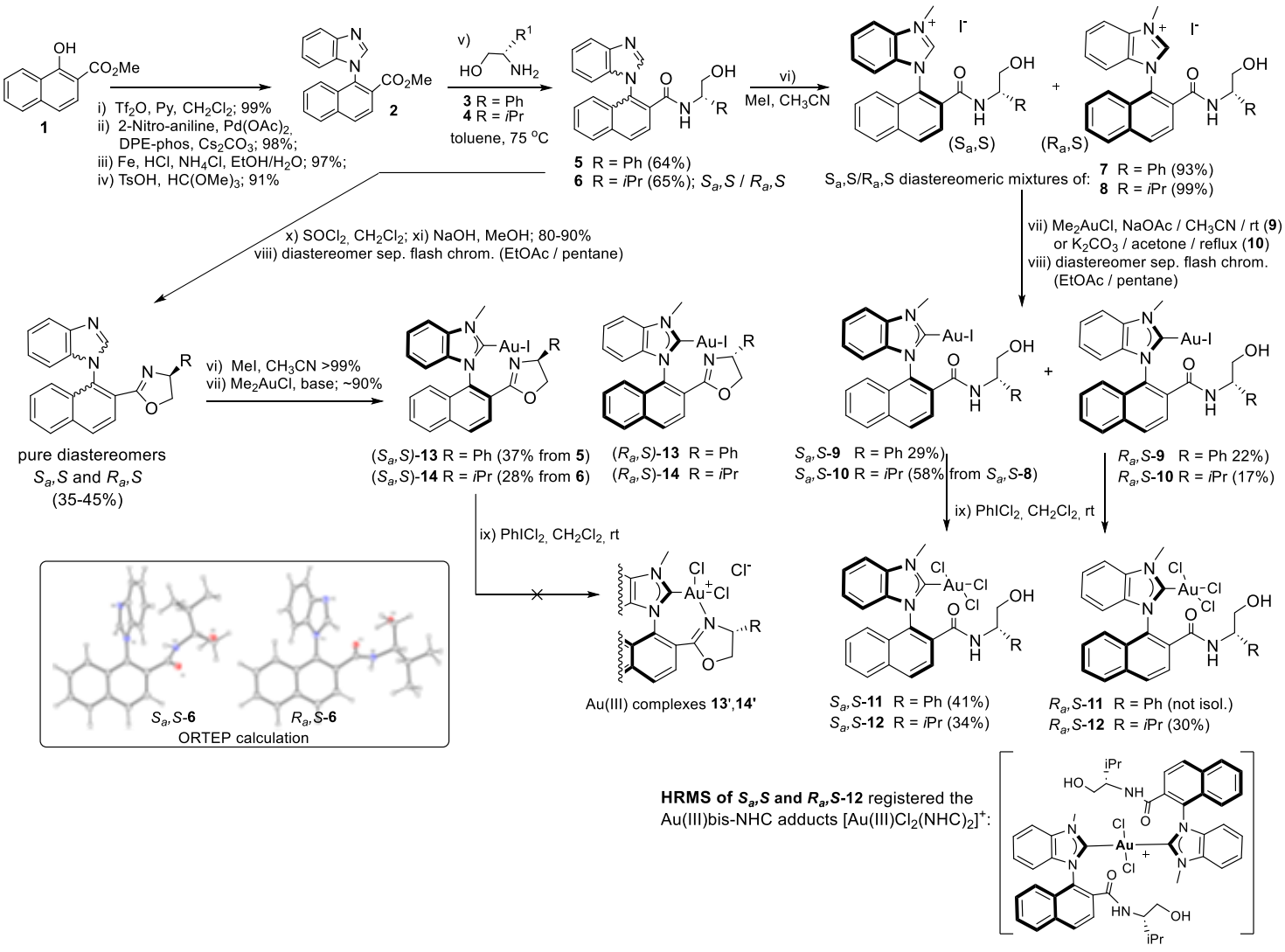
In addition to NMR (^{1}H, ^{13}C), IR and HRMS characterization of new *N*-naphthamide compounds **7**-**12**, structures of selected products (**5**, **9**, **11**) shown with full assignment of ^{1}H and ^{13}C NMR data, based on 2D NMR studies (COSY, HSQC, HMBC), are available in the Supporting Information.

Results and Discussion

Preparation of gold-NHC-*N*-naphthamide complexes

1. Pre-ligand preparation. In order to prepare novel axially chiral Au(I)- and Au(III)-NHC-naphthamide complexes (**9**, **10** and **11**, **12**) (Scheme 2), the appropriate chiral β-hydroxyamide-NHC pre-ligands **7** and **8** with a benzimidazolium-*N*-naphthyl framework, were synthesized from the respective benzimidazole precursors **5**

and **6**, which were prepared in five steps as reported previously.[27] Pd-catalyzed Buchwald-Hartwig amination of 2-nitroaniline with the phenol **1** triflate (98%), nitro reduction with iron powder (97%) and final ring closure (trimethyl orthoformate, TsOH, cat.) afforded the benzimidazole-naphthoate **2** by heating (91%) (Scheme 2). Subsequent reactions of ester **2** with enantiomerically pure aminoalcohols (*S*)-2-amino-2-phenylethan-1-ol **3** and (*S*)-2-amino-3-methylbutan-1-ol **4**, gave respectively naphthamides **5** (64%) and **6** (65%) (Scheme 2). ^{1}H and ^{13}C NMR showed that the bis-aryl product **6** with the bulky α-isopropylamide moiety (R = *i*Pr) was formed as an approximately 1:2 mixtures of axially chiral S_a,*S*-**6** and R_a,*S*-**6** diastereomers, demonstrating the restricted rotation along the N-C connecting bond in the bis-aryl benzimidazole-naphthalene product **6**. The structures of the two diastereomeric α-isopropylamides **6** were calculated (ORTEP, Scheme 2) and show that the atropoisomeric diastereomers with an axis of chirality are chemically non-equivalent, which explains the two unique set of ^{1}H and ^{13}C NMR signals. The diastereomers of amides **6** were not isolated but used in a mixture in the next step. In contrast, ^{1}H and ^{13}C NMR of the less bulky α-phenylamide **5** (R = Ph) did not show diastereomers.



Scheme 2. Synthesis of axially chiral gold(I)- and gold(III)-NHC-*N*-naphthamide complexes **9-12** and Au(I)-NHC-*N*-naphthyl-oxazolyl complexes **13-14**.

The chiral *N*-naphthyl-benzimidazolium pre-ligands **7** (93%) and **8** (99%) were obtained by benzimidazole *N*-methylation (MeI) of amides **5** and **6**, producing the characteristic change of ^{1}H NMR shift values of the H2 imidazole protons from δ ~8 ppm (imidazoles **5**, **6**) to δ ~10 ppm (imidazolium salts **7**, **8**). Both reactions afforded diastereomeric mixtures of the respective benzimidazolium salts **7** and **8**, as shown by NMR (^{1}H, ^{13}C). As mixture of atropoisomeric pre-ligands *S*$_a$,*S*-**7** and *R*$_a$,*S*-**7** (R = Ph; 1:1.3 ratio; ^{1}H NMR) were formed from non-diastereomeric benzimidazole **5**, the observed axial chirality seems to arise by internal restrictions generated by benzimidazolium formation in this case. Differently, axial chirality occurred for the bulkier isopropylamide **6** (R = *i*Pr) in the previous amidation step of chiral α-isopropylamine **4**. The inseparable *S*$_a$,*S*-**7** and *R*$_a$,*S*-**7** α-phenylamide benzimidazolium diastereomers were characterized in a mixture, while the *S*$_a$,*S*-**8** and *R*$_a$,*S*-**8** α-isopropylamide diastereomeric pre-ligands were separated by chromatography (*S*$_a$,*S*-isomer eluting first) for individual characterization (NMR, HRMS). Benzimidazolium salts (**7**, **8**) were further used in a mixture for coordination to Au(I).

2. Gold(I) coordination. Coordination of the diastereomeric mixture of *S*$_a$,*S*-**7** and *R*$_a$,*S*-**7** benzimidazolium salt**s** (R = Ph) to gold(I) by optimized conditions (Me_2SAuCl (1 eq), NaOAc (3 equiv), acetonitrile, rt 22 h) yielded the corresponding mixture of the target gold(I)-NHC-naphthamide complexes **9**. Chromatographic separation (Scheme 2) afforded the pure axially chiral gold(I)-NHC complexes *S*$_a$,*S*-**9** as an oil (29%) and *R*$_a$,*S*-**9** as a white solid (22%). Likewise, the pure *S*$_a$,*S*-**10** (16%) and *R*$_a$,*S*-**10** (17%) gold(I)-NHC complexes (R = *i*Pr) were obtained from the *S*$_a$,*S*-**8** and *R*$_a$,*S*-**8** benzimidazolium salt mixtures by gold(I) coordination (Me_2SAuCl (1 equiv), K_2CO_3 (1 equiv) in acetone, reflux, 2 h) and subsequent flash chromatography. The somewhat lower yields of gold(I)-NHC-naphthamide complex **10** (R = iPr) than complex **9** (R = Ph) indicates that the complexation is more restricted by the more sterically demanding *i*Pr substituent. An even stronger steric effect was seen in imidazolium-based Au(I) and Au(III)-NHC-oxazolyl complexes **IV**,[12] as different bulkiness of (*i*Pr *vs t*-Bu) NHC substituents gave great variation in successful transformations (69% *vs* 18%) and stability of Au-NHC complexes. Likewise, it has been seen that steric hindrance of bulky *t*-Bu-oxazoline-imidazolium pre-ligands prevented iridium complexation[28] and resulted in less successful transformation to similar Ir-NHC complexes. This effect is also discussed below for Au(I)-NHC-(2-oxazolyl) complexes **13**, **14** (Scheme 2).

Strong bases, high temperature and prolonged silica exposure seemed to lower the yields by decomposition of the gold(I)-NHC complexes. Thus, by avoiding the above described chromatographic separation of the diastereomeric mixture, the yield of gold(I) complex *S*$_a$,*S*-**10** (58%) was improved (from 16%) by gold(I) coordination of the isolated pure *S*$_a$,*S*-**8** benzimidazolium salt**.** The identity of the novel gold(I) complexes **9** and **10** were confirmed by HRMS, and the structures of the individual diastereomeric *S*$_a$,*S*-**9**, *R*$_a$,*S*-**9**, *S*$_a$,*S*-**10** and *R*$_a$,*S*-**10** complexes were proved by ^{1}H and ^{13}C NMR and 2D NMR (COSY, HSQC, ^{1}H -^{13}C-HMBC) characterization.

3. Gold(I)-to-gold (III) oxidation. The Au(III)-NHC complexes **11** and **12** were prepared by oxidation of the respective diastereomeric Au(I) complexes **9** and **10** with $PhICl_2$ in CH_2Cl_2 at rt (Scheme 2).[29] Crystalline complexes were obtained by pentane addition to the final reaction mixture. The diastereomerically pure *S*$_a$,*S*-**9**, *R*$_a$,*S*-**9**, *S*$_a$,*S*-**10** and *R*$_a$,*S*-**10** gold(I) complexes were oxidized separately to give crystalline *S*$_a$,*S*-**11** (41%), *S*$_a$,*S*-**12** (34%) and *R*$_a$,*S*-**12** (30%) gold(III)-NHC complexes, while pure *R*$_a$,*S*-**11** gold(III)-NHC could not be isolated from the respective product mixture.

^{13}C NMR studies of all *S*$_a$,*S* and *R*$_a$,*S*-diastereomeric oxidation products (**11, 12**) confirmed successful Au(I) to Au(III) oxidation. A ^{13}C NMR carbene approach has been established to confirm successful formation

of imidazole-based Au(III)-NHC carbene complexes.[30-33] ^{13}C NMR shift values of the C2 carbon in imidazole-based compounds are characteristic and can readily be used to identify actual products in synthesis sequences from imidazolium pre-ligands *via* gold(I)-NHC to gold(III)-NHC complexes.[5-11,32,34,35] Hence, the transformations of imidazolium salts to Au(I)-NHC complexes were verified by the extensive down-field changes of C2 ^{13}C NMR chemical shift (ΔδC ~ 45 ppm), going from δ ~143 ppm (N-*C*H-N) in imidazolium salts **7** and **8** to δ ~189 ppm (*carbene*-C2) in Au(I)-NHC **9** and **10**. Subsequent oxidation was confirmed by significant characteristic up-field ^{13}C NMR shifts (ΔδC ~ -35 ppm) of the carbene signals from the respective Au(I)-NHC carbene precursors **9** and **10** (δ ~189 ppm) to the Au(III)Cl_3-NHC complexes **11** and **12** (δ ~153 ppm). The up-field shift generated by oxidation is explained by the higher Lewis acidity of the Au(III) *vs*. Au(I) metal center, which induces a greater delocalization of the electron density from the benzimidazole ring to the carbene carbon atom. Our observed values are in accordance with literature values of chlorido gold(III) complexes of typical NHCs.[30-33]

The identity of the *S*$_{\alpha}$,*S*-**11** and *S*$_{\alpha}$,*S, R*$_{\alpha}$,*S*-**12** Au(III)-NHC complexes was also confirmed by (ESI) HRMS. The *S*$_{\alpha}$,*S*-**11** complex (R = Ph) revealed the characteristic HRMS isotope (^{35}Cl/^{37}Cl) pattern of the Cl_3 compound, Au(III)Cl_3-NHC (~20:20:6:1 ratio) for the M+H (*m/z* 724/726/728) molecular ion, as well as for the M+Na (*m/z* 746/748/750) and the M+K (*m/z* 762/764/766) adducts. HRMS of the corresponding S$_{\alpha}$,*S* and *R*$_{\alpha}$,*S*-**12** Au(III) complexes (R = iPr) showed the molecular ions and fragments of the respective bis-NHC Au(III) derivative Au(III)Cl_2(NHC)$_2$ (Scheme 2). ESI-HRMS spectra of similar benzimidazole based gold(III)-NHC complexes are known to be complicated, as ESI-MS conditions may give rise to dinuclear species.[32] Only the non-chloro HRMS bis-NHC molecular ion (M^+-2Cl; Au(III)(NHC)$_2$, *m/z* 971) was observed for the *S*$_{\alpha}$,*S*-**12** Au(III) complex. However, for the *R*$_{\alpha}$,*S*-**12** isomer, the characteristic Cl_2 isotope (^{35}Cl/^{37}Cl) pattern (~3 : 2 : 1 ratio) of the bis-NHC adduct, Au(III)Cl_2(NHC)$_2$, was registered for both M^+ (*m/z* 1041/1043/1045) and for M^++H (*m/z* 1042/1044/1046). Also, the de-chlorinated bis-NHC molecular ion of the non-chloro fragment (M^+- 2Cl; *m/z* 971) was seen, in accordance with literature.[34]

Attempts to prepare single crystals of Au-NHC-naphthamide complexes **9-12**, suitable for X-ray diffraction analysis, were not successful.

Preparation of gold-NHC-N-naphthyl-oxazolyl complexes

The Au(I)-NHC complexes **13,14** with the *N*-naphthyl-2-oxazolyl framework were synthesized in four steps from amides **5,6** (Scheme 2), according to the literature.[27,36] Oxazole cyclization (80-90%, $SOCl_2$), diastereomer separation (35-45% of each *S*$_{\alpha}$,*S* and *R*$_{\alpha}$,*S*) and individual imidazolium salt formation (100%, MeI), afforded the *S*$_{\alpha}$,*S* and *R*$_{\alpha}$,*S* Au(I)-NHC complexes (**13**,**14**;~90%, Me_2SAuCl, base). The pure *S*$_{\alpha}$,*S*-diastereomers were most successfully isolated and *S*$_{\alpha}$,*S*-**13**, and *S*$_{\alpha}$,*S*-**14** were obtained in 37% and 28% overall yields over four steps from diastereomeric amide (**5**, **6**) mixtures.

Oxidation of gold(I)-NHC complexes **13**, **14** with $PhICl_2$ failed to give the corresponding *C,N*-bidentate gold(III)-NHC-*N*-naphthyl-(2-oxazolyl) complexes. The observed complex decomposition may be due to a less favored seven-membered metallacyclic structures **13'**, **14'** (Scheme 2) with a strained planar Au(III) center by including oxazole *N*-coordination. The Au(I)-to-Au(III) oxidation may also provide an unstable oxazoline group, caused by the increased electron-withdrawing effect of Au(III), which might activate for nucleophilic attack on the oxazoline C=N bond. Previous attempts to prepare similar Au(III)-NHC-oxazolyl seven-membered *C,N*-bidentate complexes by Selectfluor oxidation of Au(I) precursors were unsuccessful,[36] while the more favored six-membered *P,N*-Au(III)Cl_2[SbF_6] phosphine-oxazolyl complexes **III**[9] (Scheme 1) and the corresponding Au(I)Cl precursors were stable and no oxazoline decomposition was detected. In contrast, the oxazolyl moiety caused low stability of the *C,N*-Au(III)Cl_2[SbF_6]NHC-oxazolyl complexes **IV**.[12] However, significant evidences for oxazoline-*N*-Au(III) coordination by formation of the six-membered bidentate *C,N*-Au(III)-NHC-oxazoline

chelated complex **IV** (Scheme 1) was obtained by $^{1}H,^{15}N$-HMBC 2D NMR, in particular, by the large up-field shift of the oxazoline-N ($\Delta\delta^{15}N_{oxaz}$: -71.3 ppm). The related stable *C,N*-Ir(cod)$_2$[28] and *C,N*-PtBr$_2$[37] NHC-oxazolyl complexes have been prepared in low to moderate yields, but bulkier *t*-Bu-oxazoline groups in *C,N*-Ir-NHC complexes prevented metal complexation.[28] Such steric effects may also explain the challenging lack of stability of the *C,N*-Au(III)Cl$_2$[SbF$_6$]NHC-oxazolyl complexes **IV** and the *C,N*-bidentate gold(III)-NHC-*N*-naphthyl-(2-oxazolyl) complexes (**13'**, **14'**).

Catalytic properties of gold-NHC-N-naphthyl complexes in gold-catalyzed cyclopropanation

The catalytic potential of the Au(I) and Au(III)-NHC-*N*-naphthyl complexes **9-14** was studied in the gold-catalyzed cyclopropanation reaction of propargyl ester **I** and styrene **II** (Table 1). We have previously used this model reaction for evaluation of catalytic ability of other novel gold(I) and gold(III) catalysts,[5,6,11] hence, providing a solid and well-established background for comparison. The reactions were performed by addition of a silver salt (AgSbF$_6$, 5 mol %) to a CH_2Cl_2 solution of the relevant Au complex (5 mol %, **9-14**), to generate the catalytically active cationic gold species in the mixture of propargyl acetate **I** and styrene **II**. The yield and the stereoselectivity of the vinyl-cyclopropane product **III** were determined by ^{1}H NMR. The stereoselectivity, measured as the *cis* / *trans* ratio, was based on the ratio of the singlet integrals for the respective vinylic protons (δ 5.90 and δ 6.08 ppm, structure **III**, Table 1).

In contrast to the initially established model for stereoselective cyclopropanations,[38] which explains a favored *cis* selectivity by steric interactions, we have previously shown that the stereoselective outcome is not fixed, since a more complex situation controls the stereochemistry of propargyl cyclopropanations. Our results demonstrated that the amounts of formed *cis* and *trans* isomers varies by *cis*-to-*trans* isomerization over time, and the stereoselective outcome is affected by the electronic properties, the bulkiness of substrates as well as the catalytic activity of the AuI or AuIII catalyst.[5] Some Au catalysts (e.g. BOX-Au(III) complexes **I**) (Scheme 1) were excellent for both fast cyclization into initial selective *cis*-cyclopropanes as well as subsequent complete in situ *cis*-to-*trans* isomerization. Thus, proper choice of Au catalyst successfully enabled highly selective formation of either *cis* or *trans* products (dr > 99%), and separate gold catalyzed (JohnPhosAu(I)SbF$_6$) isomerization allowed the preparation of pure *trans* diastereomers (up to 98% yield) from corresponding pure *cis* substrates. The formation of *trans* isomers is proposed to proceed by Au-catalyzed ring-opening through different relevant intermediates, as shown in the suggested *cis*-to-*trans* isomerization pathways and a more detailed discussion presented in or previous work.[5]

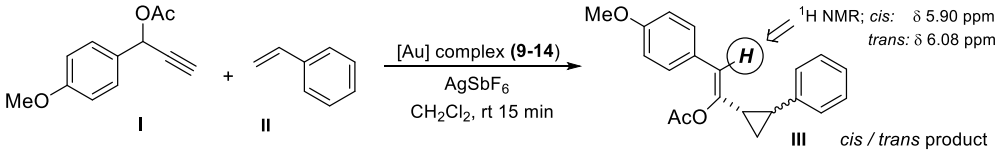
In the present studies, all the tested diastereomers of gold(I)-NHC (**9**, **10**) and gold(III)-NHC (**11**, **12**) *N*-naphthamide complexes were strong catalysts to afford cyclopropanation, as shown by complete conversion of propargyl substrate **I** into the target vinylcyclopropyl product **III** (100%, Table 1, entries 1-6) by vigorous stirring in 5-15 min. Also, predictable *trans*-stereoselectiviton p. 7)y of most reactions was excellent, as shown by up to 1:99 ratios of *cis* / *trans* cyclopropane **III** products (Table 1, entries 1-5). The results prove the combined ability of both the Au(I) and Au(III)-naphthamide complexes (*S$_a$,S*- and *R$_a$,S*-Au(I)-**9**; *S$_a$,S*-Au(I)-**10**, *S$_a$,S*-Au(III)-**11** (R = Ph) and *S$_a$,S*-Au(III)-**12** (R = iPr) to strongly activate for initial cyclopropanation as well as immediate *in situ cis*-to-*trans*-isomerization. The catalyst efficiency was demonstrated by the high-yielding preparation and isolation of the pure *trans*-isomer (91% isolated, >99% *trans* product **III**, Table 1, entry 1) provided by the *S$_a$,S*-Au(I)-**9** (R = Ph) catalyst. The diastereomeric *R$_a$,S*-Au(III)-**12** complex (R = iPr afforded slight isomerization and low *trans*-selectivity, in contrast to the *S$_a$,S*-**12** isomer. The initial product mixture (*cis / trans* ratio 30:70, 15 min) did undergo slow isomerization over time (10:90 ratio, 2 h) to give the pure *trans* product (>99%) after 16 h (Table 1, entry 6). The results may indicate that the *R$_a$,S*-stereochemistry and the bulkiness (R = iPr) reduce the *cis*-to-*trans* isomerization ability of the *R$_a$,S*-**12** complex. The corresponding *R$_a$,S*-

11 complex (R = Ph) could not be isolated from the oxidation reaction (Scheme 2) and was not available for comparison.

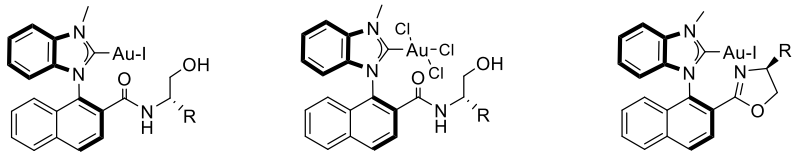
Interestingly, the related oxazoline complexes (R = Ph, *i*Pr) *Sa,S*-**13**-Au(I)-NHC and *Sa,S*-**14**-Au(I)-NHC mainly failed to catalyze cyclopropanation. Full substrate conversion was seen, but polymers were mainly observed (Table 1, entries 7,8).

Despite the axially chiral nature of the applied new gold catalysts **9-12**, no enantioselectivity was obtained (chiral HPLC) in the cyclopropanation reaction. The lack of stereocontrol is most likely due to the chiral environment provided by the ligand being too far from the reaction center.

Table 1. Catalytic studies of novel Au-NHC-*N*-naphthyl complexes[a]



Au(I) and Au(III)-NHC-*N*-naphthyl complexes:



Sa,S / *Ra,S*-Au(I)-**9**; R = Ph
Sa,S-Au(I)-**10**; R = i-Pr

Sa,S-Au(III)-**11**; R = Ph
Sa,S-Au(III)-**12**; R = *i*Pr
Ra,S-Au(III)-**12**; R = *i*Pr

Sa,S-Au(I)-**13**; R = Ph
Sa,S-Au(I)-**14**; R = *i*Pr

Entry	Gold catalyst	Functionality	Product **III** % yield[b] (% *trans*[a])	*cis : trans* ratio[a]
1	*Sa,S*-Au(I)-**9**	amide / R = Ph	> 99% (> 99% *tr*[a])	1 :99
			91% yield[c] (> 99% *tr*[c])	
2	*Ra,S*-Au(I)-**9**	amide / R = Ph	> 99%	3 : 97
3	*Sa,S*-Au(I)-**10**	amide / R = iPr	> 99%	3 : 97
4	*Sa,S*-Au(III)-**11**	amide / R = Ph	> 99%	4 : 96
5	*Sa,S*-Au(III)-**12**	amide / R = iPr	> 99%	3 : 97
6	*Ra,S*-Au(III)-**12**	amide / R = iPr	> 99%; 15 min	30 : 70
		amide / R = iPr	> 99%; 2h	10 : 90
		amide / R = iPr	> 99% (> 99% *tr*[a]); 16 h	1 :99
7	*Sa,S*-Au(I)-**13**	oxazole / R = Ph	-[d]	
8	*Sa,S*-Au(I)-**14**	oxazole / R= *i*Pr	-[d]	

[a] General procedure: Gold catalyst (5 mol%) in CH_2Cl_2 was added to a mixture of propargyl ester **I**, styrene **II**, and $AgSbF_6$ (5 mol %) and stirred vigorously until full conversion of propargyl ester **I** within 15 min. The *cis / trans* cyclopropyl **III** ratio was determined by ^{1}H NMR (ratio of integrals for singlets □ 5.90 / □ 6.08 ppm) . [b] Yield of target product **III** obtained at full conversion, determined by ^{1}H NMR. [c] Isolated product; yield and ^{1}H NMR. [d] Undefined polymer mixture.

Conclusions

A series of new pure S_a,*S* and R_a,*S* atropoisomeric diastereomers of Au(I) and Au(III)-NHC-*N*-naphthamide complexes (**9-12**; with *i*Pr and Ph groups) were prepared from appropriate axially chiral pre-ligands.

The catalytic capacity of gold-NHC-*N*-naphthyl complexes was studied in cyclopropanation. In contrast to the unsuccessful S_a,*S*-Au(I)-NHC-oxazole complexes **13** and **14**, the S_a,*S* and R_a,*S* diastereomers of Au(I) and Au(III)-NHC-*N*-naphthamide complexes **9-11** and S_a,*S*-**12** were excellent catalysts to give successful cyclopropanation (> 99% yield, 15 min). Additionally, subsequent rapid *in situ cis*-to-*trans* isomerization took place, thus affording predictable stereoselective *trans*-cyclopropyl products (*trans* > 99%) in 15 min. The R_a,*S*-Au(III)-**12** (*i*Pr) complex also gave immediate cyclopropanation, but afforded slow isomerization into pure *trans* (>99%, 16 h), indicating that the R_a,*S*-**12** *i*Pr-structure reduces the isomerization ability. No enantioselectivity was obtained in the reaction catalyzed with the axially chiral gold complexes.

The results demonstrate that the novel axially chiral Au(I)- as well as the Au(III)-NHC-*N*-naphthamide complexes (**9-12**) represent an interesting group of gold catalysts with specific catalytic properties.

Experimental Section

General. Commercial grade reagents were used without any additional purification. Dry solvents were collected from a MB SPS-800 solvent purification system. Preparation of sensitive compounds was performed under dry conditions and inert atmosphere. All reactions were monitored by NMR and/or thin-layer chromatography (TLC) using silic a gel 60 F254 (0.25 mm thickness). TLC plates were developed using UV-light (254 nm) and/or phosphomolybdenic acid with heating. Flash chromatography was performed with Merck silica gel 60 (0.040-0.063 mm). ^{1}H and ^{13}C NMR spectra were recorded either a Bruker Avance DPX 400 MHz or a Bruker Avance III 600 MHz spectrometer. Chemical shift values for ^{1}H and ^{13}C NMR are reported in ppm (δ) down-field from tetramethylsilane (TMS) as an internal standard. Coupling constants (*J*) are reported in Hz. ^{1}H and ^{13}C NMR assignments of S_a,*S*-**9**, R_a,*S*-**9** and S_a,*S*-**11**, based on 2D NMR studies (COSY, HSQC, HMBC) are available in Supp. Material. Accurate mass (HRMS) determination was performed on a "Synapt G2-S" Q-TOF instrument from Waters. Samples were ionized with an ESI probe with no chromatography separation performed before mass analysis. Calculated exact mass and spectra processing was done by Waters TM Software Masslynx V4.1 SCN871. IR spectra were recorded with a Bruker Alpha FT-IR spectrometer and OPUS V7.5 software was used for spectra analysis. Compounds **5,6,13,14** were prepared according to literature.[27]

Synthesis of benzimidazolium salts (7,8)

1-(2-Hydroxy-1-phenylethyl)carbamoyl)naphthalen-1-yl)-3-methyl-1*H*-benzo[*d*]imidazol-3-ium iodide (7). Amide **5** (117.2 mg, 0.29 mmol) and iodomethane (0.180 mL, 2.89 mmol) were dissolved in CH_3CN (10 mL) and stirred for 8h. The solvent was removed under reduced pressure to yield a diastereomeric mixture of benzimidazolium salt **7** (147.4 mg, 93%) as a pale yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 11.20 (s, 1H, N=CH-N), 10.70 (s, 1.3H, N=CH-N), 8.39 (d, *J* 7.1 Hz, 1H, Ar), 8.22 (t, *J* 8.7 Hz, 2H, Ar), 8.08 (d, *J* 8.3 Hz, 1H, Ar), 8.06 (d, *J* 8.3 Hz, 1H, Ar), 7.97 (d, *J* 8.0 Hz, 1H, Ar), 7.92 (d, *J* 8.5 Hz, 1H, Ar), 7.82 (d, *J* 8.5 Hz, 1H, Ar), 7.75-7.72 (m, 2H, Ar), 7.70-7.62 (m, 5H, Ar), 7.62-7.48 (m, 5H, Ar), 7.35-7.29 (m, 6H, Ar), 7.17-7.13 (m, 8H, Ar), 5.06-5.02 (m, 1H, NH), 4.93-4.89 (m, 1.3H, NH), 4.35 (s, 3H, CH_3), 4.16 (s, 4H, CH_3), 4.06-3.98 (m, 2H, CH_2), 3.88 (t, *J* 6.6 Hz, 1H, OH), 3.77-3.73(m, 1.3H, CH_2), 3.71-3.67 (m, 1H, CH_2), 2.96 (t, *J* 6.7 Hz, 1.3H, OH). ^{13}C NMR (600 MHz, $CDCl_3$): δ (ppm) 166.2 (C=O), 165.9 (C=O), 143.3 (N=CH-N), 143.1, 132.58 (C_q), 132.57 (C_q), 131.6 (C_q), 131.3

(C_q), 131.0 (C_q), 129.4 (C_{Ar}), 129.22 (C_{Ar}), 129.18 (C_{Ar}), 128.7 (C_{Ar}), 128.6 (C_{Ar}), 128.44 (C_{Ar}), 128.37 (C_{Ar}), 128.3 (C_{Ar}), 127.82 (C_{Ar}), 127.75 (C_{Ar}), 127.7 (C_{Ar}), 127.3 (C_{Ar}), 127.2 (C_{Ar}), 126.9 (C_{Ar}), 125.5 (C_{Ar}), 125.2 (C_{Ar}), 124.5 (C_{Ar}), 124.3 (C_{Ar}), 121.6 (C_{Ar}), 121.3 (C_{Ar}), 114.6 (C_{Ar}), 114.5 (C_{Ar}), 112.7 (C_{Ar}), 112.5 (C_{Ar}), 64.2 (CH_2), 63.8 (CH_2), 57.1 (CH), 56.8 (CH), 34.1 (CH_3), 34.0 (CH_3). IR ($CDCl_3$, cm^{-1}): 3296 (b), 3029 (w), 2948 (w), 2872 (w), 1652 (s), 1564 (s), 1529, 1457, 1377, 1257, 1042 (m), 907 (s), 723 (s). HRMS (ESI) calcd for $C_{27}H_{24}N_3O_2$ [M+] 422.1869; found 422.1872.

1-[1-Hydroxy-3-methylbutan-2-yl)carbamoyl)naphthalen-1-yl]-3-methyl-*1H*-benzo[*d*]imidazol-3-ium iodides (8). A diastereomeric mixture of amides *S*$_a$,*S*-***6*** and *R*$_a$,*S*-***6*** (365 mg, 977 mmol) and iodomethane (1368 mg, 9.64 mol, 600 mL) were dissolved in CH_3CN (10 mL) and stirred at reflux for 18 h. The product was crystallized from CH_2Cl_2/*n*-pentane to yield a diastereomeric mixture of imidazolium compounds **8** (99%). The *S*$_a$,*S*-**8** diastereomer was isolated by flash column chromatography (CH_2Cl_2/MeOH = 20:1), while the *R*$_a$,*S*-**8** diastereomer could be enriched for characterization.

S$_a$,*S*-**8**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.27 (s, 1H), 8.24 (dd, *J* 8.6, 0.9 Hz, 1H), 8.09 (d, *J* 8.5 Hz, 1H), 7.81 (dt, *J* 8.5, 0.9 Hz, 1H), 7.75 (d, *J* 8.4 Hz, 1H), 7.73 (ddd, *J* 8.4, 7.3, 1.0 Hz, 1H), 7.69 (ddd, *J* 8.2, 6.8, 1.1 Hz, 1H), 7.60 (ddd, *J* 8.4, 7.3, 1.0 Hz, 1H), 7.56 (ddd, *J* 8.3, 6.8, 1.2 Hz, 1H), 7.32 (d, *J* 8.4 Hz, 1H), 7.26 (d, *J* 5.3 Hz, 5H), 7.18 (d, *J* 8.9 Hz, 1H), 4.37 (d, *J* 0.7 Hz, 3H), 3.87 - 3.76 (m, 2H), 3.58 (ddd, *J* 11.3, 5.5, 2.8 Hz, 1H), 3.48 (t, *J* 6.0 Hz, 1H), 1.93 (h, *J* 6.8 Hz, 1H), 0.99 (d, *J* 6.8 Hz, 3H), 0.95 (d, *J* 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 143.4, 135.4, 134.6, 133.7, 132.6, 131.3, 129.3, 129.2, 128.7, 128.4, 128.2, 127.7, 125.3, 124.0, 121.7, 114.5, 112.7, 61.7, 57.8, 33.9, 29.6, 19.8, 19.2. IR (CDCl3, cm^{-1}): 3348 (b), 3051 (w), 2962 (m), 2874 (w), 1733 (w), 1650 (s), 1564 (m), 1534 (m), 1461 (m), 1378 (m), 1258 (m), 918 (m), 751 (s), 731 (s). HRMS (ESI, *m/z*): calcd for $C_{24}H_{26}N_3O_2$ [M - I] 388.2025; found 388.2026.

R$_a$,*S*-**8:** analyzed in an approx. 1:8 mixture of *S*$_a$,*S*-**8** and *R*$_a$,*S*-**8** diasteromers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.38 (s, 1H), 8.16 (d, *J* 9.5 Hz, 1H), 8.00 (d, *J* 8.4 Hz, 1H), 7.82 (dd, *J* 13.6, 8.5 Hz, 2H), 7.69 - 7.61 (m, 3H), 7.55 - 7.51 (m, 2H), 7.41 - 7.34 (m, 2H), 4.31 (s, 3H), 3.55 - 3.42 (m, 2H), 3.40 (s, 1H), 3.37 - 3.32 (m, 1H), 3.03 (t, *J* 6.2 Hz, 1H), 1.86-1.77 (m, 1H), 0.70 (dd, *J* 6.7, 1.3 Hz, 6H).

Synthesis of axially chiral Au(I)-NHC-*N*-naphthamide complexes (9,10)

1-[2-(2-Hydroxy-1-phenylethyl)carbamoyl)naphthalen-1-yl]-3-methyl-2,3-dihydro-*1H*-benzo[*d*]imidazol-2-yl)gold(I) iodides; *S*$_a$,*S*-9 and *R*$_a$,*S*-9. A diastereomeric mixture of benzimidazolium salt **7** (47.2 mg, 0.08 mmol), AuCl·SMe_2 (25.4 mg, 0.08 mmol), and sodium acetate (22.8 mg, 0.28 mmol) were dissolved in CH_3CN (6 mL) and stirred for 22 h at rt. After removal of the solvent under reduced pressure, the residue was purified by flash chromatography (EtOAc : *n*-pentane = 1:1) to afford axially chiral Au(I) complexes *S*$_a$,*S*- **9** (18.5 mg, 29%) as a brown oil and *R*$_a$,*S*- **9** (13.8 mg, 22%) as a white solid. (^{1}H and ^{13}C NMR assignments of *S*$_a$,*S*-**9** and *R*$_a$,*S*-**9**, based on 2D NMR studies (COSY, HSQC, HMBC) are available in SI).

S$_a$,*S*-**9**: ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.14 (d, *J* 8.5 Hz, 1H, Ar), 8.04 (d, *J* 8.3 Hz, 1H, Ar), 7.73 (d, *J* 8.5 Hz, 1H, Ar), 7.66-7.63 (m, 1H, Ar), 7.60 (d, *J* 8.3 Hz, 1H, Ar), 7.52-7.47 (m, 2H, Ar), 7.41 (m, 2H, Ar), 7.38-7.32 (m, 3H, Ar), 7.31-7.28 (m, 1H, Ar), 7.21 (d, *J* 8.5 Hz, 1H, Ar), 6.99 (d, *J* 8.2 Hz, 1H, NH), 6.94 (d, *J* 8.2 Hz, 1H, Ar), 5.11 (m, 1H, CH), 4.22 (s, 3H, CH_3), 3.96 (dd, *J* 4.1, 11.5 Hz, 1H, CH_2), 3.91 (dd, *J* 5.3, 11.4 Hz, 1H, CH_2), 2.47 (s, br, 1H, OH). ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm) 188.7 (C-Au), 166.6 (C=O), 138.8 (C_q), 135.5 (C_q), 134.9 (C_q), 133.7 (C_q), 132.9 (C_q), 131.2 (C_{ar}), 130.8 (C_q), 129.9 (C_q), 128.9 (2C, C_{ar}), 128.77 (C_{ar}), 128.72 (C_{ar}), 128.3 (C_{ar}), 127.9 (C_{ar}), 127.0 (2C, C_{ar}), 125.5 (C_{ar}), 125.1 (C_{ar}), 124.1 (C_{ar}), 122.9 (C_{ar}), 112.9 (C_{ar}), 111.5 (C_{ar}), 65.4 (CH_2), 55.6 (CH), 35.1 (CH_3). IR ($CDCl_3$, cm^{-1}): 3410 (b), 3060 (w), 2927 (w), 1658 (s), 1503 (m), 1440 (w), 1375 (m), 1047 (m), 910 (m), 732 (s). HRMS (ESI) calcd for $C_{27}H_{24}N_3O_2IAu$ [M+H] 746.0579; found 746.0591.

R$_a$,*S*-**9** : ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 8.17 (d, *J* 8.5 Hz, 1H, Ar), 8.03 (d, *J* 8.4 Hz, 1H, Ar), 7.87 (d, *J* 8.5 Hz, 1H, Ar), 7.65-7.61 (m, 1H, Ar), 7.49-7.45 (m, 3H, Ar), 7.34-7.30 (m, 1H, Ar), 7.30-7.27 (m, 3H, Ar), 7.17 (dd, *J*

7.8, 9.3 Hz, 2H, Ar), 7.11 (d, *J* 8.6 Hz, 1H, Ar), 7.01 (d, *J* 7.3 Hz, 1H, NH), 6.92 (d, *J* 8.2 Hz, 1H, Ar), 4.89 (q, 1H, CH), 3.91 (s, 3H, CH_3), 3.90-3.86 (m, 2H, CH_2), 2.28 (t, *J* 5.7, 1H, OH). ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm) 189.0 (C-Au), 166.7 (C=O), 138.0 (C_q), 135.4 (C_q), 135.0 (C_q), 133.4 (C_q), 132.6 (C_q), 131.3 (C_{ar}), 130.03 (C_q), 129.99 (C_q), 128.9 (2C, C_{ar}), 128.73 (C_{ar}), 128.69 (C_{ar}), 128.4 (C_{ar}), 127.8 (C_{ar}), 127.1 (2C, C_{ar}), 125.6 (C_{ar}), 125.2 (C_{ar}), 124.9 (C_{ar}), 122.7 (C_{ar}), 112.7 (C_{ar}), 111.2 (C_{ar}), 65.9 (CH_2), 56.5 (CH), 34.8 (CH_3). IR ($CDCl_3$, cm^{-1}): 3474 (b), 3288 (b), 3057 (w), 2931 (w), 1655 (s), 1526 (m), 1387 (m), 1048 (m), 910 (m), 825 (s). HRMS (ESI) calcd for $C_{27}H_{24}N_3O_2IAu$ [M+H] 746.0579; found 746.0588.

1-[2-(1-Hydroxy-3-methylbutan-2-yl)carbamoyl)naphthalen-1-yl]-3-methyl-2,3-dihydro-*1H*-benzo[*d*]imidazol-2-yl)gold(I) iodides; *S*$_{\alpha}$,*S*-10 and *R*$_{\alpha}$,*S*-10.

i) Diastereomerically pure *S*$_{\alpha}$,*S*-imidazolium **8a** (106 mg, 206 mmol), $AuCl{\cdot}SMe_2$ (62 mg, 210 mmol) and potassium carbonate (264 mg, 1.91 mol) were dissolved in acetone (15 mL) and stirred at refluxing for 2 h. The mixture was filtered through silica and solvent was removed under reduced pressure to yield gold(I) complex *S*$_{\alpha}$*S*-**10** (85 mg, 58%).

ii) A diastereomeric mixture (1:1) of *S*$_{\alpha}$,*S*-**8** and *R*$_{\alpha}$,*S*-**8** diastereomers (54.2 mg, 105 mmol), $AuCl{\cdot}SMe_2$ (31 mg, 107 mmol) and potassium carbonate (146 mg, 1.05 mol) were dissolved in acetone (7 mL) and stirred at reflux for 2 h. The crude mixture was purified with flash chromatography (EtOAc:*n*-pentane = 1:1) to yield diastereomerically pure *R*$_{\alpha}$,*S*-**10** (11.9 mg, 16%) and *R*$_{\alpha}$,*S*-**10** (12.5 mg, 17%) gold(I) complexes.

S$_{\alpha}$,*S*-**10**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* 8.6, 1H), 8.08 - 8.03 (m, 1H), 7.75 (d, *J* 8.5 Hz, 1H), 7.65 (ddd, *J* 8.2, 6.8, 1.1 Hz, 1H), 7.59 (dt, *J* 8.3, 0.9 Hz, 1H), 7.52 - 7.46 (m, 2H), 7.34 (d, *J* 15.5 Hz, 1H), 7.20 (dd, *J* 8.5, 1.1 Hz, 1H), 6.95 (d, *J* 8.2 Hz, 1H), 6.51 (d, *J* 9.2 Hz, 1H), 4.19 (s, 3H), 3.86 - 3.79 (m, 1H), 3.74 { 3.69 (m, 2H), 2.03 - 1.96 (m, 1H), 1.01 (dd, *J* 14.3, 6.7 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 188.5, 166.9, 135.6, 134.8, 134.2, 132.8, 131.2, 130.8, 129.9, 128.8, 128.7, 128.2, 125.6, 125.0, 123.8, 122.9, 112.9, 111.5, 62.0, 56.9, 35.1, 29.4, 19.8, 19.5. IR ($CDCl_3$, cm^{-1}): 3348 (b), 3051 (w), 2962 (m), 2874 (w), 1733 (w), 1650 (s), 1564 (m), 1534 (m), 1461 (m), 1378 (m), 1258 (m), 918 (m), 751 (s), 731 (s). HRMS (ESI, *m/z*): calcd for $C_{24}H_{25}N_3O_2AuINa$ [M + Na] 734.0555; found 734.0557.

R$_{\alpha}$,*S*-**10**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (dd, *J* 8.6, 0.9 Hz, 1H), 8.02 (dt, *J* 8.3, 0.9 Hz, 1H), 7.79 (d, *J* 8.5 Hz, 1H), 7.63 (ddd, *J* 8.2, 6.8, 1.1 Hz, 1H), 7.59 (d, *J* 8.3 Hz, 1H), 7.53 - 7.49 (m, 1H), 7.48 (ddd, *J* 8.2, 6.8, 1.2 Hz, 1H), 7.36 (ddd, *J* 8.3, 7.3, 1.0 Hz, 1H), 7.16 - 7.11 (m, 1H), 6.98 (dt, *J* 8.3, 0.9 Hz, 1H), 6.53 (d, *J* 8.2 Hz, 1H), 4.20 (s, 3H), 3.76 - 3.61 (m, 3H), 2.20 (t, *J* 5.5 Hz, 1H), 1.92 - 1.83 (m, *J* 6.7 Hz, 1H), 0.82 (dd, *J* 6.8, 4.7 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.2, 167.5, 135.6, 134.8, 134.2, 132.8, 131.2, 130.1, 129.9, 128.7, 128.7, 128.3, 125.7, 125.3, 124.6, 122.7, 112.9, 111.3, 63.5, 58.2, 35.0, 29.0, 19.3. IR ($CDCl_3$, cm^{-1}): 3416 (b), 2959 (m), 2874 (w), 1651 (s), 1516 (s), 1460 (m), 1440 (m), 1388 (m), 1372 (m), 1238 (m), 911 (m), 744 (s). HRMS (ESI, *m/z*): calcd for $C_{24}H_{25}N_3O_2AuINa$ [M + Na] 734.0555; found 734.0557.

Synthesis of axially chiral Au(III)Cl$_3$-NHC complexes (11, 12)

[1-(2-(2-Hydroxy-1-phenylethyl)carbamoyl)naphthalen-1-yl]-3-methyl-2,3-dihydro-*1H*-benzo[*d*]imidazol-2-yl)gold(III) trichloride; *S*$_{\alpha}$,*S*-11. *S*$_{\alpha}$,*S*-11: Diastereomerically pure gold(I) complex *S*$_{\alpha}$,*S*- **9** (15.8 mg, 0.02 mmol) and $PhICl_2$ (7.3 mg, 0.026 mmol) were dissolved in CH_2Cl_2 (2 mL) and stirred at rt for 15 min. *n*-Pentane (8 mL) was added to the solution and gave a yellow precipitate. The precipitate was filtered and washed with *n*-pentane (30 mL) and concentrated in vacuo. The crude product was purified by flash column chromatography (EtOAc/pentane = 1:1) and yielded Au(III)-NHC complex *S*$_{\alpha}$,*S*-**11**) (6.2 mg, 41%) as a yellow solid. (^{1}H and ^{13}C NMR assignment of ***S*$_{\alpha}$,*S*-11**, based on 2D NMR studies (COSY, HSQC, HMBC) are available in SI).^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.23 (d, *J* 8.5 Hz, 1H, Ar), 8.05 (d, *J* 8.3 Hz, 1H, Ar), 7.87 (d, *J* 8.5 Hz, 1H, Ar), 7.72 (d, *J* 8.4 Hz, 1H, Ar), 7.68 (t, *J* 7.5 Hz, 1H, Ar), 7.60-7.55 (m, 3H, Ar, NH), 7.48 (d, *J* 8.6 Hz, 1H, Ar), 7.43 (t, *J* 7.8 Hz, 1H, Ar), 7.30 (t, *J* 7.6 Hz, 2H, Ar), 7.26-7.22 (m, 3H, Ar), 7.17 (d, *J* 8.4 Hz, 1H, Ar), 4.94 (m, 1H,CH), 4.37 (s, 3H, CH3),

3.55 (d, *J* 11.3 Hz, 1H, CH_2), 3.21 (t, *J* 5.4 Hz, 1H, CH_2). ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm) 165.5 (C=O), 152.7 (C-Au), 138.5 (C_q), 136.2 (C_q), 135.2 (C_q), 133.8 (C_q), 133.0 (C_q), 132.4 (C_{ar}), 129.1 (C_q), 128.99 (C_{ar}), 128.93 (C_{ar}), 128.91 (C_{ar}), 128.6 (C_{ar}), 127.9 (2C, C_{ar}), 127.6 (C_q), 126.62 (2C, C_{ar}), 126.58 (C_{ar}), 126.4 (C_{ar}), 125.1 (C_{ar}), 124.1 (C_{ar}), 114.0 (C_{ar}), 111.8 (C_{ar}), 65.8 (CH_2), 55.4 (CH), 35.6 (CH_3). IR ($CDCl_3$, cm^{-1}): 3338 (b), 3063, 2926 (w), 2853 (w), 1658 (s), 1503 (s), 1262 (w), 1148 (w), 1071 (w), 1027 (w), 748 (m), 707 (m). MS (ESI): Three set of molecular ion signals with Cl_3 isotope pattern (~20 : 20 : 6 : 1 ratio): (M+H) (*m/z* 724/726/728), (M+Na) adduct (*m/z* 746/748/750) and (M+K) adduct (*m/z* 762/764/766). HRMS (ESI) calcd for $C_{27}H_{24}N_3O_2Au^{35}Cl_3$ [M + H] 724.0600; found 724.0602; calcd for $C_{27}H_{23}N_3O_2Au^{35}Cl_3Na$ [M + Na] 746.0419; found 746.0424; calcd for $C_{27}H_{23}N_3O_2Au^{35}Cl_3K$ [M + K] 762.0158; found 762.0161.

[1-(2-(1-Hydroxy-3-methylbutan-2-yl)carbamoyl)naphthalen-1-yl]-3-methyl-2,3-dihydro-*1H*-benzo[*d*]imidazol-2-yl)gold(III) trichlorides; *S*$_{\alpha}$,*S*-12 and *R*$_{\alpha}$,*S*-12. *S*$_{\alpha}$,*S*-12: Diastereomerically pure gold(I) complex *S*$_{\alpha}$,*S*-**10** (15.4 mg, 22 mmol) and $PhICl_2$ (12.4 mg, 45 mmol) were dissolved in CH_2Cl_2 (2.5 mL) and stirred at rt for 15 min. The product was crystallized from *n*-pentane and yielded product *S*$_{\alpha}$,*S*-**12** (5.8 mg, 34%). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.28 (d, *J* 8.5 Hz, 1H), 8.10 (d, *J* 8.4 Hz, 1H), 7.84 (d, *J* 8.5 Hz, 1H), 7.75 (dt, *J* 8.5, 0.9 Hz, 1H), 7.72 (ddd, *J* 8.0, 6.8, 1.1 Hz, 1H), 7.59-7.63 (m, 2H), 7.53 (dd, *J* 8.5, 0.6 Hz, 1H), 7.46 (ddd, *J* 8.3, 7.3, 0.9 Hz, 1H), 7.20 (d, *J* 8.2 Hz, 1H), 7.0 (d, *J* 8.6 Hz, 1H), 4.34 (s, 3H), 3.50-3.54 (m, 1H), 3.31 (dt, *J* 11.5, 4.7 Hz, 1H), 2.87 (ddd, *J* 3.4, 7.1, 11.0 Hz, 1H), 1.77-1.86 (m, 1H), 1.43 (dd, *J* 6.8, 5.0 Hz, 1H), 0.89 (d, *J* 7.0 Hz, 3H), 0.87 (d, *J* 7.0 Hz, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 166.2, 136.6, 135.6, 134.4, 134.1, 132.6, 129.5, 129.1, 129.1, 128.9, 127.7, 126.8, 125.6, 124.6, 114.3, 112.3, 62.7, 57.4, 36.0, 29.5, 19.4, 19.2. HRMS (ESI) showed the Au(III)bis-NHC non-chloro molecular ion, Au(III)$(NHC)_2$; calcd for $C_{48}H_{50}N_6O_4Au$ [M^+ – 2Cl] 971.3559; found 971.3554.

R$_{\alpha}$,*S*-**12**: Following the same procedure as for *S*$_{\alpha}$,*S*-**12** above, $PhICl_2$ oxidation of gold(I) complex *R*$_{\alpha}$,*S*-**10** afforded diastereomer *R*$_{\alpha}$,*S* **12** (approx. 30% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, *J* 9.6 Hz, 1H), 8.08 - 8.00 (m, 1H), 7.84 (d, *J* 8.5 Hz, 1H), 7.78 - 7.65 (m, 2H), 7.62 - 7.55 (m, 2H), 7.48 - 7.43 (m, 2H), 7.24 - 7.20 (m, 1H), 6.95 (d, *J* 7.0 Hz, 1H), 4.37 (s, 3H), 3.62 - 3.48 (m, 3H), 1.70 - 1.63 (m, 1H), 0.69 - 0.55 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.4, 153.0, 137.5, 136.2, 135.2, 133.6, 133.2, 132.5, 130.3, 129.1, 129.1, 129.0, 128.6, 127.0, 126.8, 126.6, 125.2, 124.0, 114.1, 111.7, 63.5, 58.8, 35.6, 28.9, 18.7, 18.6. IR ($CDCl_3$, cm^{-1}): 3339 (b), 3071 (w), 2960 (m), 1650 (s), 1522 (m), 1504 (m), 1457 (s), 1407 (m), 1377 (m), 909 (m), 730 (s). MS data showed the Au(III)bis-NHC adduct ([Au(III)$Cl_2(NHC)_2Cl_2$] for R_a,S-**12** Au(III) with the $AuCl_2$ isotope (^{35}Cl/^{37}Cl) pattern (~ 3 : 2 : 1 ratio): MS (ESI, *m/z*) for (M^+): *m/z* 1041/1043/1045; and for (M+H): *m/*z 1042/1044/1046. The non-chloro molecular ion, (M^+- 2Cl) 971 was also seen. HRMS registered the Au(III)bis-NHC adduct M^+: [Au(III)$Cl_2(NHC)_2^+$]; HRMS (ESI, *m/z*): calcd for $C_{48}H_{50}Au^{35}Cl_2N_6O_4$ (M^+) 1041.2936; found 1041.2936; calcd for $C_{48}H_{51}Au^{35}Cl_2N_6O_4$ (M+H) 142.3014; found 1042.2942; *m/z*); calcd for $C_{48}H_{50}N_6O_4Au$ [M^+ – 2Cl] 971.3559; found 971.3562.

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Supplementary Material

^{1}H and ^{13}C NMR spectra of novel compounds **7-12**, as well as structures of compounds **5, 9** and **11** shown with full ^{1}H and ^{13}C NMR assignments can be found in the Supplementary Material file.

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