

Gold Catalysis

Asymmetric Construction of Six-Membered Rings by Cyclization of Allenes with Dinuclear Gold Catalysis

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Abstract: A simple and efficient method for the synthesis of 1,4-dihydroarenes by gold-catalyzed 6-*endo* cyclization of benzylic allenenes has been developed. Furthermore, asymmetric hydroarylation of enantioenriched allenenes has been realized to offer a practical and convergent approach to aromatic ring-fused six-membered cycles containing a chiral stereocenter such as 1,4-dihydronaphthalenes, 1,4-dihydrodibenzo[*b,d*]thiophenes, and 4,7-dihydrobenzo[*b*]thiophenes by applying dinuclear [(dppm)Au₂Cl₂] [dppm = methylenebis(diphenylphosphane)] combined with AgOTf as the catalyst to ensure the high efficiency of chirality transfer. ESI-MS has been applied to characterize some of the key reactive dinuclear gold intermediates successfully.

1,4-Dihydroarene is an important structural motif present in natural products. Many of these compounds show exceptional biological and pharmacological activities,^[1] which has made them attractive targets for organic synthesis. Although there are some useful synthetic methods to prepare 1,4-dihydroarenes,^[2] such as Birch reduction^[3] and the aryne Diels-Alder reaction^[4] (see the Supporting Information, Scheme S1), there remain some limitations, such as over-reduction and the challenge in establishing the absolute configuration of the involved chiral center. Thus, development of mild, efficient and selective approach is still of high current interest, especially the asymmetric synthesis of 1,4-dihydroarene.

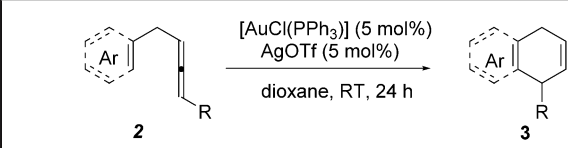
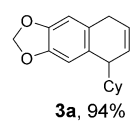
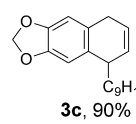
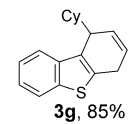
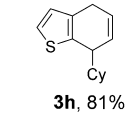
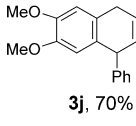
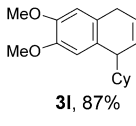
Transition metal-catalyzed cycloisomerization of allenenes has received considerable attention for the efficient and atom-economical synthesis of complex molecules in a single step.^[5] Compared with the well-developed cyclization reactions of allenenes with a highly nucleophilic O-, N-, or C-centered function-

ality,^[6] cyclization with the arene as the nucleophile with allenenes is much more challenging, due to the unfavorable breaking of the aromaticity of the benzene ring, and has thus not been well established.^[7] We reasoned that hydroarylation of benzylic allenenes would provide an efficient way to synthesize 1,4-dihydroarenes. Furthermore, asymmetric construction of 1,4-dihydroarenes may be achieved by transition metal-catalyzed hydroarylation of enantioenriched allenenes,^[8] provided that the axial chirality may be transferred to the center chirality with high efficiency.

Initially, we tried the reaction of benzylic allene **2a** in dioxane under the catalysis of [AuCl(PPh₃)]/AgBF₄,^[9] the expected 6-*endo* cyclization product **3a** was afforded in 91% yield (see the Supporting Information, Table S1, entry 1). Different silver salts were tested, fortunately, as usual the yield was improved to 99% when AgOTf was used together with [AuCl(PPh₃)] (see the Supporting Information, Table S1, entries 1–4). Other solvents, such as toluene, CH₃CN, and 1,2-dichloroethane (DCE), provided **3a** in 98%, 0%, and 93% yields, respectively (see the Supporting Information, Table S1, entries 5–7). The use of other catalysts, such as PtCl₂/AgOTf or AuCl, failed to afford better results (see the Supporting Information, Table S1, entries 8 and 9).

With the optimal conditions in hand, we proceeded to examine the scope of this gold-catalyzed intramolecular hydroarylation reaction with racemic benzyl allenenes (Table 1). A variety of aryl allenenes, including phenyl, benzothienyl, and thienyl al-

Table 1. Gold-catalyzed cyclization of **2**.^[a]

		
 3a , 94%	 3c , 90%	 3g , 85%
 3h , 81%	 3j , 70%	 3i , 87%
[a] Reaction conditions: 2 (0.2 mmol), [AuCl(PPh ₃)] (5 mol%), and AgOTf (5 mol%) in dioxane (2 mL) at room temperature.		

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lenes, were smoothly converted into the corresponding 1,4-dihydroarenes.

The next challenge of this approach was the efficient transfer of chirality of the axially chiral enantioenriched benzyl allenes. After realizing this cyclization reaction, we then began our investigation on the optimization of the reaction conditions for the highly stereoselective cyclization of the model substrate *R*-**2a**^[10] with some typical results listed in Table S2 (see the Supporting Information). We attempted to use [AuCl(PPh₃)]/AgOTf as the catalyst in dioxane first; the yield of *R*-**3a** was 97%, but the efficiency of the chirality transfer was very low and the enantiomeric excess of *R*-**3a** was only 55% from a starting allene *R*_α-**2a** with 99% ee (see the Supporting Information, Table S2, entry 1). The effect of the solvent was then explored for this transformation at room temperature. Toluene gave the best results, affording *R*-**3a** in 70% ee (see the Supporting Information, Table S2, entries 1–4). Several other silver salts in toluene were also screened. However, none surpassed AgOTf (see the Supporting Information, Table S2, entries 4–7). Interestingly, when [IPrAuCl] [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolium] was used instead of [AuCl(PPh₃)], the ee of *R*-**3a** dropped to 15% (see the Supporting Information, Table S2, entry 8), indicating the importance of the ligand. Inspired by these results, we started to try the gold complexes with a bidentate phosphine ligand. Excitingly, the ee of *R*-**3a** was improved to 97% with a yield of 98% when the reaction was catalyzed by the dinuclear complex [(dppm)Au₂Cl₂] [dppm = methylenebis(diphenylphosphane)] in combination with AgOTf (see the Supporting Information, Table S2, entry 9). This reaction did not proceed in the absence of either AgOTf or [(dppm)Au₂Cl₂] (see the Supporting Information, Table S2, entries 10 and 11). Thus, we defined the standard conditions as follows: 2.5 mol% of [(dppm)Au₂Cl₂] and 5 mol% of AgOTf in toluene at room temperature (see the Supporting Information, Table S2, entry 9).

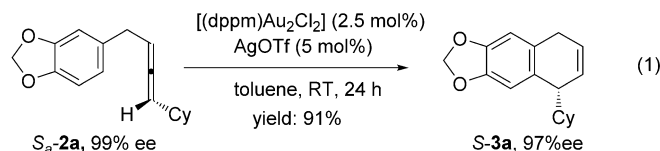
With the optimized reaction conditions in hand, the generality of the reaction was then explored and some typical results are listed in Table 2. R could be cyclohexyl (Table 2, entries 1 and 2), isobutyl (entry 3), nonyl (entry 4), and hexyl group

Table 2. Gold-Catalyzed Cyclization Reaction of <i>R</i> _α - 2 . ^[a]			
Entry	R	Yield [%] ^[b]	ee [%] ^[c]
1	Cy (<i>R</i> _α - 2a ; 99% ee)	91	99 (<i>R</i> - 3a)
2 ^d	Cy (<i>R</i> _α - 2a ; 99% ee)	92	99 (<i>R</i> - 3a)
3	<i>i</i> Bu (<i>R</i> _α - 2b ; 94% ee)	87	94 (<i>R</i> - 3b)
4	<i>n</i> -C ₉ H ₁₉ (<i>R</i> _α - 2c ; 94% ee)	91	92 (<i>R</i> - 3c)
5	<i>n</i> -C ₆ H ₁₃ (<i>R</i> _α - 2d ; 91% ee)	90	92 (<i>R</i> - 3d)

[a] Reaction conditions (unless otherwise stated): *R*_α-**2** (1.0 mmol), [(dppm)Au₂Cl₂] (2.5 mol%), and AgOTf (5 mol%) in toluene (10 mL) at room temperature; [b] yield of isolated product; [c] determined by chiral HPLC; [d] the reaction was conducted with at 4.0 mmol (1.0245 g) scale of *R*_α-**2a** in 40 mL of toluene for 36 h.

(entry 5). It is worth noting that the reaction can be easily conducted on a scale of 4.0 mmol of *R*_α-**2a** (1.0245 g) affording *R*-**3a** in a slightly higher yield (Table 2, entry 2).

Furthermore, the reaction of the enantiomer *S*_α-**2a**, prepared similarly by using (*R*)-α,α-diphenylprolinol,^[10] afforded *S*-**3a** in an excellent yield with 97% ee [Eq. (1)].



The scope of the reaction with regard to different aryl groups was also examined (Table 3). 3,4,5-Trimethoxyphenyl (*R*-**3e**) and 3,4-dimethoxyphenyl (*R*-**3f**, *S*-**3j**, and *S*-**3k**) groups were both well tolerated. Interestingly, heteroaryl-substituted optically active allenes, such as benzothiophene (*R*-**3g**) and thiophene derivatives (*R*-**3h** and *R*-**3i**) were also smoothly converted to the corresponding 1,4-dihydroarenes. Interestingly, R could also be a phenyl or 4-bromophenyl group (*S*-**3j** and *S*-**3k**).

Table 3. Gold-Catalyzed Cyclization Reaction of <i>R</i> _α - 2 . ^[a]			
 <i>R</i> - 3e , 28 h, 81%, 99% ee	 <i>R</i> - 3f , 36 h, 88%, 94% ee	 <i>R</i> - 3g , 48 h, 90%, 98% ee	 <i>S</i> - 3k , 48 h, 84%, 96% ee
 <i>R</i> - 3h , 48 h, 95%, 96% ee	 <i>R</i> - 3i , 48 h, 91%, 96% ee	 <i>S</i> - 3j , 48 h, 82%, 98% ee	

[a] Reaction conditions: *R*_α-**2** (1.0 mmol), [(dppm)Au₂Cl₂] (2.5 mol%), and AgOTf (5 mol%) in toluene (10 mL) at room temperature.

Finally, the structure and absolute configuration of *R*-**3i** was confirmed unambiguously by the X-ray single crystal diffraction study [Eq. (2) and Figure S1 in the Supporting Information].^[11]

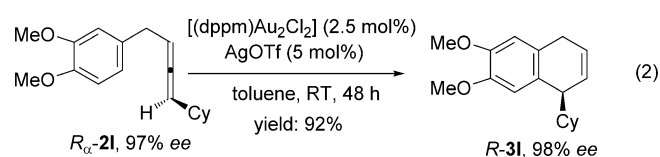


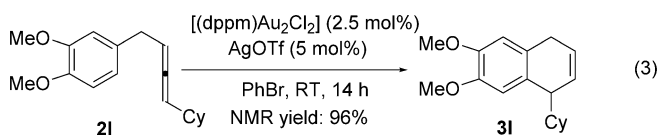
Table 4. Ligand Effects for Formation of *R*-**31**.^[a]

Entry	[Au]	Yield [%] ^[b]	ee [%] ^[c]	θ [°]
1	[IPrAuCl]	88	49.8	–
2	[(Me ₃ P)AuCl]	91	77.8	118
3	[(Ph ₃ P)AuCl]	90	81.9	145
4	[(tBu ₃ P)AuCl]	90	83.4	182
5 ^[d]	[(dppm)Au ₂ Cl ₂]	92	97.7	–

[a] Reaction conditions (unless otherwise stated): *R*_α-**21** (0.2 mmol) and catalyst (5 mol%) in toluene (2 mL); [b] yield of isolated product; [c] determined by chiral HPLC; [d] the reaction was conducted with 1.0 mmol of *R*_α-**2**, 2.5 mol% of [(dppm)Au₂Cl₂] and 5 mol% of AgOTf in 10 mL of toluene.

The effect of ligands was also explored in terms of their sizes for this transformation. The ee of *R*-**31** was found to increase with bulkier ligands (Table 4).^[12]

To capture some key reactive intermediates for the mechanism, ESI-MS was applied. After some study, we observed that the original reaction performed in toluene failed to afford stable signals. Due to the similarity of toluene with PhBr, we changed the solvent of this reaction from toluene to PhBr,^[13] which could also afford **31** in 96% NMR yield [Eq. (3)]. More importantly, the PhBr solution led to stable ESI-MS signals for reactive species involved in this reaction.



Firstly, a solution of [(dppm)Au₂Cl₂] (0.005 mmol) and AgOTf (0.01 mmol) in PhBr (2 mL) was stirred at room temperature for 10 min, then filtered and diluted with PhBr by a factor of 20. This resulting solution was transferred into the ESI source at a flow rate of 5 μL min⁻¹ [Eq. (4)]. The signal of ion [(dppm)Au₂OTf]⁺ (observed *m/z*: 927.0; *m/z* calcd for C₂₆H₂₂Au₂F₃O₃P₂S⁺: 927.0) was detected, indicating that [(dppm)Au₂OTf₂] was formed by anion exchange between [(dppm)Au₂Cl₂] and AgOTf (Figure 1 a).

Secondly, a solution of *R*_α-**21** (0.05 mmol), [(dppm)Au₂Cl₂] (0.05 mmol) and AgOTf (0.1 mmol) in PhBr (2 mL) was stirred at room temperature for 10 min [Eq. (5)]. After the same treatment as above, the signal of dinuclear gold ion **IM1** or **IM2** (observed *m/z*: 1199.2; *m/z* calcd for C₄₄H₄₆F₃O₃P₂SAu₂⁺: 1199.2) was detected (Figure 1 b).

Thirdly, a solution of *R*_α-**21** (0.2 mmol), [(dppm)Au₂Cl₂] (0.005 mmol) and AgOTf (0.01 mmol) in PhBr (2 mL) was stirred at room temperature for 8 h [Eq. (6)]. After the same treatment as above, the signals of ions *R*-**31** (observed *m/z*: 273.2; *m/z*

calcd for C₁₈H₂₅O₂⁺: 273.2), [(dppm)Au₂OTf]⁺ (observed *m/z*: 927.0; *m/z* calcd for C₂₆H₂₂Au₂F₃O₃P₂S⁺: 927.0), and [(dppm)₂Au₂OTf]⁺ (observed *m/z*: 1311.1; *m/z* calcd for C₅₁H₄₄Au₂F₃O₃P₄S⁺: 1311.1) were detected (Figure 1 c).

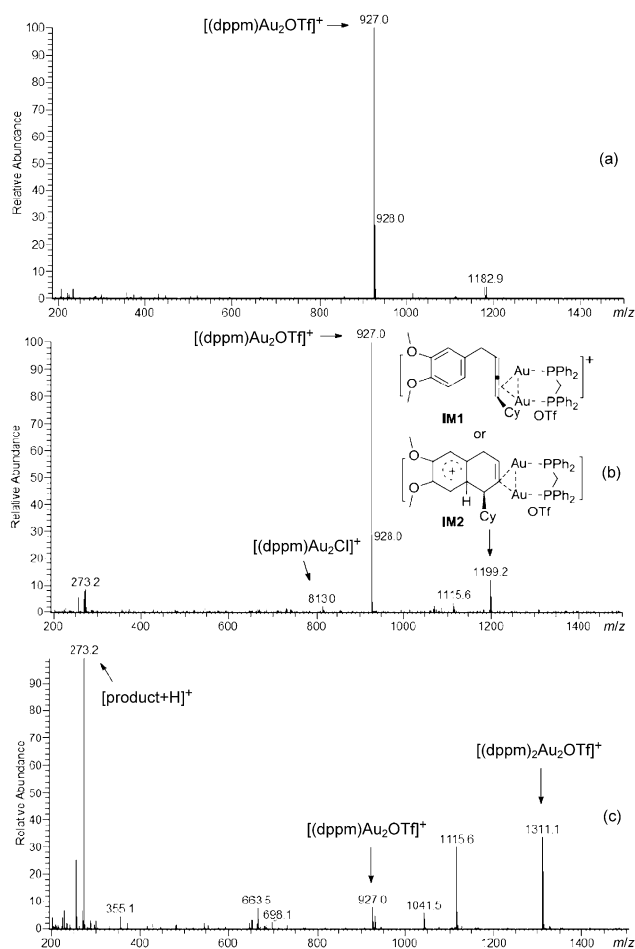
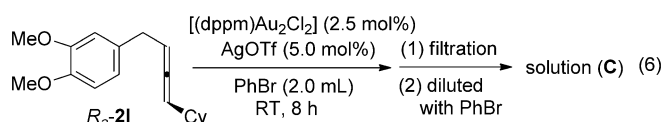
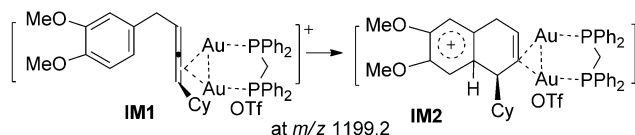
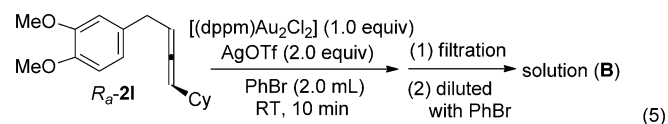
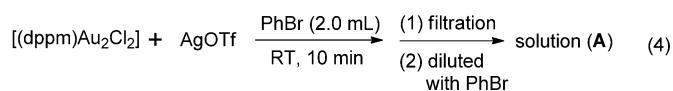
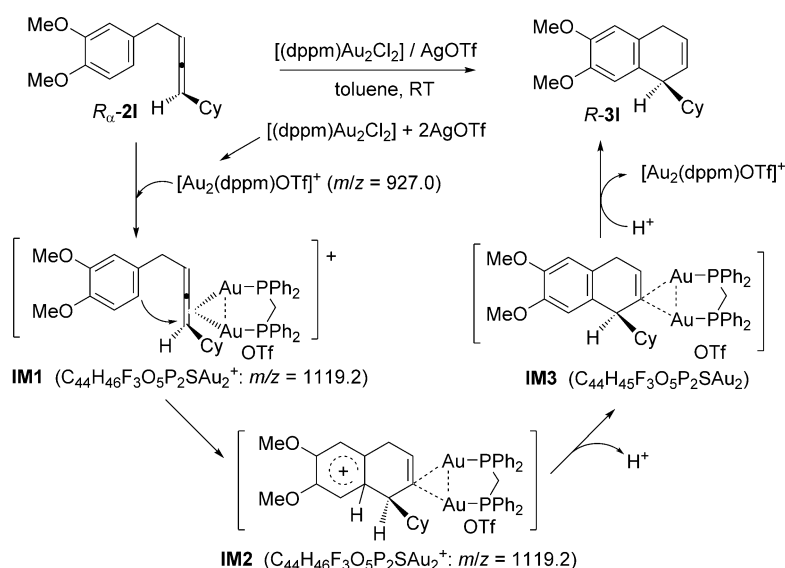


Figure 1. ESI mass spectra: a) solution A; b) solution B; c) solution C.



Scheme 1. Proposed mechanism.

Based on these facts, a mechanistic rationale for this reaction is shown in Scheme 1: nucleophilic highly stereoselective *anti*-attack of the arene at the coordinated C=C bond remote from the arene unit in the allene unit would afford the vinyl-gold species **IM2**,^[14] which ensures the efficiency of chirality transfer. Then, **IM3** was generated by releasing a proton from **IM2** to regain aromaticity. Finally, protodemetalation of **IM3** would afford the 1,4-dihydroarene **R-3I**, with regeneration of the dinuclear gold catalyst.

In conclusion, we have developed an efficient method for the synthesis of 1,4-dihydroarene by identifying a gold catalyst for the exclusive 6-*endo* cyclization of benzylic allenes. Furthermore, we have also realized the asymmetric construction of arene-fused six-membered rings, such as 1,4-dihydronaphthalenes, 1,4-dihydrodibenzo[*b,d*]thiophenes, and 4,7-dihydrobenzo[*b*]thiophenes by identifying a dinuclear gold catalyst to ensure the efficiency of chirality transfer for the hydroarylation of enantioenriched allenes. The mechanism was unveiled by the detection of some reactive dinuclear gold species by ESI-MS experiments. Further studies in this area are being carried out in our laboratory.

Experimental Section

(*R*)-1-Cyclohexyl-1,4-dihydro-6,7-methylenedioxyphthalene (**R-3a**): To a dry Schlenk tube were added sequentially AgOTf (13.0 mg, 0.05 mmol, weighed in a glove box), [(dppm)Au₂Cl₂] (21.8 mg, 0.026 mmol, weighed in a glove box), **R_α-2a** (256.6 mg, 1.0 mmol), and toluene (10 mL) under N₂. After continuous stirring for 24 h at room temperature, the reaction was complete as monitored by TLC. Filtration through a short column of silica gel (eluent: Et₂O, 3 × 20 mL), evaporation, and column chromatography on silica gel (eluent: petroleum ether) afforded **R-3a** as a liquid (233.8 mg, 91%, 99% ee). HPLC conditions: Chiralcel OD-H column, hexane/*i*PrOH = 100:0, 1.0 mL min⁻¹, λ = 214 nm, *t_R*(major) = 9.3 min, *t_R*(minor) = 12.6 min); [α]_D²⁰ = -173.0 (c = 1.03, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ = 6.65 (s, 1 H, ArH), 6.59 (s, 1 H, ArH),

6.07–5.96 (m, 1 H, =CH), 5.95–5.81 (m, 3 H, OCH₂ + =CH), 3.36–3.12 (m, 3 H, ArCH₂ + ArCH), 1.87–1.51 (m, 5 H, 2 × CH₂ + CH), 1.43–0.91 ppm (m, 6 H, 3 × CH₂); ¹³C NMR (75 MHz, CDCl₃): δ = 145.7, 145.6, 131.2, 128.3, 127.4, 125.6, 108.0, 107.5, 100.5, 46.5, 45.7, 30.8, 30.7, 27.9, 26.9, 26.5 ppm; IR (neat): ν = 3029, 2923, 2851, 2770, 1503, 1484, 1449, 1425, 1383, 1340, 1232, 1182, 1142, 1132, 1081, 1042 cm⁻¹; MS (70 eV, EI): *m/z* (%) 257 ([M⁺] + 1, 1.82), 256 ([M⁺], 9.94), 173 (100); HRMS: calcd for C₁₇H₂₀O₂ [M⁺]: 256.1463, found: 256.1460.

Acknowledgements

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Keywords: allenes • homogeneous catalysis • chirality transfer • cyclization • gold

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- [11] Crystal data for compound **R-31**: C₁₈H₂₄O₂, MW = 272.37; monoclinic; space group P2₁; final R indices [$I > 2\sigma(I)$]; R1 = 0.0570, wR2 = 0.1699; R indices (all data); R1 = 0.0693; wR2 = 0.1510; a = 9.0555 (5), b = 6.3985 (3), c = 13.9809 (9) Å; $\alpha = 90.00$, $\beta = 104.282$ (6), $\gamma = 90.00^\circ$; V = 785.04 (7) Å³; T = 293 (2) K; Z = 2; reflections collected/unique 5792/2750 (R_{int} = 0.0690); number of observations [$> 2\sigma(I)$] 2166; parameters: 184. CCDC 048430 (R-31) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.
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