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Pyridine and Quinoline Coordination

Pyridine- and Quinoline-Based Gold(III) Complexes: Synthesis, Characterization, and Application

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Abstract: Studies on gold(III) coordination of a series of prepared polydentate pyridine and quinoline based ligands are reported. Characterization (^{1}H, ^{13}C, ^{15}N NMR, and XRD) of the novel gold(III) complexes, prepared in 31–98 % yield, revealed different coordination ability of the pyridine and quinoline nitrogen atoms. Testing of catalytic activity in cyclopropanation of propargyl ester and styrene demonstrated that all the new ligated gold(III) complexes were catalytically active and outperformed $KAuCl_4$. The superior activity of the particular Au(III)-pyridine-oxazole complexes may indicate de-coordination of the pyridine-N ligand as a crucial step for efficient generation of catalytic activity.

Introduction

Homogeneous gold catalysis in organic synthesis has become a rapidly growing field within the last decades.[1] However, gold catalysis is still described as a new and young area compared to the chemistry of the more utilized and developed neighbors in the periodic table e.g. Pt, Pd, Hg, Rh, Ru and Ir.[2] This is often evidenced by the mechanism for gold catalysis being less understood and explored compared to the other transition metals.[3] The development of gold catalysis has mainly focused on gold(I) species, as shown by a large number of reported ligated gold(I) complexes utilized in various catalytic transformations.[4] Also reaction mechanisms have been studied by characterization of reactive intermediates and by corroboration of the experimental data with computational studies.[4b,4c,5] Catalysis by gold(III) has, on the other hand, been less developed and is still mainly dominated by the inorganic gold(III) salts, such as $AuCl_3$ and $KAuCl_4$.[6] However, compared to the linear gold(I) complexes, the square-planar coordination mode of gold(III) species may provide advantages in order to obtain improved control around the reaction center and, hence, influence the selectivity of the catalytic reaction. A great variety of strategies for design of mono- and polydentate ligands and their Au(III) complexes is conceivable. It is also shown that the oxidation state of gold can affect the reactivity and outcome for some organic transformation.[4a]

However, in recent years, interesting ligated gold(III) complexes are reported. Although some of the compounds are studied as catalysts in organic transformations,[7] the Au(III)-ligand concept was initially mainly developed for bioactive studies. A number of stable Au(III)-ligand complexes were designed as promising candidates for biological testing, such as antitumor agents,[8] anticancer,[9] Anti-parasitic agents,[10] antifungal,[11] inhibition of DNA/RNA synthesis,[12] and aquaporin inhibition.[13] The reported gold(III) complexes are often based on nitrogen containing ligands, such as diamine, polyamine, cyclam, bipyridyl, porphyrin, phenanthroline and terpyridine.

The limited experience and understanding of the chemistry of gold(III)-ligand species, indicates that more knowledge is needed for development of stable Au(III) complexes and for studies of their catalytic activity.

We have previously prepared gold(III) complexes based on bisoxazoline and 2-pyridylmenthol ligands, and studied their catalytic properties in cyclopropanation reactions.[14] We hereby present further studies on the synthesis of a series of new pyridyl and quinolinyl based polydentate ligands, along with gold(III) coordination studies. The catalytic ability of the new gold(III) complexes in cyclopropanation reaction is studied, as well.

Results and Discussion

Preparation of 2-(Quinolin-2-yl)- and 2-(Pyridin-2-yl)-4,5-dihydrooxazole Gold(III) Complexes, 1-Au(III) and 2-Au(III)

Ligated gold(III) complexes based on bisoxazoline,[14,15] pyridinyl-oxazolines[16] and 2,6-bisoxazoline-pyridine[17] have previously been prepared with different counterions. Given the affinity of gold(III) to coordinate to such heterocyclic ligands, we initially studied the coordination ability of gold(III) to (*S*)-4-isopropyl-2-(quinolin-2-yl)-4,5-dihydrooxazole, **1a**, and (*S*)-4-phenyl-2-(quinolin-2-yl)-4,5-dihydrooxazole, **1b**, (Scheme 1a). The coordination of the alkyl-substituted ligand (R = *i*Pr) to $AuCl_3$ seemed to give a mixture of two complexes (^{1}H NMR). Addition of NH_4PF_6 has been reported[18] to activate gold(III)

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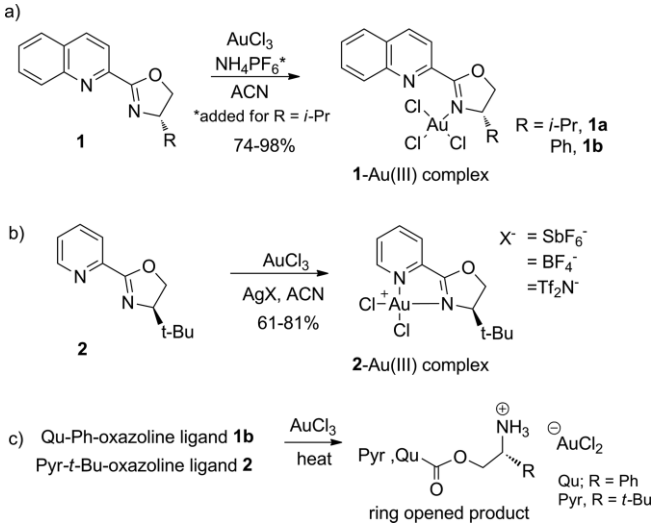
for coordination. This method allowed successful formation of the oxazole mono-coordinated crystalline **1a**-Au(III) complex as the only product (74 % yield, Scheme 1a). Addition of NH_4PF_6 was not required to efficiently obtain the corresponding **1b**-Au(III) complex (98 %) with the phenyl-substituted ligand (R = Ph).



Scheme 1. Preparation of (a) **1**-Au(III), (b) **2**-Au(III) complexes[19] and (c) Pyr-/Qu-oxazoline ring opened product.

The crystal structure (XRD) of the **1a**-Au(III) complex confirmed the formation of a mono-coordinated Au(III) complex through the oxazole-nitrogen, while no coordination of the quinoline-nitrogen had taken place (Figure 1a).

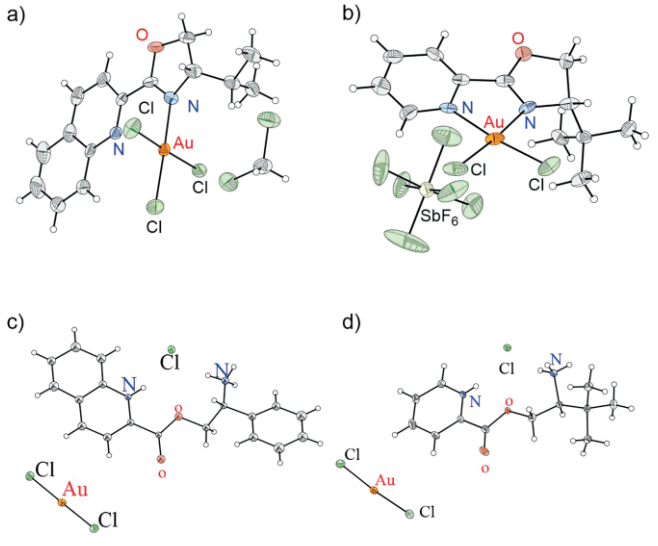


Figure 1. Crystal structures of (a) **1a**-Au(III); (b) **2**-Au(III)-SbF_6; as well as ring opened carboxylate Au(I)Cl_2 products from (c) ligand **1b**, and (d) ligand **2** (determined by XRD).

It is expected that the **1**-Au(III) complexes would be more catalytically active if both N-heteroatoms of the bidentate ligands were coordinated to gold(III). Different conditions were tested in order to facilitate exchange of the second strongly coordinated chlorine with the quinoline nitrogen (Table 1). However, none of the experiments, including varied temperature, microwave heating or addition of weakly coordinating anions, resulted in coordination of the second nitrogen to gold(III). However, an interesting difference between the quinoline ligands was identified, as the *i*Pr-substituted ligand, **1a**, had higher stability than the phenyl analogue **1b**. By heating (60 °C) the coordination solution of $AuCl_3$ and the ligand **1b**, a ring opened and gold(III) reduction minor product, the [(2-ammoniumquinoline carboxylate){Au(I)Cl_2}] complex, was identified (XRD, Figure 1c, Scheme 1c, Table 1, entry 6). The possible nucleophilic attack of water on the oxazoline ring to afford ring opening, was however, not observed for the more stable ligand **1a** at the same conditions (Table 1, entry 1). The ring opening reaction was also observed by storage of the coordination solution of $AuCl_3$ and the **1b** ligand in dichloromethane for 2–3 days. Corresponding ring opening of the oxazoline ring in the presence of water under weak basic conditions[16] or during gold(III) coordination in aqueous media[17] has been reported. In contrast to the presently observed aminocarboxylate complex formed by cleavage of C=N bond by water, we recently observed that oxazole ring opening by nucleophilic attack of strongly coordinating anions on **2**-Au(III) complexes gave a different outcome, as the nucleophilic $CF_3CO_2^-$ or NO_3^- anions attack the oxazoline-CH_2, to give cleavage of the oxazoline CH_2-O bond.[19]

Table 1. Attempted coordination of quinoline-nitrogen of ligands **1** to $AuCl_3$.[a]

Entry	Ligand	Additive	Temp.	Observation[c]
1	**1a**	_	60 °C	n.r.
2	**1a**	NH_4PF_6	r.t.	n.r.
3	**1a**	NH_4PF_6	60 °C	n.r.
4	**1a**	$AgSbF_6$	r.t.	n.r.
5	**1a**-Au(III)[b]	$AgSbF_6$	r.t.	n.r.
6	**1b**		60 °C	r.o.
7	**1a**	$AgSbF_6$	80 °C[d]	n.r.

[a] 1 equiv. $AuCl_3$ was used. [b] $AuCl_3$ was not added. [c] Abbreviations: n.r. (no reaction); r.o. (ring opening). [d] Microwave heating in a closed vial.

As the unsuccessful coordination of the quinoline nitrogen could be explained by insufficient electron density caused by electron delocalization in the benzo-fused aromatic system, the analogues pyridine ligand would be more promising for bidentate coordination. In fact, initial treatment of the pyridine-oxazoline ligand **2** (Scheme 1b) with gold(III) (1 equiv. $AuCl_3$) gave 50 % conversion of the ligand into a new product, which was initially believed to be a Au(III) complex with $AuCl_4^-$ as counterion, as reported for similar ligands.[16] However, a new minor product was also selectively formed by reflux of ligand **2** and $AuCl_3$ in acetonitrile and was identified (XRD, Figure 1d) as the ammonium-picolinate Au(I)Cl_2 complex, which is the similar ring opened product as described above (Figure 1c).

It is previously reported that ligand coordination in the presence of a silver salt of a weakly coordinating ion may give more selective coordination to gold(III) and also prevent formation of $AuCl_4^-$ complexes.[14,16] This method successfully gave crystalline **2**-Au(III) complexes with the different counterions SbF_6^-, BF_4^- and Tf_2N^- (61–82 %, Scheme 1b) by addition of the appro-

priate silver salts.[19] Preparation of a **2**-Au(III) complex by BArF counterion exchange with the NaBArF salt failed, possibly due to the lack of driving force gained by the precipitation of AgCl, using the silver salt of the counterion.

The crystal structures of **2**-Au(III) with SbF_6 as the counterions were determined (XRD, Figure 1b). In contrast to the quinoline ligands, the pyridine analogues coordinated efficiently with both heterocyclic nitrogen atoms in a bidentate Au(III) coordination mode. Only the main structure with SbF_6 as counterion is shown. However, X-ray analysis showed that the corresponding complex with $AuCl_4$ counterion also was formed. However, selective preparation of the **2**-Au(III)-SbF_6 complex was readily obtained by increasing the amount of $AgSbF_6$ from 1.2 to 2 equivalents in order to suppress the formation of the unwanted $AuCl_4$ counterion.

The different coordination abilities of pyridine and quinoline nitrogen atoms to the gold(III), shown by XRD (Figure 1a, b), were also clearly recognized by ^{1}H NMR. Monitoring of the gold coordination experiments of quinoline and pyridine based ligands, afforded a convenient method for identifying selective mono- or bidentate Au(III) coordination modes (Figure 2). Coordination of pyridine-oxazoline ligand **2** to Au(III) and formation of the **2**-Au(III) complexes gave strong and significant deshielding effects and large peak shifts ($\Delta\delta^1H_{coord} = \delta^1H_{complex} - \delta^1H_{ligand}$) of most pyridine protons ($\Delta\delta^1H_{coord}$ up to 0.8 ppm, Figure 2a). Whereas pyridine coordinates through its nitrogen, the delocalized aromatic electron structure of the benzo-fused quinoline analogue prohibits N-coordination to gold(III), as shown by the moderate deshielding effect and peak shifts of the quinoline protons H3 and H4 ($\Delta\delta^1H_{coord}$ 0.2–0.6 ppm, Figure 2b). In particular, protons H5–8 in the benzo-fused quinoline part were weakly affected by coordination and experience minor deshielding ($\Delta\delta^1H_{coord} < 0.2$ ppm). The selective coordination effect was seen by ^{1}H NMR for both the complexes **1a**-Au(III) and **1b**-Au(III) and demonstrates that no nitrogen-gold(III) coordination of quinoline takes place.

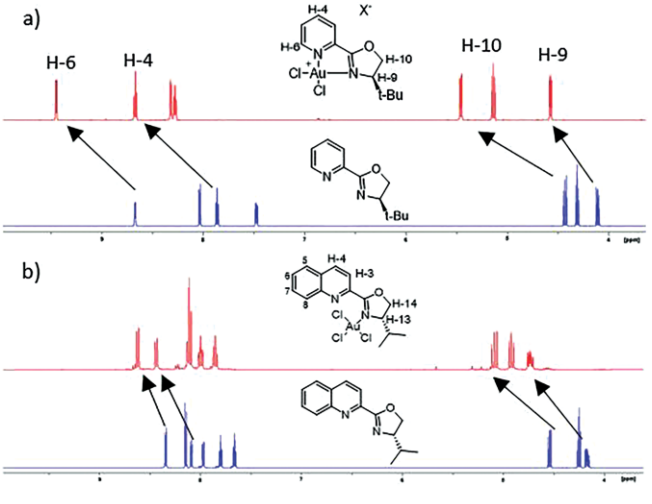
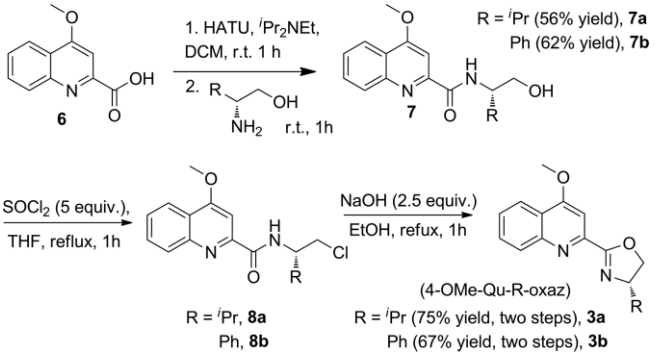


Figure 2. ^{1}H NMR study (δ = 4–10 ppm) of $AuCl_3$ coordination experiments of ligands (a) **2** and (b) **1a**.

As ^{15}N NMR chemical shifts have proven to give valuable information on metal coordination,[20] the observed coordination effect in ^{1}H NMR was corroborated by the change in ^{15}N NMR shifts by coordination ($\Delta\delta^{15}N_{coord} = \delta^{15}N_{complex} - \delta^{15}N_{ligand}$). In a recent study,[19] we observed that both nitrogen atoms in the **2**-Au(III) complexes were clearly affected by coordination, as shown by large differences of both the pyridine nitrogen ($\Delta\delta^{15}N_{coord}$ –87.5 ppm) and the oxazoline nitrogen ($\Delta\delta^{15}N_{coord}$ –41.1ppm) by ^{1}H,^{15}N HMBC in CD_3CN, indicating bidentate Au(III) coordination of the pyridine-oxazoline ligand **2**. In contrast, similar studies of the **1a**-Au(III) complex, indicated that the quinoline nitrogen was hardly affected by coordination, as shown by a minor NMR peak change ($\Delta\delta^{15}N_{coord}$ 2.2 ppm). Mono-coordination of the oxazoline nitrogen was demonstrated by the large difference of the oxazoline nitrogen signal upon coordination ($\Delta\delta^{15}N_{coord}$ –76.2 ppm).

Different impact on the oxazoline nitrogen atoms by coordination of the pyridine and the quinoline complexes was seen. Larger $\Delta\delta^{15}N_{coord}$ and stronger coordination of Au(III) to the oxazoline nitrogen was observed for the mono-dentate quinoline based complex ($\Delta\delta^{15}N_{coord}$ –76.2 ppm) than the di-coordinated pyridine complex ($\Delta\delta^{15}N_{coord}$ –41.1 ppm). Additionally, ^{13}C NMR clearly showed that the aromatic carbons of quinoline ligands are less affected by coordination (^{13}C NMR spectra, see Figure S1, Supp. Info.)

In order to increase the electron density of the quinoline nitrogen to improve the coordination ability, the 4-methoxy substituted analogues of ligands **1**, ligands **3**, were synthesized according to the synthetic route described in Scheme 2.



Scheme 2. Preparation of 4-methoxy substituted quinoline ligands **3a** and **3b**.

The 4-OMe quinoline substituted ligands **3a** (*i*Pr) and **3b** (Ph) were attempted coordinated to gold(III) by the same methods as above, in the presence and absence of silver salt (Scheme 1). However, no AgCl precipitate was observed by silver salt addition and ^{1}H NMR of the coordination solutions indicated unsuccessful coordination of the quinoline nitrogen. Refluxing the reaction mixtures in acetonitrile overnight had no further effect. These observations were corroborated with ^{15}N NMR of ligand **3b** to confirm the observed results. Mono-coordination of the ligand through the oxazoline nitrogen was similarly seen by the respective large and small NMR differences of the oxazoline and quinoline nitrogen signals ($\Delta\delta^{15}N_{coord,\ oxaz}$ –74.0 ppm and $\Delta\delta^{15}N_{coord,Qu}$ –1.0 ppm).

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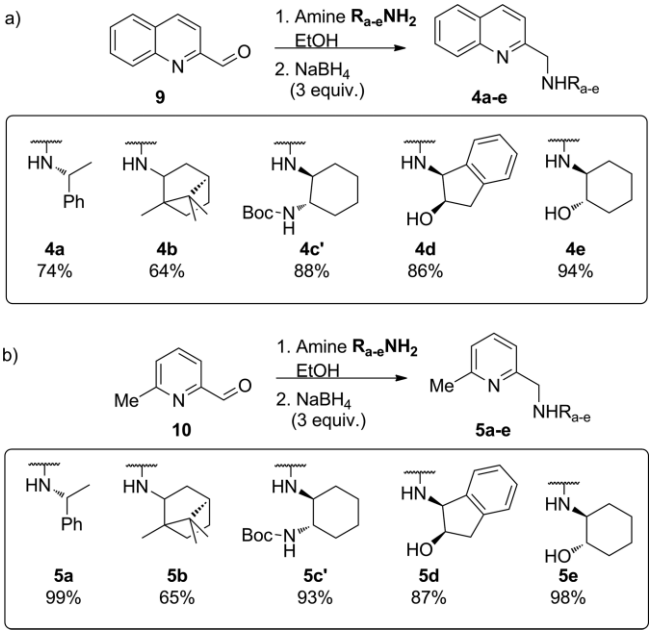
Synthesis of Potential Pyridine and Quinoline Based Ligands for Gold(III) Coordination

To further explore the selective quinoline and pyridine coordination patterns, a series of new quinoline and pyridine based Au(III)-ligand complexes were prepared, replacing the oxazoline ring with other heteroatom units. The 10 new potential ligands for gold(III) coordination were synthesized (**4a**–**e** and **5a**–**e**, 47–99 % yield) by two-step reductive amination of quinolone-2-carbaldehyde **9** or 6-methyl-picolinaldehyde **10**, and the appropriate amine $R_{a-e}NH_2$, (Scheme 3). Deprotection of *N*-Boc-compounds **4c′** and **5c′** yielded amines **4c** and **5c** (52–70 %).



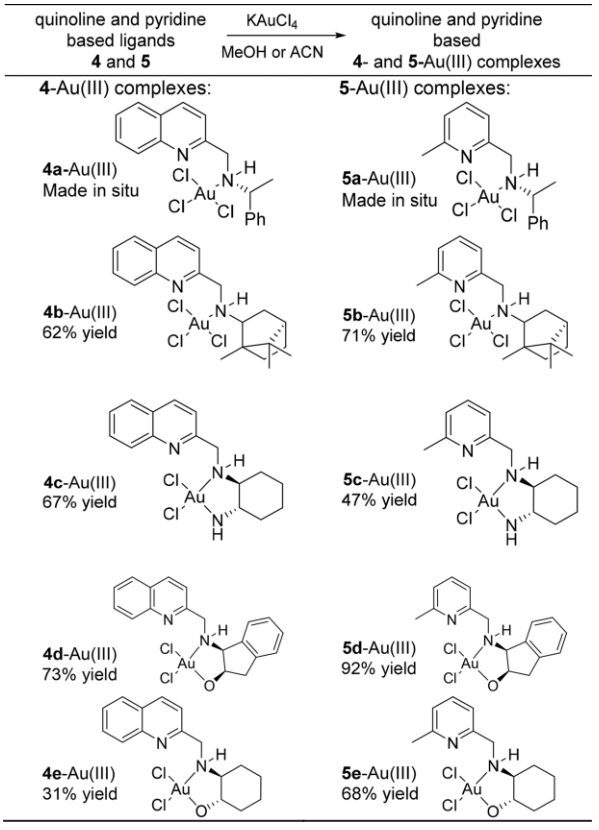
Scheme 3. Preparation of quinoline- and pyridine-based ligands (a) **4a**–**e** and (b) **5a**–**e** through reductive amination.

Gold(III) Coordination Studies of Ligands 4a–e and 5a–e

All ligands **4** and **5** readily coordinated to give Au(III) complexes (31–92 %, Table 2). Despite the polydentate nature of the ligands (*N*,*N*-bi, *N*,*N*,*N*-tri; *N*,*N*,*O*-tri), no coordination of neither the quinoline nor the pyridine nitrogen atoms took place, as only amino, di-amino and amino-alkoxylate complexes were formed. This was shown by full characterization of all complexes and was also clearly recognized by ^{1}H NMR (Figure 3). Only small changes in ^{1}H NMR chemical shifts (0.1–0.2 ppm) of heteroaromatic protons were observed upon coordination, indicating lack of coordination of the heteroaromatic nitrogen atoms, as discussed above (Figure 2).

Moderate to high yields of the monoamino-ligated Au(III) complexes of *N*,*N*-ligands **4b** and **5b** (42–82 %) were obtained. Non-coordination of heterocyclic nitrogen atoms was also seen by formation of the respective *N*,*N*-diamino complexes (62–71 %) from the possible *N*,*N*,*N*-tridentate ligands **4c** and **5c**. Coordination of the analogue potential *N*,*N*,*O*-tridentate aminocyclohexanol ligands **4e** and **5e** to gold(III) readily took place to afford the *N*,*O*-bidentate complexes **4e**-Au(III) and **5e**-Au(III) (31–68 %). No coordination of the aromatic nitrogen was observed. The potential *N*,*N*,*O*-tridentate aminoindenol ligands **4d** and **5d** showed similar coordination behavior, affording the

Table 2. Formation of Au(III) complexes of quinoline and pyridine based ligands **4** and **5**. Proposed structures of **4**- and **5**-Au(III) complexes.



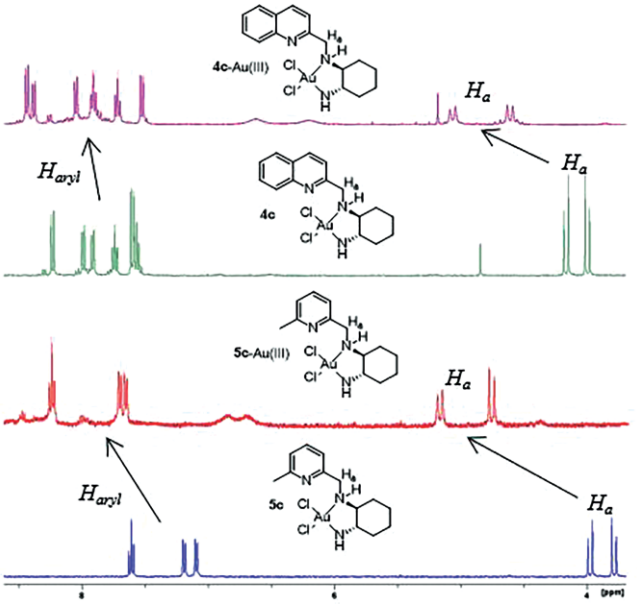


Figure 3. ^{1}H NMR study of $KAuCl_4$ coordination experiments of ligands **4c** and **5c**.

N,O-bidentate complexes **4d**-Au(III) and **5d**-Au(III) (73–92 %, Table 2).

Different stability of the quinoline and pyridine based complexes was observed. Whereas the quinoline complex **4d**-Au(III) started to decompose in one day in acetonitrile, the pyridine complex **5d**-Au(III) remained stable. This trend was seen for all complexes. The quinoline/pyridine benzylic CH_2-group may be a weak point, exposed for nucleophilic attack by traces of water in the solvent. Specially coordination of **4a** and **5a** to Au(III) resulted in complexes sensitive to water, hence these complexes were not isolated, but complexed and used directly in situ in the reaction. When suitable crystals for X-ray analysis were attempted grown for **4c**-Au(III) and **5c**-Au(III), complex **4c**-Au(III) decomposed to give crystals of diaminocyclohexane dihydrochloride, while **5c**-Au(III) formed crystals, but not proper quality for X-ray analysis.

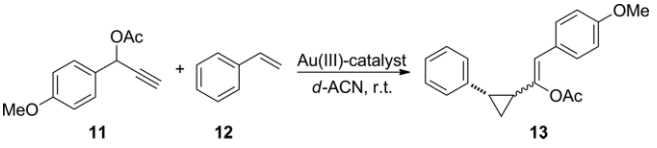
Even though larger ^{1}H NMR peak changes ($\Delta\delta^1H_{coord}$) were seen for the aromatic protons of compound **5c** than of compound **4c** upon coordination (Figure 3), ^{15}N NMR of the **5c**-Au(III) complex indicated no coordination of the pyridine nitrogen ($\Delta\delta^{15}N_{coord}$ −13.9 ppm) by addition of Au(III).

It seems like one chloride is readily exchanged, while the second requires more energy. When coordination of compound **5c** was attempted, using $AgSbF_6$ to facilitate chloride exchange and coordination of the pyridine nitrogen, the compound seemed to decompose, and a complex mixture was observed by ^{1}H NMR.

Catalytic Activity

The gold-catalyzed cyclopropanation of propargyl **11** and alkene **12** was selected as the model reaction for investigation of the catalytic ability of the new gold(III) catalyst (Table 3). This reaction has previously been thoroughly investigated (^{1}H NMR) with similar gold(III) catalysts,[14] thus providing a solid background for comparison. A difference in catalytic activity was observed for the pyridine and quinoline complexes (entries 1–5), as **2**-Au(III) and **1**-Au(III) gave full conversion in 5 min and 12–24 hours, respectively. The Au(III) complexes of the methoxy activated quinoline, **3**-Au(III), afforded faster conversion than the non-substituted complexes (entry 5/24 h; entry 7 /12 h). Comparable reactivity was observed in the presence of the quinoline and pyridine complexes **4**-Au(III) and **5**-Au(III), having the oxazoline ring replaced by other heteroatom units (entries 8–17). Although they were less active than the oxazoline based complexes above (entries 1–7), the catalytic activity of **4**-Au(III) and **5**-Au(III) complexes were definitively larger than the nearly non-catalytic $KAuCl_4$ salt (entries 18–19). $KAuCl_4$ seems to be to solvated in acetonitrile, blocking any catalyst activity of the gold center. Even if the Au(III) complexes of ligands **4** and **5** proved to be unstable, they seem to be transformed into new catalytically active species by ligand modification, as they remained catalytically active. As discussed above, the ligand may undergo benzylic cleavage, leaving gold coordinated to the chlorides and the respective amine ($R_{a\text{-}f}NH_2$). Hence, decomposition of the complexes does not generate the highly active $AuCl_3$, which, in contrast, gave immediate conversion, even by low catalyst loading (2 mol-%, entry 21). The disadvantage of $AuCl_3$ is, however, instability and low reproducibility, as shown by immediate decomposition into black precipitate. The large reactivity difference of **4**-Au(III) and **5**-Au(III) complexes compared to $AuCl_3$, illustrates the deactivating effect of an alkylamine ligand on the gold catalyst.

Table 3. Studies of catalytic activity of new gold(III) complexes in cyclopropanation of propargyl ester **11** and styrene **12**.



11 **12** **13**

Entry	Au(III) cat.[a]	Time	Conversion[b]	*Cis:trans*-ratio
1	**2**-Au(III)-SbF_6	5 min	100 %	60/40
		12 h		14/86
2	**2**-Au(III)-BF_4	5 min	100 %	56/44
		12 h		26/74
3	**2**-Au(III)-Tf_2N	5 min	100 %	54/46
		24 h		27/73
4	**1a**-Au(III)	12 h	100 %	79/21
5	**1b**-Au(III)	24 h	94 %	68/32
6	**3a**-Au(III)	< 12 h	100 %	77/23
7	**3b**-Au(III)	< 12 h	100 %	67/33
8	**4a**-Au(III)	24 h	79 %	80/20
9	**4b**-Au(III)	24 h	100 %	76/24
10	**4c**-Au(III)	12 h	100 %	78/22
11	**4d**-Au(III)	24 h	82 %	76/24
12	**4e**-Au(III)	24 h	90 %	84/16
13	**5a**-Au(III)	12 h	100 %	78/22
14	**5b**-Au(III)	24 h	100 %	86/14
15	**5c**-Au(III)	24 h[d]	100 %	71/29
16	**5d**-Au(III)	24 h	90 %	79/21
17	**5e**-Au(III)	< 24 h	100 %	81/19
18	$K(AuCl_4)$	24 h	0 %	–
19	$K(AuCl_4)$[c]	24 h	< 5 %	<99/>1
20	Box-*i*Pr-Au(III)[d]	15 min	100 %	70/30
		12 h		10/90
21	$AuCl_3$[e]	5 min	100 %	83/17
		12 h		83/17

[a] 5 mol-% catalyst was used unless stated otherwise. [b] Percent conversion of propargyl substrate (^{1}H NMR). [c] 10 mol-% of $K(AuCl_4)$ was used. [d] Previous reported reaction repeated in *d*-ACN for comparison.[14] [e] 2 mol-% of $AuCl_3$ was used.

Our previous study on Box-Au(III) complexes proved their strong catalytic effect both on cyclopropanation and subsequent in situ *cis*-to-*trans* isomerization (90 % *trans* in 12 h, entry 20). Similar unique dual properties were identified for the present **2**-Au(III) N-pyridine coordinated complexes (up to 86 % *trans* in 12 h; entries 1–3). The non-heterocycle-coordinated **1**-Au(III), and **4**-Au(III) and **5**-Au(III) complexes afforded less efficient conversions.

In a recent study, monitoring a different alkoxycyclization reaction by ^{1}H,^{15}N HMBC, a large peak shift ($\Delta\delta^{15}N_{rx}$ = $\delta^{15}N_{coord}$ − $\delta^{15}N_{diss}$ = +83.3 ppm) of the pyridine nitrogen of the **2**-Au(III) complex was observed during the reaction.[19] This most likely reflects dissociation of the pyridine nitrogen throughout the reaction, which activates the complex for coordination to the substrate. This correlates with the reactivity dif-

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ference we observe between the **2**-Au(III) and **3**-Au(III), **4**-Au(III) and **5**-Au(III) complexes, which may indicate de-coordination of the pyridine-N ligand as a crucial step for efficient generation of catalytic activity.

Despite the chiral nature of the applied Au(III) complexes, no enantioselectivity was observed, and racemic cyclopropyl products **13** were obtained (HPLC).

Conclusion

Our study on the coordination ability of new polydentate pyridine- and quinoline-oxazoline based ligands to gold(III) (^{1}H, ^{13}C, ^{15}N NMR and XRD) showed formation (61–98 %) of N-oxazoline Au(III) complexes, with selective coordination of pyridine nitrogen, whereas quinoline nitrogen atoms failed to undergo complexation. Attempts to activate the quinoline nitrogen for coordination (heat, microwave, silver salts additives, increased quinoline electron density) were unsuccessful.

To further explore the selective quinoline and pyridine coordination patterns, a series of new quinoline and pyridine based Au(III)-ligand complexes were prepared (31–92 %), replacing the oxazoline ring with other heteroatom units. However, the obtained complexes were formed by selective coordination of the *N*,*N*- or *N*,*O*-heteroatom units, whereas pyridine and quinoline nitrogen coordination was unsuccessful.

The catalytic ability of all of the described new gold(III) complexes were screened in a cyclopropanation reaction of styrene using propargyl ester. While all complexes were catalytically active, the pyridine coordinated **2**-Au(III) complexes had similar unique catalytic properties as our previously studied Box-Au(III) complexes. Hence, the studies may indicate that pyridine-nitrogen de-coordination ability is significant in order to generate highly efficient catalytic activity.

Experimental Section

General: Commercial grade reagents were used as received. Dry solvents were collected from a solvent-purification system. All reactions were monitored by thin-layer chromatography (TLC) using silica gel 60 F254 (0.25-mm thickness) or by ^{1}H-NMR. Flash chromatography was carried out using silica gel 60 (0.040–0.063 mm). High Throughput Flash Purification (HPFP) was performed on pre-packed cartridges. ^{1}H and ^{13}C NMR spectra were recorded using a 400 or 600 MHz spectrometer, while ^{1}H,^{15}N HMBC was recorded suing a 600 MHz spectrometer. Chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) or *d*-ACN. Coupling constants (*J*) are reported in Hertz (Hz). The attributions of the chemical shifts were determined using COSY, HSQC and HMBC NMR experiments. Accurate mass determination in either positive or negative mode was performed with a "Synapt G2-S" Q-TOF instrument from Waters. Samples were ionized with an ASAP probe (APCI) or ESI probe, and no chromatographic separation was used before the mass analysis. Calculated exact mass and spectra processing was done by Waters TM Software Masslynx V4.1 SCN871. Single crystal X-ray data was acquired using a Bruker D8 Venture diffractometer with the APEX3 suit, integrated with SAINT V9.32B, solved with XT and refined with XL using Olex2 as GUI. The cif files were edited with encipher 1.4 and molecular graphics were produced with Mercury 3.8. ORTEP plots are shown in the thesis and all metric data, including reflection data, are contained in the respective cif files. Propargyl ester **11**[21] and **2**-Au(III)-SbF_6/BF_4/NTf_2 complexes[19] were prepared according to literature procedures. The ligands (*S*)-4-*tert*-butyl-2-(2-pyridyl)oxazoline, (*S*)-4-isopropyl-2-(quinolin-2-yl)-4,5-dihydrooxazole and (*R*)-4-phenyl-2-(quinolin-2-yl)-4,5-dihydrooxazole were commercially available. Crystal structures (Figure 1a-d).

CCDC 1951650 {for **1a**-Au(III)}, 1951651 {for **2**-Au(III) SbF_6}, 1951652 {for ring opened carboxylate Au(I)Cl_2 product from ligand **1b**}, and 1951653 {for ring opened carboxylate Au(I)Cl_2 product from ligand **2**} contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

General Method 1: Synthesis of Pyridine- and Quinoline-based Ligands: Quinoline-2-carbaldehyde **9** or 6-methylpicolinaldehyde **10** (1 equiv.) and the selected chiral amine (1 equiv.) were dissolved in dry EtOH (0.15 molar solution) under a nitrogen atmosphere. The reaction mixture was stirred until full conversion into imine was observed by ^{1}H NMR (around 1 hour), before $NaBH_4$ (3 equiv.) was added directly to the reaction mixture. When ^{1}H NMR showed full reduction to amine, the reaction was quenched with HCl (1 M). Aqueous NaOH solution (1 M) was subsequent added until basic solution, before the water phase was extracted with DCM (3 × 30 mL). The combined organic phases were dried with anhydrous Na_2SO_4, filtered and dried under reduced pressure. If the product needed additional purification, it was done as indicated for each compound.

General Method 2: Coordination of ligands to gold(III). Ligands **4a**–**e** or **5a**–**e** were dissolved in ACN and added $KAuCl_4$ (1 equiv.). The mixture was stirred for 15–60 minutes before white precipitate from KCl was removed and the complex was dried under reduced pressure. If the product needed additional treatment, it was done as indicated for each compound.

General Method 3: Testing of catalytic ability in cyclopropanation reaction. The propargyl ester **11** (5 mg, 1 equiv.) and styrene **12** (4 equiv.) was dissolved in *d*-ACN (0.6 mL) and added the gold-catalyst (5 mol-%) dissolved in *d*-ACN. The reaction progress was monitored by ^{1}H NMR at 5 min, 30 min, 1 h, 2 h, 5 h, 12 h, 24 h. The results are presented in Table 3. The ^{1}H NMR shifts are in accordance with characterized product previously reported.[14]

(*S*)-*N*-(1-Hydroxy-3-methylbutan-2-yl)-4-methoxyquinoline-2-carboxamide (7a): 4-Methoxyquionoline-2-carboxylic acid **6** (147 mg, 0.723 mmol) was dissolved in dichloromethane (15 mL) and added DIPEA (0.65 mL, 3.72 mmol) and HATU (413 mg, 1.085 mmol). The reaction mixture was stirred for 1 hour before (*R*)-2-amino-3-methylbutan-1-ol (230 mg, 2.23 mmol) dissolved in dichloromethane (2 mL) was added. The solution was stirred for an additional hour, before the reaction mixture was poured into aqueous HCl (0.1 M, 5 mL). The mixture was extracted with dichloromethane (3 × 10 mL). The combined organic phases were washed with conc. aqueous $NaHCO_3$ solution (10 mL) and water (10 mL). The aqueous phases were reextracted with DCM before the combined organic phases were dried with anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (*n*-pentane/EtOAC, 1:1, R_f = 0.33) to give 120 mg (58 %, 0.416 mmol) of the product, **7a**, as a colorless oil. ^{1}H NMR (400 MHz, [D]Chloroform) δ = 8.52 (d, *J* = 8.5, 1H), 8.21 (ddd, *J* = 8.4, 1.6, 0.8, 1H), 8.07–8.00 (m, 1H), 7.73 (ddd, *J* = 8.4, 6.8, 1.5, 1H), 7.69 (d, *J* = 0.9, 1H), 7.56 (ddd, *J* = 8.3, 6.9, 1.2, 1H), 4.12 (s, 3H), 3.96 (dtd, *J* = 8.2, 6.6, 3.3, 1H), 3.87 (td, *J* = 10.6, 10.0, 6.4, 2H), 2.89 (s, 1H), 2.19–2.02 (m, 1H), 1.07 (t, *J* = 6.4, 6H). ^{13}C NMR (101 MHz, [D]Chloroform) δ = 165.7,

163.7, 151.0, 147.5, 130.3, 129.2, 126.9, 122.1, 122.0, 97.9, 64.4, 58.0, 56.2, 29.3, 19.7, 18.8; HRMS (APCI/ASAP, *m/z*): 289.1553 (calcd. $C_{16}H_{21}N_2O_3$, 289.1552, $[M + H]^+$); HRMS (APCI/ASAP, *m/z*): 289.1553 (calcd. $C_{16}H_{21}N_2O_3$, 289.1552, $[M + H]^+$).

(*S*)-4-Isopropyl-2-(4-methoxyquinolin-2-yl)-4,5-dihydrooxazole (3a): (*S*)-*N*-(1-hydroxy-3-methylbutan-2-yl)-4-methoxy-quinoline-2-carboxamide **7a** (90 mg, 0.312 mmol) was dissolved in dry THF (3 mL) and added thionyl chloride (114 µL, 1.56 mmol). The reaction mixture was refluxed for 1.5 hours before the reaction was quenched with sat. aqueous $NaHCO_3$ solution and extracted with dichloromethane (3 × 10 mL). The combined organic phases were dried with anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude product, **8a**, was subsequently dissolved in dry ethanol (3 mL) and added sodium hydroxide (37 mg, 0.925 mmol). The reaction mixture was refluxed for one hour before water (10 mL) was added. The mixture was extracted with dichloromethane (3 × 10 mL) and the combined organic phases were washed with sat. aqueous sodium chloride solution (20 mL), dried with anhydrous sodium sulfate and concentrated under reduced pressure. Purification with silica gel column chromatography (*n*-pentante: EtOAc, 1:1, R_f = 0.19) yielded 63 mg (63 %, 0.233 mmol) of the ligand **3a** as a white powder. ^{1}H NMR (400 MHz, [D_3]acetonitrile) δ = 8.21 (dd, *J* = 8.3, 1.5, 1H), 8.01 (dt, *J* = 8.4, 0.9, 1H), 7.77 (ddd, *J* = 8.4, 6.8, 1.5, 1H), 7.65–7.51 (m, 2H), 4.54 (dd, *J* = 9.7, 8.4, 1H), 4.25 (t, *J* = 8.4, 1H), 4.16 (ddd, *J* = 9.8, 8.3, 6.5, 1H), 4.10 (s, 3H), 1.84 (dt, *J* = 13.3, 6.7, 1H), 1.05 (d, *J* = 6.7, 3H), 0.96 (d, *J* = 6.7, 3H); ^{13}C NMR (101 MHz, [D_3]acetonitrile) δ = 163.9, 163.5, 149.5, 149.4, 131.3, 130.3, 128.0, 122.6, 122.6, 100.8, 73.8, 71.7, 56.9, 33.8, 19.1, 18.7; HRMS (APCI/ASAP, *m/z*): 271.1445 (calcd. $C_{16}H_{19}N_2O_2$, 271.1447, $[M + H]^+$).

(*S*)-*N*-(2-Hydroxy-1-phenylethyl)-4-methoxyquinoline-2-carboxamide (7b): 4-Methoxyquionoline-2-carboxylic acid **6** (145 mg, 0.714 mmol) was dissolved in dichloromethane (15 mL) and added DIPEA (0.65 mL, 3.72 mmol) and HATU (413 mg, 1.085 mmol). The reaction mixture was stirred for 1 hour before (*R*)-2-amino-2-phenylethan-1-ol (282 mg, 2.88 mmol) dissolved in dichloromethane (2 mL) was added. The solution was stirred for an additional hour, before the reaction mixture was poured into aqueous HCl (0.1 M, 5 mL). The mixture was extracted with dichloromethane (3 × 10 mL). The combined organic phases were washed with conc. aqueous $NaHCO_3$ solution (10 mL) and water (10 mL). The aqueous phases were reextracted with DCM before the combined organic phases were dried with anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (*n*-pentane/EtOAC, 1:1, R_f = 0.29) to give 147 mg (64 %, 0.457 mmol) of the product, **7b**, as a colorless oil. ^{1}H NMR (400 MHz, [D]Chloroform) δ = 8.94 (d, *J* = 7.5, 1H), 8.22 (ddd, *J* = 8.4, 1.5, 0.7, 1H), 8.04 (ddd, *J* = 8.6, 1.3, 0.7, 1H), 7.73 (ddd, *J* = 8.5, 6.9, 1.5, 1H), 7.70 (s, 1H), 7.57 (ddd, *J* = 8.2, 6.9, 1.2, 1H), 7.50–7.36 (m, 4H), 7.38–7.29 (m, 1H), 5.31 (td, *J* = 6.6, 4.2, 1H), 4.12 (s, 3H), 4.13–4.01 (m, 2H), 2.78 (t, *J* = 6.2, 1H); ^{13}C NMR (100 MHz, [D]Chloroform) δ = 165.3, 163.7, 150.8, 147.5, 138.9, 130.3, 129.3, 129.0 (2C), 128.0, 127.0, 126.9 (2C), 122.2, 122.0, 97.9, 67.0, 56.6, 56.2; HRMS (APCI/ASAP, *m/z*): 323.1395 (calcd. $C_{19}H_{19}N_2O_3$, 323.1396, $[M + H]^+$).

(*S*)-2-(4-Methoxyquinolin-2-yl)-4-phenyl-4,5-dihydrooxazole (3b): (*S*)-*N*-(2-hydroxy-1-phenylethyl)-4- methoxyquinoline-2-carboxamide **7b** (137 mg, 0.425 mmol) was dissolved in dry THF (3 mL) and added thionyl chloride (155 µL, 2.125 mmol). The reaction mixture was refluxed for 1.5 hours before the reaction was quenched with sat. aqueous $NaHCO_3$ solution and extracted with dichloromethane (3 × 10 mL). The combined organic phases were dried with anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude product, **8b**, was subsequently dissolved in dry ethanol (3 mL) and added sodium hydroxide (46 mg, 1.150 mmol). The reaction mixture was refluxed for one hour before water (10 mL) was added. The mixture was extracted with dichloromethane (3 × 10 mL) and the combined organic phases were washed with sat. aqueous sodium chloride solution (20 mL), dried with anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified with silica gel column chromatography (*n*-pentante: EtOAc, 1:1, R_f = 0.20), yielding 86 mg (67 %, 0.283 mmol) of the ligand **3b** as a white powder. ^{1}H NMR (400 MHz, [D_3]acetonitrile) δ = 8.23 (dd, *J* = 8.3, 1.5, 1H), 8.05 (d, *J* = 8.4, 1H), 7.79 (ddd, *J* = 8.4, 6.8, 1.5, 1H), 7.64 (s, 1H), 7.63 (ddd, *J* = 8.0, 6.9, 0.9, 1H), 7.40–7.32 (m, 5H), 5.49 (dd, *J* = 10.3, 8.3, 1H), 4.94 (dd, *J* = 10.3, 8.6, 1H), 4.36 (t, *J* = 8.5, 1H), 4.10 (s, 3H).^{13}C NMR (100 MHz, [D_3]acetonitrile) δ = 165.3, 163.6, 149.4, 149.3, 143.6, 131.4, 130.4, 129.7 (2C), 128.6, 128.2, 127.9 (2C), 122.7, 122.7, 101.0, 76.1, 71.0, 57.0; HRMS (APCI/ASAP, *m/z*): 305.1293 (calcd. $C_{19}H_{17}N_2O_2$, 305.1290, $[M + H]^+$).

(*R*,*E*)-*N*-(1-Phenylethyl)-1-(quinolin-2-yl)methanimine (4a′): Quinoline-2-carbaldehyde **9** (39 mg, 0.248 mmol) was dissolved in dry EtOH (5 mL) and added (*R*)-1-phenylethan-1-amine a (32 µL, 0.248 mmol) dropwise. The reaction mixture was stirred for 1.5 hours before solvent was removed under reduced pressure. No purification was needed. Drying gave 63 mg (97 %, 0.241 mmol) of the desired product **4a′** as a pale yellow powder. ^{1}H NMR (600 MHz, [D]Chloroform) δ = 8.64 (s, 1H), 8.26 (d, *J* = 8.5, 1H), 8.19 (d, *J* = 8.5, 1H), 8.12 (d, *J* = 8.5, 1H), 7.84 (d, *J* = 8.6, 1H), 7.74 (dd, *J* = 6.8, 1.4, 1H), 7.58 (dd, *J* = 6.8, 1.4, 1H), 7.47 (d, *J* = 7.6, 2H), 7.36 (t, *J* = 7.6, 2H), 7.29–7.26 (m, 1H), 4.72 (q, *J* = 6.7, 1H), 1.65 (d, *J* = 6.7, 3H); ^{13}C NMR (150 MHz, [D]Chloroform) δ = 161.0, 155.1, 147.8, 144.6, 136.2, 129.8, 129.6, 128.8, 128.5 (2C), 127.7, 127.4, 127.1, 126.8 (2C), 118.7, 69.6, 24.6; HRMS (APCI/ASAP, *m/z*): 261.1390 (calcd. $C_{18}H_{17}N_2$, 261.1392, $[M + H]^+$).

(*R*)-1-Phenyl-*N*-(quinolin-2-ylmethyl)ethan-1-amine (4a): Compound **4a′** (34 mg, 0.131 mmol) was dissolved in dry EtOH (3 mL) under a nitrogen atmosphere and added $NaBH_4$ (15 mg, 0.392 mmol) in EtOH (2 mL). The mixture was stirred overnight before the reaction mixture was quenched with HCl (2 M). The mixture was then added aq. NaOH solution (1 M) until basic solution and extracted with diethyl ether (3 × 10 mL). The combined organic phases were dried with anhydrous Na_2SO_4, filtered and dried under reduced pressure. The procedure yielded 26 mg, (76 %, 0.099 mmol) of **4a** as a colorless oil. ^{1}H NMR (600 MHz, [D]Chloroform) δ = 8.07 (d, *J* = 8.4, 1H), 8.06 (d, *J* = 8.3, 1H), 7.78 (dd, *J* = 8.1, 1.4, 1H), 7.69 (ddd, *J* = 8.4, 6.8, 1.5, 1H), 7.50 (ddd, *J* = 8.1, 6.7, 1.2, 1H), 7.44–7.38 (m, 2H), 7.36–7.33 (m, 3H), 7.27–7.24 (m, 1H), 3.95 (s, 2H), 3.91 (q, *J* = 6.6, 1H), 1.46 (d, *J* = 6.6, 3H). ^{13}C NMR (100 MHz, [D]Chloroform) δ = 160.3, 147.8, 145.5, 136.3, 129.4, 129.1, 128.5 (2C), 127.5, 127.3, 127.0, 126.8 (2C), 126.0, 120.7, 58.3, 53.7, 24.5; HRMS (APCI/ASAP, *m/z*): 263.1546 (calcd. $C_{18}H_{19}N_2$, 263.1548, $[M + H]^+$).

(*E*)-1-(Quinolin-2-yl)-*N*-[(4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl]methanimine (4b′): Quinoline-2-carbaldehyde (27 mg, 0.172 mmol) was dissolved in dry EtOH (5 mL) and added (*R*)-(+)-bornylamine **b** (26 mg, 0.172 mmol) dissolved in EtOH (2 mL). The reaction mixture was stirred for 1.5 hours before solvent was removed under reduced pressure. No purification was needed. Drying gave 48 mg (96 %, 0.164 mmol) of the desired product as a pale yellow powder. ^{1}H NMR (600 MHz, [D_3]acetonitrile) δ = 8.45 (s, 1H), 8.30 (d, *J* = 8.6, 1H), 8.18 (d, *J* = 8.5, 1H), 8.06 (d, *J* = 8.4, 1H), 7.95 (dd, *J* = 8.2, 1.4, 1H), 7.77 (ddd, *J* = 8.4, 6.8, 1.4, 1H), 7.62 (ddd, *J* = 8.1, 6.9, 1.2, 1H), 3.68 (ddd, *J* = 10.2, 4.3, 2.1, 1H), 2.31–2.22 (m, 2H),

1.85 (ddq, *J* = 11.8, 7.8, 4.0, 1H), 1.76 (t, *J* = 4.5, 1H), 1.41–1.29 (m, 3H), 1.02 (s, 3H), 0.96 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (150 MHz, [D$_3$]acetonitrile) δ = 161.5, 155.9, 148.4, 137.1, 130.4, 129.9, 129.2, 128.5, 127.9, 118.8, 75.5, 51.1, 48.9, 46.1, 37.8, 29.0, 28.7, 19.6, 18.7, 13.4; HRMS (APCI/ASAP, *m/z*): 293.2018 (calcd. $C_{20}H_{25}N_2$, 293.2018, $[M + H]^+$).

(4*R*)-1,7,7-Trimethyl-*N*-(quinolin-2-ylmethyl)bicyclo[2.2.1]heptan-2-amine (4b): Compound **4b′** (31 mg, 0.106 mmol) was dissolved in dry EtOH (3 mL) under a nitrogen atmosphere and added $NaBH_4$ (12 mg, 0.318 mmol) in EtOH (2 mL). The mixture was stirred overnight before the reaction mixture was quenched with HCl (2 M). The mixture was then added aq. NaOH solution (1 M) until basic solution and extracted with diethyl ether (3 × 10 mL). The combined organic phases were dried with anhydrous Na_2SO_4, filtered and dried under reduced pressure. The procedure yielded 21 mg, (67 %, 0.071 mmol) of **4b** as a pale oil. ^{1}H NMR (600 MHz, [D]Chloroform) δ = 8.10 (d, *J* = 8.5, 1H), 8.05 (d, *J* = 8.4, 1H), 7.79 (dd, *J* = 8.2, 1.5, 1H), 7.69 (ddd, *J* = 8.4, 6.8, 1.5, 1H), 7.54–7.48 (m, 2H), 4.11 (dd, *J* = 54.7, 13.8, 2H) 2.93 (ddd, *J* = 10.0, 4.2, 2.0, 1H), 2.20–2.15 (m, 1H), 1.94 (ddd, *J* = 13.2, 9.4, 4.3, 1H), 1.72 (ddq, *J* = 12.1, 8.0, 4.0, 1H), 1.63 (t, *J* = 4.6, 1H), 1.32 (tdd, *J* = 12.2, 4.6, 2.0, 1H), 1.24 (ddd, *J* = 12.2, 9.4, 4.5, 1H), 0.96–0.93 (m, 1H), 0.91 (s, 3H), 0.87 (s, 3H), 0.84 (s, 3H). ^{13}C NMR (150 MHz, [D]Chloroform) δ = 161.3, 147.7, 136.2, 129.3, 129.0, 127.5, 127.3, 125.9, 120.7, 63.3, 55.2, 48.9, 48.4, 45.1, 38.0, 28.5, 27.5, 19.9, 18.7, 14.3; HRMS (APCI/ASAP, *m/z*): 295.2173 (calcd. $C_{20}H_{27}N_2$, 295.2174, $[M + H]^+$).

***tert*-Butyl{(1*S*,2*S*)-2-[(Quinolin-2-ylmethyl)amino]-cyclohexyl}-carbamate (4c′):** The target compound was prepared as described in General method 1 starting with quinoline-2-carbaldehyde (84 mg, 0.532 mmol) and *tert*-butyl [(1*S*,2*S*)-2-aminocyclohexyl]-carbamate **c′** (114 mg, 0.532 mmol). No purification was necessary. The method yielded 166 mg (88 %, 0.467 mmol) of the desired product as a pale white powder, mp. 110–112 °C. ^{1}H NMR (600 MHz, [D]Chloroform) δ: 8.32 (d, *J* = 8.2, 1H), 8.11(d, *J* = 8.2, 1H), 7.81 (d, *J* = 8.2, 1H), 7.70 (t, *J* = 6.9, 1H), 7.53 (t, *J* = 7.6, 1H), 7.34 (d, *J* = 8.8, 1H), 4.18 (dd, *J* = 74.3, 17.0, 2H), 3.35 (br.s, 1H), 2.30 (dt, *J* = 20.4, 3.7, 2H), 2.14–2.11 (m, 1H), 1.71–1.69 (m, 1H), 1.65–1.63 (m, 1H), 1.53 (s, 9H), 1.33–1.29 (m, 1H), 1.24–1.20 (m, 1H), 1.16–1.11 (m, 1H), 1.05–0.99 (m, 1H); ^{13}C NMR (150 MHz, [D]Chloroform) δ = 156.1, 147.7, 136.5, 129.8, 129.0, 127.6, 127.3, 126.1, 120.5, 79.0, 60.0, 54.8, 51.8, 32.9, 32.5, 28.6 (3C), 24.8, 24.6; HRMS (APCI/ASAP, *m/z*): 356.2338 (calcd. $C_{21}H_{30}N_3O_2$, 356.2333, $[M + H]^+$).

(1*S*,2*S*)-*N*1-(Quinolin-2-ylmethyl)cyclohexane-1,2-diamine (4c): Compound **4c′** (100 mg, 0.281 mmol) was dissolved in EtOH (2 mL) and added cons. HCl (1 mL). the reaction mixture was stirred overnight before NaOH was added until the solution was basic. The water phase was extracted with diethyl ether (4 × 30 mL). The combined organic phases were dried with anhydrous Na_2SO_4, filtered and dried under reduced pressure, yielding 50 mg (70 %, 0.196 mmol) of the deprotected product as a pale wax. ^{1}H NMR (600 MHz, [D]Chloroform) δ = 8.11 (d, *J* = 8.4, 1H), 8.05 (d, *J* = 8.5, 1H), 7.79 (d, *J* = 8.1, 1H), 7.70–7.67 (m, 1H), 7.53 (dd, *J* = 8.4, 1.3, 1H), 7.52–7.46 (m, 1H), 4.15 (dd, *J* = 106.0, 14.6, 2H), 2.48 (dddd, *J* = 10.9, 9.3, 4.2, 1.4, 1H), 2.20–2.14 (m, 2H), 1.91–1.89 (m, 1H), 1.75–1.67 (m, 3H), 1.30–1.21 (m, 3H), 1.16–1.07 (m, 2H).^{13}C NMR (150 MHz, [D]Chloroform) δ = 161.2, 147.7, 136.3, 129.3, 129.0, 127.5, 127.3, 126.0, 120.7, 64.1, 55.5, 55.3, 36.0, 31.6, 25.32, 25.26; HRMS (APCI/ASAP, *m/z*): 256.1809 (calcd. $C_{16}H_{22}N_3$, 256.1814, $[M + H]^+$).

(1*S*,2*R*)-1-[(Quinolin-2-ylmethyl)amino]-2,3-dihydro-1*H*-inden-2-ol (4d): The target compound was prepared as described in General method 1 starting with quinoline-2-carbaldehyde (62 mg, 0.394 mmol) and (1*S*,2*R*)-1-amino-2,3-dihydro-1*H*-inden-2-ol **d** (58 mg, 0.389 mmol). Drying gave 99 mg (86 %, 0.341 mmol) of the desired product as a beige oil. ^{1}H NMR (600 MHz, [D]Chloroform) δ = 8.14 (d, *J* = 8.4, 1H), 8.08 (d, *J* = 8.5, 1H), 7.82 (dd, *J* = 8.1, 1.4, 1H), 7.72 (ddd, *J* = 8.4, 6.9, 1.4, 1H), 7.53 (ddd, *J* = 8.1, 6.9, 1.2, 1H), 7.50–7.47 (m, 1H), 7.39 (d, *J* = 8.4, 1H), 7.25–7.24 (m, 3H), 4.41 (dd, *J* = 69.5, 16.3, 2H), 4.36 (dt, *J* = 5.0, 3.5, 1H), 4.19 (d, *J* = 4.6, 1H), 3.02 (d, *J* = 3.4, 2H); ^{13}C NMR (150 MHz, [D]Chloroform) δ = 160.5, 147.3, 132.7, 141.1, 136.9, 129.9, 128.6, 127.9, 127.6, 127.4, 126.6, 126.4, 125.4, 124.4, 120.2, 71.5, 67.8, 54.3, 39.2; HRMS (APCI/ASAP, *m/z*): 291.1492 (calcd. $C_{19}H_{19}N_2O$, 291.1497, $[M + H]^+$).

(1*R*,2*R*)-2-[(Quinolin-2-ylmethyl)amino]cyclohexan-1-ol (4e): The target compound was prepared as described in General method 1 starting with quinoline-2-carbaldehyde (32 mg, 0.204 mmol) and (1*R*,2*R*)-2-aminocyclohexan-1-ol **e** (23 mg, 0.200 mmol). Drying gave 49 mg (94 %, 0.191 mmol) of **4e** as a pale powder, mp. 90–92 °C. ^{1}H NMR (600 MHz, [D$_4$]Methanol) δ = 8.31 (d, *J* = 8.4, 1H), 8.04 (dd, *J* = 8.4, 1.2, 1H), 7.93 (dd, *J* = 8.1, 1.4, 1H), 7.76 (ddd, *J* = 8.4, 6.8, 1.5, 1H), 7.59 (ddd, *J* = 7.9, 6.8, 0.8, 1H), 7.58 (d, *J* = 8.5, 1H), 4.14 (dd, *J* = 101.2, 14.6, 2H), 3.39 (ddd, *J* = 10.4, 9.0, 4.4, 1H), 2.42 (ddd, *J* = 10.8, 9.2, 4.1, 1H), 2.18–2.15 (m, 1H), 2.00–1.97 (m, 1H), 1.74 (dt, *J* = 11.7, 2.4, 2H), 1.35–1.17 (m, 4H); ^{13}C NMR (150 MHz, [D$_4$]Methanol) δ = 161.2, 148.6, 138.4, 131.0, 129.1, 129.0, 128.9, 127.6, 122.0, 74.7, 64.1, 52.9, 35.3, 31.0, 25.7, 25.6; HRMS (ESI, *m/z*): 257.1659 (calcd. $C_{16}H_{21}N_2O$, 257.1654, $[M + H]^+$).

(*R*)-*N*-[(6-Methylpyridin-2-yl)methyl]-1-phenylethan-1-amine (5a): The target compound was prepared as described in General method 1 starting with 6-methylpicolinaldehyde (78 mg, 0.647 mmol) and (*R*)-1-phenylethan-1-amine **a** (0.68 mL, 0.578 mmol). Drying gave 129 mg (99 %, 0.570 mmol) of the desired product as a colorless oil. ^{1}H NMR (600 MHz, [D]Chloroform) δ = 7.48 (dd, *J* = 7.6, 1.0, 1H), 7.38–7.36 (m, 2H), 7.35–7.31 (m, 2H), 7.28–7.22 (m, 1H), 7.00 (dd, *J* = 9.4, 7.7, 2H), 3.83 (q, *J* = 6.6, 1H), 2.53 (s, 3H), 1.41 (d, *J* = 6.6, 3H).^{13}C NMR (150 MHz, [D]Chloroform) δ = 159.1, 157.9, 145.6, 136.5, 128.4 (2C), 126.9, 126.8 (2C), 121.3, 119.2, 58.1, 53.2, 24.5 (2C); HRMS (APCI/ASAP, *m/z*): 227.1549 (calcd. $C_{15}H_{19}N_2$, 227.1548, $[M + H]^+$).

(4*R*)-1,7,7-Trimethyl-*N*-[(6-methylpyridin-2-yl)methyl]bicyclo-[2.2.1]heptan-2-amine (5b): The target compound was prepared as described in General method 1 starting with 6-methylpicolinaldehyde (58 mg, 0.480 mmol) and (*R*)-(+)-bornylamine **b** (74 mg, 0.480 mmol). Drying gave 80 mg (65 %, 0.310 mmol) of the desired product as a colorless oil. ^{1}H NMR (600 MHz, [D]Chloroform) δ = 7.51 (t, *J* = 7.6, 1H), 7.15 (d, *J* = 7.6, 1H), 6.99 (d, *J* = 7.6, 1H), 3.87 (dd, *J* = 45.7, 14.4, 2H), 2.86 (ddd, *J* = 10.0, 4.2, 2.0, 1H), 2.53 (s, 3H), 2.16–2.11 (m, 1H), 1.90 (ddd, *J* = 13.2, 9.4, 4.3, 1H), 1.70 (tt, *J* = 12.0, 3.9, 2H), 1.61 (t, *J* = 4.6, 1H), 1.28 (tdd, *J* = 12.1, 4.7, 2.0, 1H), 1.21 (ddd, *J* = 12.3, 9.4, 4.6, 1H), 0.93–0.89 (m, 1H), 0.88 (s, 3H), 0.86 (s, 3H), 0.84 (s, 3H). ^{13}C NMR (150 MHz, [D]Chloroform) δ = 160.1, 157.7, 136.5, 121.2, 119.0, 63.0, 54.7, 48.8, 48.4, 45.1, 37.9, 28.5, 27.5, 24.5, 19.9, 18.7, 14.3; HRMS (APCI/ASAP, *m/z*): 259.2177 (calcd. $C_{17}H_{27}N_2$, 259.2174, $[M + H]^+$).

***tert*-Butyl((1*S*,2*S*)-2-{[(6-Methylpyridin-2-yl)methyl]amino}-cyclohexyl)carbamate (5c′):** The target compound was prepared as described in General method 1 starting with 6-methylpicolinaldehyde (116 mg, 0.958 mmol) and *tert*-butyl [(1*S*,2*S*)-2-aminocyclohexyl]carbamate **c′** (189 mg, 0.882 mmol). Drying gave 262 mg (93 %, 0.819 mmol) of the desired product as a white powder. ^{1}H NMR (600 MHz, [D]Chloroform) δ = 7.51 (t, *J* = 7.6, 1H), 7.06 (d, *J* = 7.6, 1H), 7.01 (d, *J* = 7.6, 1H), 5.59 (br. s, 1H), 3.93 (dd, *J* = 76.5, 15.5, 2H), 3.30 (br. s, 1H), 2.59 (s, 3H), 2.25–2.21 (m, 2H), 2.11–2.08 (m, 1H), 1.70–1.63 (m, 2H), 1.46 (s, 9H), 1.35–1.23 (m, 2H), 1.89–1.13 (m, 2H), 1.07–1.03 (m, 1H); ^{13}C NMR (150 MHz, [D]Chloroform) δ = 159.4,

158.0, 156.1, 136.7, 121.4, 119.3, 79.0, 60.0, 54.6, 51.2, 32.9, 32.0, 28.5 (3C), 24.7 (2C), 24.4; HRMS (APCI/ASAP, *m/z*): 320.2332 (calcd. $C_{18}H_{30}N_3O_2$, 320.2338, $[M + H]^+$).

(1*S*,2*S*)-*N*1-[(6-Methylpyridin-2-yl)methyl]cyclohexane-1,2-diamine (5c): Compound **5c′** (150 mg, 0.281 mmol) was dissolved in EtOH (2 mL) and added cons. HCl (1 mL). The reaction mixture was stirred for 3 hours before NaOH was added until the solution was basic. The water phase was extracted with diethyl ether (4 × 30 mL). The combined organic phases were dried with anhydrous Na_2SO_4, filtered and dried under reduced pressure, yielding 52 mg (51 %, 0.237 mmol) of the deprotected product as a pale yellow oil. ^{1}H NMR (600 MHz, [D]Chloroform) δ = 7.52 (t, *J* = 7.6, 1H), 7.13 (d, *J* = 7.6, 1H), 7.01 (d, *J* = 7.6, 1H), 3.95 (dd, *J* = 105.3, 14.3, 2H), 2.58–2.56 (m, 1H), 2.55 (s, 3H), 2.26 (ddd, *J* = 11.1, 9.7, 4.0, 1H), 2.12–2.10 (m, 1H), 2.01–1.99 (m, 1H), 1.75–1.69 (m, 2H), 1.29–1.22 (m, 3H), 1.13–1.10 (m, 1H); ^{13}C NMR (150 MHz, [D]Chloroform) δ = 159.3, 157.9, 136.8, 121.5, 119.1, 63.0, 55.4, 52.0, 34.8, 31.4, 25.2, 25.0, 24.4; HRMS (APCI/ASAP, *m/z*): 220.1816 (calcd. $C_{13}H_{22}N_3$, 220.1814, $[M + H]^+$).

(1*S*,2*R*)-1-{[(6-Methylpyridin-2-yl)methyl]amino}-2,3-dihydro-1*H*-inden-2-ol (5d): The target compound was prepared as described in General method 1 starting with 6-methylpicolinaldehyde (69 mg, 0.570 mmol) and (1*S*,2*R*)-1-amino-2,3-dihydro-1*H*-inden-2-ol **d** (84 mg, 563 mmol). Drying gave 126 mg (87 %, 0.495 mmol) of the desired product as a white powder, mp. 107–109 °C(dec). ^{1}H NMR (600 MHz, [D]Chloroform) δ = 7.56 (t, *J* = 7.7, 1H), 7.38–7.36 (m, 1H), 7.24–7.21 (m, 3H), 7.10 (d, *J* = 7.5, 1H), 7.06 (d, *J* = 7.7, 1H), 4.38–4.36 (m, 1H), 4.11 (dd, *J* = 43.2, 15.0, 2H), 4.14 (d, *J* = 4.6, 1H), 3.02–3.00 (m, 2H), 2.56 (s, 3H); ^{13}C NMR (150 MHz, [D]Chloroform) δ = 159.1, 158.2, 142.6, 141.1, 137.1, 127.8, 126.6, 125.4, 124.2, 121.9, 119.3, 71.1, 67.3, 52.6, 39.2, 24.2; HRMS (APCI/ASAP, *m/z*): 255.1494 (calcd. $C_{16}H_{19}N_2O$, 255.1497, $[M + H]^+$).

(1*R*,2*R*)-2-{[(6-Methylpyridin-2-yl)methyl]amino}cyclohexan-1-ol (5e): The target compound was prepared as described in General method 1 starting with 6-methylpicolinaldehyde (25 mg, 0.206 mmol) and (1*R*,2*R*)-2-aminocyclohexan-1-ol **e** (23 mg, 0.200 mmol). Drying gave 43 mg (98 %, 0.195 mmol) of the desired product as a white powder, mp. 53–55 °C. ^{1}H NMR (600 MHz, [D_3]-acetonitrile) δ = 7.57 (t, *J* = 7.8, 1H), 7.14 (d, *J* = 7.6, 1H), 7.06 (d, *J* = 7.6, 1H), 3.84 (dd, *J* = 109.0, 14.2, 2H), 3.17 (ddd, *J* = 10.7, 9.1, 4.4, 1H), 2.46 (s, 3H), 2.21 (ddd, *J* = 11.2, 9.1, 4.0, 1H), 2.03 (m, 1H), 1.91–1.87 (m, 1H), 1.67–1.64 (m, 2H), 1.28–1.14 (m, 3H), 1.02 (tdd, *J* = 12.7, 11.0, 3.4, 1H); ^{13}C NMR (150 MHz, [D_3]acetonitrile) δ = 161.3, 158.6, 137.7, 122.0, 119.9, 74.6, 64.5, 52.8, 34.8, 31.5, 25.8, 25.3, 24.4; HRMS (ESI, *m/z*): 221.1652 (calcd. $C_{13}H_{21}N_2$, 221.1654, $[M + H]^+$).

1a-Au(III); (*S*)-4-Isopropyl-2-(quinolin-2-yl)-4,5-dihydrooxazole $AuCl_3$ Complex: NH_4PF_6 (4 mg, 0.025 mmol) and $AuCl_3$ (6 mg, 0.02 mmol) were dissolved in ACN and stirred for 15 min before (*S*)-4-isopropyl-2-(quinolin-2-yl)-4,5-dihydrooxazole (5 mg, 0.021 mmol) was added. The reaction mixture was stirred for 30 min before ACN was removed under reduced pressure. The crude mixture was dissolved in DCM (5 mL) and extracted with water (3 × 7 mL). The organic phase was dried with anhydrous Na_2SO_4, filtered and removed under reduced pressure. Drying gave 10 mg (74 %, 0.015 mmol) of the gold(III) complex as a pale yellow powder. ^{1}H NMR (400 MHz, [D_3]acetonitrile) δ = 8.62 (ap. d, *J* = 8.7, 1H), 8.44 (ap. d, *J* = 8.6, 1H), 8.13–8.09 (m, 2H), 8.00 (ddd, *J* = 8.5, 6.9, 1.5, 1H), 7.85 (ddd, *J* = 8.2, 6.9, 1.2, 1H), 5.09 (dd, *J* = 10.6, 9.4, 1H), 4.92 (dd, *J* = 9.4, 8.2, 1H), 4.74 (ddd, *J* = 10.6, 8.1, 3.7, 1H), 2.55 (ddq, *J* = 10.5, 6.9, 3.4, 1H), 1.33 (dd, *J* = 7.9, 7.2, 6H); ^{13}C NMR (100 MHz, [D_3]acetonitrile) δ = 167.8, 147.6, 141.3, 139.9, 133.1, 131.4, 131.0, 130.2, 129.4, 129.3, 121.9, 74.2, 71.6, 31.0, 19.0, 16.1; ^{15}N NMR (61 MHz, [D_3]acetonitrile) δ = –66.5, –215.5; HRMS (ESI, *m/z*): found 503.0809 (calcd. $C_{16}H_{19}N_2O_2ClAu$, 503.0801, $[M - Cl + MeOH]^+$) (X-ray: CCDC 1951650).

1b-Au(III); (*R*)-4-Phenyl-2-(quinolin-2-yl)-4,5-dihydrooxazole $AuCl_3$ Complex: $AuCl_3$ (20 mg, 0.066 mmol) and (*R*)-4-phenyl-2-(quinolin-2-yl)-4,5-dihydrooxazole (18 mg, 0.066 mmol) were dissolved in ACN (4 mL) and stirred overnight before ACN was removed under reduced pressure. Drying gave 37 mg (98 %, 0.064 mmol) of the gold(III) complex as a pale yellow powder. ^{1}H NMR (600 MHz, [D_3]acetonitrile) δ = 8.66 (ap. d, *J* = 8.4, 1H), 8.38 (ap. d, *J* = 8.5, 1H), 8.21 (ap. d, *J* = 8.5, 1H), 8.14 (ap. d, *J* = 8.3, 1H), 7.99 (ddd, *J* = 8.4, 6.9, 1.4, 1H), 7.86 (ddd, *J* = 8.2, 6.9, 1.2, 1H), 7.70–7.69 (m, 2H), 7.54–7.52 (m, 3H), 5.87 (t, *J* = 10.8, 1H), 5.52 (dd, *J* = 10.6, 9.4, 1H), 5.06 (dd, *J* = 11.0, 9.4, 1H); ^{13}C NMR (100 MHz, [D_3]acetonitrile) δ = 167.8, 147.7, 141.6, 139.9, 136.2, 133.1, 131.5, 131.1 (2C), 131.0, 130.7 (2C), 130.3, 130.1, 129.3, 122.1, 79.4, 70.4. HRMS; could not be detected, due to low stability.

3a-Au(III); (*S*)-4-Isopropyl-2-(4-methoxyquinolin-2-yl)-4,5-dihydrooxazole $AuCl_3$ Complex: $AuCl_3$ (11 mg, 0.035 mmol) and (*S*)-4-isopropyl-2-(4-methoxyquinolin-2-yl)-4,5-dihydrooxazole (10 mg, 0.035 mmol) were dissolved in ACN (2 mL) and stirred for 15 min before ACN was removed under reduced pressure. the complex was purified by precipitation from DCM in *n*-pentane. Drying gave18 mg (89 %, 0.031 mmol) of the gold(III) complex as a yellow powder. ^{1}H NMR (600 MHz, [D_3]acetonitrile) δ = 8.36 (d, *J* = 8.5, 1H), 8.28 (dd, *J* = 8.4, 0.7, 1H), 7.95 (ddd, *J* = 8.4, 6.9, 1.4, 1H), 7.77 (ddd, *J* = 8.3, 6.9, 1.1, 1H), 7.48 (s, 1H), 5.08 (dd, *J* = 10.5, 9.4, 1H), 4.91 (dd, *J* = 9.3, 8.2, 1H), 4.72 (ddd, *J* = 10.5, 8.2, 3.8, 1H), 4.15 (s, 3H), 1.14 (d, *J* = 7.0, 1H), 1.12 (d, *J* = 6.8, 1H); ^{13}C NMR (100 MHz, [D_3]acetonitrile) δ = 168.0, 165.3, 148.4, 142.6, 133.1, 130.3, 129.9, 123.4, 123.1, 101.8, 74.2, 71.7, 57.7, 31.0, 19.0, 16.2. HRMS; could not be detected, due to low stability.

3b-Au(III); (*S*)-2-(4-Methoxyquinolin-2-yl)-4-phenyl-4,5-dihydrooxazole $AuCl_3$ Complex: $AuCl_3$ (8 mg, 0.028 mmol) and (*S*)-2-(4-methoxyquinolin-2-yl)-4-phenyl-4,5-dihydrooxazole (8 mg, 0.028 mmol) were dissolved in ACN (2 mL) and stirred for 15 min before ACN was removed under reduced pressure. the complex was purified by precipitation from DCM in *n*-pentane. Drying gave15 mg (89 %, 0.025 mmol) of the gold(III) complex as a yellow powder. ^{1}H NMR (600 MHz, [D_3]acetonitrile) δ = 8.31–8.29 (m, 2H), 7.93 (ddd, *J* = 8.4, 6.9, 1.3, 1H), 7.77 (ddd, *J* = 8.2, 7.3, 1.3, 1H), 7.69–7.67 (m, 2H), 7.60 (s, 1H), 7.53–7.52 (m, 3H), 5.86 (t, *J* = 10.8, 1H), 5.52 (dd, *J* = 10.5, 9.4, 1H), 5.05 (dd, *J* = 11.0, 9.4, 1H), 4.18 (s, 3H); ^{13}C NMR (100 MHz, [D_3]acetonitrile) δ = 168.0, 165.3, 148.8, 142.8, 136.2, 133.1, 131.0, 130.6 (2C), 130.4, 130.1 (2C), 130.0, 123.4, 123.1, 102.0, 79.3, 70.4, 57.8; ^{15}N NMR (61 MHz, CD_3CN) δ = –89.0, –211.6. HRMS; could not be detected, due to low stability.

2-Au(III)-X, X = SbF_6, BF_4, NTf_2; (*S*)-4-*tert*-Butyl-2-(2-pyridyl)oxazoline $AuCl_2X$ Complexes: The pyridine-oxazoline **2**-Au(III)-X complexes with X = SbF_6, BF_4 or NTf_2 anions, were prepared and characterized (NMR, HRMS) according to literature.[19] Crystals for X-ray analysis were grown for **2**-Au(III)-SbF_6 complex by slow diffusion of *n*-pentane into a dichloromethane solution of the complex (X-ray: CCDC 1951651).

4b-Au(III) Complex: The complex was prepared according to General method 2, starting with ligand **4b** (8 mg, 0.027 mmol) and $KAuCl_4$ (10 mg, 0.027 mmol). Drying gave 10 mg (62 %, 0.017 mmol) of **4b**-Au(III) complex as a yellow oil. ^{1}H NMR (600 MHz, [D_3]acetonitrile) δ = 8.41 (d, *J* = 8.6, 1H), 8.08 (d, *J* = 8.6, 1H), 8.01 (d, *J* = 8.2, 1H), 7.84 (t, *J* = 7.3, 1H), 7.68 (t, *J* = 7.3, 1H), 7.49 (d, *J* = 8.6, 1H),

4.60 (dd, *J* = 79.8, 16.6, 2H), 3.48–3.47 (m, 1H), 2.33–2.29 (m, 1H), 1.90–1.87 (m, 1H), 1.82–1.81 (m, 1H), 1.76–1.69 (m, 2H), 1.46–1.44 (m, 1H), 1.33–1.30 (m, 1H), 1.15 (s, 3H), 0.94 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (150 MHz, [D$_3$]acetonitrile) δ = 151.4, 147.2, 139.2, 131.7, 129.1, 129.1, 128.9, 128.4, 120.8, 66.3, 50.1, 50.0, 49.7, 45.1, 32.9, 28.2, 28.1, 19.5, 18.6, 13.9. HRMS; could not be detected, due to low stability.

4c-Au(III) Complex: The complex was prepared according to General method 2, starting with ligand **4c** (8 mg, 0.031 mmol) and $KAuCl_4$ (12 mg, 0.031 mmol). The complex precipitated immediately after mixing in ACN and was filtered and washed with more ACN. Drying gave 11 mg (67 %, 0.021 mmol) of **4c**-Au(III) complex as a yellow powder. ^{1}H NMR (600 MHz, [D$_4$]Methanol) δ = 8.42 (d, *J* = 8.1, 1H); 8.39 (d, *J* = 8.1, 1H), 7.98 (d, *J* = 8.1, 1H), 7.83 (ddd, *J* = 14.3, 7.2, 5.8, 1H), 7.66 (t, *J* = 7.2, 1H), 7.51 (d, *J* = 8.3, 1H), 5.10 (d, *J* = 17.2, 1H), 4.71 (d, *J* = 17.2, 1H), 3.22–3.18 (m, 1H), 3.04–2.98 (m, 1H), 2.54–2.52 (m, 1H), 2.20 (m, 1H), 1.71–1.66 (m, 2H), 1.59–1.46 (m, 2H), 1.30–1.27 (m, 1H), 1.09–1.07 (m, 1H); ^{13}C NMR (150 MHz, [D$_4$]Methanol) δ = 154.0, 148.1, 139.2, 131.3, 130.0, 129.3, 129.0, 128.4, 121.6, 70.6, 66.0, 52.6, 33.9, 31.2, 25.6, 25.0; HRMS (ESI, *m/z*): 486.1014 (calcd. $C_{16}H_{20}N_3ClAu$, 486.1011, [M – Cl]$^+$).

4d-Au(III) Complex: The complex was prepared according to General method 2, starting with ligand **4d** (8 mg, 0.028 mmol) and $KAuCl_4$ (10 mg, 0.028 mmol). Drying gave 11 mg (73 %, 0.020 mmol) of **4d**-Au(III) complex as a yellow solid. ^{1}H NMR (600 MHz, [D$_3$]acetonitrile) δ = 8.39 (d, *J* = 8.2, 1H), 8.08 (d, *J* = 8.2, 1H), 7.99 (d, *J* = 7.8, 1H), 7.83 (t, *J* = 7.8, 1H), 7.67 (d, *J* = 7.8, 1H), 7.64 (d, *J* = 7.8, 1H), 7.49 (d, *J* = 8.7, 1H), 7.41 (d, *J* = 7.8, 1H), 7.37 (d, *J* = 7.8, 1H), 7.34 (t, *J* = 7.6, 1H), 4.89 (q, *J* = 6.1, 1H), 4.83 (d, *J* = 6.1, 1H), 4.67 (d, 2H), 3.33 (dd, *J* = 16.6, 6.6), 3.10 (dd, *J* = 16.6, 5.8, 1H); ^{13}C NMR (150 MHz, [D$_3$]acetonitrile) δ = 152.1, 147.4, 143.2, 139.1, 135.1, 131.7, 131.6, 129.3, 129.1, 128.8, 128.4, 128.4, 127.2, 126.8, 120.7, 71.0, 65.4, 49.5, 39.8; HRMS (ESI, *m/z*): 557.0466 (calcd. $C_{19}H_{18}N_2OCl_2Au$, 557.0462, [M + H]$^+$).

4e-Au(III) Complex: The complex was prepared according to General method 2, starting with ligand **4e** (8 mg, 0.031 mmol) and $KAuCl_4$ (12 mg, 0.031 mmol) in methanol. The complex was purified by precipitation in acetonitrile, followed by filtration. Drying gave 5 mg (31 % yield, 90 % purity, 0.010 mmol) of **4e**-Au(III) complex as pale crystals. ^{1}H NMR (400 MHz, [D$_4$]Methanol) δ = 8.19 (d, *J* = 8.8, 1H), 7.90 (d, *J* = 8.1, 1H), 7.77 (d, *J* = 7.8, 1H), 7.60 (ddd, *J* = 8.3, 7.0, 1.3, 1H), 7.44 (ddd, *J* = 8.0, 7.0, 1.1, 1H), 7.33 (d, *J* = 8.4, 1H), 4.47 (dd, *J* = 48.1, 15.7, 2H), 3.51–3.48 (m, 1H), 2.91–2.86 (m, 1H), 2.09–2.07 (m, 1H), 1.90–1.88 (m, 1H), 1.83–1.81 (m, 1H), 1.66–1.64 (m, 1H), 1.59–1.57 (m, 1H), 1.34–1.32 (m, 1H), 1.21–1.15 (m, 2H); ^{13}C NMR (100 MHz, [D$_4$]Methanol) δ = 153.3, 148.4, 139.3, 131.6, 129.9, 129.3, 128.5, 121.0, 71.9, 64.6, 49.4, 35.6, 28.2, 25.4, 25.0. HRMS; could not be detected, due to low stability.

5b-Au(III) Complex: The complex was prepared according to General method 2, starting with ligand **5b** (8 mg, 0.031 mmol) and $KAuCl_4$ (12 mg, 0.031 mmol). Drying gave 12 mg (71 %, 0.022 mmol) of **5b**-Au(III) complex as a yellow solid. ^{1}H NMR (600 MHz, [D$_3$]acetonitrile) δ = 7.76 (t, *J* = 7.8, 1H), 7.28 (d, *J* = 7.8, 1H), 7.22 (d, *J* = 7.4, 1H), 4.35 (dd, *J* = 90.5, 15.8, 2H), 3.32–3.30 (m, 1H), 2.54 (s, 1H), 2.27–2.25 (m, 1H), 1.87–1.86 (m, 1H), 1.80–1.79 (m, 1H), 1.66–1.63 (m, 2H), 1.43–1.40 (m, 1H), 1.27–1.24 (dd, *J* = 13.7, 3.9, 1H), 1.04 (s, 3H), 0.92 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (150 MHz, [D$_3$]acetonitrile) δ = 159.0, 149.6, 139.3, 124.4, 120.8, 65.7, 50.0, 49.6, 45.1, 32.8, 28.2, 28.1, 26.5, 24.1, 19.5, 19.6, 13.7. HRMS; could not be detected, due to low stability.

5c-Au(III) Complex: The complex was prepared according to General method 2, starting with ligand **5c** (8 mg, 0.035 mmol) and $KAuCl_4$ (13 mg, 0.035 mmol). The complex was purified by crystallization in ACN. Filtration followed by drying gave 8 mg (47 %, 0.016 mmol) of **5c**-Au(III) complex as yellow crystals. ^{1}H NMR (600 MHz, [D$_4$]Methanol) δ = 7.75 (t, *J* = 7.7, 1H), 7.32 (d, *J* = 7.7, 1H), 7.25 (d, *J* = 7.4, 1H), 4.90 (d, *J* = 14.0, 1H), 4.42 (d, *J* = 15.7, 1H), 3.12 (br. s, 1H), 2.73 (s, 3H), 2.45 (br. s, 1H), 2.15–2.14 (m, 1H), 1.71–1.65 (m, 2H), 1.51–1.42 (m, 2H), 1.25–1.23 (m, 1H), 1.10–1.04 (m, 1H); ^{13}C NMR (150 MHz, [D$_4$]Methanol) δ = 160.3, 151.8, 139.3, 124.6, 121.8, 70.1, 65.9, 52.2, 33.8, 30.9, 25.5, 24.9, 24.2; HRMS (ESI, *m/z*): 450.1017 (calcd. $C_{13}H_{20}N_3ClAu$, 450.1011, [M – Cl]$^+$).

5d-Au(III) Complex: The complex was prepared according to General method 2, starting with ligand **5d** (8 mg, 0.031 mmol) and $KAuCl_4$ (12 mg, 0.031 mmol). Drying gave 15 mg (92 %, 0.029 mmol) of **5d**-Au(III) complex as a yellow solid. ^{1}H NMR (600 MHz, [D$_3$]acetonitrile) δ = 7.77 (t, *J* = 7.6, 1H), 7.57 (d, *J* = 7.3, 1H), 7.44–7.43 (m, 1H), 7.40–7.35 (m, 2H), 7.29 (d, *J* = 7.6, 1H), 7.25 (d, *J* = 7.6, 1H), 4.87–4.85 (m, 1H), 4.73 (d, *J* = 5.7, 1H), 4.47–4.46 (m, 2H), 3.19 (ddd, *J* = 147.3, 16.6, 6.8, 2H), 2.56 (s, 3H); ^{13}C NMR (CD_3CN, 150 MHz) δ = 159.1, 150.4, 143.1, 139.2, 135.2, 131.2, 128.4, 127.1, 126.8, 124.3, 120.7, 70.9, 65.2, 49.2, 39.7, 24.2. HRMS; could not be detected, due to low stability.

5e-Au(III) Complex: The complex was prepared according to General method 2, starting with ligand **5e** (8 mg, 0.036 mmol) and $KAuCl_4$ (14 mg, 0.036 mmol). Drying gave 12 mg (68 % yield, 92 % pyrity, 0.025 mmol) of **5e**-Au(III) complex as a yellow solid. ^{1}H NMR (600 MHz, [D$_3$]acetonitrile) δ = 7.75 (t, *J* = 7.7, 1H), 7.27 (d, *J* = 7.7, 1H), 7.20 (d, *J* = 7.7, 1H), 4.35 (dd, *J* = 54.5, 15.3, 2H), 3.66–3.62 (m, 1H), 2.99–2.94 (m, 1H), 2.54 (s, 3H), 2.11–2.09 (m, 1H), 2.05–2.02 (m, 1H), 1.79–1.72 (m, 2H), 1.47–1.41 (m, 1H), 1.32–1.27 (m, 3H); ^{13}C NMR (150 MHz, [D$_3$]acetonitrile) δ = 159.1, 150.4, 139.2, 124.3, 120.5, 71.1, 64.8, 48.3, 34.7, 27.4, 24.6, 24.3, 24.2; HRMS (ESI, *m/z*): 451.0857 (calcd. $C_{13}H_{19}N_2OClAu$, 451.0851, [M – Cl]$^+$).

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