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Gold-Catalyzed Tandem Annulations of Pyridylhomopropargylic Alcohols with Propargyl Alcohols

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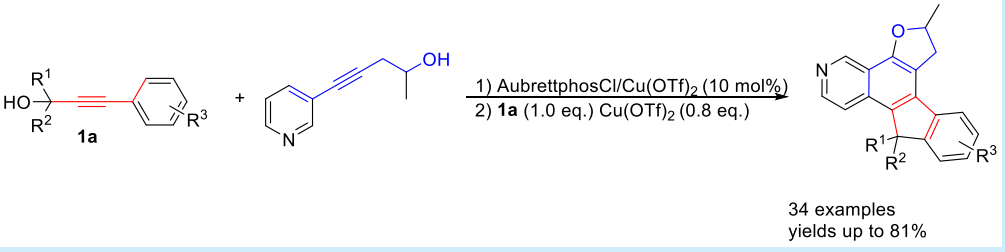

ABSTRACT: A gold-catalyzed tandem annulation of propargylic alcohols and pyridylhomopropargylic alcohols is achieved, providing an atom-economical approach to a diverse set of polycyclic dihydrobenzofurans in good yields. The reaction proceeds via the 5-*endo-dig* cyclization/Meyer−Schuster rearrangement/Friedel−Crafts-type pathway. In this way, three C−C bonds and one C−O bond form to give a polycyclic skeleton in a one-pot process. Moreover, the products exhibit unique optical properties, which reveal their potential application value.

Homogeneous gold catalysis is an effective method to synthesize various complex molecules based on the selective activation of C−C multiple bonds in the presence of hetero- and carbonucleophiles.[1] In particular, gold-catalyzed tandem cyclization is successfully utilized in the synthesis of diverse polycyclic architectures. Pioneering works were reported by the Hashmi,[2] Toste,[3] and Zhang[4] groups. In 2014, gold-catalyzed tandem cycloisomerization was demonstrated by Ye's group in the synthesis of functionalized indole derivatives, whereby a single metal center served a dual-catalytic role in two different catalytic cycles, which provided a new type of concurrent tandem catalysis.[5] There are several challenging tasks in this field that need to be overcome, such as matching the rates of each catalytic cycle and the compatibility of the catalyst with substrates and intermediates.[6] As part of our interest in this type of transformation and propargyl alcohol chemistry, we envisioned that the combination of gold and copper catalysis to synthesize polycyclic skeleton compounds from propargyl alcohol could be possible.

It is well known that the polycyclic dihydrobenzofuran skeletons exist in a wide range of pharmacologically relevant natural products and biologically active molecules, such as cystibenetrimerol A, melapinol B, and carasiphenol C (Figure 1).[7] Therefore, great endeavors have been devoted to building polycyclic dihydrobenzofuran skeletons.[8] In 2014, Lu and coworkers reported a intramolecular nucleophilic addition between the carbon−palladium bond and cyanogen initiated by the nucleopalladation of alkynes.[9] Subsequently, the Liu group described an endo-cycloisomerization/C−H activation

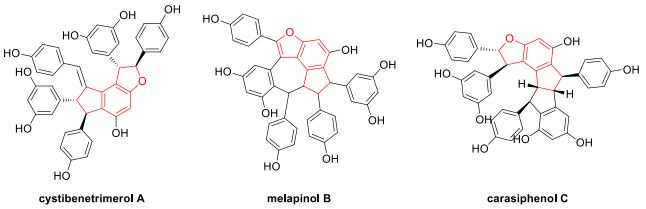

Figure 1. Representative bioactive molecules.

cascade reaction leading to the practical synthesis of 2,3-dihydronaphtho[1,2-*b*]furans.[10] There are also some other types of transformations that collaborate with the intramolecular cycloisomerization of alkynols to build tricyclic compounds, such as the Povarov reaction[11] and Prins-type cyclization.[12] However, a cascade reaction of alkynols that constructs polycyclic compounds with tetracyclic or pentacyclic skeletons has rarely been explored.[13] Therefore, the development of a novel protocol for their preparation is highly desirable. Herein we report an efficient synthesis of dihydrobenzofuran-alkaloid-type polycycles from 3-(4,5-dihy-

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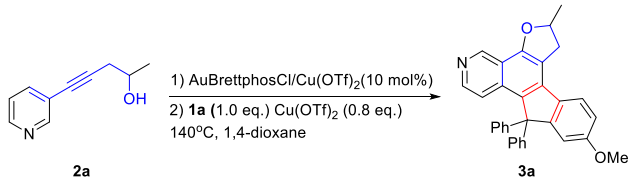
drofuran-2-yl)pyridine and propargyl alcohol through a tandem 5-*endo-dig* cyclization/Meyer−Schuster rearrangement/Friedel−Crafts reaction sequence.

We initiated our study by using propargyl alcohol **1a** and 5-(pyridin-3-yl)pent-4-yn-2-ol **2a** as the model substrates to optimize the reaction conditions. After screening a range of reaction conditions, we isolated the desired polycyclic dihydrobenzofuran derivative **3a** in 76% yield using the catalysts BrettphosAuCl/$Cu(OTf)_2$ (10 mol %) in the first step and the oxidant $Cu(OTf)_2$ (0.8 equiv) in the second step (Table 1, entry 1). When the reaction proceeded in one step

Table 1. Optimization of the Reactions Conditions[a]



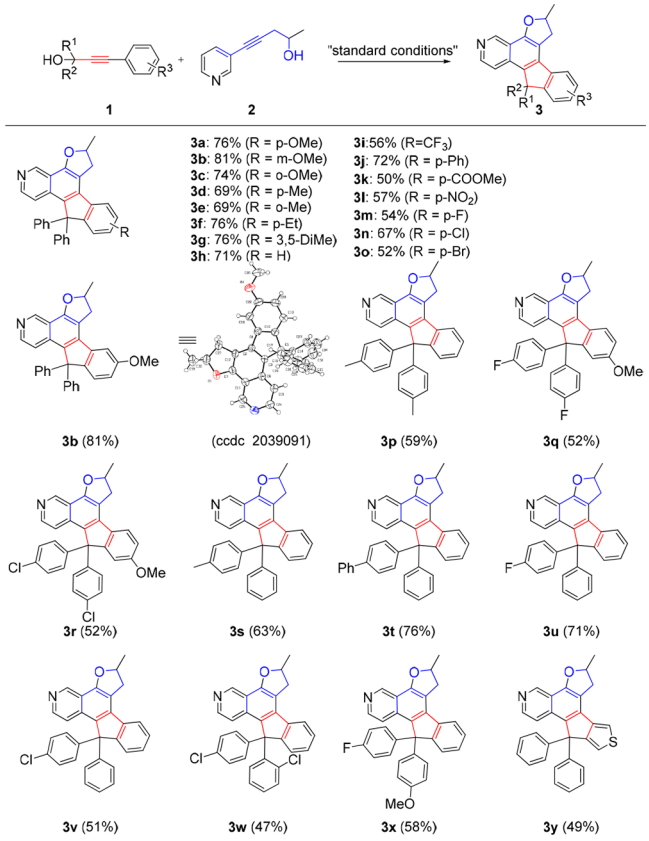
entry	variations from reaction conditions	yield (%)[b]
1		76
2	only $Cu(OTf)_2$ used	10
3	only $Sc(OTf)_3$ used	27
4	only AgOTf used	38
5	only AuBrettPhosCl used	14
6	AuBrettPhosCl/AgOTf (10 mol %) used	58
7	AuBrettPhosCl/$AgNTf_2$ (10 mol %) used	51
8	AuBrettPhosCl/$AgSbF_6$ (10 mol %) used	40
9	$Au(PPh)_3Cl$ instead of AuBrettphosCl	46
10	AuJohnPhosCl instead of AuBrettphosCl	45
11	$Au(PPh)_3NTf_2$ instead of AuBrettphosCl	53
12	AuXPhosNTf$_2$ instead of AuBrettphosCl	36
13	PhCl instead of 1,4-dioxane	41
14	$PhCH_3$ instead of 1,4-dioxane	64
15	100 °C instead of 140 °C	32
16	120 °C instead of 140 °C	42
17	Ar instead of air	74

[a]Reaction conditions: A mixture of alkynol **2a** (0.15 mmol, 1.5 equiv) and catalyst (10 mol %) was added to 1,4-dioxane (0.1 M) at 140 °C under an air atmosphere. After 7 h, propargyl alcohol **2a** (0.1 mmol, 1.0 equiv) and $Cu(OTf)_2$(0.8 equiv) were added, and the reaction mixture was stirred at the reported temperature for another 12 h. [b]Isolated yields.

under Lewis acid $Cu(OTf)_2$, $Sc(OTf)_3$, AgOTf, and BrettphosAuCl catalysts, the desired product was afforded in low yields (entries 2−5). Afterward, several representative Ag catalysts were employed in this system instead of $Cu(OTf)_2$, and the desired products were obtained in 40−58% yields (entries 6−8). Following this approach, several gold catalysts with different steric characteristics and electronic were also tested, but they were all inferior to AuBrettphosCl (entries 9−12). The influence of solvents on the reaction was then investigated, but other solvents led to no improvement (entries 13 and 14). Moreover, decreasing the temperature resulted in a significant drop in yield (entries 15 and 16). Finally, replacing air with argon had almost no effect on the yield of the reaction (entry 17), which indicated that $Cu(OTf)_2$ may play a major role in the oxidation process of the reaction.

With the optimized reaction conditions, the applicability of the tandem cycloaddition reaction was explored by employing 5-(pyridin-3-yl)pent-4-yn-2-ol with various propargylic alcohols. As illustrated in Scheme 1, electron-donating groups of methoxyl and methyl on different positions of the aromatic

Scheme 1. Substrate Scope of Tertiary Propargylic Alcohols[a]



[a]Unless otherwise specified, all reactions were performed on a 0.1 mmol scale under the standard conditions. Isolated yields.

ring (R^3) afforded the desired products (**3a−3e**) in moderate to high yields ranging from 69 to 81%. The structure of **3b** was identified by X-ray crystal structure analysis. (See the Supporting Information.) Propargylic alcohols substituted with other electron-donating groups (Et, 3, 5-*di*Me, **1f**, **1g**) and electron-withdrawing groups (CF_3, Ph, COOMe, NO_2, halogen, **1h−1o**) at the para positions of the benzene ring were tested, and the cyclization products **3h−3o** were obtained in moderate to good yields. The reaction also proceeded well with symmetrical propargylic alcohols with different electronic natures (Me, F, Cl, **1p**, **1q**, **1r**,) on the aromatic rings of R^1 and R^2. Unsymmetrical propargylic alcohol substrates (**1s−1x**) containing either electron-donating (Me, OMe) or -withdrawing (Ph, F, Cl) groups on the phenyl rings (R^1, R^2) did not affect the reaction (**3s−3x**). To our delight, the sensitive substituent thiophene (**1y**) was well tolerated in this transformation in 49% yield.

Subsequently, pyridylhomopropargylic alcohols **2** bearing electron-donating (Me) or electron-withdrawing groups (F and Cl) on the heterocyclic (R^2) generated the expected products **3z−3ac** in 14−22% yields, as illustrated in Scheme 2. Compounds **2** bearing parent pyridine (Scheme 1) are much better than those bearing functionalized pyridine (**3z−3ac**) due to the substituents on pyridine (**2z−2ac**) that reduced the electrophilicity of the four-position of pyridine and suppressed

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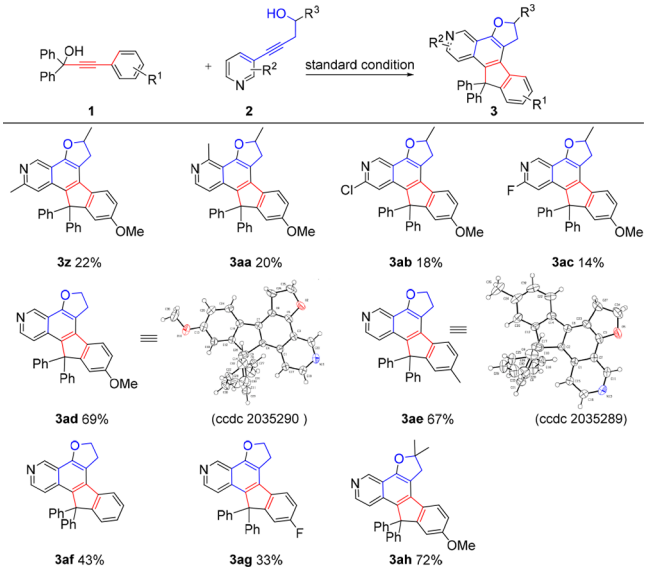
Scheme 2. Substrate Scope of Pyridylhomopropargylic Alcohols[a]



[a]Unless otherwise noted, all reactions were performed under standard conditions. Isolated yields.

the intramolecular nucleophilic addition. Tertiary and primary homopropargylic alcohols (**1ad**−**1ah**) also proceeded well, giving the annulation products **3ad** and **3ah** in 33−72% yields. The structures of **3ad** and **3ae** were confirmed by X-ray crystallographic analysis. (See the Supporting Information.)

After diverse dihydrobenzofuran molecules were obtained, we turned our interest to the photophysical properties of synthesized dihydrobenzofurans **3**. As we all know, most of the conjugated frameworks are fluorescent at low concentrations. Fluorescence will weaken or even cease in solid or aggregated states due to the aggregation-caused quenching (ACQ) effect. To our delight, when we concentrated on the fluorescence properties of dihydrobenzofurans **3**, we found that most of the solid products **3** showed bright blue-green light emissions (Table 2, Figures 2 and 3). Surprisingly, the crystal sample **3b** exhibited green luminescence centered at 501 nm, and after grinding in a mortar, the luminescence presented a blue-shift emission toward 469 nm and intensification of luminescence. These properties of mechanochromic fluorescence may

Table 2. Photophysical Properties of Compounds of 3

entry	compound	λ_{max} (nm)	λ_{em} (nm)	Φ_F (%)
1	**3b** (crystal)	294	501	7.01
2	**3b** (powder)	332	469	5.14
3	**3c**	334	494	2.68
4	**3d**	343	495	2.68
5	**3h**	351	487	5.22
6	**3j**	333	502	10.45
8	**3n**	344	489	3.25
9	**3o**	342	479	2.01
10	**3p**	338	488	2.65
11	**3q**	346	501	1.89
12	**3s**	338	487	3.42
13	**3t**	306	522	1.79
14	**3y**	352	478	3.15

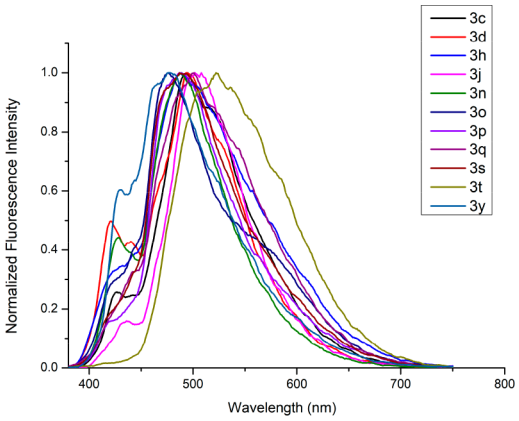


Figure 2. Fluorescence spectra of compounds **3**.

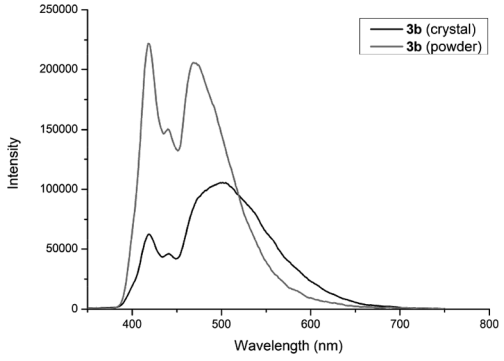
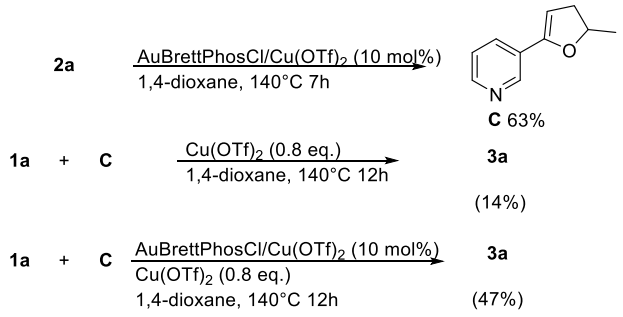


Figure 3. Fluorescence spectra of compound **3b** crystal and powder.

indicate a promising perspective on their practicality in optoelectronic devices.

To gain insight into the reaction mechanism, some control experiments were carried out (Scheme 3). In the reaction of 5-

Scheme 3. Mechanistic Study



(pyridin-3-yl)pent-4-yn-2-ols (**2a**) with BrettphosAuCl/Cu(OTf)$_2$ (10 mol %) in 1,4-dioxane, the 5-*endo-dig* cycloisomerization product 3-(5-methyl-4,5-dihydrofuran-2-yl)-pyridine **C** was isolated in 63% yield. When **C** and **1a** were allowed to conduct with Cu(OTf)$_2$ (0.8 equiv), the product **3a** was obtained in 14% yield. When **C** and **1a** proceeded under the standard conditions, the product **3a** could be isolated in 47% yield, which may indicate that the gold catalyst plays an important role in two different catalytic cycles, whereby a nearly stoichiometric amount of Cu(OTf)$_2$ may act as the oxidant during the formation of **3**.

On the basis of the aforementioned results and the reported literature,[14] a plausible mechanistic hypothesis for this cascade

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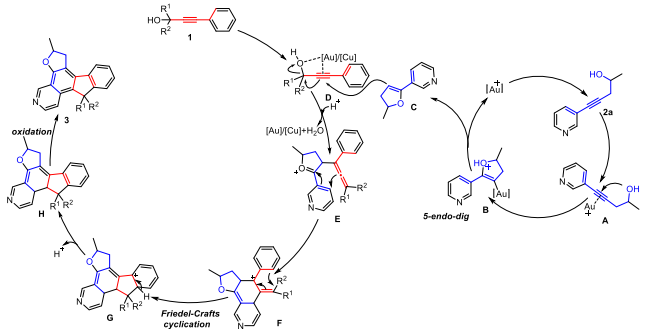
annulation reaction is put forward in Scheme 4. The mechanism is initiated by coordination of the Au complex to

Scheme 4. Plausible Catalytic Cycles



the triple bond of alkynol **2** to form intermediate **B** via 5-*endo-dig* cyclization, followed by protodemetalation to give 2,3-dihydrofuran **C** and release of the catalytic Au(I) complex. Propargyl alcohol **1** undergoes a Meyer−Schuster rearrangement in the presence of the Au(I) complex and $Cu(OTf)_2$ and affords intermediate **E** via an intermolecular nucleophilic attack of 2,3-dihydrofuran **C**. This intermediate **E** undergoes intramolecular nucleophilic addition to yield the intermediate **F**, which undergoes Friedel−Crafts alkylation and the release of a proton to furnish intermediate **H**. Finally, the oxidation of intermediate **H** generates the product **3**.

In summary, we have introduced a gold/copper-promoted concurrent tandem catalysis system for the construction of structurally diversified polycyclic dihydrobenzofurans from easily prepared alkynol substrates. The sequences involve 5-*endo-dig* cycloisomerization, Meyer−Schuster rearrangement, and Friedel−Crafts-type pathways. The products act as valuable building skeletons in many biologically active compounds and optical materials. The photophysical properties of synthesized compounds were also investigated, and the interesting properties of the mechanochromic fluorescence indicate its potential application value. Further properties and applications of the polycyclic dihydrobenzofuran skeletons will be further pursued by our work team.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c04070.

Experimental procedures, crystallographic data, compound characterization, and NMR spectra (PDF)

Accession Codes

CCDC 2035289−2035290 and 2039091 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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