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Gold(I)-catalyzed stereoselective cyclization of 1,3-enyne aldehydes by a 1,3-acyloxy migration/Nazarov cyclization/aldol addition cascade†

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Stereoselective synthesis of bicyclo[3.3.0]octenones from chiral 1,3-enyne aldehydes bearing propargylic acetates is described. The method is based on a Au(I)-catalyzed domino sequence with concomitant transfer of chirality involving 1,3-acyloxy migration followed by Nazarov cyclization and an unprecedented aldol addition. The method furnishes densely functionalized bicyclic structures in high yields, with up to 97% ee and good diastereoselectivity.

Introduction

In recent years, Au(I) complexes have yielded powerful catalysts for the activation of alkynes, giving rise to a diversity of new and efficient catalytic transformations leading to high molecular complexity.[1] Among them, Au(I)-catalyzed reactions of enynes bearing propargylic carboxylates have been found to be especially versatile.[2] A particularly valuable feature of Au-catalysis is that it enables sequential formation of numerous C–C bonds *via* cascading cycloisomerization processes. Herein, we document a stereoselective process in which acyclic propargylic enynes with a pendant aldehyde are converted into optically active, highly functionalized diquinanes. The cascade reaction proceeds through 1,3-acyloxy migration, Nazarov cyclization, and aldol addition. Thus, in one step the method leads to the generation of functionalized, fused five-membered rings bearing three contiguous stereocenters (Fig. 1).

In a pioneering study, Zhang and Wang reported the Au(I)-catalyzed synthesis of cyclopentenones from readily available enyne ester.[3] The proposed mechanism involves 1,3-acyloxy migration followed by Nazarov cyclization, [1,2]-hydride shift, deauration, and hydrolysis of the intermediate cyclopentadienyl acetate formed (**C**, Fig. 2a).[4] In light of the mechanistic model, we wondered whether aldehydes incorporated into the starting enynes would be trapped *in situ* by **C** and form diquinanes (**2**).[5] The consequence of such a process is to add an unprecedented aldol addition reaction to the cascade that includes 1,3-migration and Nazarov cyclization.[6] This would require that aldehydes in the starting enynes are compatible with and survive the intervening steps and thereby subsequently be engaged as electrophiles. In an ideal scenario, Au(I) would function as a catalyst in all three fundamental steps of the cascading sequence: 1,3-acyloxy migration, Nazarov cyclization, and aldol reaction. In 2009, Malacria and Fensterbank demonstrated that the Au(I)–vinylcarbene[7] formed from Nazarov cyclization (**5**) could participate in intramolecular cyclopropanations with substrates incorporating olefin side chains (Fig. 2b).[4,8] Importantly, this is the sole example of concomitant transfer of chirality from an enantioenriched propargylic acetate. The fact that optically active propargyl acetates furnish optically active cycloalkanes led to the suggestion of an intermediate "bent-allene" complex (**A**)[4,9] that serves as a conduit for the transmission of the stereochemical information in the starting materials to enantioenriched products.[10] Accordingly, starting from a readily accessible chiral linear precursor, the domino reaction would be envisioned to give rise to highly functionalized optically active bicyclo[3.3.0]octenones with the configuration of the starting propargyl acetate potentially determining the configuration of all three stereocenters in the final product.

We recently reported the first asymmetric total synthesis of (−)-merochlorin A (**7**), relying on the key Au(I)-catalyzed reaction cascade described herein to access the diquinane core (Fig. 3).[11]

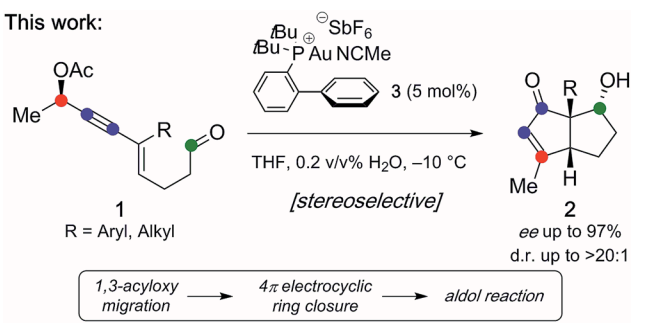

Fig. 1 Au(I)-catalyzed cascade reaction in this work.

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† Electronic supplementary information (ESI) available. CCDC 1517154–1517155 and 1913669. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9sc02828e

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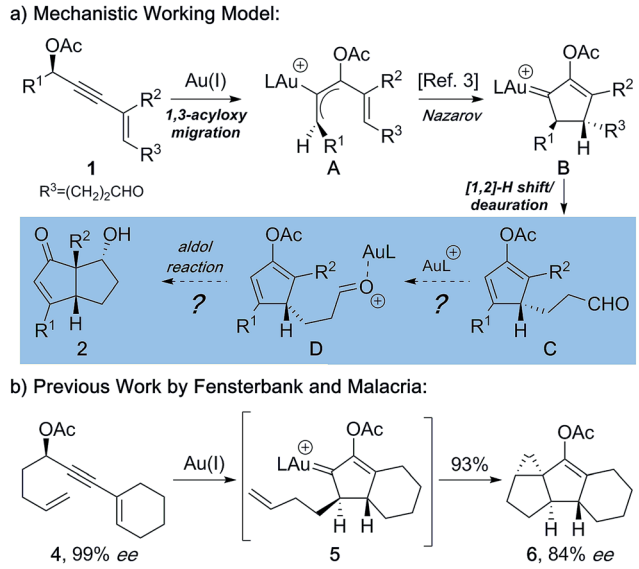


Fig. 2 (a) Mechanistic working model for the process developed by Zhang. (b) Previous work by Fensterbank and Malacria with concomitant transfer of chirality.

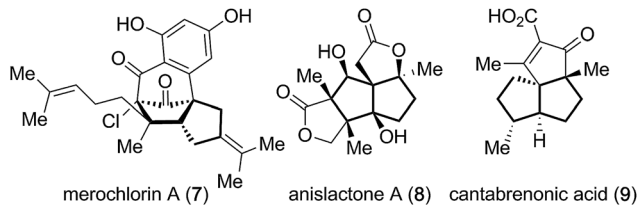
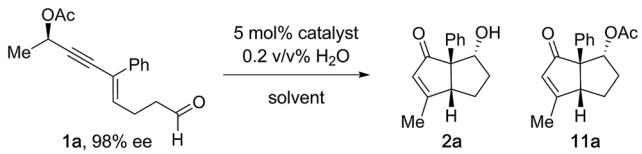


Fig. 3 Representative natural products incorporating a diquinane core.

Table 1 Optimization of reaction conditions[a]



Entry	Catalyst	Solvent	Yield **2**[b]	Yield **11a**[b]	ee[c]	d.r.
1	$AuCl_3$	THF	42%	—	79%	85 : 15
2[d]	$AuClPPh_3$	THF	67%	—	44%	81 : 19
3[d]	**10**[e]	THF	61%	—	67%	81 : 19
4	**3**	THF	71%	6%	91%	85 : 15
5	**3**	CH_2Cl_2	19%	74%	92%	74 : 26
6	**3**	Acetone	51%	23%	91%	88 : 12
7	**3**	Dioxane	50%	18%	91%	60 : 40
8[f]	**3**	**THF**	**76%**	—	**93%**	**89 : 11**

[a] Reaction conditions: 5 mol% catalyst, 0.2 vol% H_2O, solvent (0.05 M), 0.09–0.11 mmol **1a**, and RT. [b] Yields of isolated products. [c] Enantiomeric excess determined by supercritical fluid chromatography (SFC) on a chiral stationary phase and reported for the major diastereomer. [d] 5 mol% $AgSbF_6$ was added. [e] Ipr = 1,3-bis(2,6-diisopropylphenyl)imidiazol-2-ylidene. [f] Reaction was performed at −10 °C for 24 h.

Intrigued by the significant potential of this transformation, we were interested in investigating this novel reaction cascade because of its general applicability as a synthetic method for the synthesis of optically active bicyclo[3.3.0]octanes, which are abundant structural motifs in natural products such as anislactone A (**8**) and cantabrenonic acid (**9**).[12]

Results and discussion

Our synthetic studies commenced with the investigation of readily available chiral enyne (*R*)-**1a** (98% ee, Table 1). Thus, **1a** was treated with various gold complexes. While $AuCl_3$, $AuCl(PPh_3)/AgSbF_6$, and Ipr $AuCl/AgSbF_6$ (**10**) furnished enone **2a** in either poor yield or with poor chirality transfer, the treatment of **1a** with 5 mol% Au(MeCN)(JohnPhos)SbF_6 (Echavarren's catalyst, **3**)[13] in THF gave **2a** in 71% yield, with 91% ee and a d.r. of 85 : 15 (entry 4). It is noteworthy that 6% of aldol acetate **11a** was isolated, a product arising from acetate transfer during the terminating aldol reaction. Furthermore, initial screening revealed that the reaction benefits from the presence of 0.2 vol% H_2O in the reaction mixture (see the ESI†), which is consistent with prior reports of H_2O favoring the formation of **A**.[4a] Screening of reaction media (entries 4–7) revealed that solvents other than THF led to decreased d.r. and increased formation of acetate **11a**. Interestingly, when the reaction was conducted in CH_2Cl_2 in the absence of water, aldol acetate **11a** was found to be the dominant product (entry 5).

When the influence of the reaction temperature was investigated, optimal performance was found at −10 °C, leading to 76% of the desired bicyclo[3.3.0]octenone with 93% ee and 89 : 11 d.r. (entry 8).

With the optimized reaction conditions in hand, the scope of this method was examined next (Table 2). To this end, arenes incorporating various substituents were examined. Electron withdrawing groups (CF_3, CO_2Me, Cl, and F) were well tolerated, leading to the isolation of the corresponding pentalenes in high yields with high ee (**2a–2f**). *ortho*-Fluorinated arene **2g** showed some deleterious effects on chirality transfer. Strikingly, however, a d.r. of >20 : 1 was observed. A 3-naphthyl group was also compatible affording **2h** in 86% yield with 91% ee. Electron donating groups were found to be problematic.[14] However, the cyclization of protected aniline and phenol proceeded smoothly, furnishing the corresponding enones **2i** and **2j** in high yield with high ee. The observed diastereoselectivity may be explained by the consideration of a pair of possible transition states **TS1** and **TS2** (Table 2), in which the former suffers from destabilizing non-bonding interactions which are absent in the latter.

We next examined enyne aldehydes substituted with aliphatic groups. Enyne **1k** bearing a methyl substituent was found to be a suitable substrate, affording **2k** in 63% yield with 90% ee, albeit with poor diastereoselectivity. Nevertheless, introduction of a sterically more demanding isopropyl led to increased 90 : 10 d.r. (**2l**). A benzyloxy-substituted alkyl chain was tolerated to give **2m** in 72% yield with 95% ee. Pentalene **2n** including a benzoyl-protected alcohol is an intermediate of the total synthesis of (−)-merochlorin A (**7**)[11] and was obtained with excellent transfer of chirality (97% ee) from the acyclic starting material (98% ee).

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These findings considerably expand the utility of the procedure developed, as it allows for the synthesis of highly functionalized aliphatic bicyclo[3.3.0]octenones. The absolute configuration was determined by X-ray crystallographic analysis of **2e** and **2j**, which confirmed the mechanistic model established by Fensterbank and Malacria for **6** (Fig. 4, see ESI†).

A salient feature of this transformation is the formation of a quaternary center at a ring junction. Such substitution would otherwise be cumbersome to access *via* conventional synthetic approaches such as α-arylation or alkylation of this sterically hindered position.

To further demonstrate the utility of this method, we were curious to explore whether the aldehyde is able to undergo the aldol reaction when placed at a different position within the starting material. For this purpose, we synthesized enyne **12** (d.r. >20 : 1) using Enders' SAMP protocol (see the ESI†).[15] Remarkably, triquinane **13** was isolated as a single diastereomer in 60% yield when **12** was subjected to the standard reaction conditions (5 mol% **3**, 0.2 vol% H_2O, and THF) at room temperature (Fig. 5). Furthermore, propargylic enyne **14** (E/Z = 6 : 1) underwent smooth cyclization to give enone **15** (74%, with 78% ee) as a single diastereomer. The absolute configuration of **15** was determined by X-ray crystallographic analysis. Much to our delight, the Au(I)-catalyzed reaction cascade developed herein is thus useful for the synthesis of enantioenriched bicyclo[3.3.0]octane, spiro[4.4]nonane and tricyclo[6.3.0.0^{1,5}] undecane systems.

In 1974, Mukaiyama and co-workers reported the reaction of vinyl acetates with acetal- and carbonyl compounds in the presence of strong Lewis acids ($TiCl_4$, $SnCl_4$, and $BF_3 \cdot Et_2O$) to afford the corresponding aldol products in modest yield.[8] In light of this report, the described aldol reaction of a cyclopentadienyl acetate in the presence of the unarguably poor Lewis acidic Au(I)-catalyst is remarkable.[16,17] In principle, two different mechanistic pathways can be proposed (Fig. 6). Acetate **16**, formed after initial 1,3-acyloxy migration/Nazarov cyclization, may first be hydrolyzed under the employed

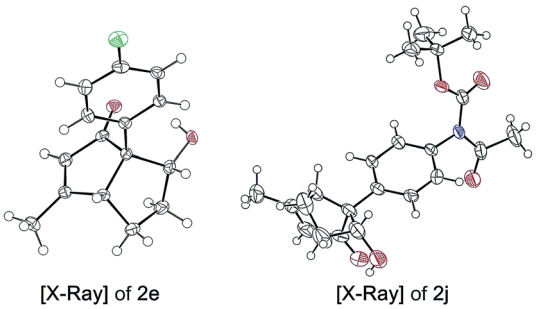
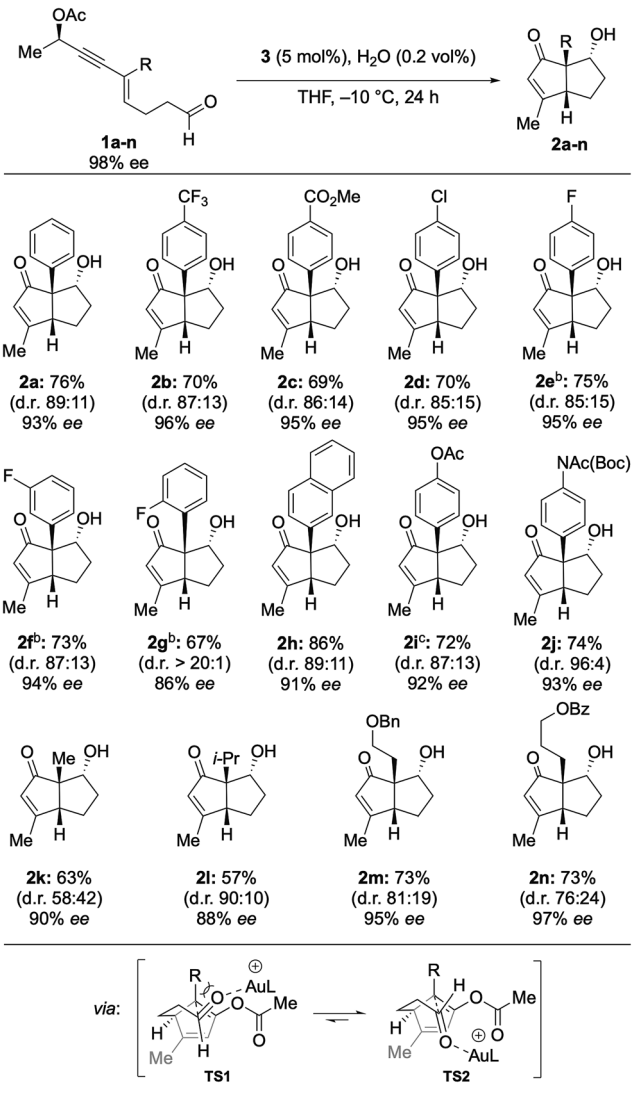


Fig. 4 Absolute configuration assigned by X-ray crystallographic analysis of (*R,R,R*)-**2e** and (*R,R,R*)-**2j**. For ORTEP representations the thermal ellipsoids are shown at 50% probability.

Table 2 Substrate scope of the stereoselective 1,3-acyloxy migration/Nazarov cyclization/aldol addition sequence[a]



[a] Reaction conditions: 5 mol% **3**, 0.2 vol% H_2O, THF (0.05 M), and −10 °C. Enantiomeric excess reported for the major diastereomer. [b] Reaction warmed to RT after 16 h. [c] Isolated yield over two steps from the primary alcohol.

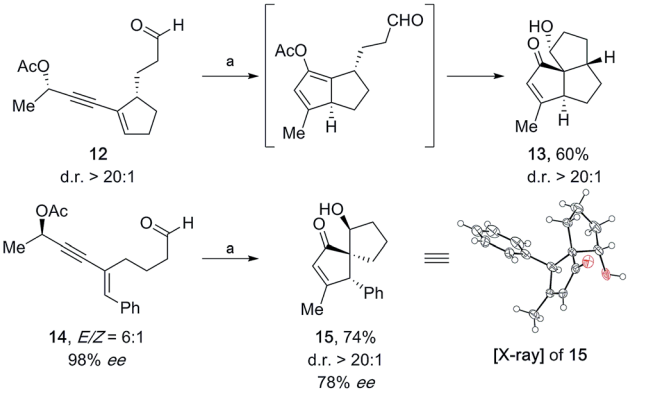


Fig. 5 Synthesis of tricyclo[6.3.0.0^{1,5}]undecane **13** and spiro[4.4]nonane **15**. Reagents and conditions: 5 mol% **3**, 0.2 v/v% H_2O, THF (0.05 M), RT, and 24 h. For ORTEP representations the thermal ellipsoids are shown at 50% probability.

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standard reaction conditions (Table 1, entry 8) to give cyclopentadienyl enolate **17**, which then undergoes an intramolecular aldol reaction to afford pentalene **1**. Importantly, while the initial hydrolysis may be mediated by the Au(I)-catalyst, this pathway fails to account for the formation of acetate **11**. Alternatively, the aldol reaction could proceed directly from the enol acetate to give **18**, which then could either undergo hydrolysis to produce enone **1** or suffer intramolecular acetate transfer to afford acetate **11**.

Optimization studies (Table 1) revealed that the Au(I)-catalyzed tandem 1,3-acyloxy migration/Nazarov cyclization/aldol reaction sequence occurs in the absence of water. In particular, if the reaction is conducted in dry solvents such as THF or CH_2Cl_2, acetate **11a** is isolated as the major product (Fig. 7A). Furthermore, isolated enol acetate **19** does not participate in intramolecular aldol reactions or hydrolysis under the standard reaction conditions in the absence of the Au(I)-catalyst (Fig. 7B). However, the treatment of **19** with 5 mol% Echavarren's catalyst (**3**) furnished the desired products **2a** and **11a** in high yield. In summary, these results suggest that the Au(I)-catalyst is involved in all three reaction steps and the terminal aldol reaction indeed proceeds directly from the enol acetate. Nevertheless, the possibility of a second operative pathway *via* initial hydrolysis of **19** in wet solvent in the presence of the Au(I)-catalyst cannot be entirely excluded.

In summary, we surmise that the water present under the standard reaction conditions primarily suppresses the acetate transfer *via* hydrolysis of oxocarbenium ion intermediate **18** (Fig. 6).

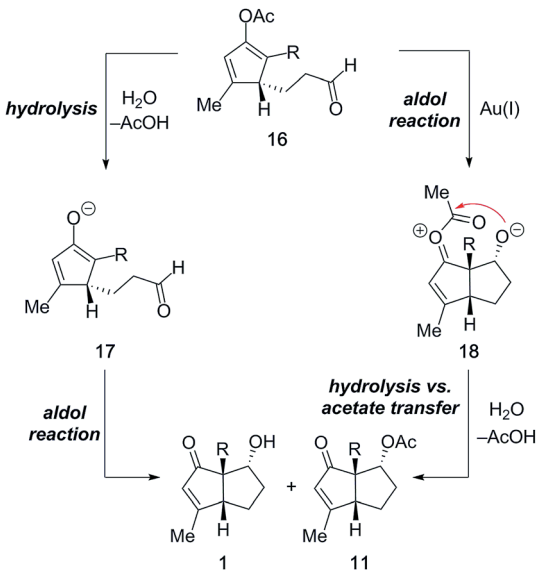

Fig. 6 Mechanistic options for the terminal aldol reaction.

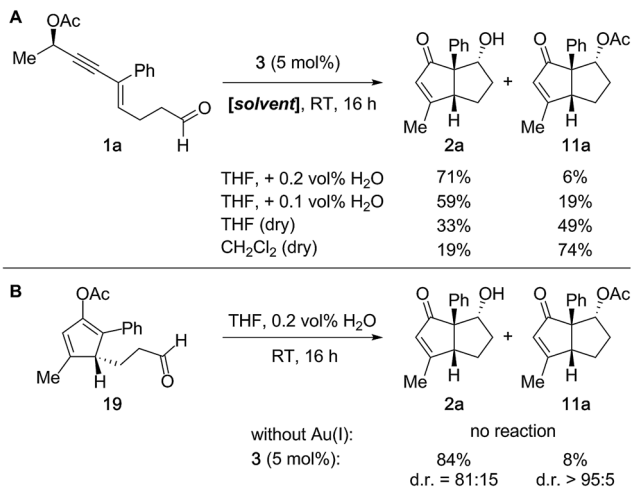

Fig. 7 Experiments to elucidate the mechanism of the terminal aldol reaction of cyclopentadienyl acetate **19**.

Conclusions

In conclusion, a Au(I)-catalyzed stereoselective tandem 1,3-acyloxy migration/Nazarov cyclization/aldol addition cascade has been developed. In a single step, this method allows for the generation of two rings bearing three contiguous stereocenters, one of them being quaternary. The bicyclo[3.3.0]octenones obtained are isolated in high yields and with high stereoselectivity. The ability of intermediate cyclopentadienyl acetates to undergo an intramolecular Au(I)-catalyzed aldol reaction constitutes a reactivity pattern with great potential to provide the foundation for new cascading sequences leading to highly functionalized building blocks. Studies to apply this method to complex systems and to include it in further total syntheses of natural products are currently ongoing in our laboratories and will be reported in due course.

Conflicts of interest

The authors declare no conflict of interest.

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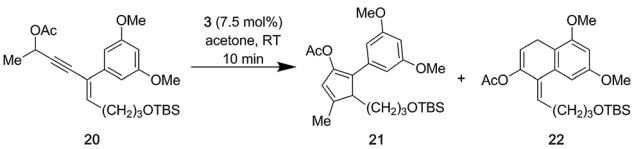

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