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# *p*-TsOH Promoted Au(I)-Catalyzed Consecutive Endo Cyclization of Yne-Tethered Ynamide: Access to Benzofused Dihydroisoquinolones

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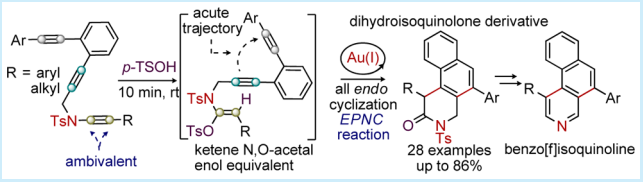
Supporting Information

**ABSTRACT:** A novel synthetic route to benzo[*f*]dihydroisoquinolone through a *p*-TsOH promoted cascade cyclization of easily accessible diyne-tethered ynamides in the presence of a Au(I)-catalyst is described. This reaction unveils a broad substrate scope, constructing a wide range of benzo[*f*]dihydroisoquinolones in good yields. The diyne-tethered ynamides are synthesized from inexpensive *o*-iodoaniline through Sonogashira couplings and the Cu-mediated C−N bond formation. The role of *p*-TsOH is examined, and the reaction pathway is also deduced. The benzo[*f*]isoquinoline scaffold is constructed from benzo[*f*]dihydroisoquinolones.




Isoquinoline derivatives are potentially useful building blocks widely found in natural products and pharmaceutically active compounds (Figure 1).[1] In general, the isoquinoline frameworks

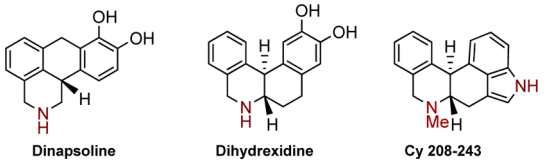
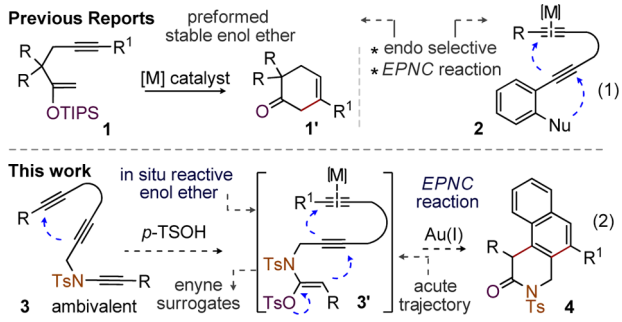



**Figure 1.** Isoquinoline derivatives containing natural products.

are readily manufactured from the dihydroisoquinolone motifs.[2] The benzo[*f*]isoquinolines, another class of fused N-heterocycles, structurally resemble the isoquinoline derivatives. Thus, the benzo[*f*]isoquinolines analogues, which can be easily accessed from benzo[*f*]dihydroisoquinolones, show interesting biological properties as do isoquinoline derivatives. With our current research interest in ynamides, we intend to investigate Au(I)-catalyzed cascade cyclization of diyne-tethered ynamide, which will eventually lead to the step-efficient synthesis of an unprecedented benzo[*f*]dihydroisoquinolone core (eq 2, Scheme 1).[3−5]

In general, the preformed alkyne-bearing enol-ethers **1** [alkyl/silyl enol ethers, and silyl ketene amides] are efficiently employed in Au-catalyzed cyclizations (Scheme 1).[6] In contrast, the intramolecular cyclization of an in situ generated vinyl-Au-species, formed through an *exo*/*endo*-cyclization of enol-ethers and a pendant alkyne moiety in **1**, with the tethered-yne motif, is less explored.[7] Likewise, cascade *electrophile promoted nucleophilic cyclization* (EPNC) of diyne-bearing species **2** directly constructs polyfused heterocycles in a single operation; these transformations explicitly involve 5-*endo*-dig/6-*endo*-dig cyclizations.[8] Despite this notable success, the cascade reaction of diyne-tethered ynamide is so far unprecedented (Scheme 1). We thus envisaged the formation of benzo[*f*]dihydroisoquinolone **4**

**Scheme 1. Ynamide As Enol Equivalent for Cascade Cyclization/1,5-Enyne Cycloisomerization Strategy**




through the cascade EPNC reaction of transient enol-ether **3′** (ketene *N*,*O*-acetal), readily generated involving the facile attack of *p*-TsOH to the ambivalent ynamide **3** in situ (eq 2, Scheme 1).[9] We could foresee a 6-*endo*-dig cyclization of **3′** with the suitably substituted yne motif in the presence of a Au(I)-catalyst to form a six-membered vinyl-gold intermediate, a perfect 1,5-enyne precursor, which subsequently undergoes cyclization followed by aromatization to result **4** (eq 2, Scheme 1).[10] We herein show a convergent synthetic manifestation engendering benzo[*f*]dihydroisoquinolones from easily accessible diyne-tethered ynamides through Au-catalysis in the presence of *p*-TsOH.

To directly access the benzo[*f*]dihydroisoquinolone skeleton, investigation was initiated to examining Brønsted acid promoted Au(I)-catalyzed consecutive *endo*-cyclizations of diyne-tethered ynamide **3a**. Accordingly, compound **3a** was synthesized from the inexpensive 2-iodoaniline involving consecutive Sonogashira reactions followed by C−N bond formation in four steps with overall appreciable yield.[11] The ynamide unit is usually

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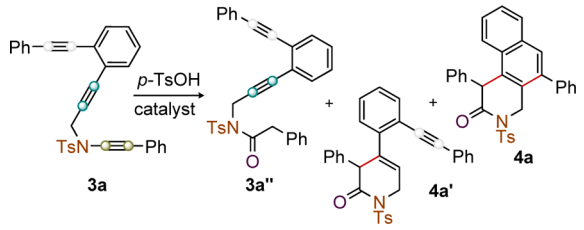
**Table 1. Optimization of the Reaction Conditions**[a]




| entry | catalyst (mol %)[b] | solvent | yield (%)[c] 3a″ | 4a′ | 4a |
|---|---|---|---|---|---|
| 1 | **A** (5) | $CH_3CN$ | – | | |
| 2 | **A** (5) | dioxane | 6 | 35 | 50 |
| 3 | **A** (5) | dioxane | 80 | – | – |
| 4 | **B** (5) | dioxane | 45 | 20 | 20 |
| 5 | **C** (5) | dioxane | 10 | 35 | 40 |
| 6 | **D** (5) | dioxane | – | 40 | 48 |
| 7 | **E** (5) | dioxane | 79 | 5 | – |
| 8 | **F** (5) | dioxane | 82 | – | – |
| 9 | **A** (5) | DCE | trace | – | – |
| 10 | **A** (5) | dioxane/DCE | 0 | 25 | 62 |
| **11**[d] | **A (5)** | **dioxane/DCE** | **0** | **5** | **83** |
| 12[d] | **B** (5) | dioxane/DCE | – | 30 | 60 |
| 13[d] | **D** (5) | dioxane/DCE | – | 30 | 50 |
| 14 | **G** (5) | dioxane/DCE | 85 | – | – |
| 15 | **H** (5) | dioxane/DCE | 82 | – | – |

[a]Reactions were carried out using **3a** (0.2 mmol), *p*-TsOH (0.3 mmol), and catalyst (5.0 mol %) in solvent (3.0 mL) at rt−80 °C for 24 h. [b]Catalyst **A**: JohnphosAu(I) (NCMe)]$^+SbF_6^-$; **B**: JohnphosAuNTf$_2$; **C**: JohnphosAuCl + AgSbF$_6$; **D**: IPrAuCl + AgSbF$_6$; **E**: $Ph_3PAuCl$ + AgSbF$_6$; **F**: $Ph_3PAuCl$ + AgNTf$_2$; **G**: AgSbF$_6$; **H**: AgNTf$_2$. [c]Isolated yields. [d]Reaction was conducted by stirring **3a** and *p*-TsOH in dioxane for 10 min followed by addition of catalyst in DCE and continued for 4 h at rt, and finally heating the resulting mixture for 20 h at 80 °C.

responsive to acid catalysts and $H_2O$; we could thus anticipate the formation of amide **3a″**, dihydropyridinone **4a′**, and the desired **4a** from **3a** (Table 1).

To validate workable conditions for the construction of **4a**, an investigation was initiated exposing **3a** to *p*-TsOH (1.5 equiv) in the presence of Echavarren's catalyst A (5.0 mol %) in $CH_3CN$ at room temperature (rt); to our dismay, **3a** did not survive, providing a complex mixture (entry 1). Gratifyingly, **4a** (50%) was isolated along with **3a″** (6%) and **4a′** (35%), when the reaction was performed in dioxane at rt (entry 2); in contrast, reaction at 80 °C exclusively delivered **3a″** (entry 3). The use of JohnphosAuNTf$_2$ led to a poor amount of **4a** (entry 4). The use of a combination of catalysts (JohnphosAuCl/IPrAuCl with AgSbF$_6$ and $Ph_3PAuCl$ and AgSbF$_6$/AgNTf$_2$) was inferior (entries 5−8). Catalyst **A** thus appeared to be the best (entry 2). The effect of solvents was next surveyed. The reaction of **3a** with catalyst **A** and *p*-TsOH in $ClCH_2CH_2Cl$ (DCE) provided a trace amount of **3a″** with incomplete consumption of **3a** at 80 °C (entry 9); the inadequate solubility of *p*-TsOH in DCE is presumably responsible for the poor outcome. Results from entries 2 and 9 thus inspired us to scrutinize the mixture of solvents for this study. Interestingly, the reaction in dioxane and DCE (1:2) resulted in a 62% yield of **4a**, **4a′** (25%), and **3a″** (0%) at rt (entry 10). Due to this observation, the reaction was pursued by performing it at various temperatures through sequential addition of reagents.[11] Complete consumption of **3a** surprisingly occurred, when **3a** and *p*-TsOH were stirred in dioxane at rt for 10 min; subsequently, catalyst **A** in DCE was introduced and the reaction was continued at rt until the disappearance of the intermediate species; finally, heating the resulting mixture at 80 °C for 20 h led to **4a** in 83% yield (entry 11). Under the identical conditions in entry 11, other catalysts turned moderate (entries 12 and 13). Regrettably, reaction under Ag-catalysis exclusively provided **3a″** (entries 14 and 15).

We next set out to examine the scope of Au-catalyzed cascade cyclization of diyne-tethered ynamides **3** for the construction of benzo[*f*]dihydroisoquinolone skeletons **4** and **5** (Figures 2 and 3). First, ynamide **3** having a variation of substitutions on the aryl moiety on the alkyne terminus was surveyed under the catalytic conditions shown in entry 11, Table 1 (Figure 2). The ynamide **3a** produced **4a** in 83% yield. Interestingly, cascade cyclization of ynamides **3b** and **3c** (*o*-substitution on the aryl group) provided a 1:1 mixture of two atropisomers of the corresponding **4b** and **4c**

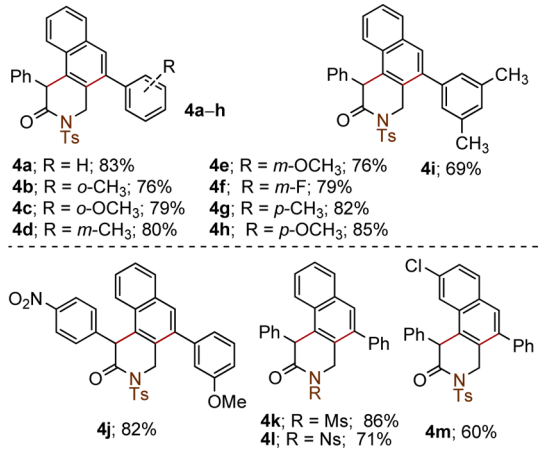



**Figure 2.** Substrate Scope **I**. Reactions were carried out using **3** (0.2 mmol), *p*-TsOH (0.3 mmol), catalyst **A** (5.0 mol %) in dioxane/DCE (1:2, 3.0 mL) at rt−80 °C for 24 h. Isolated yields.

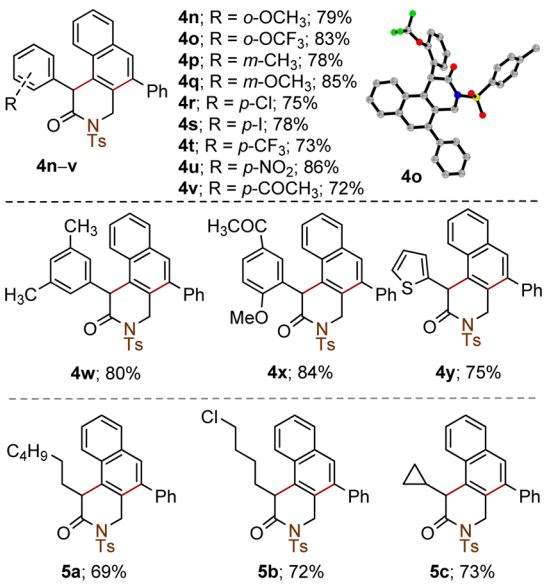



**Figure 3.** Substrate Scope **II**. Reactions were carried out using **3** (0.2 mmol), *p*-TsOH (0.3 mmol), catalyst **A** (5.0 mol %) in dioxane/DCE (1:2, 3.0 mL) at rt−80 °C for 24 h. Isolated yields.



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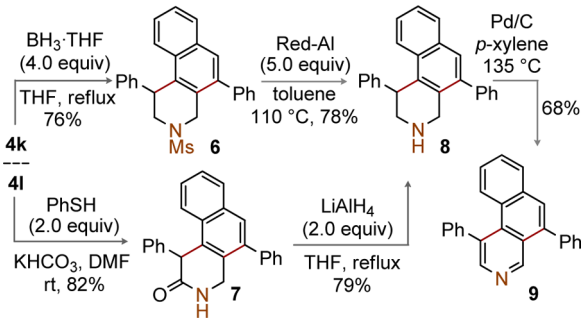
in good yields. The *m*- and *p*-substitution on the aryl moiety in the alkyne terminus did not affect the reaction outcome affording **4d**–**f** (76–80%), **4g** (82%), **4h** (85%), and **4i** (69%). Ynamide **3j** [different aryl moiety on alkyne and ynamide terminus] smoothly underwent cascade cyclization to yield 82% of **4j**. The N-Ms/-Ns protecting groups were tolerated providing the desired **4k** and **4l** in good yields. Similarly, **4m** was constructed in 60% yield.

Next, the effect of substitutions on the ynamide terminus in **3** was examined for the Au-catalyzed cascade cyclization (Figure 3). The substitutions at the *o*-, *m*-, or *p*- position on the aryl moiety at the ynamide terminus in **3** did not show a pronounced effect, constructing the respective **4n**–**v** in good yields. The structure of **4o** was further confirmed by X-ray crystallographic analysis (Figure 3).[11] The modifiable functional groups $-NO_2$ and $-COCH_3$ were inert under the optimized conditions; the $-CF_3$, Cl, and I moieties did not show an adverse effect and were tolerated. Likewise, the benzo[*f*]dihydroisoquinolones **4w** (80%) and **4x** (84%) were readily accessed from **3w** and **3x** holding two-methyl or OMe and COMe substituents on the aryl moiety at the ynamide terminus. Gatifyingly, the thiophenyl bearing ynamide **3y** effectively underwent cyclization to provide **4y** in 75% yield. The effect of the aliphatic substituent at the ynamide terminus in **3** was next surveyed (Figure 3). Pleasingly, the alkyl moiety containing ynamides under the optimized conditions delivered the nonseparable mixture of rotamer of the designed products **5a**/**5a′** = 5:1 and **5b**/**5b′** = 7:1 in 69% and 72% yield, respectively.[11] The cyclopropyl group on the ynamide survived in the reaction, generating the mixture of rotamers **5c** and **5c′** = 4:1 in 73% yield.[11] Thus, the current method developed for benzo[*f*]dihydroisoquinolones synthesis from diyne-tethered ynamides proved to be general and broad (Figures 2 and 3).

We next explored the makeover of benzo[*f*]dihydroisoquinolone to benzo[*f*]isoquinoline. The $B_2H_6$ mediated amide reduction of **4k** followed by N-Ms deprotection of **6** with Red-Al furnished 1,5-diphenyl-1,2,3,4-tetrahydrobenzo[*f*]-isoquinoline **8** (Scheme 2). The reductive cleavage of the N-Ns

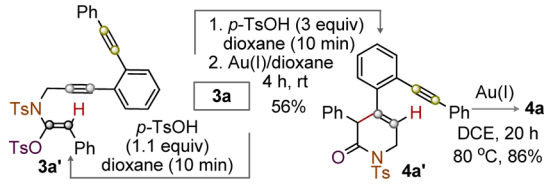
**Scheme 2. Synthesis of Benzo[*f*]isoquinoline Derivative**




moiety of **4l** provided **7**; subsequently $LiAlH_4$ reduction of the amide moiety of **7** directly led to **8** (Scheme 2). Finally, oxidative dehydrogenation of **8** with Pd/C delivered 1,5-diphenylbenzo-[*f*]isoquinoline **9** in 68% yield (Scheme 2).[11]

The participation of transient ketene *N,O*-acetal **3a′** (outlined in eq 2, Scheme 1) for the synthesis of **4** from **3** under the Au(I)-catalyzed cascade cyclization is established with the characterization of **3a′** (NMR and HRMS study), which is rapidly obtained in situ from **3a** and *p*-TsOH in dioxane at rt in 10 min (Scheme 3). Furthermore, the isolation of monocyclic species

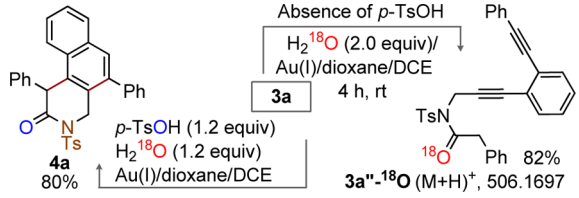
**Scheme 3. Control Experiment**




**4a′** confirms the participation of the Au-vinyl complex (Scheme 3), when the reaction was performed with the Au-catalyst and *p*-TsOH (3.0 equiv) in dioxane for 4 h at rt. Subsequently, heating **4a′** with a Au-catalyst in DCE at 80 °C delivered **4a** (Scheme 3).[9a,b]

To further support the involvement of **3a′** and the source of oxygen in this transformation, the reaction of **3a** with a Au-catalyst in $H_2{}^{18}O$ (in the absence of *p*-TsOH) was conducted. The amide product **3a″-$^{18}$O** with the insertion of $^{18}O$ has exclusively been obtained (HRMS, Scheme 4).[11] While the

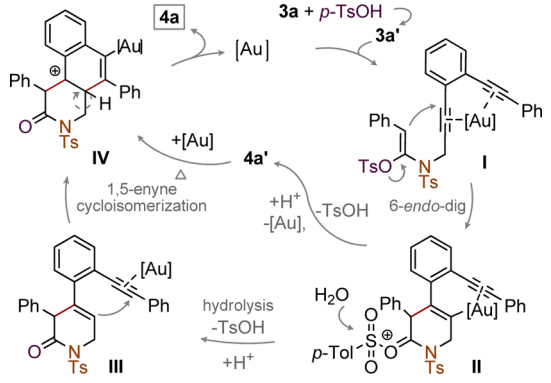
**Scheme 4. Isotopic Labeling Experiment**




reaction of **3a** with *p*-TsOH in $H_2{}^{18}O$ under Au-catalysis delivered **4a** (80%); the incorporation of $^{18}O$ is not observed (HRMS, Scheme 4).[11] It appears that the attack of *p*-TsOH to **3a** is facile over $H_2O$, resulting in the rapid formation of enol-ether **3a′** (Scheme 3).

On the basis of the studies shown in Schemes 3 and 4, the probable mechanistic path for the synthesis of **4** from **3** is deduced (Scheme 5).[5e] The reaction initiates with the formation

**Scheme 5. Plausible Mechanistic Cycle**




of ketene *N,O*-acetal **3a′**, which is realized through the attack of *p*-TsOH to the keteniminium intermediate of ynamide **3a**. Although both alkyne motifs undergo activation by a Au-catalyst, the stereoelectronic effect on ketene N,O-acetal **I** favors 6-*endo*-dig cyclization with the proximal Au(I) activated alkyne unit to afford monocyclic vinyl–Au species **II**.[7] The intermediate **II** undergoes hydrolysis to result **III** and simultaneously proceeds in the intramolecular cyclization of the ene moiety with the Au-activated alkyne species to attain **IV**. Finally, aromatization and



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protodeauration of **IV** affords the benzo[*f*]dihydroisoquinolone **4a** releasing the Au-complex for the next cycle. On the other hand, the formation of **4a′**, a 1,5-enyne surrogate, is possible with the removal of TsOH through the attack of $H_2O$ on **II** and protodeauration, as evident in Scheme 3.[5h,10] At elevated temperature, **4a′** undergoes 6-*endo* cyclization to generate **IV** under Au-catalysis.[10]

In summary, a novel synthetic route to benzo[*f*]dihydroisoquinolone through the *p*-TsOH promoted cascade cyclization of the easily accessible diyne-tethered ynamides in the presence of a Au(I) catalyst was demonstrated. The reaction exhibited broad scope and tolerated common functional groups. Benzo[*f*]isoquinoline was realized through the peripheral modifications of benzo[*f*]dihydroisoquinolone. The reaction pathway was deduced based on the detailed studies of intermediates. Application of this method for the construction of a structurally complex framework is currently being pursued.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02946.

Experimental procedures (PDF)
Compound characterization data (PDF)
Crystallographic data for **4o** (CIF)

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### Notes

The authors declare no competing financial interest.

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(11) See the Supporting Information.


## ■ NOTE ADDED AFTER ASAP PUBLICATION

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