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Nazarov Cyclization

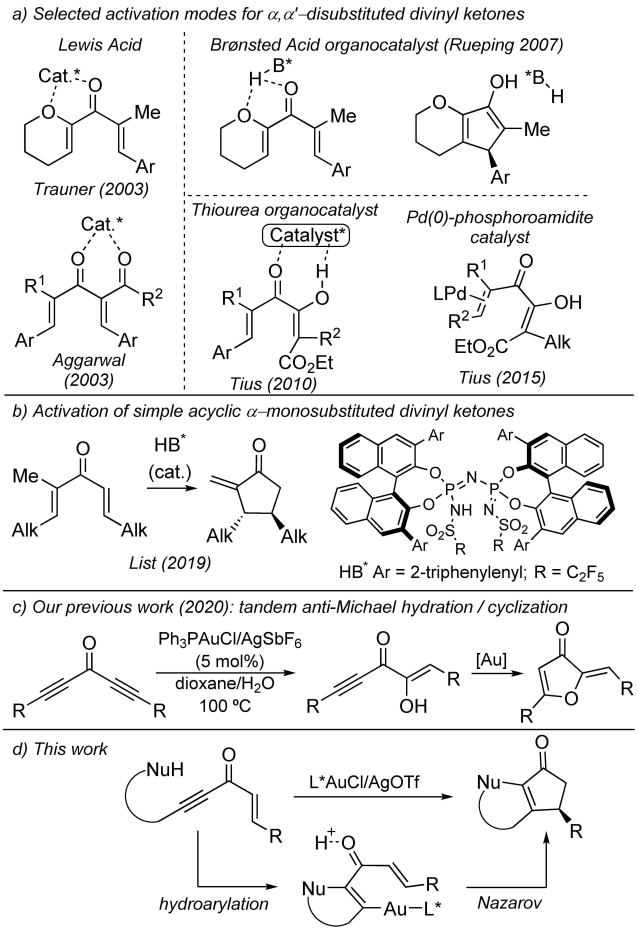
Asymmetric Gold(I)-Catalyzed Tandem Hydroarylation–Nazarov Cyclization: Enantioselective Access to Cyclopentenones

*Marta Solas, Samuel Suárez-Pantiga, and Roberto Sanz**

Abstract: The asymmetric synthesis of cyclopentachromenones from gold-catalyzed reaction of readily available skipped alkenynones is described. This cascade reaction involves an initial *anti*-Michael hydroarylation of the ynone moiety to form a gold-functionalized dialkenylketone intermediate, followed by a Nazarov cyclization that proceeds in an unprecedented enantioselective manner. Excellent enantiomeric ratios and chemical yields are obtained under mild reaction conditions.

Cyclopentenones are functional scaffolds for several transformations that allow access to bioactive target molecules.[1] Nazarov cyclization is among the most straightforward and commonly used methods for synthesizing this relevant core.[2] Nevertheless, its enantioselective version by means of asymmetric catalysis has demonstrated more challenges.[3] Notable advances have been achieved since 2003, when the first examples of the Nazarov cyclization under asymmetric catalysis were reported.[4] However, some of these pioneering contributions required sub- or stoichiometric amounts of the catalyst. In 2007, Rueping utilized chiral Brønsted acid organocatalysts to achieve the enantioselective synthesis of cyclopentenones (Scheme 1a).[5]

Since then, various approaches to asymmetric Nazarov reactions have been reported employing Lewis acid catalysts,[6] or chiral organocatalysts,[3b,7,8] or a combination of both metal Lewis acid and an organocatalyst.[9] These strategies are based on carbonyl activation by the chiral catalyst. Tius and Ateşin reported the only case in which chirality was achieved through an alternative approach through a Pd-π-allyl complex generated after coordination to one alkene moiety of a Pd^0 complex bearing a phosphoramidite ligand, affording densely substituted cyclopentenones (Scheme 1a).[6d] Because of the spatial distance between the carbonyl group bonded to the chiral catalyst and the newly generated stereocenters, the design of the starting divinyl ketone plays a crucial role in achieving high enantioselectivities. For instance, polarized divinyl ketones[10] bearing an electron-donating group at one of the α-positions and an electron-withdrawing group at the other α-position were revealed as excellent substrates for asymmetric Nazarov cyclizations. Functionalities able to stabilize the cationic charge more efficiently over one of the α-positions were also introduced, controlling the formation of the alkene and avoiding the formation of isomers.[9b] Notably, Rawal reported the enantioselective Nazarov cyclization of non-polarized dienones using Cr-salen complexes.[6c] In most cases, only divinyl ketones having substituents at both α-positions were employed as suitable precursors for the asymmetric Nazarov cyclization. Only



Scheme 1. Previous work concerning asymmetric Nazarov cyclizations and our tandem gold-catalyzed approach.

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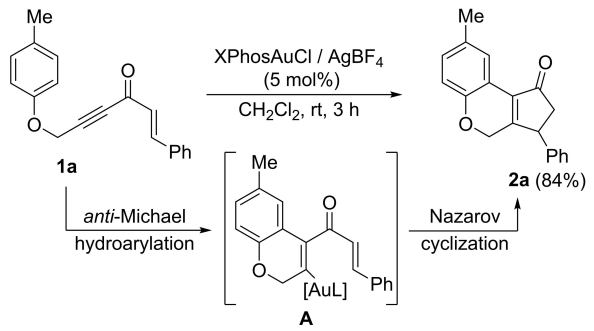
recently, List described the enantioselective synthesis of cyclopentenones using simple non-activated α-methyl-substituted divinyl ketones and a confined Brønsted acid catalyst (Scheme 1b).[8]

The use of unconventional substrates in Nazarov cyclization has emerged considerably in recent years.[11] The development of gold catalysis has played a prominent role in designing Nazarov-like reactions forming 5-membered ring cycles.[12] Notably, Toste described the enantioselective synthesis of cyclopentenones from enantioenriched propargyl pivalates by Au^I-catalyzed Rautenstrauch rearrangement.[13] Despite the challenges of asymmetric gold(I)-catalysis, the same group designed a ligand-controlled enantioselective dearomative Rautenstrauch rearrangement to obtain cyclopenta[*b*]indoles.[14]

Recently, we have described the synthesis of furanones from easily accessible skipped diynones[15] employing gold catalysis.[16] After initial Au-catalyzed alkyne activation, the reaction proceeds by an unusual *anti*-Michael hydration and subsequent *endo*-cyclization (Scheme 1c). Inspired by these findings, we envisaged that dienones could be accessed by replacing one of the alkynes with an alkene group. An organogold dialkenyl ketone intermediate would be formed after alkyne activation followed by the addition of a suitable nucleophile. Considering that similar complexes have very low basicity compared with other C(sp^2)–Au bonds,[17] we envisioned that carbonyl activation by the in situ generated proton could occur. If the dienone intermediate adopts *s*-trans/*s*-trans conformation faster than protodeauration of the alkenyl organogold bearing suitable chiral ligands,[18] an asymmetric Nazarov cyclization could be achieved, affording enantioenriched cyclopentenones (Scheme 1d).

To test our hypothesis, we designed a skipped alkenynone **1a**,[19] which would undergo an initial hydroarylation.[20] After some optimization, we found that XPhosAuCl, in combination with $AgBF_4$, afforded cyclopenta[*c*]chromenone **2a** in high yield (Scheme 2).[19] To account for its formation, we assumed that the initial hydroarylation takes place in an *anti*-Michael manner[21] giving rise to an alkenyl gold intermediate like **A**, which could evolve via a Nazarov cyclization to the final cyclopentenone **2a**. At this stage, it is not clear if **A** is protodeaurated prior to the cyclization or not, which would be crucial for the success of an enantioselective version of this process by using chiral gold complexes as catalysts.

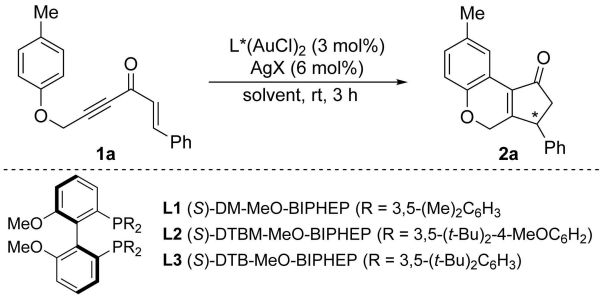


Scheme 2. Proof of concept: tandem hydroarylation–Nazarov cyclization of skipped alkenynone **1a**.

Interestingly, this gold(I)-catalyzed tandem transformation provides access to cyclopenta[*c*]chromenone derivatives in a straightforward manner from simple and readily available starting materials. These compounds combine the attractive 2*H*-chromene core[22] with the cyclopentanone moiety. So, the scope of this process was tested with respect to the aryl moiety involved in the initial hydroarylation and the alkene substituents (Table S2).[19] Then, we decided to tackle if our initial proposal for developing a new strategy for enantioselective Nazarov cyclizations could be successful.

Using model alkenynone **1a**, we tested the reaction using various gold catalysts bearing chiral ligands. After an initial screening (see Table S3),[19] we selected three chiral BIPHEP-like bisphosphines (Table 1). Our initial essays with **L1**–**L3** in CH_2Cl_2 (rt, 3 h) using $AgSbF_6$ afforded cyclopentenone **2a** in high yields and good enantioselectivities, especially with **L2** and **L3** (entries 1–3). Curiously, the use of DCE as the solvent provides better *ee* values with **L1** (entries 4–6). A subsequent counteranion screening with this ligand (entries 7–9) led to an excellent *ee* when employing AgOTf (entry 9). In conjunction with **L2** and **L3**, this silver salt provides enantioselectivities similar to those achieved with $AgSbF_6$ (entries 10 and 11). Therefore, the combination

Table 1: Optimization of the reaction conditions for the enantioselective synthesis of **2a**.[a]



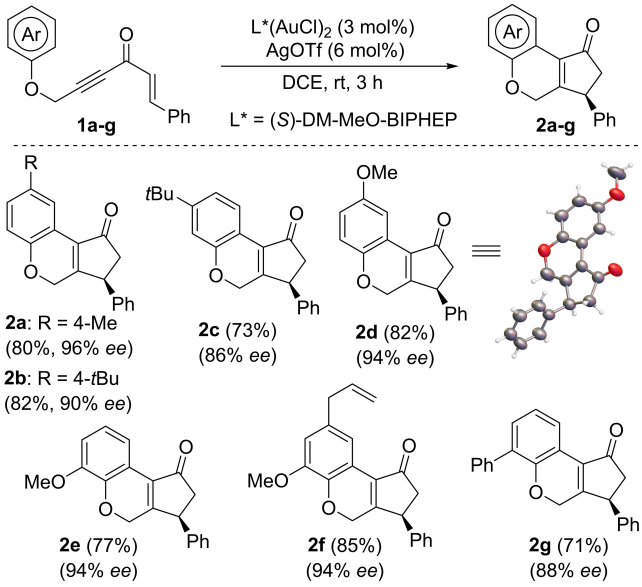
Entry	L*	X	Solvent	Yield **2a**[b]	*ee*[c]
1	**L1**	SbF_6	CH_2Cl_2	80	66
2	**L2**	SbF_6	CH_2Cl_2	65	87
3	**L3**	SbF_6	CH_2Cl_2	57	81
4	**L1**	SbF_6	DCE	83	84
5	**L2**	SbF_6	DCE	70	50
6	**L3**	SbF_6	DCE	60	68
7	**L1**	BF_4	DCE	71	76
8	**L1**	NTf_2	DCE	77	76
9	**L1**	OTf	DCE	80	96
10	**L2**	OTf	CH_2Cl_2	38[d]	88
11	**L3**	OTf	CH_2Cl_2	37[e]	76
12[f]	**L1**	OTf	DCE	75	94
13[g]	**L1**	OTf	DCE	78	88

[a] Reactions were conducted with **1a** (0.2 mmol) and the catalyst in 2 mL of the corresponding solvent. [b] Isolated yield. [c] Determined by HPLC analysis. [d] Significant amounts of diketone **3a**, arising from hydration of the alkyne were obtained (see Supporting Information for details). [e] Uncomplete conversion. [f] Carried out at 0 °C. [g] Carried out with 3 mol% of AgOTf.

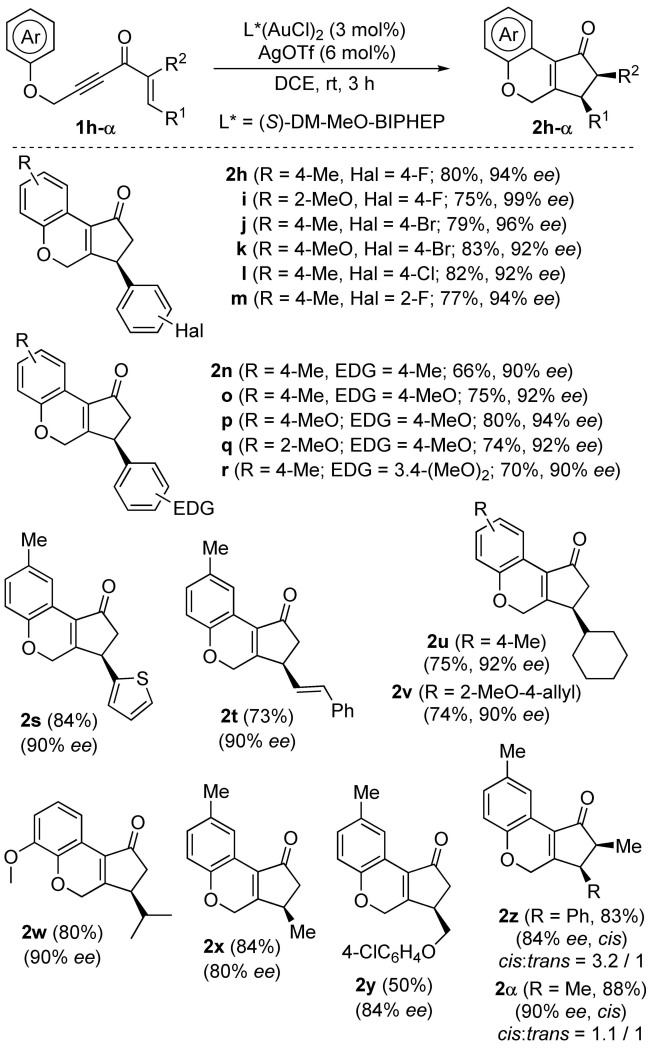
of **L1** with AgOTf was selected as optimal reaction conditions. An additional experiment lowering the reaction temperature did not improve the enantioselectivity (entry 12). Finally, with only 1 equiv. of AgOTf, similar yield and *ee* value were obtained (entry 13).[23]

The optimized reaction conditions were then employed to evaluate the substrate scope for this new enantioselective synthesis of cyclopentenones. First, alkenynones **1a–g** bearing different aryl frameworks and a β-styrenyl group were tested (Scheme 3). The reaction with substrates bearing aryl rings functionalized with alkyl, aryl, or alkoxy groups at *para*-, *meta*- and *ortho*-positions proceeds efficiently with high yields and enantioselectivities. The absolute configuration of compounds **2** was inferred from the X-ray diffraction of **2d**, revealing a (*S*)-configuration for the generated stereocenter.[24] In addition, the influence of the alkene geometry was studied by using (*Z*)-**1a** (as 6/1 mixture of *Z*/*E* isomers). Its reaction led to the opposite enantiomer but with lower enantioselectivity (68 % *ee*).

The effect of β-substituent on alkenynones **1** was then studied, as summarized in Scheme 4. When using olefins with aromatic groups bearing halogen atoms at different positions, the corresponding cyclopentenones **2h–m** were obtained in high yields and excellent enantioselectivies. Similarly, electron-rich aromatic rings were also well-tolerated as R substituents providing access to cyclopentenones **2n–r** with good yields and high *ee* values. Alkenynones bearing a heterocycle, or an additional alkenyl group at the R position, were also suitable substrates leading to **2s** and **2t**, respectively, with high enantioselectivities. In addition, primary and secondary (*c*)-alkyl groups were evaluated as β-substituents of the alkenynone, and, gratifyingly, the desired cyclopentenones **2u–x** were obtained in high yields and enantioselectivities, even with a substrate possessing a simple methyl group (**2x**). Moreover, a



Scheme 3. Scope of *O*-aryl moiety for the enantioselective synthesis of cyclopentenones **2**.

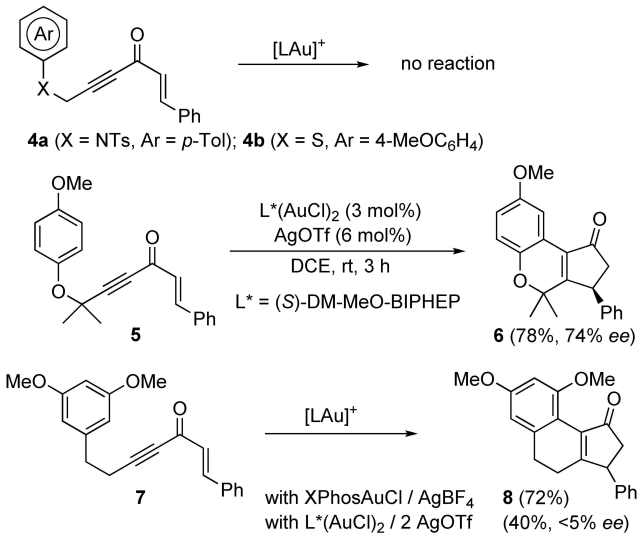


Scheme 4. Scope of alkene moiety for the enantioselective synthesis of cyclopentenones **2**.

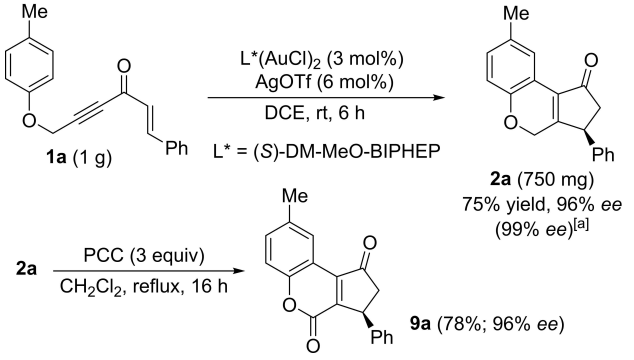
substrate bearing a functionalized alkyl group was also successfully realized (**2y**). Finally, the cyclization of α,β-disubstituted alkenynones **1z** and **1α** was evaluated. In these cases, mixtures of diastereoisomers were obtained favoring the *cis*-cyclopentenones, which were afforded with good enantioselectivities.

As the initial hydroarylation reaction has also been described for other alkyne-containing aromatics, related substrates were synthesized and evaluated (Scheme 5). Disappointingly, sulfonamide **4a** and sulfide **4b** did not evolve under the established conditions, even when employing the non-chiral XPhosAuCl catalyst. Changing the –O–CH_2– tether by a –O–$C(Me)_2$– one, alkenynone **5**, led to the expected cyclopentenone **6** in high yield and with good enantioselectivity. Moreover, with ketone **7**, bearing a –CH_2–CH_2– tether, the tandem reaction proceeds efficiently leading to **8**, although with almost no enantioselectivity.

Interestingly, the scale-up reaction using 1 g of **1a** can be conducted efficiently, providing 750 mg of **2a** with 96 % *ee* and with only a slight decrease in the yield (Scheme 6). In



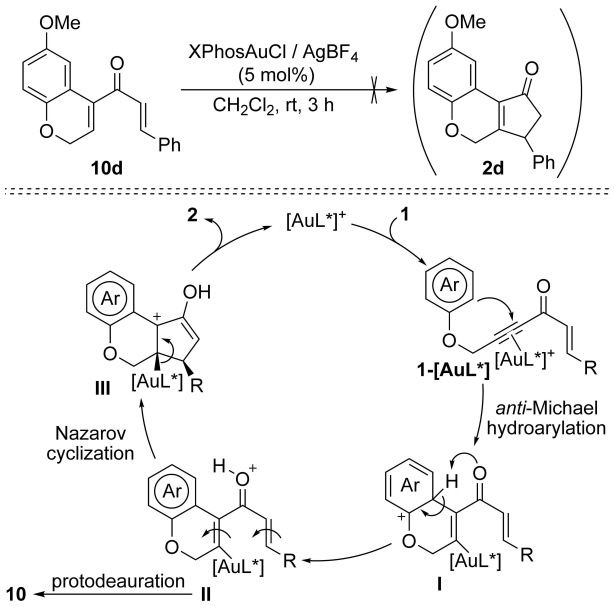
Scheme 5. Limitations and further scope of the enantioselective hydroarylation–Nazarov cyclization.



Scheme 6. Gram-scale experiment and further derivatization. [a] *ee* value within parenthesis is obtained by recrystallization after column chromatography.

addition, a pure enantiomeric sample of **2a** could be obtained by recrystallization after chromatographic purification. In addition, a synthetic application of the product is shown in a further transformation involving oxidation to the coumarin derivative **9a** without erosion of the enantiomeric excess (Scheme 6).

A control experiment with dialkenyl ketone **10d** was conducted to gain more mechanistic insights into the reaction. As shown in Scheme 7, when this plausible intermediate was treated with the gold catalyst under the established reaction conditions, no evolution occurred, thus suggesting that free chromene derivatives **10** are not involved as intermediates. Our mechanistic proposal implies the initial activation of the alkyne by the gold complex, **1-[AuL*]**, that triggers an *anti*-Michael hydroarylation reaction leading to cationic intermediate **I**. The removal of a proton, to recover the aromaticity, could be assisted by the carbonyl group favoring the formation of an intermediate such as **II** in which a competitive protodemetallation, leading to **10**, could be slowed down, allowing subsequent



Scheme 7. Control experiment and the postulated mechanism.

Nazarov cyclization. In this way, intermediate **III** would be formed in which the stereogenic center has been created in an enantioselective manner due to the presence of the chiral complex attached to the molecule and the control over the absolute sense of conrotation. Similar to silicon-directed Nazarov cyclizations,[9b] the gold complex in the intermediate **III** may be decisive in controlling the alkene formation and avoiding alternative isomers. Finally, demetallation and further tautomerization would lead to the cyclopenta-[*c*]chromenones **2** (Scheme 7).

In conclusion, an unconventional approach to the asymmetric catalytic Nazarov cyclization has been described, probably due to the crucial formation of an alkenylgold intermediate. Accessible chiral bisphosphine-gold complexes enable an enantioselective cascade reaction affording cyclopenta[*c*]chromenones with high enantiomeric excess, employing skipped alkenynones as substrates. The coordination of the gold catalyst to the alkyne prompted *anti*-Michael hydroarylation followed by the Nazarov cyclization. The method is scalable and conveniently conducted at room temperature achieving cyclopentenones in good yields and excellent enantioselectivities. This approach could be useful in designing related enantioselective cascade reactions employing unconventional precursors.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Asymmetric Catalysis · Cyclopentenones · Gold · Hydroarylation · Nazarov Cyclization

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[24] Deposition Number 2122998 (for **2d**) 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.

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