

Tridentate Ligands

Studies towards Pyridine-Based *N,N,O*-Gold(III) Complexes: Synthesis, Characterization and Application

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Abstract: Gold(III) coordination of new chiral polydentate (*N,N,O*-pyridine based ligands is reported. Successful coordination afforded novel chiral *N,N,O*-tridentate Au(III) complexes with the 2-pyridyl-6-[(1*S,2S,5R*)-neomenthol-1-yl]pyridine ligand (¹H, ¹³C, ¹⁵N NMR, HRMS, IR, XRD). The chiral 2-aryl-6-alkylpyridine alcohol ligands were prepared from 2,6-dibromopyridine

by initial stereoselective addition to (−)-menthone and (+)-camphor, respectively, and subsequent Suzuki cross-coupling with a series arylboronic acids. Testing of catalytic activity in propargyl cyclopropanation demonstrated that the new *N,N,O*-ligated gold(III) complex was highly catalytic active and outperformed AuCl₃.

Introduction

Gold(III) complexes are less developed and have received less attention as catalysts in organic synthesis compared to their gold(I) counterparts. Catalysis by gold(III) is still mainly dominated by inorganic gold(III) salts, such as AuCl₃ and K(AuCl₄).^[1] Different from the linear coordination mode of Au(I) complexes, Au(III) complexes prefer a square-planar geometry, which allows for better tuning of the spatial environment of the gold centre by ligand design. Thus, the Au(III) complexes may have a greater potential to achieve chemo- and enantioselectivity by being able to bring the ligand(s) closer to the substrate through its square-planar geometry. Initially, the Au(III)-ligand concept was mainly developed for bioactive studies. A number of stable Au(III)-ligand complexes were designed as promising candidates for biological testing.^[2]

A great variety of strategies for design of mono- and polydentate ligands for Au(III) complexes is conceivable. Several heteroatoms have been shown to coordinate to gold(I), while the coordination behavior of gold(III) is different, and nitrogen is recognized as the heteroatom which most readily coordinates to Au(III). However, the actual *N*-functional group affects the strength of the resulting Au-N bond, and amines, normally form strong, irreversible tethers to Au(III), whilst *N*-amide coordination seems to require stabilized carbonyl groups, such as

benzamide and picolinamide.^[3] Most *N*-coordinated gold(III) complexes are based on aliphatic di-/poly-amines or *N*-heterocycles, such as (bi-/ter-)pyridines, oxazoline,^[4a–4d] porphyrin,^[4e] phenanthroline,^[4f] and cyclam.^[2i] Several catalytically active^[4a,4c,5] *N,O*-coordinated Au(III) complexes with ligands, such as PicAuCl₂ based and pyridine derivatives with chelating oxygen functionalities, have been developed.^[6] In contrast to the unaided *O*-Au(III) coordination of carboxylic acids, alcohols may need deprotonation by base treatment to afford *O*-Au(III) coordination.^[4c] Known methods for arene C-H-activation of aryl ligands afford C-Au bond formation and C-coordinated Au(III) arene complexes.^[7]

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 and studied the catalytic properties of gold(III) complexes based on bisoxazoline and 2-pyridylmenthol ligands,^[4a] as well as pyridyl and quinolinyl based polydentate ligands.^[8] Given the affinity of gold(III) to coordinate to *N*-heterocyclic ligands, we wanted to study the coordination ability of gold(III) to other pyridine based ligands. We hereby present further studies on the synthesis of a series of new chiral pyridyl-alcohol (neomenthol, isoborneol) based (*N,N,O*-polydentate ligands, along with gold(III) coordination studies. The catalytic ability of new pyridine based gold(III) complexes is studied, as well.

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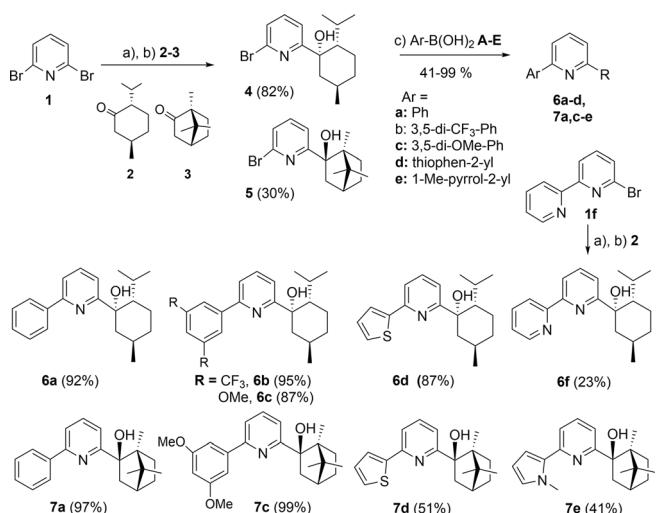
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Results and Discussion

Preparation of Chiral 2-Aryl-6-alkylpyridine Alcohol (6,7) Ligands

Chiral 2-aryl-6-alkylpyridine alcohols **6–7** were synthesized^[9] in two steps from 2,6-dibromopyridine (**1**), chiral ketones, (−)-menthone (**2**) and (+)-camphor (**3**), and aryl boranes **A–E** (Scheme 1). Initial treatment of dibromopyridine **1** with BuLi

enabled stereoselective addition to the chiral ketones **2–3** to give chiral monoalkylated 2-Br-6-alkyl-pyridine alcohols **4–5** in 82 and 30 % yields, respectively. Subsequent Suzuki cross-coupling of monobromopyridines **4–5** with various boronic acids **A–E** gave the new chiral 2-aryl-6-alkylpyridine alcohols **6–7** in moderate to excellent yields (41–99 %). These products represent potential *N,O*-bidentate or (*N/S/C*),*N,O*-tridentate ligands. The possible *N,N,O*-tridentate dipyridyl ligand **6f** was directly synthesized (23 %) by lithiation of commercially available 6-bromo-2,2'-bipyridine (**1f**) and (–)-menthone (**2**).



a) BuLi, THF, -80 °C; b) chiral ketone **2–3**; c) ArB(OH)₂ **A–E**; Pd(PPh₃)₄, K₂CO₃, dioxane:H₂O, 70 °C.

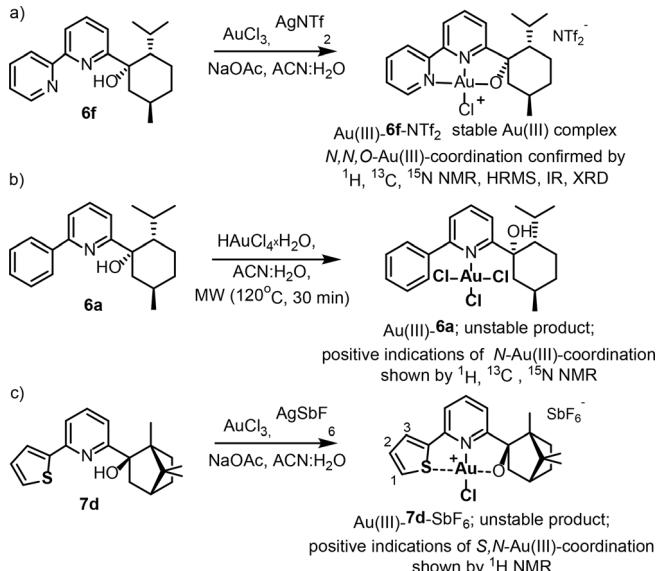
Scheme 1. Preparation of chiral 2-aryl-6-alkylpyridine alcohol ligands (**6–7**).

Au(III) Ligand Coordination

Based on our previous experience of incorporation of 2-substituted pyridines in Au(III) complexes,^[8] coordination studies of the prepared 2-aryl-6-alkylpyridine alcohols **6–7**, being potential (*N/C/S*),*N,O*-tridentate ligands, were carried out. NMR analysis is a useful method used in our group to monitor ligand-to-gold coordination.^[8,9] In the present study, the chemical shift variation of the triplet for the central pyridine proton on C4 turned out to be a diagnostic parameter for *N*-coordination.^[8,9] In the present study, the chemical shift variation of the triplet for the central pyridine proton on C4 turned out to be a diagnostic parameter for *N*-coordination.^[8,9] The characteristic deshielding effect on this proton shown as a shift to higher ppm values is reported as $\Delta\delta^1\text{H}_{\text{coord}} = \delta^1\text{H}_{\text{complex}} - \delta^1\text{H}_{\text{ligand}}$. ¹H, ¹⁵N HMBC was also used to assign pyridine-nitrogens and to verify the large coordination shift to lower ppm values expected by pyridine *N*-coordination, reported as $\Delta\delta^{15}\text{N}_{\text{coord}} = \delta^{15}\text{N}_{\text{complex}} - \delta^{15}\text{N}_{\text{ligand}}$. Our previous results have shown that values of $\Delta\delta^1\text{H}_{\text{coord}}$ up to 0.7 ppm and $\Delta\delta^{15}\text{N}_{\text{coord}}$ up to –80 ppm indicate successful pyridine *N*-coordination.^[8,10]

Attempted gold(III) coordination of the pyridine based ligands **6–7** showed varied results, greatly depending on the pyridine 2,6-substituents, as well as the reaction conditions. A series of experimental coordination conditions were tested, including varied amounts of the gold source (AuCl₃, KAuCl₄; 1–2.5 equiv.), base treatment (KOAc, NaOAc, NaH), solvent (ACN, with or without water added), heating (r.t. to 70 °C), activation by silver salt additives (AgSbF₆ or AgNTf₂), different work-up and crude product treatment. After a series of coordination experiments for formation of the *N,N,O*-tridentate Au(III)-**6f** complex of the bipyridine ligand **6f**, optimized conditions based on AuCl₃ (2.5 equiv.) and the mild base KOAc (6 equiv.) in ACN/H₂O, afforded the *N,N,O*-tridentate Au(III)-**6f** complex with the AuCl₄[–] anion, as a single product, as shown by NMR. The bipyridine *N,N*-coordination was indicated by ¹H NMR, showing large shifts of the pyridine hydrogens ($\Delta\delta^1\text{H}_{\text{coord}} > 0.5$ ppm), characteristic for gold *N*-coordination of both pyridine nitrogens. The O-coordination was indicated by the disappearance of the broad OH peak at $\delta = 4.8$ ppm. HRMS in positive and negative mode showed correct ion for the *N,N,O*-tridentate coordinated Au(III)-**6f** complex, as well as AuCl₄[–] as the counter anion.

It is known that ligand coordination in the presence of a silver salt of a weakly coordinating ion may give more selective coordination to gold(III) by counterion exchange and thus, prevent the formation of AuCl₄[–] complexes.^[4a,4c] Application of this coordination protocol allowed for successful formation of Au(III) complexes with non-auric counterions. Quantitative conversion to the corresponding Au(III)-**6f**-NTf₂ (Scheme 2a) and Au(III)-**6f**-SbF₆ complexes was obtained by treatment of ligand **6f** with KAuCl₄ (1.3 equiv.), KOAc (3 equiv.) and AgNTf₂ or AgSbF₆ (1.3 equiv.), respectively, by stirring over-night in an acetonitrile/water mixture.



Scheme 2. Au(III) coordination studies of ligands **6f**, **6a** and **7d**.

The formation of Au(III)-**6f**-NTf₂ complex was studied by NMR (Figure 1). The *N,N*-coordination was demonstrated by ¹H NMR, showing pronounced deshielding effect on the bipyridine hydrogens H1',2',3',6' ($\Delta\delta^1\text{H}_{\text{coord}}$ 0.4–0.6 ppm), as expected for gold *N*-coordination of both pyridine nitrogens (Figure 1a). The O-coordination was indicated by the disappearance of a broad OH peak at $\delta = 4.8$ ppm. ¹H, ¹⁵N HMBC (Figure 1a) allowed assignment of the respective two pyridine nitrogens in ligand **6f** and the Au(III)-**6f** complex, as correlation was seen between the corresponding central pyridine nitrogens N_{centr} and H5' and

H7', as well as between the terminal pyridine nitrogens N_{term} and H1', H2' and H4'. Judging from ¹H, ¹⁵N HMBC, N_{term} seems to be more affected by coordination than N_{centr} as shown by the higher shift difference; $\Delta\delta^{15}\text{N}_{\text{term,coord}} = -80.1$ ppm vs. $\Delta\delta^{15}\text{N}_{\text{centr,coord}} = -49.9$ ppm. This observation may be explained by selective intramolecular hydrogen bond formation between N_{centr} and OH in the more rigid part of the original ligand **6f** molecule before Au(III) treatment. The proximity of the O-coordinated gold also strongly affected the menthol group (Figure 1b). In particular, a strong deshielding effect was observed for the H6_{eq} and H7 menthol protons, as shown by the large $\Delta\delta^1\text{H}_{\text{coord}} = 0.44$ ppm and $\Delta\delta^1\text{H}_{\text{eq,coord}} = 0.61$ ppm. An important proof of O-coordination is the large $\Delta\delta^{13}\text{C}_{\text{coord}}$ > 25 ppm of the benzylic carbon C1 on the menthol moiety [moving from ¹³C 77.3 ppm (CDCl₃) to ¹³C 105.5 ppm (CD₃CN)]. Also, IR spectroscopy revealed absence of any OH absorption band, verifying the O-coordination mode. The NTf₂ counterion was identified by ¹⁹F NMR.

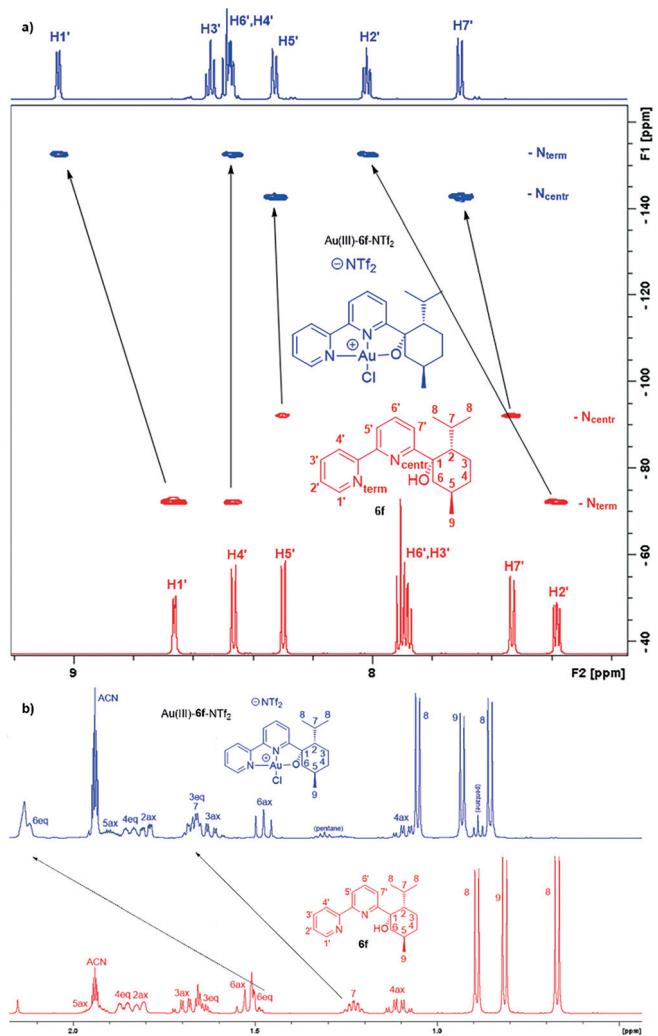


Figure 1. Au(III) coordination study of ligand **6f**; a) ¹H, ¹⁵N HMBC NMR (¹H NMR: $\delta = 7.2$ –9.2 ppm and ¹⁵N NMR: -40 to -160 ppm) and b) ¹H NMR ($\delta = 0.0$ –2.2 ppm).

The coordination of the other potential N,O-bidentate and X,N,O-tridentate Au(III) ligands **6a**–**c** and **7a**–**e** (X = N, C or S)

were more challenging. Some ligands may interact with Au(III) by treatment of AuCl₃ or KAuCl₄, but their possible complex structures were not confirmed, as the ligands failed to give stable Au(III) complexes. Other ligands showed a promising shift change ($\Delta\delta^1\text{H}$ up to 0.6 ppm), but the formed products were shown to be the respective protonated pyridinium salt, possibly with anionic gold counterion. A few experiments only gave recovery of the ligands. However, also potential N-Au(III) coordination was observed, as shown by promising $\Delta\delta^1\text{H}_{\text{coord}}$ of approx. 0.7–0.8 ppm and $\Delta\delta^{15}\text{N} > -100$ ppm, but these possible ligated Au(III) complexes were formed in mixtures with other products and seemed to decompose during workup and isolation.

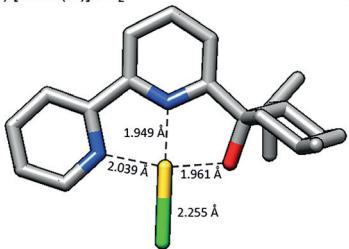
Several attempts were made for C–H-activation of the aryl-substituted ligands **6a**–**c** to give C–Au bond formation and C,N,O-Au(III) complexes. Multiple microwave heating experiments^[7] were made with ligand **6a**, varying the reaction time, combination of solvents (water, acetonitrile and methanol) and gold salts (HAuCl₄ hydrate and AuCl₃). However, no activation for C–Au bond formation was obtained, as indicated by ¹H and ¹³C NMR. Still, ¹H, ¹⁵N-HMBC NMR showed formation of a pyridine-N-coordinated Au(III)–**6a** complex, as seen by $\Delta\delta^{15}\text{N}_{\text{coord}}$ of -102.4 ppm of the pyridine nitrogen (Scheme 2b). The electron-deficient and electron rich aryl ligands **6b** and **6c** also failed to give the desired C–Au(III) complexes.

Sulfur is compatible with Au(I), e.g. in the commercially available reagent Me₂SAu(I)Cl used for ligand exchange. To study possible formation of S,N-bidentate or S,N,O-tridentate Au(III) complexes, the thiophene ligand **7d** was tested with a series of experimental conditions to obtain S-coordination to Au(III). In fact, a new promising coordinated product was obtained by AuCl₃ treatment in the presence of AgSbF₆ in a mixture of ACN/H₂O. Careful work-up with Na₂SO₄ removal of the water solvent afforded a crude product of high purity (Figure S1, Supporting Information). NMR revealed a characteristic pyridine coordination pattern with the promising $\Delta\delta^1\text{H}_{\text{coord}} = 0.71$ ppm. Also the $\Delta\delta^1\text{H}_{\text{coord}}$ (≈ 0.5 ppm) for thiophene H1 proton indicates S-Au(III) coordination. Thus, the product was assumed to be the Au(III)–**7d**-SbF₆ complex (Scheme 2c), although it was not concluded whether an S,N,O-tridentate, N,O-bidentate, or S,N-bidentate complex was formed, but the appearance of a broad peak (spanning ≈ 3 ppm in width) might indicate that the OH-group was not coordinated. Attempts to form crystals for XRD analysis were unsuccessful and caused decomposition.

Single crystals of the Au(III)–**6f**-NTf₂ complex were successfully obtained by slow diffusion of *n*-pentane into a dichloromethane solution of the complex. X-ray single crystal analysis confirmed the formation of a N,N,O-tridentate Au(III) complex through the bipyridine nitrogens and the alcoholate oxygen (Figure 2a). A shorter Au–N distance was seen for the central pyridine; Au–N_{centr} (1.949 Å) < the Au–N_{term} (2.039 Å). Also a slight distortion from the square planar Au(III) geometry was observed. The atoms form an almost ideal plane (mean deviations from the plane of < 0.2 Å), and only small deviations from linear/right angles of the coordinating atoms are imposed by the ligand framework. Importantly, X-ray analysis confirmed the formation of the Au–O bond, which often is difficult to verify

by NMR and HRMS by the presence of only one counterion and the absence of residual electron density attributable to an OH. The crystal structure of our previously reported analogous *N,N,O*-pyridine-menthol-Au(III) complex^[8] is shown for comparison (Figure 2b).

a) [6f-Au(III)]NTf₂



b) Pyr-Menth-Au(III) (Paper I)

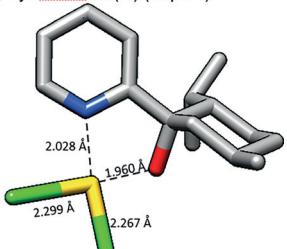


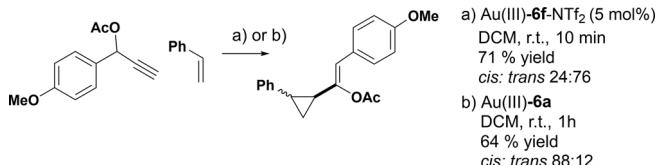
Figure 2. Crystal structures (XRD) of a) *N,N,O*-Au(III) Au(III)-6f-NTf₂ and b) the *N,O*-Au(III) analogues pyr-menth-Au(III) complex.^[8]

Catalytic Activity of Au(III) Complexes

The catalytic activity of the *N,N,O*-tridentate Au(III)-6f-NTf₂ complex and monodentate Au(III)-6a was investigated in a model reaction. Complex Au(III)-6f-NTf₂ was highly active in the cyclopropanation between propargyl acetate and styrene (Scheme 3), causing complete consumption of the propargyl substrate in <10 min. The cyclopropyl product, obtained in 71 % yield, was formed as a 24:76 *cis/trans* mixture (52 %de). High amounts of the *trans* diastereomer in the model reaction has previously been shown for bisoxazoline [BOX-Au(III)] complexes by our group to be a result of the additional ability of some active gold complexes^[4a] to rapidly transform the initially formed *cis* product into the isomerized *trans* product (full conversion 10 min; 92:18 *cis/trans*; vs. 24 h; 10:90 *cis/trans*). The BOX-Au(III) complexes represent an interesting group of gold catalysts, being superior to other tested catalysts, including AuCl₃, for combined cyclopropanation and isomerization. The Au(III)-6f-NTf₂ complex had similar specific and unique properties as BOX-Au(III), and even stronger catalytic ability for isomerization. The slightly increased reaction time needed to reach full conversion with the pyridine-*N*-coordinated Au(III)-6a complex (1 h, 88:12, *cis/trans*) is in accordance with our previous studies, indicating that replacement of Au(III) chlorides with chelating heteroatom ligands give increased Au(III) catalytic activity.^[8,10] The studies indicate that the pyridine-nitrogen decoordination ability of the second pyridine moiety is significant in order to generate highly efficient catalytic activity. No discernible enantiomeric excess was observed for any of the diastereomers.

Conclusion

Through our present studies on the coordination ability of new pyridine alcohol ligands to gold(III), successful *N,N,O*-gold(III) coordination of a new polydentate bis-pyridine alcohol ligand was obtained. Stable *N,N,O*-tridentate Au(III)-6f-X complexes (X = AuCl₄⁻, NTf₂⁻, SbF₆⁻) with the chiral 2-pyridyl-6-[(1*S,2S,5R*)-



Scheme 3. Propargyl cyclopropanation; model reaction for evaluation of catalytic activity of Au(III) complexes.

neomenthol-1-yl]pyridine ligand were prepared and characterised (¹H, ¹³C, ¹⁵N NMR, HRMS, IR, XRD).

A series of eight chiral 2-aryl-6-alkylpyridine alcohol ligands **6–7**, with potential *Z,N,O*-tridentate coordination ability (*Z* = *N*, *S* or *C*), were prepared from 2,6-dibromopyridine, (–)-menthone or (+)-camphor, respectively, and appropriate arylboronic acids. However, only ligand **6f** successfully gave stable *N,N,O*-tridentate coordinated Au(III) complexes.

The catalytic ability of the Au(III)-6f-NTf₂ complex was tested in propargyl cyclopropanation and demonstrated that the new ligated gold(III) complex had similar unique strong catalytic properties as our previously studied Box-Au(III) complexes.

The present study demonstrates the importance of ligand design, as the Au(III)-coordination ability and the activity and stability of the Au(III) complexes were strongly depending on the structure of the 2-aryl-6-alkylpyridine alcohol ligands.

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 ¹H-NMR. Flash chromatography was carried out using silica gel 60 (0.040–0.063 mm). High Throughput Flash Purification (HTFP) was performed on pre-packed cartridges. ¹H, ¹³C NMR, ¹H, ¹⁵N HMBC NMR spectrum were recorded in CDCl₃ or CD₂Cl₂, using a 400 or a 600 MHz Bruker spectrometer. ¹H and ¹³C chemical shifts are reported in ppm (δ), using the residual solvent signal as internal standard. ¹H and ¹³C NMR characterization is reported in the experimental part following the numbering given in Supporting Information for ligands **6b,c,d,f** and **7c,d** and corresponding Au(III) complexes [Au(III)-**6f** and Au(III)-**6a**]. Accurate mass determination, HRMS, in positive or negative mode was performed with a “Synapt G2-S” Q-TOF instrument from Waters. Samples were ionized with an ASAP probe, and no chromatographic separation was used before the mass analysis. 1-(4-Methoxyphenyl)prop-2-yn-1-yl acetate^[11] was prepared according to literature procedures.

Synthesis of Chiral 2-Bromo-6-alkylpyridine Alcohols (4,5)

(1*R,2*R,5*S*)-1-(6-Bromopyridin-2-yl)-2-isopropyl-5-methylcyclohexan-1-ol (4):** 2,6-Dibromopyridine (755 mg, 3.45 mmol) was dissolved in DEE (50 mL) and cooled to –78 °C. nBuLi (1.7 mL, 2 M, 3.4 mmol) was added dropwise before the reaction mixture was warmed to –40 °C. The mixture was cooled to –78 °C and (–)-menthone (0.58 mL, 3.36 mmol) was added dropwise. The reaction mixture was warmed to r.t. and stirred for additional 2 hours. The reaction mixture was quenched with water (20 mL) and extracted with DEE (3 × 20 mL). The combined organic phases were dried with anhydrous Na₂SO₄, filtered and removed in vacuo. The crude product was purified with silica gel column chromatography (*n*-

pentane/EtOAc, 9:1, $R_f = 0.30$) to yield the product as a colorless oil, 795 mg (82 %, 2.55 mmol). The spectroscopic data corresponds well with that reported previously.^[12]

(1*R*,*2R*,*4R*)-2-(6-Bromopyridin-2-yl)-1,7,7-trimethylbicyclo-[2.2.1]heptan-2-ol (5): 2,6-Dibromopyridine (817 mg, 3.45 mmol) was dissolved in DEE (50 mL) and cooled to -78 °C. *n*BuLi (2 mL, 2 M, 4 mmol) was added dropwise before the reaction mixture was warmed to -40 °C. The mixture was cooled to -78 °C and (1*R*)-(+)camphor (514 mg, 3.38 mmol) was added dropwise. The reaction mixture was warmed to r.t. and stirred for 4 hours. The reaction mixture was quenched with water (20 mL) and extracted with DEE (3 × 20 mL). The combined organic phases were dried with anhydrous Na₂SO₄, filtered and removed under vacuum. The crude product was purified with silica gel column chromatography (DCM, $R_f = 0.41$) to yield the product as a white powder, 314 mg (30 %, 1.01 mmol). The spectroscopic data corresponds well with that reported previously.^[12]

Synthesis and Characterization of Chiral 2-Aryl-6-alkyl Pyridine Alcohols (6,7): General procedure A: Chiral 2-bromopyridine 4-5 (1 equiv.), aryl boronic acid or boron pinacol ester A-E (1-2 equiv.), K₂CO₃ (3 equiv.) and Pd(PPh₃)₄ (5-10 mol-%) were dissolved in a mixture of dioxane (1-2 mL) and water (0.5 mL) under N₂-atmosphere. The solution was heated to 70 °C and stirred overnight or until full conversion as determined by TLC. Water (10 mL) was added, the product was extracted with DCM. The organic phase was washed with brine (10 mL) and dried with anhydrous Na₂SO₄. The solvent was removed in vacuo before the crude product was purification by silica gel column chromatography yielding the pure 2-aryl-6-alkylpyridines 6a-d and 7a,c-e.

(1*R*,*2R*,*5S*)-2-Isopropyl-5-methyl-1-(6-phenylpyridin-2-yl)cyclohexan-1-ol (6a): Phenylboronic acid (A) (35 mg, 0.284 mmol), Pd(PPh₃)₄ (16 mg, 0.01 mmol), (1*R*,*2R*,*5S*)-1-(6-bromopyridin-2-yl)-2-isopropyl-5-methylcyclohexan-1-ol (74 mg, 0.24 mmol) and K₂CO₃ (130 mg, 0.941 mmol) were dissolved in dioxane (2 mL) and water (2 mL) under nitrogen atmosphere. The mixture was stirred under reflux for 3 hours before water was added. The water phase was extracted with DEE (3 × 10 mL) and the combined organic phases were dried with anhydrous Na₂SO₄, filtered and removed in vacuo. Silica gel column chromatography (*n*-pentane/EtOAc, 10:1, $R_f = 0.46$) and drying yielded the product as a colorless oil, 67 mg (92 %, 0.261 mmol). The spectroscopic data corresponds well with that reported previously.^[9b]

(1*R*,*2R*,*5S*)-1-[6-[3,5-Bis(trifluoromethyl)phenyl]pyridin-2-yl]-2-isopropyl-5-methylcyclohexan-1-ol (6b): [3,5-Bis(trifluoromethyl)phenyl]boronic acid (B) (53 mg, 0.205 mmol), Pd(PPh₃)₄ (3 mg, 0.008 mmol), (1*R*,*2R*,*5S*)-1-(6-bromopyridin-2-yl)-2-isopropyl-5-methylcyclohexan-1-ol (4) (53 mg, 0.170 mmol) and K₂CO₃ (76 mg, 0.550 mmol) were dissolved in dioxane (2 mL) and water (0.5 mL) under nitrogen atmosphere. The mixture was stirred under reflux for 3 hours before water was added. The water phase was extracted with DEE (3 × 10 mL) and the combined organic phases were dried with anhydrous Na₂SO₄, filtered and removed in vacuo. Silica gel column chromatography (*n*-pentane/EtOAc, 10:1, $R_f = 0.81$) and drying yielded the product as a colorless oil, 72 mg (95 %, 0.162 mmol). ¹H NMR (600 MHz, CDCl₃) δ (ppm): 8.47–8.39 (m, 2H), 7.93 (s, 1H), 7.88 (t, $J = 7.8$ Hz, 1H), 7.72 (dd, $J = 7.7, 0.7$ Hz, 1H), 7.43 (d, $J = 7.9$ Hz, 1H), 2.06–1.96 (m, 1H), 1.92 (dt, $J = 13.0, 3.1$ Hz, 1H), 1.81–1.68 (m, 3H), 1.63 (ddd, $J = 13.2, 3.7, 2.2$ Hz, 1H), 1.44–1.34 (m, 1H), 1.30–1.23 (m, 1H), 1.09 (qd, $J = 12.7, 3.8$ Hz, 1H), 0.92 (d, $J = 6.6$ Hz, 3H), 0.85 (d, $J = 7.0$ Hz, 3H), 0.71 (d, $J = 7.0$ Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ (ppm): 166.3, 151.7, 140.9, 138.3, 132.3 (q, ²J_{C,F} = 34.1 Hz, 2C), 126.9 (d, ³J_{C,F} = 3.3 Hz, 2C), 125.1 (q, ¹J_{C,F} =

272.7 Hz, 2C), 122.6 (h, ³J_{C,F} = 3.9 Hz), 119.5, 118.7, 77.6, 50.8, 50.0, 35.3, 28.6, 27.7, 23.7, 22.4, 22.0, 18.6; HRMS (ASAP, *m/z*): found 446.1992 (calc. C₃₁H₂₅F₆NO, 446.1920 [M + H]⁺).

(1*S*,*2S*,*5R*)-1-[6-(3,5-Dimethoxyphenyl)pyridin-2-yl]-2-isopropyl-5-methylcyclohexan-1-ol (6c): Following general procedure A, 2-bromopyridine 4 (100.1 mg, 0.320 mmol) was treated with (3,5-dimethoxyphenyl)boronic acid (C) (115.4 mg, 0.640 mmol) in the presence of catalytic Pd(PPh₃)₄ (19.0 mg, 0.016 mmol) and K₂CO₃ (136.0 mg, 0.984 mmol) to give 2,6-disubstituted pyridine 6c (103.1 mg, 87 %) after workup and purification (1:25 EtOAc:*n*-pentane) as a colourless oil. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.77 (t, $J = 7.8, 1$ H, H12), 7.60 (d, $J = 7.7, 1$ H, H13), 7.28 (d, $J = 7.8, 1$ H, H11), 7.19 (d, $J = 2.3, 2$ H, H16), 6.54 (t, $J = 2.3, 1$ H, H18), 5.58 (bs, 1H, OH), 3.87 (s, 6H, H19), 2.00 (m, 1H, H5_{ax}), 1.91 (m, 1H, H4_{eq}), 1.74 (qd, $J = 12.8, 3.4$ Hz, 1H, H3_{ax}), 1.58–1.70 (m, 3H, H2_{ax}, H3_{eq} and H6_{eq}), 1.38 (t, $J = 12.6, 1$ H, H6_{ax}), 1.27 (hept d, $J = 6.9, 1.9, 1$ H, H7), 1.07 (qd, $J = 12.7, 3.7$ Hz, 1H, H4_{ax}), 0.91 (d, $J = 6.6, 3$ H, H9), 0.84 (d, $J = 6.8, 3$ H, H8), 0.69 (d, $J = 7.0, 1$ H, H8); ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 165.0 (C10), 161.2 (C17), 154.2 (C14), 140.9 (C15), 137.8 (C12), 118.41 (C13), 118.04 (C11), 105.0 (C16), 101.3 (C18), 55.5 (C19), 50.71 (C6), 50.16 (C2), 35.4 (C4), 28.6 (C5), 27.5 (C7), 23.7 (C8), 22.43 (C9), 22.08 (C3), 18.6 (C8); HRMS (ESI): found 370.2387 (calc. 370.2387, 370.2382 [M + H]⁺).

(1*S*,*2S*,*5R*)-2-Isopropyl-5-methyl-1-[6-(thiophen-2-yl)pyridin-2-yl]cyclohexan-1-ol (6d): Following general procedure A, 2-bromopyridine 4 (50.7 mg, 0.160 mmol) was treated with (thiophene-2-yl)boronic acid (D) (33.6 mg, 0.240 mmol) in the presence of catalytic Pd(PPh₃)₄ (18.6 mg, 0.016 mmol) and K₂CO₃ (68.6 mg, 0.480 mmol) to give 2,6-disubstituted pyridine 6d (44.1 mg, 87 %) after workup and purification (1:30 EtOAc/pentane) as a white powder. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.70 (t, $J = 7.8, 1$ H, H12), 7.61 (d, $J = 3.5, 1$ H, H16), 7.53 (d, $J = 7.7, 1$ H, H13), 7.39 (d, $J = 5.0, 1$ H, H18), 7.18 (d, $J = 7.8, 1$ H, H11), 7.11 (dd, $J = 4.9, 3.8$ Hz, 1H, H17), 5.32 (bs, 1H, OH), 2.00 (m, 1H, H5), 1.90 (m, 1H, H4_{eq}), 1.74 (qd, $J = 12.8, 3.4$ Hz, 1H, H3_{ax}), 1.66 (dq, $J = 13.0, 3.5$ Hz, 1H, H3_{eq}), 1.58–1.63 (m, 2H, H2 and H6_{eq}), 1.36 (t, $J = 12.6, 1$ H, H6_{ax}), 1.28 (hept d, $J = 6.9, 1.7$ Hz, 1H, H7), 1.06 (qd, $J = 12.6, 3.8$ Hz, 1H, H4_{ax}), 0.91 (d, $J = 6.6, 3$ H, H9), 0.84 (d, $J = 6.8, 3$ H, H8), 0.69 (d, $J = 7.0, 3$ H, H8); ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 165.2 (C10), 149.9 (C14), 144.5 (C15), 137.7 (C12), 128.0 (C17), 127.7 (C18), 124.7 (C16), 117.5 (C11), 116.4 (C13), 77.1 (C1), 50.6 (C6), 50.1 (C2), 35.3 (C4), 28.6 (C5), 27.6 (C7), 23.6 (C8), 22.4 (C9), 22.0 (C3), 18.5 (C8); HRMS (ASAP, *m/z*): found 316.1742 (calc. C₁₉H₂₆NOS, 316.1735 [M + H]⁺).

(1*S*,*2S*,*5R*)-1-[6-[2,2'-Bipyridin-6-yl]-2-isopropyl-5-methylcyclohexan-1-ol (6f): 6-Bromo-2,2'-bipyridine (1f) (497.2 mg, 2.115 mmol) was dissolved in dry DEE and cooled to -80 °C. *n*BuLi (850 μL, 2.5 M in hexane, 2.125 mmol) was added dropwise and the solution stirred until it reached -40 °C before being cooled back to -80 °C. (-)-Menthone (2) (367 μL, 2.379 mmol) diluted in DEE (1 mL) was added dropwise, and the solution was stirred overnight and warmed to r.t. The solution was quenched with sat. NH₄Cl (25 mL), extracted into DCM (3 × 20 mL), washed with brine (20 mL), dried with Na₂SO₄. Removal of the solvent in vacuo and purification by flash column chromatography (1:15 NEt₃:petroleum ether) and product recrystallised from ACN by dropwise addition of water, yielding product 6f (150.5 mg, 23 %) as white crystals. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 8.69 (dm, $J = 4.7, 1$ H, H19), 8.41 (d, $J = 8.0, 1$ H, H16), 8.33 (d, $J = 7.7, 1$ H, H13), 7.85 (t, $J = 7.8, 1$ H, H12), 7.83 (td, $J = 11.5, 1.8$ Hz, 1H, H17), 7.37 (d, $J = 7.8, 1$ H, H11), 7.32 (ddd, $J = 7.4, 4.8, 0.9$ Hz, 1H, H18), 5.42 (bs, 1H, OH), 2.01 (m, 1H, H5_{ax}), 1.92 (m, 1H, H4_{eq}), 1.76 (qd, $J = 12.9, 3.4$ Hz, 1H, H3_{ax}), 1.65–1.71 (m, 2H, H2_{ax} and H3_{eq}), 1.62 (ddd, $J = 13.1, 3.2, 2.5$ Hz, 1H, H6_{eq}), 1.40 (t, $J =$

12.6, 1H, H_{6ax}), 1.28 (hept d, J = 6.9, 1.5, 1H, H7), 1.08 (qd, J = 12.6, 3.6, 1H, H_{4ax}), 0.92 (d, J = 6.8, 3H, H9), 0.84 (d, J = 6.8, 3H, H8), 0.69 (d, J = 7.0, 1H, H8); ¹⁵N NMR (60.8 MHz, d₃-ACN) δ (ppm): -72.4 (between C15 and C19), -92.4 (between C10 and C14). ¹H NMR was in accordance with literature data.^[9b]

(1R,2R,4R)-1,7,7-Trimethyl-2-(6-phenylpyridin-2-yl)bicyclo[2.2.1]heptan-2-ol (7a): Following general procedure A, 2-bromopyridine 5 (100.0 mg, 0.322 mmol), was treated with phenylboronic acid (**A**) (43.2 mg, 0.355 mmol) in the presence of catalytic Pd(PPh₃)₄ formed in situ from Pd(OAc)₂ (3.6 mg, 0.016 mmol), PPh₃ (25.4 mg, 0.097 mmol) and NEt₃ (135 μ L, 0.967 mmol) and K₂CO₃ (66.0 mg, 0.478 mmol) to give 2,6-disubstituted pyridine **15d** (95.8 mg, 97 %) after workup and purification (DCM) as a white oil. The spectroscopic data corresponds well with that reported previously.^[9b]

(1R,2R,4R)-2-[6-(3,5-Dimethoxyphenyl)pyridin-2-yl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (7c): Following general procedure A, 2-bromopyridine 5 (50.1 mg, 0.161 mmol) was treated with (3,5-dimethoxyphenyl)boronic acid (**C**) (53.9 mg, 0.296 mmol) in the presence of catalytic Pd(PPh₃)₄ (9.9 mg, 0.009 mmol) and K₂CO₃ (66.0 mg, 0.478 mmol) to give 2,6-disubstituted pyridine **7c** (59.0 mg, 100 %) after workup and purification (1:10 EtOAc/pentane) as a colourless oil. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.70 (t, J = 7.8, 1H, H13), 7.58 (d, J = 7.8, 1H, H14), 7.39 (d, J = 7.8, 1H, H12), 7.17 (d, J = 2.3, 2H, H17), 6.53 (t, J = 2.3, 1H, H19), 5.27 (s, 1H, OH), 3.85 (s, 6H, H20), 2.34 (dt, J = 14.1, 3.8, 1H, H_{6eq}), 2.20 (d, J = 14.0, 1H, H_{6ax}), 1.92 (t, J = 4.4, 1H, H5), 1.81 (m, 1H, H_{4eq}), 1.24–1.37 (m, 5H, H_{3eq}, H_{4ax} and H10), 0.85 (m, 7H, H_{3ax}, H7 and H9); ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 163.2 (C11), 161.1 (C18), 154.5 (C15), 141.0 (C16), 136.6 (C13), 119.3 (C12), 118.5 (C14), 105.0 (C17), 101.1 (C19), 82.8 (C1), 55.4 (C20), 53.5 (C8), 50.5 (C2), 45.4 (C5), 44.1 (C6), 30.8 (C3), 27.0 (C4), 21.3 (C10), 21.2 (C9), 10.0 (C7); HRMS (ASAP, m/z): found 368.2223 (calc. C₂₃H₃₀NO₃, 368.2226 [M + H]⁺).

(1R,2R,4R)-1,7,7-Trimethyl-2-[6-(thiophen-2-yl)pyridin-2-yl]-bicyclo[2.2.1]heptan-2-ol (7d): Following general procedure A, 2-bromopyridine 5 (50.0 mg, 0.161 mmol), was treated with (thiophene-2-yl)boronic acid (**D**) (22.7 mg, 0.177 mmol) in the presence of catalytic Pd(PPh₃)₄ formed in situ from Pd(OAc)₂ (1.8 mg, 0.008 mmol), PPh₃ (12.7 mg, 0.048 mmol) and NEt₃ (68 μ L, 0.484 mmol), and K₂CO₃ (68.0 mg, 0.492 mmol) to give 2,6-disubstituted pyridine **7d** (25.6 mg, 51 %) after workup and purification (1:10 acetone:n-pentane) as a colourless oil. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.65 (t, J = 7.8, 1H, H13), 7.58 (dd, J = 3.7, 1.0, 1H, H17), 7.53 (d, J = 7.8, 1H, H14), 7.38 (dd, J = 5.0, 1.0, 1H, H19), 7.30 (d, J = 7.8, 1H, H12), 7.10 (dd, J = 5.0, 3.7, 1H, H18), 4.96 (s, 1H, OH), 2.31 (dt, J = 14.1, 3.8, 1H, H_{6eq}), 2.20 (d, J = 14.0, 1H, H_{6ax}), 1.92 (t, J = 4.4, 1H, H_{5eq}), 1.80 (m, 1H, H_{4eq}), 1.23–1.35 (m, 7H, H_{3eq}, H_{4ax} and H10), 0.91 (s, 3H, H9), 0.89 (s, 3H, H7), 0.86 (m, 1H, H_{3ax}); ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 163.4 (C11), 150.3 (C15), 144.9 (C16), 136.5 (C13), 128.0 (C18), 127.7 (C19), 124.4 (C17), 118.6 (C12), 116.5 (C14), 82.8 (C1), 53.5 (C8), 50.5 (C2), 45.4 (C5), 43.7 (C6), 30.8 (C3), 26.9 (C4), 21.3 (C10), 21.2 (C9), 9.8 (C7); HRMS (ASAP, m/z): found 314.582 (calc. C₁₉H₂₄NOS, 314.1579 [M + H]⁺).

(1R,2R,4R)-1,7,7-Trimethyl-2-[6-(1-methyl-1H-pyrrol-2-yl)pyridin-2-yl]bicyclo[2.2.1]heptan-2-ol (7e): Following general procedure A, 2-bromopyridine 5 (50.0 mg, 0.161 mmol), was treated with 1-Methyl-2-pyrroleboronic acid pinacol ester (**E**) (72.4 mg, 0.350 mmol) in the presence of catalytic Pd(PPh₃)₄ formed in situ from Pd(OAc)₂ (3.8 mg, 0.0017 mmol), PPh₃ (25.9 mg, 0.099 mmol) and NEt₃ (68 μ L, 0.484 mmol), and K₂CO₃ (136.5 mg, 0.988 mmol) to give 2,6-disubstituted pyridine **7e** (20.8 mg, 41 %) after workup and purification (1:1 DCM/pentane) as an orange oil. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.63 (t, J = 7.9, 1H, H13), 7.45 (dd, J =

7.9, 0.6, 1H, H14), 7.23 (d, J = 7.8, 1H, H12), 6.73 (t, J = 2.2, 1H, H19), 6.62 (dd, J = 3.8, 1.8, 1H, H17), 6.18 (dd, J = 3.7, 2.6, 1H, H18), 5.30 (s, 1H, OH), 4.00 (s, 3H, H20), 2.33 (dt, J = 14.1, 3.8, 1H, H_{6eq}), 2.13 (d, J = 14.1, 1H, H_{6ax}), 1.92 (t, J = 4.4, 1H, H5), 1.82 (m, 1H, H_{4eq}), 1.28–1.36 (m, 2H, H_{3eq} and H_{4ax}), 1.27 (s, 3H, H10), 1.00 (m, 1H, H_{3ax}), 0.92 (s, 3H, H9), 0.83 (s, 3H, H7); ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 162.3 (C11), 150.4 (C15), 136.2 (C13), 131.8 (C16), 126.7 (C19), 119.4 (C14), 117.4 (C12), 111.3 (C17), 107.8 (C18), 83.1 (C1), 53.5 (C8), 50.6 (C2), 45.4 (C5), 44.6 (C6), 37.6 (C20), 30.7 (C3), 27.1 (C4), 21.4 (C10), 21.2 (C9), 10.3 (C7); HRMS (ASAP, m/z): found 311.2127 (calc. C₂₀H₂₇N₂O, 311.2123 [M + H]⁺).

Synthesis and Characterization of Au(III) Complexes

Au(III)-6f-NTf₂: Chiral bipyridine alcohol ligand **6f** (5.1 mg, 0.016 mmol) was stirred with KAuCl₄ (8.0 mg, 0.021 mmol) in ACN (0.5 mL) and KOAc (5.1 mg, 0.052 mmol) in H₂O (0.3 mL). AgNTf₂ (8.3 mg, 0.021 mmol) in ACN (0.4 mL) was added and the solution stirred for 1.5 h. H₂O (1 mL) was added and the solution extracted with DCM (3 × 1 mL) without inclusion of AgCl precipitate. Removal of solvent in vacuo yielded pure **[6f-Au(III)]NTf₂** (13.5 mg, 100 %). ¹H NMR (600 MHz, d₃-ACN) δ (ppm): 9.05 (d, J = 5.6, 1H, H19), 8.54 (td, J = 7.9, 1.4, 1H, H17), 8.49 (t, J = 8.1, 1H, H12), 8.47 (d, J = 8.1, 1H, H16), 8.33 (d, J = 8.1, 1H, H13), 8.02 (ddd, J = 7.9, 5.9, 1.6, 1H, H18), 7.71 (d, J = 8.2, 1H, H11), 2.11 (m, 1H, H_{6eq}), 1.90 (m, 1H, H_{5ax}), 1.84 (m, 1H, H_{4eq}), 1.80 (ddd, J = 12.4, 4.1, 1.8, 1H, H_{2ax}), 1.57–1.72 (m, 3H, H_{3ax}, H_{3eq} and H7), 1.48 (dd, J = 12.7, 12.7, 1H, H_{6ax}), 1.08 (qd, J = 12.3, 4.1, 1H, H_{4ax}), 1.05 (d, J = 6.8, 3H, H8), 0.93 (d, J = 6.7, 3H, H9), 0.85 (d, J = 6.9, 3H, H8); ¹³C NMR (150 MHz, d₃-ACN) δ (ppm): 177.0 (C10), 158.8 (C15), 151.9 (C14), 149.8 (C19), 145.8 (C17), 145.7 (C12), 131.3 (C18), 127.5 (C16), 126.9 (C11), 124.9 (C13), 120.9 (q, J = 320.6, CF₃), 105.5 (C1), 51.8 (C6), 51.3 (C2), 34.7 (C4), 30.0 (C7), 28.7 (C5), 23.7 (C8), 22.1 (C9), 21.3 (C3), 19.9 (C8); ¹⁵N NMR (60.8 MHz, d₃-ACN) δ (ppm): -142.7 (between C10 and C14), -152.6 (between C15 and C19); HRMS (ESI): found 541.1326 (calc. C₂₀H₂₅N₂OClAu, 541.1321 [M]⁺); HRMS (ESI-): found 279.9177 (calc. for C₂NO₄F₆S₂, 279.9173 [M]⁻); CCDC No: 2023898.

Au(III)-6f-SbF₆: Chiral bipyridine alcohol ligand **6f** (5.0 mg, 0.016 mmol) was stirred with KAuCl₄ (7.9 mg, 0.021 mmol) in ACN (0.5 mL) and KOAc (4.7 mg, 0.048 mmol) in H₂O (0.3 mL). AgSbF₆ (7.2 mg, 0.021 mmol) in ACN (0.4 mL) was added and the solution stirred for 1.5 h. H₂O (1 mL) was added and the solution extracted with DCM (3 × 1 mL) without inclusion of AgCl precipitate. Removal of solvent in vacuo yielded pure **[6f-Au(III)]SbF₆** (13.1 mg, 100 %). ¹H NMR (600 MHz, d₃-ACN) δ (ppm): 9.06 (dd, J = 5.8, 1.0, 1H, H19), 8.54 (td, J = 7.9, 1.5, 1H, H13), 8.49 (t, J = 8.1, 1H, H12), 8.47 (dd, J = 8.1, 1.0, 1H, H16), 8.32 (dd, J = 8.0, 0.7, 1H, H13), 8.02 (ddd, J = 7.7, 5.9, 1.5, 1H, H18), 7.71 (dd, J = 8.2, 0.6, 1H, H11), 2.13 (m, 1H, H_{6eq}), 1.90 (m, 1H, H_{5ax}), 1.85 (m, 1H, H_{4eq}), 1.80 (ddd, J = 12.4, 4.1, 1.8, 1H, H_{2ax}), 1.57–1.72 (m, 3H, H_{3ax}, H_{3eq} and H7), 1.48 (dd, J = 12.9, 12.8, 1H, H_{6ax}), 1.09 (qd, J = 12.6, 4.1, 1H, H_{4ax}), 1.06 (d, J = 6.8, 3H, H8), 0.93 (d, J = 6.7, 3H, H9), 0.86 (d, J = 6.9, 3H, H8); ¹³C NMR (150 MHz, d₃-ACN) δ (ppm): 177.0 (C10), 158.8 (C15), 151.9 (C14), 149.9 (C19), 145.9 (C17), 145.7 (C12), 131.3 (C18), 127.5 (C16), 126.9 (C11), 124.9 (C13), 105.5 (C1), 51.8 (C6), 51.4 (C2), 34.8 (C4), 30.0 (C7), 28.8 (C5), 23.7 (C8), 22.2 (C9), 21.3 (C3), 19.9 (C8); ¹⁵N NMR (60.8 MHz, d₃-ACN) δ (ppm): -142.8 (between C10 and C14), -152.7 (between C15 and C19); HRMS (ESI): found 541.1321 (calc. C₂₀H₂₅N₂OClAu, 541.1321 [M]⁺); HRMS (ESI-): found 234.8944 (calcd for SbF₆, 234.8942 [M]⁻).

Au(III)-6a: Ligand **6a** (6 mg, 0.019 mg) and HAuCl₄·2H₂O (9 mg, 0.023 mmol) was dissolved in a mixture of acetonitrile (3 mL) and water (1 mL) in a closed microwave vial. The reaction mixture was heated to 120 °C in the microwave for 30 min, before the solvent was removed under reduced pressure. Small amounts of NH₄⁺ from

hydrolysed acetonitrile under the reaction condition was observed by ^1H and ^{15}N NMR. The complex was attempted purified by bases, however low stability of the complex in the presence of bases hindered removal of this side-product. ^1H NMR (600 MHz, CD_3CN) δ = 8.58 (t, J = 8.1 Hz, 1H, H12), 8.16 (dd, J = 8.0, 1.0 Hz, 1H, H11), 7.97 (d, J = 8.3 Hz, 1H, H13), 7.92–7.82 (m, 2H, H17), 7.78–7.67 (m, 3H, H16, H18), 1.89–1.82 (m, 4H, H2, H3, H4, H5, H6), 1.76 (dq, J = 13.6, 3.6 Hz, 1H, H3), 1.70–1.53 (m, 2H, H3, H6), 1.35–1.13 (m, 2H, H4, H7), 0.95 (d, J = 6.2 Hz, 3H, H9), 0.85 (d, J = 6.8 Hz, 3H, H8), 0.74 (d, J = 6.8 Hz, 3H, H8); ^{13}C NMR (151 MHz, CD_3CN) δ = 162.5 (C10), 148.1 (C12), 133.2 (C18), 131.4 (C15), 130.4 (C16), 128.6 (C17), 124.9 (C11), 122.7 (C13), 79.1 (C1), 50.1 (C2), 48.2 (C6), 34.3 (C10), 28.4 (C9), 28.3 (C7), 23.2 (C8), 21.64 (C9), 21.55 (C3), 18.3 (C8); ^{15}N NMR (61 MHz, CD_3CN) δ = -194.5.

General Procedure for Testing of Catalytic Activity: The catalytic activity of Au(III) complexes was evaluated in cyclopropanation reaction as described below. The propargyl ester (1 equiv.) and styrene (4 equiv.) were dissolved in (*d*)-DCM and added the gold-catalyst (5 mol-%) dissolved in (*d*)-DCM. The reaction progress was monitored by ^1H NMR or TLC, while the *cis/trans* ration were determined by ^1H NMR. The crude product was purified by silica column chromatography (*n*-pentane/ethyl acetate, 10:1). Reactivity data, yield and enantioselectivity for the different Au-catalyst is presented in the main text.

Deposition Number 2023898 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Keywords: N,N,O-gold(III) complexes · Pyridine · Tridentate catalyst

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