

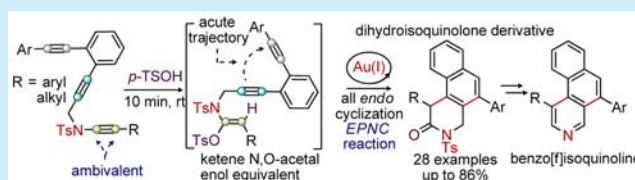
# *p*-TsOH Promoted Au(I)-Catalyzed Consecutive Endo Cyclization of Yne-Tethered Ynamide: Access to Benzofused Dihydroisoquinolones

Sanatan Nayak, Nayan Ghosh, B. Prabagar, and Akhila K. Sahoo\*

School of Chemistry, University of Hyderabad, Hyderabad-500046, India

**S** 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).<sup>1</sup> In general, the isoquinoline frameworks

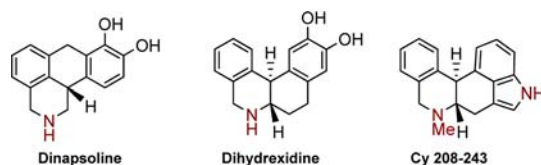
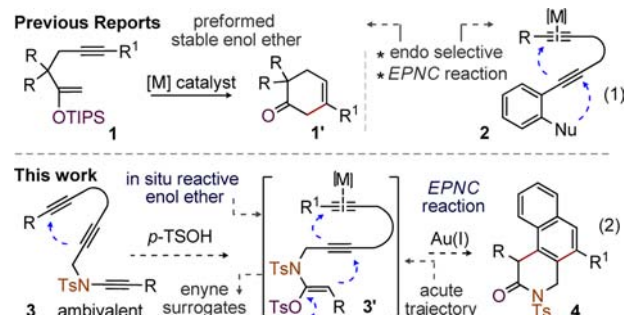


Figure 1. Isoquinoline derivatives containing natural products.

are readily manufactured from the dihydroisoquinolone motifs.<sup>2</sup> The benzo[*f*]isoquinolones, another class of fused N-heterocycles, structurally resemble the isoquinoline derivatives. Thus, the benzo[*f*]isoquinolones 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).<sup>3–5</sup>

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).<sup>6</sup> 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.<sup>7</sup> 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.<sup>8</sup> 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

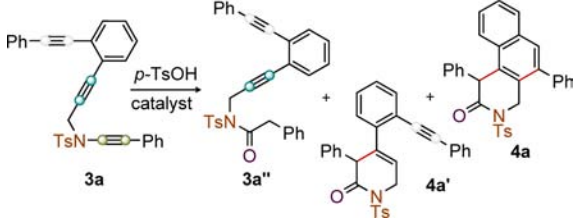


through the cascade EPNC reaction of transient enol-ether **3'** (ketene *N,O*-acetal), readily generated involving the facile attack of *p*-TsOH to the ambivalent ynamide **3** in situ (eq 2, Scheme 1).<sup>9</sup> We could foresee a *6-endo-dig* cyclization of **3'** with the suitably substituted yne 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).<sup>10</sup> 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 examine 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.<sup>11</sup> The ynamide unit is usually

Received: October 12, 2015

Published: November 2, 2015

Table 1. Optimization of the Reaction Conditions<sup>a</sup>


entry	catalyst (mol %) <sup>b</sup>	solvent	yield (%) <sup>c</sup>		
			3a''	4a'	4a
1	A (5)	CH <sub>3</sub> CN	–	–	–
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 <sup>d</sup>	A (5)	dioxane/DCE	0	5	83
12 <sup>d</sup>	B (5)	dioxane/DCE	–	30	60
13 <sup>d</sup>	D (5)	dioxane/DCE	–	30	50
14	G (5)	dioxane/DCE	85	–	–
15	H (5)	dioxane/DCE	82	–	–

<sup>a</sup>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. <sup>b</sup>Catalyst A: JohnphosAu(I) (NCMe)<sup>+</sup>SbF<sub>6</sub><sup>–</sup>; B: JohnphosAuNTf<sub>2</sub>; C: JohnphosAuCl + AgSbF<sub>6</sub>; D: IPrAuCl + AgSbF<sub>6</sub>; E: Ph<sub>3</sub>PAuCl + AgSbF<sub>6</sub>; F: Ph<sub>3</sub>PAuCl + AgNTf<sub>2</sub>; G: AgSbF<sub>6</sub>; H: AgNTf<sub>2</sub>. <sup>c</sup>Isolated yields. <sup>d</sup>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<sub>2</sub>O; 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<sub>3</sub>CN 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<sub>2</sub> led to a poor amount of **4a** (entry 4). The use of a combination of catalysts (JohnphosAuCl/IPrAuCl with AgSbF<sub>6</sub> and Ph<sub>3</sub>PAuCl and AgSbF<sub>6</sub>/AgNTf<sub>2</sub>) 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<sub>2</sub>CH<sub>2</sub>Cl (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.<sup>11</sup> 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

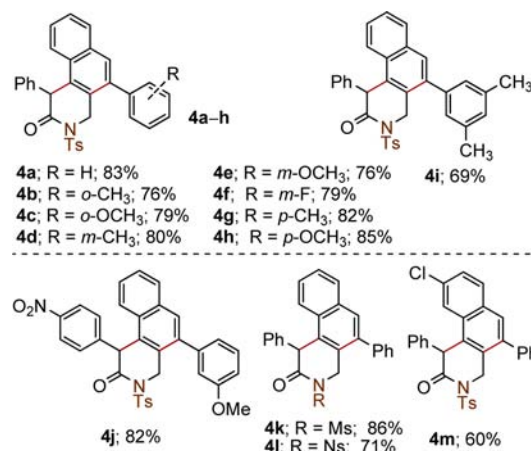


Figure 2. Substrate Scope I. Reactions were carried out using **3** (0.2 mmol), *p*-TsOH (0.3 mmol), catalyst A (5.0 mol %) in dioxane/DCE (1:2, 3.0 mL) at rt–80 °C for 24 h. Isolated yields.

**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**

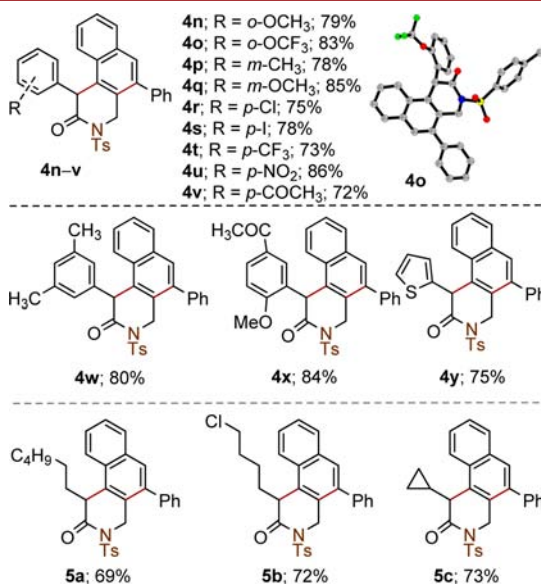


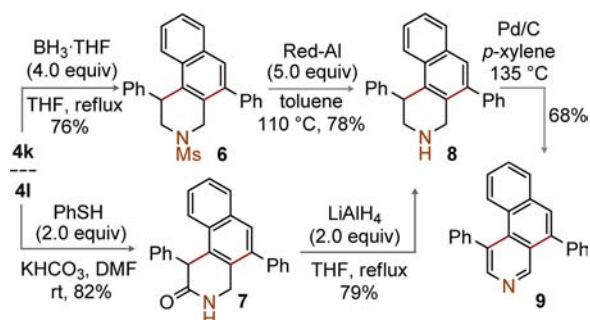
Figure 3. Substrate Scope II. Reactions were carried out using **3** (0.2 mmol), *p*-TsOH (0.3 mmol), catalyst A (5.0 mol %) in dioxane/DCE (1:2, 3.0 mL) at rt–80 °C for 24 h. Isolated yields.

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 (Scheme 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).<sup>11</sup> The modifiable functional groups –NO<sub>2</sub> and –COCH<sub>3</sub> were inert under the optimized conditions; the –CF<sub>3</sub>, 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. Gatingly, 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.<sup>11</sup> The cyclopropyl group on the ynamide survived in the reaction, generating the mixture of rotamers **5c** and **5c'** = 4:1 in 73% yield.<sup>11</sup> 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<sub>2</sub>H<sub>6</sub> 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

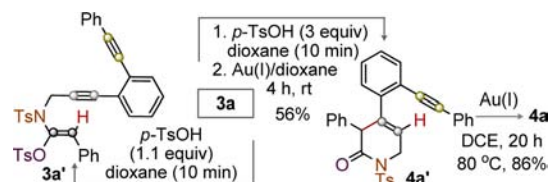
### Scheme 2. Synthesis of Benzo[*f*]isoquinoline Derivative



moiety of **4l** provided **7**; subsequently LiAlH<sub>4</sub> 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).<sup>11</sup>

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

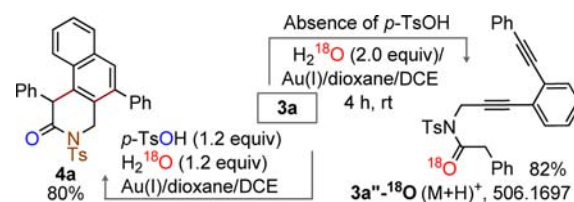
### Scheme 3. Control Experiment



**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).<sup>9a,b</sup>

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<sub>2</sub><sup>18</sup>O (in the absence of *p*-TsOH) was conducted. The amide product **3a''**-<sup>18</sup>O with the insertion of <sup>18</sup>O has exclusively been obtained (HRMS, Scheme 4).<sup>11</sup> While the

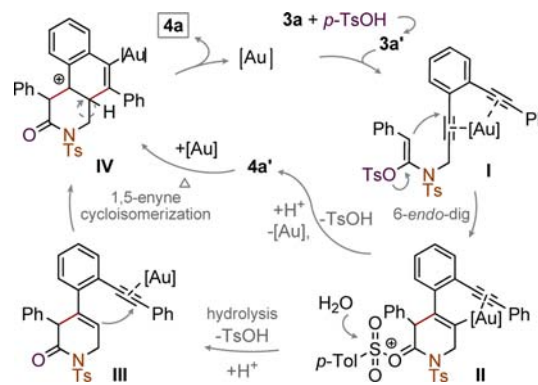
### Scheme 4. Isotopic Labeling Experiment



reaction of **3a** with *p*-TsOH in H<sub>2</sub><sup>18</sup>O under Au-catalysis delivered **4a** (80%); the incorporation of <sup>18</sup>O is not observed (HRMS, Scheme 4).<sup>11</sup> It appears that the attack of *p*-TsOH to **3a** is facile over H<sub>2</sub>O, 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).<sup>5c</sup> 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**.<sup>7</sup> 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



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<sub>2</sub>O on II and protodeauration, as evident in Scheme 3.<sup>5h,10</sup> At elevated temperature, 4a' undergoes 6-*endo* cyclization to generate IV under Au-catalysis.<sup>10</sup>

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)

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: akhilchemistry12@gmail.com; akssc@uohyd.ac.in.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This manuscript is dedicated to Prof. D. Basavaiah, School of Chemistry, University of Hyderabad for the development of the Baylis–Hillman–Basavaiah (BHB) reaction and for his 65th birthday. S.N, N.G., and P.B. thank CSIR, India for a fellowship. Mr. Krishna Chari, UoH is thanked for the X-ray crystallographic analysis.

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(11) See the Supporting Information.

## ■ NOTE ADDED AFTER ASAP PUBLICATION

Scheme 4 was corrected on November 3, 2015.