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Asymmetric intramolecular hydroamination of allenes using mononuclear gold catalysts.

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ABSTRACT: The intramolecular gold catalyzed asymmetric hydroamination of allenes was studied screening a series of mononuclear gold(I) and (III) complexes in combination with silver salts. Among the various chiral mono-phosphine and diaminocarbene ligands tried, the best catalysts arose from mononuclear gold(I) complexes synthesized from BINOL based phosphoramidite ligands. The latest were improved by addition of bulky substituents at specific positions of the BINOL scaffold. The resulting gold(I) complexes were combined with selected

silver salts to afford efficient catalysts for intramolecular hydroamination of allenes at room temperature or below, with good conversions and enantioselectivities.

INTRODUCTION. Amines are ubiquitous in natural products, building blocks and targets for fine chemicals, farming-related chemicals and compounds of pharmaceutical interest.¹ The hydroamination of unactivated alkenes and allenes is the shortest synthetic route to secondary and tertiary amines. For the enantioselective synthesis of optically pure amines, the most studied and privileged hydroamination method is metal-catalysis. Lanthanides and actinides (f-block) were widely screened and significant achievements were reported for intramolecular reactions.^{1b,c,g,2} Group 4 metal (Zr, Ti)^{1c,3} or main-group metal (Mg, Li)^{1c,4} complexes led also to valuable results. By comparison, applications in asymmetric catalysis of transition metals from groups 3-11 (d-block) remain scarce but offer a broader functional group tolerance and substrate scope.^{1c,5,8f} Moreover, the development of recoverable catalysts may favour groups 3-11 metals which can lead to stable and easy to handle organometallic catalysts.

Along the past years, the usefulness of gold⁶ was pointed out on various C-C multiple bond substrates like alkynes,^{6,7} alkenes,^{6,8} allenes,^{6,9} and dienes^{6,10} for both intra- and intermolecular hydroamination reactions as well as for diaminations. These results may be quite surprising as far as gold(I) can be considered as a challenging metal for asymmetric catalysis as highlighted recently by Fürstner et al.¹¹ First, these authors stressed gold(I) privileges a linear-dicoordination geometry¹² which positions the ligand and the activated substrate in a trans fashion restricting thus the asymmetric induction. Tri and tetracoordination of gold(I) proved to be less common.^{12,13} Second, though the reaction mechanism appears to depend on the nature of the nucleophile,^{14,15} gold(I) catalyzed reactions are considered to be outer-sphere in most cases, the metal coordinating the substrate pi-system and the nucleophile attacking from the back side

which is far away from the chiral ligand. To overcome such drawbacks, 3 strategies have been developed in gold(I) catalyzed asymmetric catalysis and to some extent to hydroamination reactions.

The first one implies the use of chiral phosphate anions like TRIP in combination with a gold(I) complex to create a tight ion pair. The resulting chiral binding pocket proved to be highly efficient for some asymmetric intramolecular hydroamination of allenes.^{9u,v} The chiral phosphate counterion was shown to act as a ligand bonded to the gold species all along the hydroamination reaction.¹⁶

The second concept implies the use of chiral dinuclear gold(I)-phosphine complexes. Due to the broad choice of bisphosphine ligands, this approach has been versatile for some inter- and intramolecular asymmetric hydroamination of allenes and alkenes.^{6,8,9} Surprisingly, little has been reported on the role of the second gold atom and the importance of gold-gold interactions in the catalytic course and therefore in the asymmetric induction. Moreover a recent report from Widenhoefer et al.^{9a} has shed light on difficulties arising from the use of binuclear gold catalysts. Indeed, a decreasing enantioselectivity of the gold-catalyzed intermolecular hydroamination of allenes was observed while in the meantime conversions increased. As assumed by the authors, whereas one gold center of the bis(gold)catalyst participates in the allene activation/C-N bond formation, the second one is apparently free to coordinate the *N*-allylic carbamate product leading to a less selective catalyst species.

The third strategy developed in gold(I) catalyzed asymmetric catalysis implies the use of mononuclear gold(I) complex relying mainly on chiral phosphoramidite and diaminocarbene ligands. Though that approach has been efficient for various asymmetric organic reactions,^{6b,17,18}

it has until recently^{11,19} not been applied to hydroamination reactions and remains promising.

While the work reported herein was in progress in our laboratory, Fürstner et al. reported seminal examples of gold(I)-phosphoramidite catalysts for asymmetric intramolecular hydroamination reactions of allenes.¹¹

From a mechanistic point of view, gold(I) catalyzed hydroamination reactions proved to be intriguing. Indeed, with poor nucleophiles, gold cationic complexes were shown to be the main catalysts as far as no Brønsted acid was generated by coordination of the cationic gold species with weakly basic amine reagents.¹⁴ However, stronger nucleophiles including ammonia and hydrazine proved to lead to two potent catalysts, a Brønsted acid and an amine-gold complex. The latest was shown to catalyze exclusively the hydroamination reaction in several examples. In the case of enantiopure allene substrates, the reaction with amines proceeded smoothly with high chirality transfer excluding thus the acid species as the main catalyst.¹⁵ Though suffering of a narrow reaction scope almost limited to disubstituted allenes, such chirality transfer and memory of chirality have emerged as useful tools in organic chemistry.^{15j} Moreover, the nucleophilicity of the amine reagent seems directing the nature of the catalyst species for the hydroamination reaction. Whereas an outer-sphere mechanism seems to be applied to weak amines which add in an anti-fashion to the gold complex,^{9f,t,x, 14} an inner-sphere mechanism may be preferred for stronger nucleophiles.^{9p, 15h} However, some gold amide complexes were recently shown to be unreactive in the amination of alkynes suggesting that the inner sphere mechanism for addition to pi-bonds may not be preferred in some cases.²⁰ Interestingly, Ujaque et al. have compared by calculations the mechanisms of acid and gold catalyzed hydroamination of alkenes and dienes.²¹ Whereas the acid-catalyzed process was shown as concerted, the gold-catalyzed reaction was found to be stepwise for the nucleophile-assisted and counterion-assisted pathways. Indeed, a

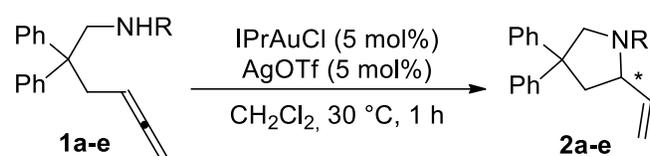
proton-transfer agent, i.e the nucleophile or the counterion, was crucial to lower the energy barrier for the proton transfer step. Toste, Goddard et al. studied through calculations and experiments the intramolecular aminoauration of unactivated alkenes providing evidence of an anti-addition mechanism for alkene aminoauration.²² However, once prepared, such assumed catalytic intermediates didn't allow the hydroamination reaction to proceed leading only to the unreacted alkenes. The authors concluded that was due to the high energy barrier calculated for the protodeauration step.²² The latter was recently shown to be also the turnover limiting step for gold(I)-catalyzed intramolecular allene hydroalkoxylation.^{23a} The active mono(gold)vinyl complex proved to be in equilibrium with an inert off-cycle bis(gold) vinyl complex. In addition, the reversibility of C-Nuc bond formation was evidenced and may play an important role in the stereoselectivity of gold(I) catalyzed hydrofunctionalization.^{22,23} Furthermore, nucleophile concentration proved to be critical for the stereochemical outcome of intermolecular hydroamination reactions of allenes.^{9h} At high nucleophile concentrations, the amine addition was fast and favored a two-step no intermediate pathway with high level of chirality transfer. At low nucleophile concentration, a planar allene-gold intermediate was formed and induced a loss of chirality. In addition, steric hindrance at the allylic positions was shown to determine the possible isomeric forms of the bent, cationic η^1 -gold(I) transition species.²⁴

On the whole, according to the previous statements, the deep understanding of gold catalyst activity along with the achievement of highly selective gold catalyzed hydroamination of allenes and alkenes are still challenging fields. Hence, following our interest on hydroamination and aza-Michael reactions catalyzed by copper and gold complexes²⁵ and considering the inadequacy of applications of chiral mononuclear gold(I) species to asymmetric hydroamination,^{11,19} we would

like to report herein our own results on asymmetric intramolecular hydroamination of allenes using mononuclear gold catalysts.

RESULTS AND DISCUSSION. In order to study the substituent effect on amine reactivity, we performed preliminary studies on the racemic intramolecular hydroamination of allene with amine substrates **1a-e** using IPrAuCl as pre-catalyst along with 5 mol% AgOTf (Table 1). The catalysis proceeded well for electron poor amine substrates (entries 1-4). Indeed, almost quantitative conversions were obtained in 1 hour at 30 °C.

Table 1. Amine substitution effect on reactivity.

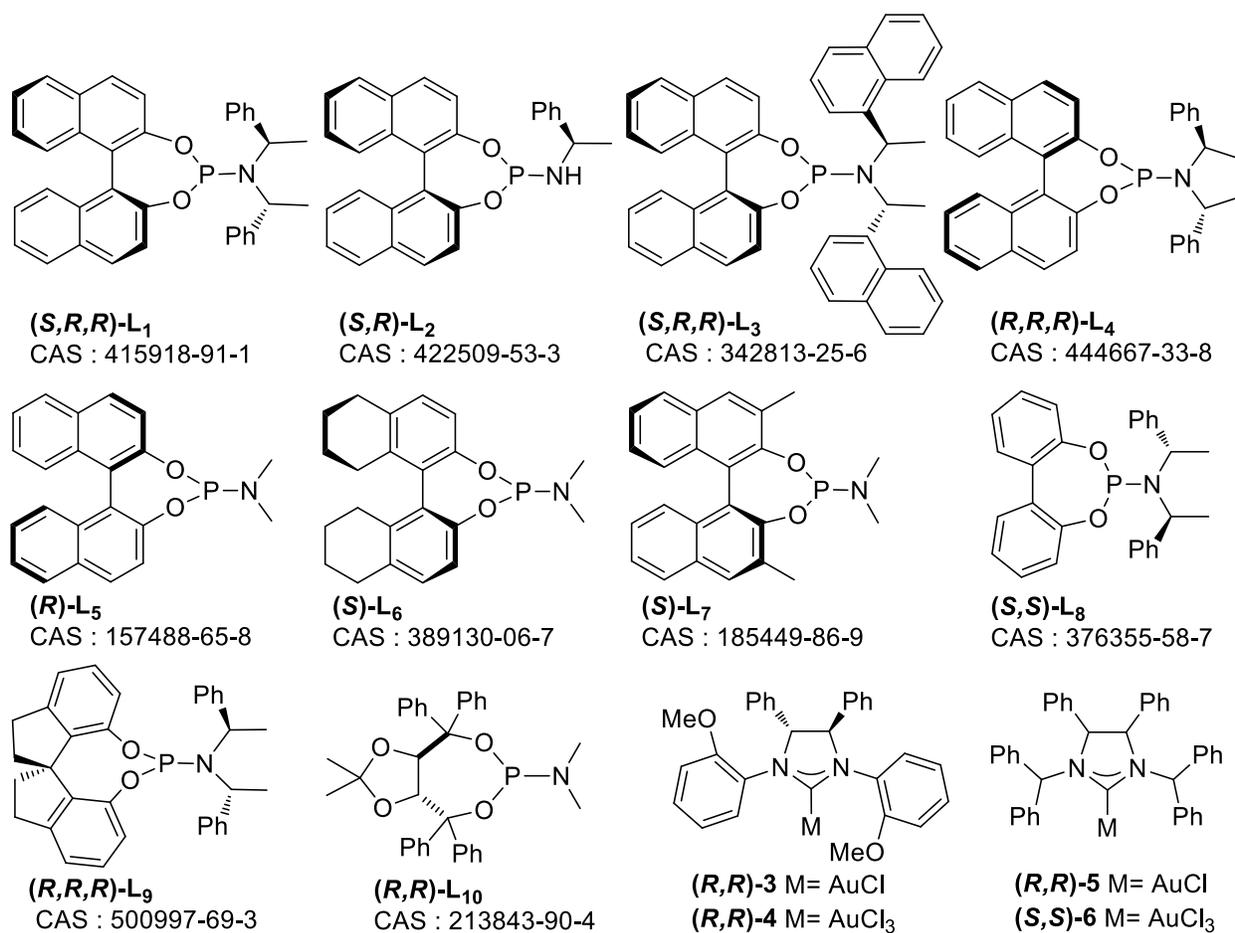


Entry	Reagent 1a-e	R	Product 2a-e conversion (%) ^a
1	1a	CBz	>95
2	1b	Ts	>95
3	1c	Boc	>95
4	1d	CONHPh	>95
5	1e	Bn	>77 ^b

^a Measured by NMR. ^b At 80 °C for 66 h in toluene.

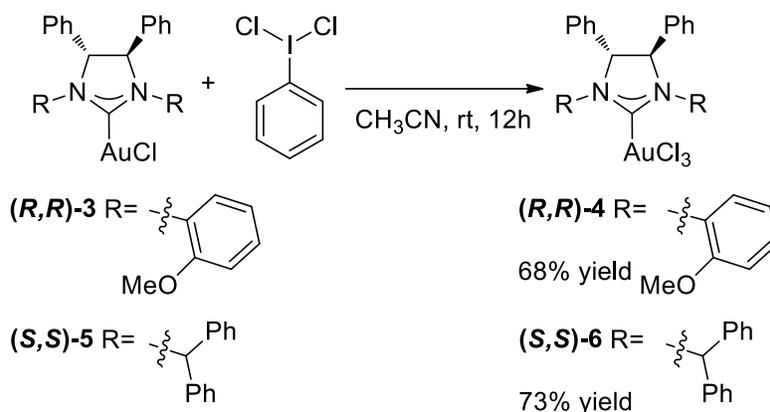
By comparison, a poor reactivity was observed for electron rich *N*-benzyl allene amine **1e** which required a stronger and much longer heating (80 °C, 66 hours) to reach a 77% conversion (entry 5). A first study on asymmetric intramolecular hydroamination of allenes using mononuclear

Chart 1. Ligands and complexes used for the screening of mononuclear gold(I) and (III) catalysts.



substrates when binuclear gold(I) catalysts were used.^{9t,x,z} In addition, as highlighted in the introduction of the present work, the carbamate function was shown to participate in a low barrier mechanistic hydroamination pathway through carbamate tautomerization assisted by a triflate anion acting as a proton shuttle.²¹ Our screening started with mononuclear gold(I) complexes **3** and **5** based on diaminocarbene ligands²⁶ but poor conversions and enantioselectivities were obtained (Chart 1 and Table 2 entries 1, 3). New gold(III) diaminocarbene complexes **4** and **6** were synthesized and tested in the asymmetric intramolecular hydroamination of allene **1a** (Scheme 1 and Table 2, entries 2, 4). Gold(III) pre-catalyst **4**

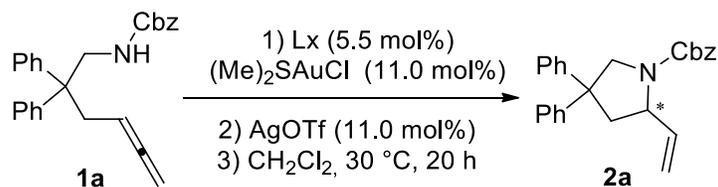
Scheme 1. Mononuclear diaminocarbene gold(III) catalysts synthesis.



displayed a high conversion and a poor enantioselectivity whereas complex **6** was inactive. The result obtained using **4** can be explained by the coordination of one of the neighboring methoxy substituent to the gold(III) center; such effect was already reported to significantly enhance activity of gold catalyzed hydrofunctionalization of allenes.^{9p} We next switched to mononuclear gold(I) complexes issued from phosphoramidite ligands (Chart 1, table 2). First, **L**₁ based on BINOL and the Whitesell amine was used affording product **2a** with high conversion (95%) and average enantiomeric excess (ee) (42%) (Table 2, entries 5-6). The enantioselectivity of **2a** proved to be stable along time, a same ee value being measured for 1 and 20 hours of reaction (entrie 5). It was worth noting the ee of the reaction product **2a** appeared to be proportional to the ee value of the chiral ligand **L**₁ suggesting the absence of nonlinear effects (see supporting information Table S1 and Figure S1).²⁷ Next, as shown by the use of phosphoramidite ligands **L**₂-**L**₅, any change on the chiral amine fragment proved to have a negative effect on the conversion and/or the enantioselectivity (table 2, entries 7-10). Moreover, the switch from ligand Monophos **L**₅ to **L**₆, that is to say the change from a BINOL scaffold to a partially hydrogenated

one, led to a decrease of the conversion (entries 10-11) and demonstrated the negative effect of an increase of the ligand dihedral angle. The change to ligand **L₈** based on a biphenyl scaffold had an even more dramatic effect, no conversion being observed (entry 13). It was worth noting the 3,3'-substitution of the BINOL backbone by two methyl substituents (**L₇**) led to a significant increase of the enantioselectivity (from 16 to 33% ee, entries 10,12). The spiro phosphoramidite ligand **L₉** afforded the best ee (47%), whereas taddol based ligand **L₁₀** gave a poor one (15%) (entries 14-15). Except for these last two ligands which are based on different diol scaffolds, it appeared the chirality of the BINOL fragment was the key factor controlling the stereochemistry of the product **2a**, both displaying the same configuration (entries 5-12).

Table 3. Screening of binuclear gold(I).

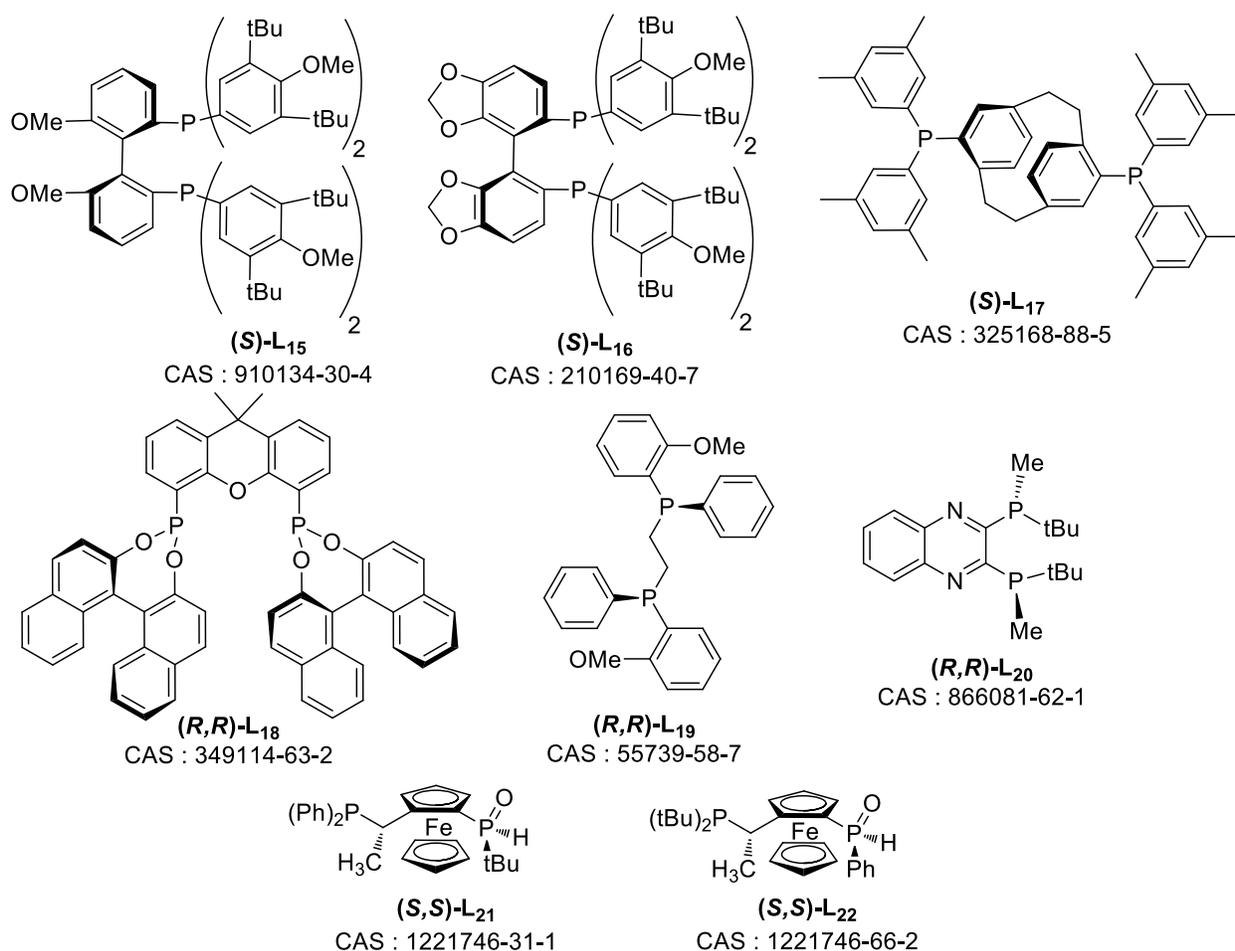


Entry	Ligand (Lx)	Conversion ^a (%)	Ee (%) ^b	Configuration ^c
1	(<i>S</i>)- L₁₅	90	42	<i>R</i>
2 ^d	(<i>S</i>)- L₁₆	0	-	-
3	(<i>S</i>)- L₁₇	90	21	<i>R</i>
4	(<i>R,R</i>)- L₁₈	90	18	<i>S</i>
5	(<i>R,R</i>)- L₁₉	90	7	<i>S</i>
6	(<i>R,R</i>)- L₂₀	90	21	<i>R</i>
7 ^e	(<i>S,S</i>)- L₂₁	0	-	-
8 ^e	(<i>S,S</i>)- L₂₂	0	-	-

^a) Measured by ¹H NMR. ^b) Measured by HPLC at 220 nm. ^c) Determined from HPLC by comparison of previous work. ^d) Performed with AgClO₄ in toluene. ^e) Same with a (1/1) gold / ligand ratio.

By comparison to mononuclear gold(I) catalysts, dinuclear gold(I) catalysts didn't afford better conversions and enantioselectivities within the same experimental conditions, (Table 3 and Chart 2). A maximum of 90% conversion and 42% ee was reached with biphep ligand **L15** (entry 1). However, it was previously reported gold(I) catalyst based on **L15** could lead to a much higher enantioselectivity for product **2a** provided different anions, solvents and reaction temperatures were used.^{9x} Surprisingly, the change for **L16** with a Segphos backbone led to complete loss of reactivity (entry 2). The use of trans-ligands **L17** and **L18** (entries 3-4) or P-chiral phosphines **L19** and **L20** (entries 5-6) afforded **2a** in high conversions but moderate enantioselectivities. Finally, the use of chiral secondary phosphine oxides **L21** and **L22** didn't allow any reaction (entries 7-8).

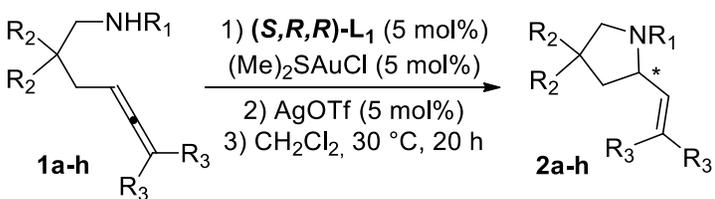
Chart 2. Ligands used for the screening of binuclear gold(I) catalysts.



Regarding our screening of mononuclear gold(I) complexes issued from phosphoramidite ligands, we chose to focus on ligand **L**₁ though **L**₉ was found to be the best hit of our study. Indeed, BINOL-based phosphoramidite ligands¹⁷ appeared to afford us broader possibilities of derivatization as compared to the spiro-based ligands.²⁸

In order to check the substituent effects on the selectivity of the reaction, we screened several substrates using ligand **L**₁ (Table 4).

Table 4. Substituent effects on enantioselectivity.



Entry	R ₁	R ₂	R ₃	Conversion (%) ^a	Ee (%) ^b
1	CBz	Ph	H	2a >95	42
2	Ts	Ph	H	2b >95	-32
3	Boc	Ph	H	2c >95	41
4	CONHPh	Ph	H	2d >95	28
5 ^c	Bn	Ph	H	2e >95	0
6	CBz	Ph	Me	2f 93	22
7	CBz	Me	H	2g >95	9
8	CBz	-(CH ₂) ₅ -	H	2h >95	7

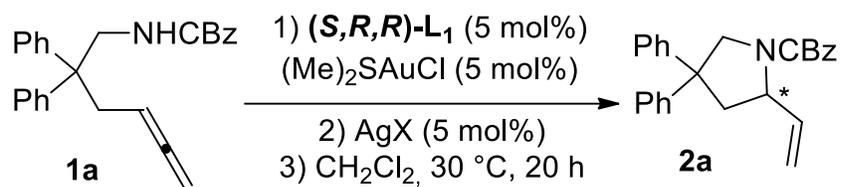
^a Measured by ¹H NMR. ^b Measured by HPLC. ^c Performed at 100 °C for 20 h.

First, we reinvestigated the substituent effect on amine reactivity. All reactions afforded an almost quantitative conversion at 30 °C in 20 h, except for *N*-benzyl allenyl substrate **1e** which required a 100 °C heating (entry 5). Regarding the enantioselectivity, CBz and Boc substituents were by far the most appropriate with values of 42 and 41% ee, the *N*-urea allenyl substrate

leading to a 28% ee (entries 1, 3, 4). By offering a 32% ee, the tosyl group was less selective and induced a reversal of the stereoselectivity (entry 2). No enantioselectivity could be observed for *N*-benzyl allenyl reagent **1e** (entry 5). Mononuclear gold(I) catalyst based on phosphoramidite ligand **L1** appeared to be sensitive to substituents on the allene moiety. For example, *N*-carbamate tris-substituted allene substrate **1f** afforded only a 22% ee (entry 6). The change of substituents at the C2 position of the 4,5-hexadienyl chain had even a more critical effect on the stereochemical outcome of the hydroamination reaction, enantioselectivities being very low for methyl and cyclohexyl substituents (entries 1, 7, 8). A similar trend was observed when binuclear gold(I) catalysts were used though enantioselectivities were higher.^{9x}

We next focused on the influence of the anion on the conversion and enantiomeric excess (Table 5). Among the various silver salts screened, triflate, tosylate and perchlorate anions appeared to be the most appropriate (entries 1-10). Moreover, when no ligand and gold were used, silver triflate was not catalysing the hydroamination of **1a** (entry 6). When product **2a** was formed, the enantioselectivity and the nature of the ion pairing were found unrelated in our reaction conditions. Gold(I) catalyst based on **L1** proved to be non-reactive when associated with chiral TRIP phosphate anion, even when stronger reaction conditions were used (entries 11-12).

To pursue our study on the influence of reaction parameters, various solvents were screened (Table 6). Except for acetonitrile (entry 13), reaction was running quite well in polar or apolar solvents (entries 1-12). However, we noticed enantiomeric excesses were higher when reactions were performed in apolar aromatic solvents (entries 3-7) and concluded tight ion pairs were critical to reach high levels of enantioselectivity. By decreasing the temperature to 0 °C and to -20 °C, the reaction was not proceeding in dichloromethane and THF (entries 2,9) but it was running smoothly in toluene reaching respectively 62 and 67% ee (entries 4,5).

Table 5. Silver salt screening.

Entry	AgX	Conversion (%) ^a	Ee (%) ^b	Configuration ^c
1	AgSbF ₆	>95	24	<i>S</i>
2	AgClO ₄	85	41	<i>S</i>
3	AgBF ₄	>95	36	<i>S</i>
4	AgNTf ₂	>95	26	<i>S</i>
5	AgOTf	>95	42	<i>S</i>
6 ^d	AgOTf	0	-	-
7 ^e	AgOTs	>95	46	<i>R</i>
8	AgPNB	0	-	-
9	AgNO ₃	0	-	-
10	AgBARF	>95	19	<i>S</i>
11 ^{f,g}	(<i>R</i>)-AgTRIP	0	-	-
12 ^g	(<i>S</i>)-AgTRIP	0	-	-

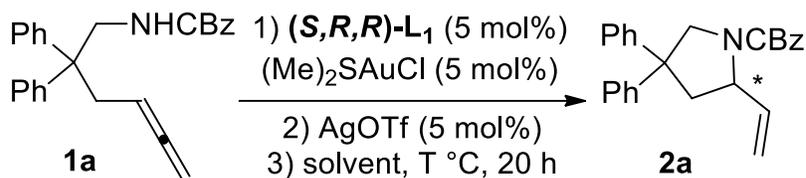
^a Measured by ¹H NMR. ^b Measured by HPLC at 220 nm.

^c Determined by HPLC (see supporting information).

^d Performed without **(Me)₂SAuCl** and **L₁**. ^e Performed with **(R,S,S)-L₁**.

^f For 74 h. ^g less than 10% conversion in toluene at 100 °C for 26 h.

That last enantioselectivity was obtained with a reduced conversion suggesting a longer reaction time was needed. Moreover, the reaction outcome remained unchanged upon removal of AgCl by filtration through CeliteTM of the phosphoramidite mononuclear gold(I) cationic species prepared prior to the catalysis (entry 1). Hence, no “silver effect” was observed in our gold catalyzed hydroamination reactions.²⁹

Table 6. Solvent screening.

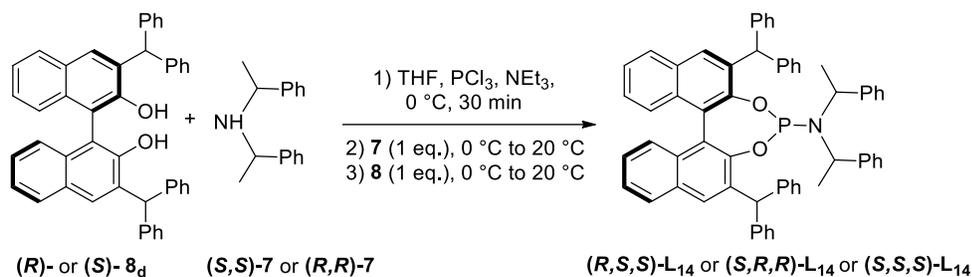
Entry	Solvent	T(°C)	Conversion (%) ^a	Ee (%) ^b
1 ^c	CH ₂ Cl ₂	30	>95	42
2 ^d	CH ₂ Cl ₂	0	0	-
3	Toluene	30	>95	52
4	Toluene	0	>95	62
5	Toluene	-20	25	67
6	Benzene	30	>95	57
7	<i>m</i> -xylene	30	>95	51
8	THF	30	>95	47
9 ^d	THF	0	0	-
10	1,4-dioxane	30	>95	51
11	CH ₃ NO ₂	30	>95	31
12	CF ₃ CH ₂ OH	30	>95	29
13	CH ₃ CN	30	10	36

^a Measured by ¹H NMR. ^b Measured by HPLC at 220 nm. ^c Same result using catalyst purified by filtration over Celite™. ^d Same result at -20°C for 20h.

Considering our results and the general trends in gold(I) catalyzed asymmetric reactions,¹⁷ a series of phosphoramidite ligands related to **L**₁ was foreseen. Based on the Whitesell amine and on BINOL, these ligands would carry bulky substituents at the 3,3' positions of the BINOL scaffold (see **Chart 3**, Table 7 and supporting information).³⁰ As illustrated by some MM2 calculations, we were confident such phosphoramidite ligands would afford an enhanced steric

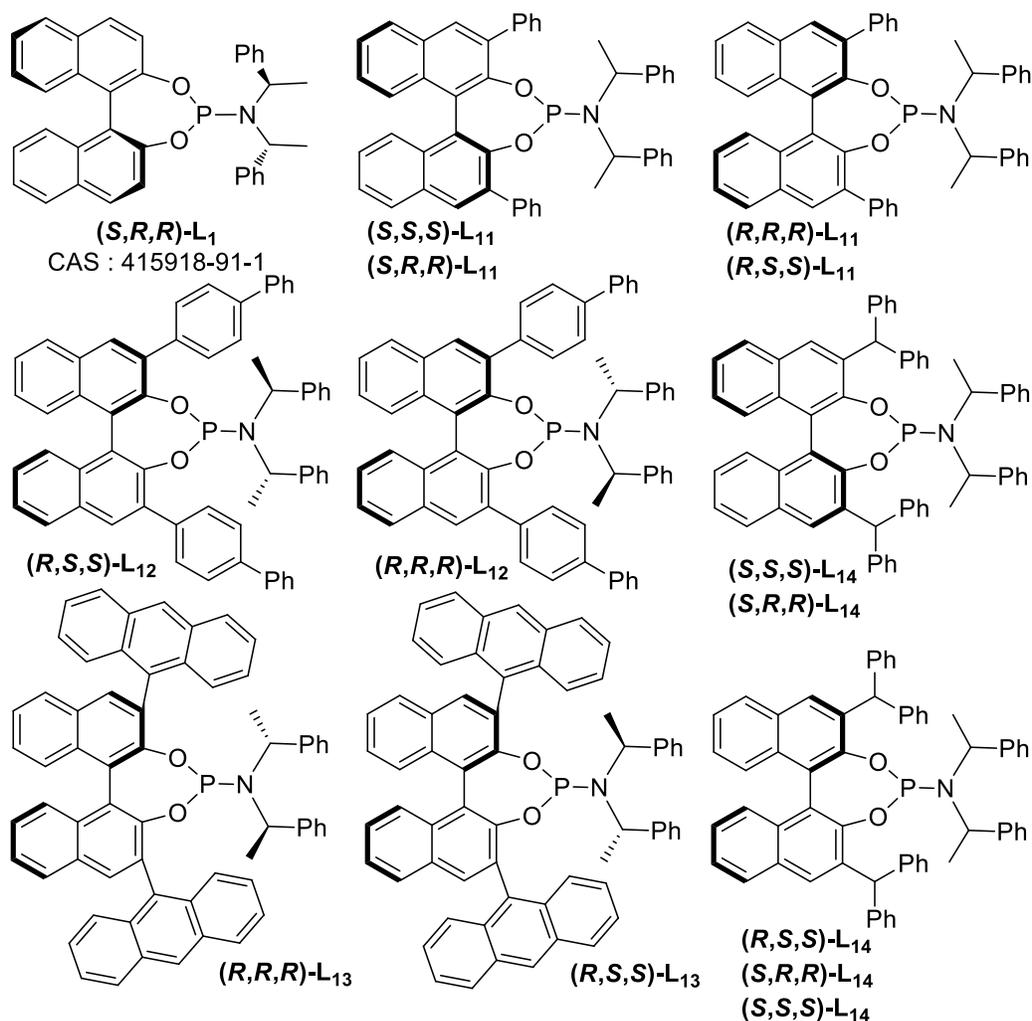
hindrance around the gold(I) catalytic center and would lead to a better enantioselectivity (see supporting information Chart S1).

Scheme 2. Synthesis of 3,3'-dibenzhydryl substituted phosphoramidite ligand **L₁₄**.

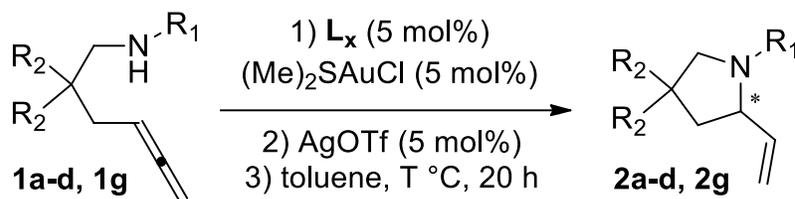


The new phosphoramidite ligand **L₁₄** was synthesized by reaction of functionalized BINOL (*R*) or (*S*)-**8d** with PCl_3 and the Whitesell amine **7** of defined configuration (Scheme 2). All the other 3,3'-substituted ligands (Chart 3) were prepared according the same synthetic pathway and already reported procedures (see supporting information). First, catalytic tests were performed on the most appropriate substrate, i.e. **1a**, performing the reactions with our best experimental conditions, in toluene at $-20\text{ }^\circ\text{C}$ for 20 h with AgOTf (Table 7, Chart 3). We started by studying again **L₉** but no significant increase of enantioselectivity was observed and conversion was reduced (entry 1). The use of phosphoramidite ligand **L₁** confirmed the enhanced ee previously obtained and showed a close correlation between conversions and the ligand configurations (entries 2, 3). We next studied the four stereoisomers of phosphoramidite ligand **L₁₁** bearing phenyl substituents. Again, conversions were highly dependent on the ligand configuration, values being quite disparate (entries 4-7). With an average 55% conversion and a good 78% ee, ligand (*S,R,R*)-**L₁₁** afforded the best result (entry 7). A final attempt was run at $-40\text{ }^\circ\text{C}$ but no reaction occurred (entry 8). Substrates **1b-d,g** were then tested using ligand (*S,R,R*)-**L₁₁** at $-20\text{ }^\circ\text{C}$

Chart 3. Tuned phosphoramidite ligands used for the screening of mononuclear gold(I) catalyst.



for 20 h. By offering a 44% ee, compound **1b** bearing a tosyl group was less selective and induced a reversal of the stereoselectivity, conversion being high (entry 9). Compound **1c** with a Boc substituent afforded a good enantioselectivity (66% ee) but conversion was moderate (entry 10). The *N*-urea allenyl substrate **1d** led to average enantiomeric excess and conversion (entry 11). Finally, the reaction of compound **1g** at 0°C afforded a 68% conversion along with a moderate enantioselectivity of 15% in spite of the presence of a Cbz substituent (entry 12). This confirmed any change of substituent at the C2 position of the reagent 4,5-hexadienyl chain

Table 7. Screening of mononuclear gold(I) catalyst based on tuned phosphoramidite ligands.

Entry	R ₁	R ₂	Ligand (L_x)	T (°C)	Conversion ^a (%)	Ee (%) ^b	Configuration ^c
1	CBz	Ph	(<i>R,R,R</i>)-L ₉	-20	2a 30	50	<i>R</i>
2	CBz	Ph	(<i>S,R,R</i>)-L ₁	-20	2a 5	65	<i>S</i>
3	CBz	Ph	(<i>R,S,S</i>)-L ₁	-20	2a 25	67	<i>R</i>
4	CBz	Ph	(<i>R,S,S</i>)-L ₁₁	-20	2a 5	71	<i>R</i>
5	CBz	Ph	(<i>R,R,R</i>)-L ₁₁	-20	2a >95	31	<i>R</i>
6	CBz	Ph	(<i>S,S,S</i>)-L ₁₁	-20	2a 30	31	<i>S</i>
7	CBz	Ph	(<i>S,R,R</i>)-L ₁₁	-20	2a 55	78	<i>S</i>
8	CBz	Ph	(<i>S,R,R</i>)-L ₁₁	-40	2a 0	-	-
9	Ts	Ph	(<i>S,R,R</i>)-L ₁₁	-20	2b >95	-44	-
10	Boc	Ph	(<i>S,R,R</i>)-L ₁₁	-20	2c 26	66	-
11	CONHPh	Ph	(<i>S,R,R</i>)-L ₁₁	-20	2d 62	52	-
12	CBz	Me	(<i>S,R,R</i>)-L ₁₁	0	2g 68	15	-
13	CBz	Ph	(<i>R,R,R</i>)-L ₁₂	-20	2a >95	24	<i>R</i>
14	CBz	Ph	(<i>R,S,S</i>)-L ₁₂	-20	2a >95	78	<i>R</i>
15	CBz	Ph	(<i>R,S,S</i>)-L ₁₂	-30	2a 17	78	<i>R</i>
16	CBz	Ph	(<i>R,R,R</i>)-L ₁₃	-20	2a >95	40	<i>R</i>
17	CBz	Ph	(<i>R,S,S</i>)-L ₁₃	-20	2a >95	21	<i>R</i>
18	CBz	Ph	(<i>R,S,S</i>)-L ₁₄	-20	2a 75	66	<i>R</i>
19	CBz	Ph	(<i>S,R,R</i>)-L ₁₄	-20	2a 86	16	<i>R</i>
20	CBz	Ph	(<i>S,S,S</i>)-L ₁₄	-20	2a 90	4	<i>R</i>

^a Measured by ¹H NMR. ^b Measured by HPLC at 220 nm. ^c Determined from HPLC by comparison with previous work (see supporting information).

lead to a critical decrease of the product enantiomeric excess. As previously observed for **L**₁, the chirality of **L**₁₁ BINOL fragment was the key factor controlling the stereochemistry of the product **2a**; both were shown to display the same configuration. This same stereoselectivity was observed for two configurations of phosphoramidite ligand **L**₁₂ bearing biphenyl substituents (entries 13-14). Product **2a** was afforded in high 95% conversions and good 78% ee for (*R,S,S*)-**L**₁₂. The latest was allowed to react with reagent **1a** at -30 °C but the enantioselectivity was not improved and a low conversion was obtained (entry 15). Phosphoramidite ligand **L**₁₃ functionalized by anthracenyl substituents led also to high conversions (95%) but average to modest ee (21-40%) were obtained (entries 16-17). Finally, phosphoramidite ligand **L**₁₄ bearing benzhydryl substituents afforded **2a** in good to high conversions (75-90%) along with low to good ee (4-66%), configuration (*R,S,S*) being the best (entries 18-20). It was worth noting the chirality of the **L**₁₄ BINOL fragment was no longer controlling the stereochemistry of the product **2a** as far as both displayed opposite configurations (entries 15-16). Regarding all these synthesized phosphoramidite ligands, the best asymmetric induction was obtained by combining opposite stereochemical configurations on respectively, the BINOL fragment and the Whitesell amine part, privileged ligand configurations being (*R,S,S*) or (*S,R,R*). The best conversions and ee were obtained by running the reaction at -20 °C and using phosphoramidite ligand (*R,S,S*)-**L**₁₂.

CONCLUSIONS. The gold catalyzed asymmetric intramolecular hydroamination of allenes was studied screening a series of mononuclear gold (I) and (III) complexes in combination with silver salts. Among the various chiral mono-phosphine and diaminocarbene ligands tried, the best catalysts arose from mononuclear gold(I) complexes built on BINOL based phosphoramidite ligands. The latest were improved by addition of bulky substituents at the specific 3,3'-positions

of the BINOL scaffold. The resulting gold (I) complexes were combined with selected silver salts to afford efficient catalysts for intramolecular hydroamination of allenes at room temperature or below, with good conversions and enantioselectivities. In the future, such mononuclear gold(I) catalysts may be a good alternative solution to binuclear gold(I) catalysts, when selectivity issues are encountered owing to the presence of two gold centers, the first being part of the most active and selective catalyst, the second leading to a competing unselective catalyst species.^{9a}

EXPERIMENTAL SECTION.

General Remarks.

All solvents were dried using standard methods and stored over molecular sieves (4 Å). All silver salts were weighted in a glovebox. All reactions were carried out under a dry nitrogen atmosphere and were at least repeated twice. Analytical thin layer chromatography (TLC) was performed on Macherey pre-coated 0.20 mm silica gel Alugram Sil 60 G/UV254 plates. Flash chromatography was carried out with Macherey silica gel (Kieselgel 60). ¹H (300 MHz), ¹³C (75 MHz) and ³¹P (121 MHz) spectra were acquired on a Bruker Avance spectrometer. Chemical shifts (δ) are reported downfield of Me₄Si in ppm and coupling constants are expressed in Hz. 1,3,5-trimethoxybenzene and 1,2,4,5-tetrachlorobenzene were used as internal standards when needed. Infrared spectra were recorded on a ThermoScientific-Nicolet 6700 spectrometer; the samples being prepared with KBr powder. HPLC was performed on a Hitachi LaChromElite equipment with a micropump, a Peltier oven and a DAD detector. HRMS-ESI analyses were performed at CUMA-Pharm. Dept.-University Lille Nord de-France. Elemental analyses were performed at UCCS, University Lille Nord de France. AuS(Me)₂Cl was prepared following related procedures.³² BARF and TRIP silver salts were prepared as reported.^{33,34} Amino-allene substrates were synthesized following reported procedures: **1a**,^{9z} **1b**,³⁵ **1c**,^{9z} **1d**,^{9f} **1e**,³⁵ **1f**,³⁵ **1g**,^{9x} **1h**.¹¹ Except for **L14**; phosphoramidite ligands were prepared according reported procedures: **L11**,^{30e} **L12**,^{30e} **L13**.^{17b} Gold(I) diaminocarbene complexes **3** and **5** were synthesized as reported.²⁶ See supporting information for further details.

General Procedure (Ligand screening). In a glovebox, AuS(Me)₂Cl (2.9 mg, 0.01 mmol) and the corresponding ligand (0.01 mmol) are disposed in a first Schlenk flask. Dry dichloromethane (1 mL) is added under a nitrogen atmosphere and the resulting mixture is stirred at room temperature for 2 hours. Afterwards, the solvent is evaporated under vacuum and the resulting solid is dried 30 minutes before addition of AgOTf (2.3 mg, 0.009 mmol) in a glovebox. Dry dichloromethane (1 mL) is added under nitrogen and the resulting solution is stirred for 30 minutes before being transferred to a second Schlenk containing amino-allene substrate **1a** (68.9 mg, 0.18 mmol). After 20 hours of stirring at 30 °C, the solution is filtered through a pad of silica gel using dichloromethane as solvent. After evaporation of solvent under vacuum, the resulting oil is analyzed by ¹H NMR and HPLC.

General procedure (Silver salt screening). In a glovebox, 0.01 mmol of AuS(Me)₂Cl (2.9 mg) and 0.01 mmol of (*S,R,R*)-**L1** (5.4 mg) are disposed in a first Schlenk flask. Dry dichloromethane (1 mL) is then added under a nitrogen atmosphere and the resulting mixture is stirred for two hours at room temperature. Afterwards, the solvent is evaporated under vacuum and the resulting solid is dried 30 minutes before addition of AgOTf (0.009 mmol) in a glovebox. Dry dichloromethane (1 mL) is added under nitrogen atmosphere and the resulting solution is stirred for 30 minutes before being transferred in a second Schlenk flask containing amino-allene substrate **1a** (0.18 mmol, 68.9 mg). After 20 hours under stirring at 30 °C, the solution is filtered through a pad of silica gel using dichloromethane as solvent. After evaporation of solvents under vacuum, the resulting oil is analyzed by ¹H NMR and HPLC.

General procedure (Solvent screening). In a glovebox, AuS(Me)₂Cl (0.01 mmol, 2.9 mg) and (*R,S,S*)-**L1** (0.01 mmol, 5.4 mg) were added to a Schlenk flask. Dry solvent (1 mL) is then added under a nitrogen atmosphere and the resulting mixture is stirred for two hours at room temperature.

Afterwards, the solvent is evaporated under vacuum and the resulting solid is dried 30 minutes before addition of AgOTf (0.009 mmol, 2.3 mg) in a glovebox. The corresponding dry solvent (1 mL) is added under a nitrogen atmosphere and the resulting solution is stirred for 30 minutes before being transferred in a second Schlenk flask containing amino-allene substrate **1a** (0.18 mmol, 68.9 mg). After 20 hours under stirring at 30 °C, the solution is filtered through a pad of silica gel using dichloromethane as solvent. After evaporation of solvents under vacuum, the resulting oil is analyzed by ¹H NMR and HPLC.

General procedure (Temperature screening). In a glovebox, AuS(Me)₂Cl (0.01 mmol, 2.9 mg) and (*R,S,S*)-**L1** (0.01 mmol, 5.4 mg) are added to a Schlenk flask. Dry toluene (1 mL) is then added under a nitrogen atmosphere and the resulting mixture is stirred for two hours at room temperature. Afterwards, the solvent is evaporated under vacuum and the resulting solid is dried 30 minutes before addition of AgOTf (0.009 mmol, 2.3 mg) in a glovebox. Dry toluene (1 mL) is then added under a nitrogen atmosphere and the resulting solution is stirred for 30 minutes before being transferred in a second Schlenk flask containing amino-allene substrate **1a** (0.18 mmol, 68.9 mg). After 20 hours under stirring at the corresponding temperature, the solution is filtered through a pad of silica gel using dichloromethane as solvent. After evaporation of solvents under vacuum, the resulting oil is analyzed by ¹H NMR and HPLC.

(*R,S,S*)-(+)-(2,6-dibenzhydryl -3,5-dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']dinaphthalen-4-yl)bis(1-phenylethyl)amine (*R,S,S*)-L14**.** In a first flame dried Schlenk flask, dry and degassed THF (1mL) is disposed under nitrogen and cooled at 0 °C. NEt₃ (1.02 mmol, 138 μL) followed by PCl₃ (0.17 mmol, 85 μL of a 2M solution) are added under nitrogen and the mixture is stirred at 0 °C for 30 minutes. Afterwards, (*S,S*)-bis[1-phenylethyl]amine (*S,S*)-**7** (0.17 mmol, 39 μL) is added

at 0 °C and the solution is stirred and warmed up to room temperature for 4 hours. In a second flame dried Schlenk, compound **(R)-8d** (0.17 mmol, 106 mg) is disposed and dried by dissolving in dry toluene (1mL) and evaporation of the resulting solution under vacuum (2 times). Then, the resulting dried **(R)-8d** is dissolved in dry and degassed THF (1 mL) and transferred by cannula to the first Schlenk at 0 °C. After being stirred at room temperature overnight (12 h), the reaction is quenched by adding dichloromethane (10 mL) followed by brine (20 mL). After extraction, the organic phase is dried over Na₂SO₄ and evaporated under vacuum. The solid residue is purified by flash chromatography on silica gel using a (1/1) mixture of petroleum ether and toluene (R_f = 0.6). After evaporation of solvents under vacuum and further washes with acetone and petroleum ether, compound **(R,S,S)-L₁₄** is obtained as a white solid (0.12 mmol, 105 mg, 71%). ¹H NMR (300 MHz, CDCl₃): δ 1.56 (br s, 3H), 2.15 (br s, 3H), 4.47 (br s, 1H), 4.83 (br s, 1H), 5.90 (s, 1H), 6.27 (s, 1H), 6.75-7.20 (m, 20H), 7.20-7.60 (m, 18H), 7.66 (d, J = 8.3 Hz, 1H), 7.74 (d, J = 8.3 Hz, 1H). ³¹P NMR (121.5 MHz, CDCl₃): δ 142.5. ¹³C NMR (75 MHz, CDCl₃): δ 50.3 (CH₃), 50.3 (CH₃), 52.8 (CH), 122.8 (C), 122.8 (C), 124.6 (CH), 124.7 (CH), 125.8 (CH), 125.9 (CH), 126.3 (CH), 126.4 (CH), 126.7 (CH), 126.9 (CH), 127.2 (CH), 127.9 (CH), 128.3 (CH), 128.3 (CH), 128.4 (CH), 128.5 (CH), 128.5 (CH), 128.8 (CH), 129.4 (CH), 129.7 (C), 130.0 (CH), 130.3 (CH), 131.0 (C), 131.4 (CH), 132.0 (C), 132.5 (C), 135.5 (C), 135.6 (C), 142.6 (C), 143.2 (C), 144.3 (C), 144.4 (C), 148.2 (C), 148.5 (C), 148.6 (C). HMRS (ESI) m/z calcd for C₆₂H₅₁NO₂P : 872.3652 [MH⁺], found : 872.3644. [α]_D²⁰ = +62 (CH₂Cl₂, c 0.1g/100ml).

(S,S,S)-(-)-(2,6-dibenzhydryl-3,5-dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']dinaphthalen-4-yl)bis(1-phenylethyl)amine (S,S,S)-L₁₄ Compound is prepared from **(S)-8d** and amine **(S,S)-7** using the same procedure than **(R,S,S)-L₁₄**. [α]_D²⁰ = -187 (CH₂Cl₂, c 0.1g/100ml).

(S,R,R)-(-)-(2,6-dibenzhydryl-3,5-dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']dinaphthalen-4-yl)bis(1-phenylethyl)amine (S,R,R)-L₁₄ Compound is prepared from **(R)-8d** and amine **(R,R)-7** using the same procedure than **(R,S,S)-L₁₄**. $[\alpha]_D^{20} = -39$ (CH₂Cl₂, c 0.1g/100ml).

Benzyl-2,2-dimethyl-4,5-hexadienyl-carbamate (1g) Following a related procedure,^[5x] dry diisopropylamine (1.7 mL, 10 mmol) and dry THF (5 mL) are added in an oven dried Schlenk flask. The solution is then cooled down to 0 °C and *n*BuLi (1.2 eq., 12 mmol, 7.5mL, 1.6 M solution) is added under nitrogen. After one hour of stirring at room temperature, dry isobutyronitrile (0.9 mL, 10 mmol) diluted in dry THF (3 mL) is added under nitrogen. After a second hour of stirring at room temperature, propargyl bromide (1.2 eq., 12 mmol, 1.5 mL, 80 wt.% solution in toluene) is added under nitrogen and the solution is stirred overnight at room temperature. Then, 10 mL of distilled water are added, the layers are separated and the aqueous layer is extracted with Et₂O (3x10 mL). The combined organic layers are dried over MgSO₄ and concentrated under vacuum to afford 2,2-dimethyl-4-pentynenitrile as a slightly yellow oil, which is used for the next step without any further purification due to its volatility. In an oven dried Schlenk flask, paraformaldehyde (2 eq., 20 mmol, 0.63 g) and CuBr (0.4 eq., 4.2 mmol, 0.6 g) are diluted in dry 1,4-dioxane (10 mL). Then, dry diisopropylamine (2 eq., 20 mmol, 3 mL) and the oil obtained previously are added under nitrogen. After being stirred at reflux overnight, the solution is filtered through a pad of silica gel with dichloromethane/petroleum ether [1:1]. Evaporation of solvents affords 2,2-dimethylhexa-4,5-dienitrile as a slightly yellow oil which is used without any further purification step due to its volatility. In an oven dried Schlenk flask, dry Et₂O (20 mL) and LiAlH₄ (26 mmol, 0.5 g) are added to the oil obtained previously. After being stirred at room temperature overnight, the solution is neutralized at 0°C with H₂O and NaOH_{aq} (6M). After filtration through a pad of Celite, the organic layer is dried over MgSO₄ and

concentrated under vacuum to afford 2,2-dimethylhexa-4,5-dien-1-amine as a slightly yellow oil which is used without any further purification step due to its volatility. The resulting product is added in a flask with benzyl chloroformate (1.2 eq., 12 mmol, 1.6 mL), ethanol (40 mL), distilled water (16 mL) and NaHCO_{3aq} (1M, 24 mL). After 45 minutes of stirring at room temperature, saturated NaCl_{aq} (50 mL) was added, the layers are separated and the resulting aqueous layer is extracted with Et₂O (3x10 mL). The combined organic layers are dried over MgSO₄ and concentrated under vacuum to afford a colorless oil which is purified by flash chromatography using a (9/1) petroleum ether/EtOAc solvent mixture (R_f = 0.4). After evaporation of solvents under vacuum, compound **1g** is obtained as a colorless oil (1.3 mmol, 0.34 g, 13% overall yield over 4 steps). ¹H NMR (300 MHz, CDCl₃): δ 0.89 (s, 6H), 1.93 (m, 2H), 3.06 (d, 2H, J= 6.9), 4.64 (m, 2H), 4.82 (bs, 1H), 5.06 (m, 3H), 7.35 (m, 5H). ¹³C NMR (75 MHz, CDCl₃): δ 24.7, 35.4; 39.1, 50.5, 66.8, 73.9, 85.8, 128.2; 128.3, 128.6, 136.7, 156.8, 209.8 (CO). HMRS (ESI) m/z calcd for C₁₆H₂₂NO₂ : 260.16451 [MH⁺], found : 260.16308.

Benzyl-4,4-dimethyl-2-vinylpyrrolidine-1-carboxylate (2g). Isolated after flash chromatography with petroleum ether/ethylacetate (8/2), R_f = 0.7, as a colorless oil (quantitative). ¹H NMR (300 MHz, CDCl₃): δ 1.02 (s, 3H), 1.09 (s, 3H), 1.53 (m, 1H), 1.91 (dd, 1H, J= 8.1 Hz), 3.11 (d, 1H, J= 11.1 Hz), 3.45 (dd, 1H, J= 12.3 Hz), 4.35 (m, 1H), 5.12 (m, 4H), 5.81 (m, 1H), 7.35 (m, 5H). ¹³C NMR (75 MHz, CDCl₃) as mixture of 2 rotamers: δ [26.3, 26.5], [37.2, 37.7], [46.4, 47.3], [59.5, 59.6], 60.1, 66.7, [114.2, 114.7], 127.8 (4C_{Ar}), 128.5 (1C_{Ar}), 137.0, [139.3, 140.0], [155.2, 155.6] (CO). HMRS (ESI) m/z calcd for C₁₆H₂₂NO₂ : 260.16451 [MH⁺], found : 260.16298. Enantiomeric excess (ee) is measured by HPLC using Regis (*S,S*)-Whelk 01TM CSP, at 25°C, with (90/10) *n*hexane/*i*PrOH, 1 mL/min, λ = 220 nm, t_R (minor) = 17.0 min. and t_R (major) = 25.6 min. Ee was too low to measure any [α]_D²⁰.

(4*R*,5*R*)-1,3-bis(2-methoxyphenyl)-4,5-diphenyl-imidazolin-2-ylidene gold trichloride (4).

This new compound was prepared following a related procedure.³¹ In a flame dried Schlenk tube are disposed and dried a stirring bar, Au(I) complex **3** (67 mg, 0.1 mmol) and iodobenzene dichloride (55 mg, 0.15 mmol). Under nitrogen, acetonitrile (3 mL) is added and the reaction is stirred overnight (c.a. 12h) at room temperature. Diethylether is then added to precipitate a solid which is further washed with petroleum ether. After recrystallization (dichloromethane / petroleum ether) and drying under vacuum, compound **4** is obtained as a yellow solid (50 mg, 0.07 mmol, 68%). ¹H NMR (300 MHz, CDCl₃) : δ 4.00 (s, 6H), 5.49 (s, 2H), 6.95 (m, 4H), 7.35 (m, 4H), 7.47 (m, 10H). ¹³C NMR (75 MHz, CDCl₃) : δ 56.5 (2CH₃), 76.2 (2CH), 112.6 (CH_{Ar}), 113.7 (CH_{Ar}), 121.3 (CH_{Ar}), 124.8 (C), 125.7 (C), 127.4 (CH_{Ar}), 129.6 (CH_{Ar}), 130.1 (CH_{Ar}), 130.7 (CH_{Ar}), 131.7 (CH_{Ar}), 136.9 (C), 154.3 (C), 170.0 (C_{Au}). [α]_D²⁰ = +179 (CH₂Cl₂, 0.2 g / 100 ml). HRMS (ESI+): m/z calcd for C₂₉H₂₇N₂O₂AuCl₃ [MH⁺]: 737.0798; found: 737.0600. Anal. calcd (%) for (C₂₉H₂₆AuCl₃N₂O₂ + 1 CH₂Cl₂): C, 43.79; H, 3.43; N, 3.40; found C, 43.26; H, 3.28; N, 3.44.

(4*S*,5*S*)-1,3- dibenzhydryl 4,5-diphenyl-imidazolin-2-ylidene gold(III) trichloride (6).

This compound was prepared following a related procedure.³¹ In a flame dried Schlenk tube are disposed and dried a stirring bar, Au(I) complex **5** (100 mg, 0.13 mmol) and iodobenzene dichloride (70 mg, 0.19 mmol). Under nitrogen, acetonitrile (3 mL) is added and the reaction is stirred overnight (c.a. 12 h) at room temperature. Diethylether is then added to precipitate a solid which is further washed with petroleum ether. After recrystallization (dichloromethane / petroleum ether) and drying under vacuum, compound **6** is obtained as a yellow solid (79 mg, 0.09 mmol, 73%). ¹H NMR (300 MHz, CDCl₃) : δ 4.76 (s, 2H), 6.65 (s, 2H), 7.05 (m, H_{Ar}), 7.36 (m, H_{Ar}). ¹³C NMR (75 MHz, CDCl₃) : δ 68.5 (2CH), 74.5 (2CH), 129.9 (4CH_{Ar}), 129.6 (4CH_{Ar}), 129.3 (4CH_{Ar}), 129.2

(5CH_{Ar}), 129.1 (3CH_{Ar}), 128.5 (2CH_{Ar}), 128.3 (4CH_{Ar}), 126.0 (4CH_{Ar}), 135.1 (2C), 137.6, 138.2 (4C), 171.6 (C_{Au}). $[\alpha]_D^{20} = -14$ (CH₂Cl₂, 0.2 g / 100 ml). HRMS (ESI⁺): m/z calcd for C₄₁H₃₅AuCl₃N₂ [MH⁺]: 857.1526; found: 857.1995. Anal. calcd (%) for (C₄₁H₃₄AuCl₃N₂ + ½ CH₂Cl₂): C, 55.35; H, 3.92; N, 3.11; found: C, 54.94, H, 3.90, N, 3.14.

ASSOCIATED CONTENT

Supporting Information. Additional data, experimental procedures and characterizations for other compounds, copies of ¹H and ¹³C NMR spectra of all final products (new or reported), copies of HRMS spectra of new compounds, copies of HPLC analyses.

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Notes

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ABBREVIATIONS

TLC, thin layer chromatography; GC, gas chromatography; HPLC, high pressure chromatography; CSP, chiral stationary phase; NMR, nuclear magnetic resonance; HRMS, high resolution mass spectroscopy; ESI, electrospray ionization; THF, tetrahydrofuran; TRIP, 3,3'-bis(2,4,6-triisopropylphenyl)-1,1'-binaphthyl-2,2'-diyl hydrogenphosphate; BARF, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate; PNB, para-nitrobenzoate; CBz, benzylcarbamate; Ts, tosyl; Bn, benzyl; Boc, tert-butyl carboxylate; NTf, trifluoromethaneimide; IPr, 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene.

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SYNOPSIS.

