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Gold-Catalyzed [1,5]-Hydride Shift onto Unactivated Alkynes To Trigger an Intermolecular Diels–Alder Reaction

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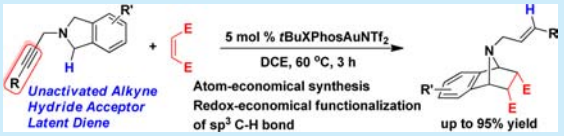
Supporting Information

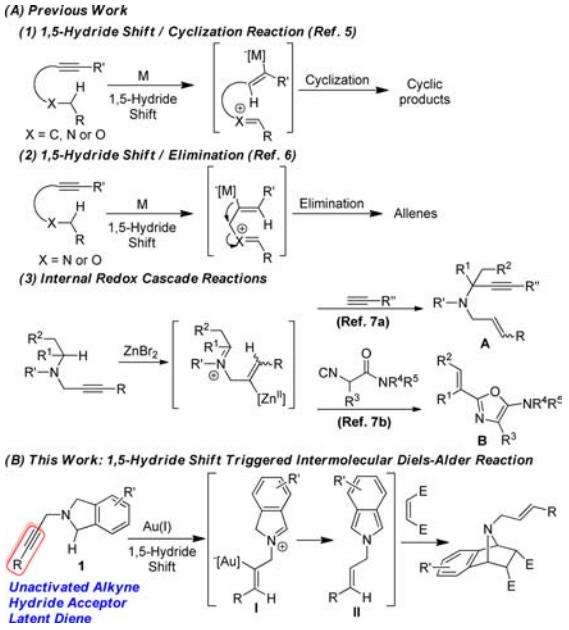
ABSTRACT: A [1,5]-hydride shift of sp^3 C–H onto an unactivated carbon–carbon triple bond catalyzed by a gold(I) complex enabled *N*-propargylisoindolines to be latent dienes and therefore triggered an intermolecular Diels–Alder reaction with dienophiles. This protocol provides an atom-economical and straightforward approach to access a wide range of polycyclic skeletons in high yields and with excellent diastereoselectivities from easily accessible molecules.



The direct functionalization of inactive C–H bonds undoubtedly represents one of the most ideal strategies for the synthesis of structurally complex molecules.[1] [1,*n*]-Sigmatropic hydrogen shift/cyclization reactions have been a redox-economical strategy to functionalize sp^3 C–H bonds and have turned out to be very useful in organic synthesis.[2−4] In most cases, an activated hydride acceptor, basically an electronically deficient unsaturated bond, is required to be located in an appropriate position to a hydride donor. Previous elegant studies have indicated that the presence of π-Lewis acid catalysts has enabled unactivated alkynes to serve as hydride acceptors to participate in cascade [1,5]-hydride shift/ring-closing reactions (Scheme 1A−1).[5] Additionally, [1,5]-hydride shift/elimination reactions, very unique methods for the preparation of allenes, have been established by Che, Gagosz, Ma, and others (Scheme 1A-2).[6] Moreover, the zwitterionic intermediates, generated from the [1,5]-hydride shift of propargylic amines, were also able to react with terminal alkynes and isonitriles, furnishing products **A** and **B**, respectively (Scheme 1A-3).[7] Herein, we will describe that a [1,5]-hydride shift of sp^3 C–H onto the unactivated carbon–carbon triple bond catalyzed by a gold(I) complex enabled *N*-propargylisoindolines to be latent dienes capable of undergoing an intermolecular Diels–Alder reaction with dienophiles,[8] directly giving rise to polycyclic molecules (Scheme 1B).

During our continuous endeavors directed toward the C–H functionalization reaction by using [1,*n*]-hydride shift strategy,[9] we initially investigated a transformation of **1a** under the catalysis of a gold(I) complex to identify if it was possible to undergo a hydride shift/cyclization reaction[2a,b] and to generate tricyclic product **C** under degassed conditions (eq 1). However, the proposed product **C** was not detected. On the contrary, an unanticipated molecule **D** was isolated in a 14% yield, which was presumably generated from a reaction between a diene species, cinnamylisoindole **IIa** in situ formed from [1,5]-hydride shift of **1a**, with trace amounts of residual oxygen in glassware and solvent (eq 1).[10] Indeed, the yield of **D** could be improved to 67% by conducting the reaction under the atmosphere of air,

Scheme 1. Alkynes Served as Hydride Acceptors in the Cascade Reactions



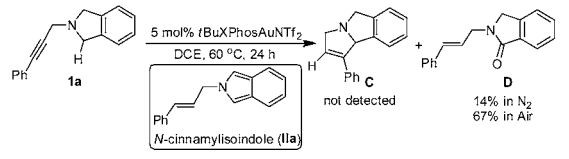


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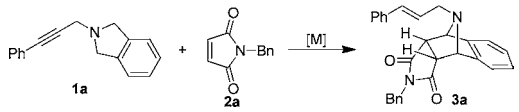
Table 1. Optimization of Reaction Conditions



entry	[M] (5 mol %)	soln	temp (°C)	time (h)	yield[a] (%)
1	*t*-BuXPhosAuNTf$_2$	DCE	60	3	89
2	PdCl$_2$	DCE	60	24	<5
3	PtCl$_2$	DCE	60	24	<5
4	Ph$_3$PAuCl	DCE	60	24	*b*
5	JohnPhosAuCl	DCE	60	24	*b*
6	JohnPhosAuSbF$_6$	DCE	60	3	40
7	IPrAuSbF$_6$	DCE	60	3	81
8	IPrAuNTf$_2$	DCE	60	3	88
9	*t*-BuXPhosAuNTf$_2$	DCE	20	24	47
10	*t*-BuXPhosAuNTf$_2$	THF	60	24	51
11	*t*-BuXPhosAuNTf$_2$	MeCN	60	24	39
12	*t*-BuXPhosAuNTf$_2$	PhMe	60	24	24
13	*t*-BuXPhosAuNTf$_2$	CHCl$_3$	60	24	38

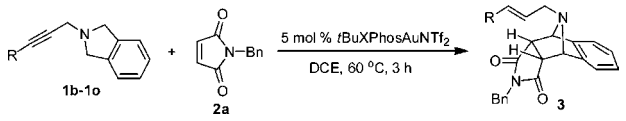
[a]Yield of the isolated product. [b]No reaction was observed. DCE = 1,2-dichloroethane.

which could clearly indicate the occurrence of the reaction between cinnamylisoindole **IIa** and oxygen, leading to the generation of oxidized product **D**. In addition, ^{1}H NMR studies identified the intermediate **IIa** to confirm the hypothesis on the [1,5]-hydride transfer occurred in **1a** under the catalysis of gold(I), leading to the efficient formation of cinnamylisoindole **IIa** (see the Supporting Information for ^{1}H NMR spectra).[11] Interestingly, the allene resulting from the [1,5]-hydride shift/elimination process, which commonly occurred in other processes,[6] was not observed in this case.

The findings inspired us to envisage that if a dienophile was introduced to the reaction, a cascade [1,5]-hydride shift/intermolecular Diels–Alder reaction[12] would be created. To our delight, a reaction of **1a** with *N*-benzylmaleimide (**2a**) was indeed able to undergo the desired cascade reaction to give *endo*-adduct **3a** as a single diastereomer in a high yield (89%) under the promotion of *t*-BuXPhosAuNTf$_2$[13] at 60 °C under N$_2$ (Table 1, entry 1). Other commonly used π-Lewis acids, such as PdCl$_2$ and PtCl$_2$,[14] showed no catalytic activity for this transformation (entries 2 and 3). Either the counterion or ligand of gold(I) complexes exerted significant effect on the catalytic activity. For instance, gold chloride complexes were unable to promote the reaction (entries 4 and 5), and JohnPhosAuSbF$_6$[15] gave a poor yield (entry 6). In sharp contrast, the highly cationic gold complexes enabled the reaction to proceed smoothly, in particular, under the assistance of an appropriate ligand (entries 1, 7, and 8). When the reaction was performed at 20 °C in 1,2-dichloroethane (DCE), a lower yield (47%) was obtained, prolonging the reaction time to 24 h (entry 9). A final evaluation of solvents showed that DCE is the most suitable media to allow the reaction and gives the highest yield (entries 1 and 10–13).

Having established the optimal reaction conditions, the generality of the transformation for arylalkynylisoindolines **1** was subsequently examined (Table 2). A variety of substrates **1b–o** with different substituents adjacent to the carbon–carbon triple bond were treated with *N*-benzylmaleimide (**2a**) in the presence of 5 mol % of *t*-BuXPhosAuNTf$_2$ in DCE at 60 °C. All of the arylalkynylisoindolines underwent the [1,5]-hydride shift/intermolecular Diels–Alder cycloaddition very smoothly and gave **3b–o** in high yields and with excellent *endo*-selectivity

Table 2. Scope of Arylalkynylisoindoline Substrates[a]



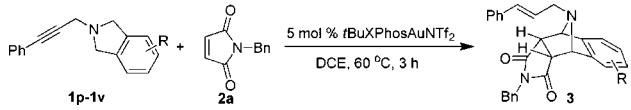
entry	**1** (R)	**3**	yield[b] (%)
1	**1b** (2-MeC$_6$H$_4$)	**3b**	88
2	**1c** (3-MeC$_6$H$_4$)	**3c**	84
3	**1d** (4-MeC$_6$H$_4$)	**3d**	95
4	**1e** (2-MeOC$_6$H$_4$)	**3e**	91
5	**1f** (3-MeOC$_6$H$_4$)	**3f**	92
6	**1g** (4-MeOC$_6$H$_4$)	**3g**	89
7	**1h** (2-ClC$_6$H$_4$)	**3h**	53
8	**1i** (3-ClC$_6$H$_4$)	**3i**	77
9	**1j** (4-ClC$_6$H$_4$)	**3j**	84
10	**1k** (2-MeO$_2$CC$_6$H$_4$)	**3k**	77
11	**1l** (3-MeO$_2$CC$_6$H$_4$)	**3l**	78
12	**1m** (4-MeO$_2$CC$_6$H$_4$)	**3m**	75
13	**1n** (*E*-C$_6$H$_5$CH=CH)	**3n**	82
14	**1o** (H)	**3o**	89

[a]The reaction was carried out with **1** (0.1 mmol) and *N*-benzylmaleimide **2a** (1.2 equiv) in the presence of 5 mol % of *t*-BuXPhosAuNTf$_2$ in DCE (1.0 mL) under N$_2$. The resulting solution was stirred for 3 h at 60 °C. [b]Yield of the isolated product.

(Table 2). Generally, the introduction of an electron-rich substituent to the arylalkynyl moiety of the substrate **1** led to a relatively cleaner reaction in comparison with those bearing an electron-withdrawing group (entries 1–6 vs 10–12). Interestingly, in the cases of alkynylisoindolines with a chlorophenyl substituent, the substitution pattern exerted an apparent impact on the conversion. As a consequence, the *m*- and *p*-chlorophenylalkynylisoindolines **1i** and **1j** resulted in considerably higher yields than *o*-chlorophenylalkynylisoindoline **1h** (entries 8 and 9 vs 7). Moreover, *E*-styrylalkynylisoindoline **1n** could furnish the product **3n** in 82% yield (entry 13). More significantly, an unsubstituted substrate, 2-(prop-2-yn-1-yl)-isoindoline **1o**, could also be nicely tolerated to give corresponding polycyclic product in an 89% yield (entry 14).

Additionally, the variation of substituent on the isoindoline moiety was also tolerated to undergo the cascade reaction cleanly and furnished polycyclic heterocycles in high yields (Table 3).Basically, either the electronic feature of the substituent or the

Table 3. Scope of Isoindoline Substrates[a]



entry	**1** (R)	**3**	yield[b] (%)
1	**1p** (4-Cl)	**3p**	90
2	**1q**(5-Cl)	**3q**	91
3	**1r** (5-Me)	**3r**	88
4	**1s** (5,6-Me$_2$)	**3s**	89
5	**1t** (5-OMe)	**3t**	88
6	**1u** (5-CF$_3$)	**3u**	89
7	**1v** (5-NO$_2$)	**3v**	78

[a]The reaction was carried out with **1** (0.1 mmol) and *N*-benzylmaleimide **2a** (1.2 equiv) in the presence of 5 mol % of *t*-BuXPhosAuNTf$_2$ in DCE (1.0 mL) under N$_2$. The resulting solution was stirred for 3 h at 60 °C. [b]Yield of the isolated product.

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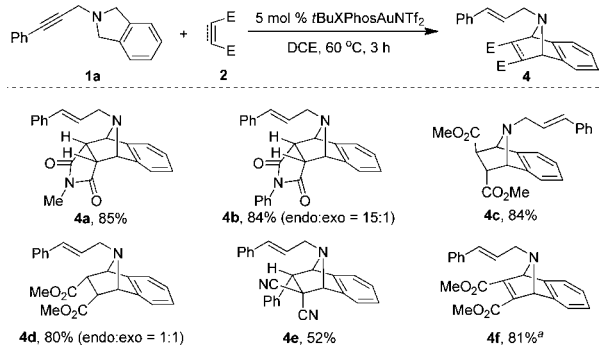
Scheme 2. Scope of Dienophiles



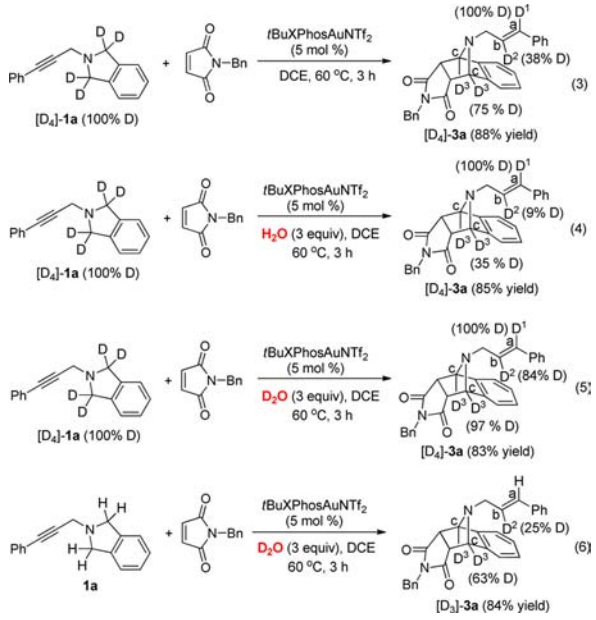
[a]The reaction was carried out with **1** (0.1 mmol) in the presence of 5 mol % of *t*-BuXPhosAuNTf$_2$ in DCE (1.0 mL) at 60 °C under N_2 for 3 h. The solution was then cooled to 20 °C, dimethyl acetylenedicarboxylate was added, and the resulting solution was stirred for 1 h.

substitution pattern has little influence on the reaction performance. Thus, the presence of electron-donating or electron-withdrawing groups on the isoindoline led to the generation of desired products in almost identical yields (entries 1−6) except that the 5-NO_2-substituted isoindoline (**1v**) gave a relatively lower, but still good, yield (78%, entry 7).

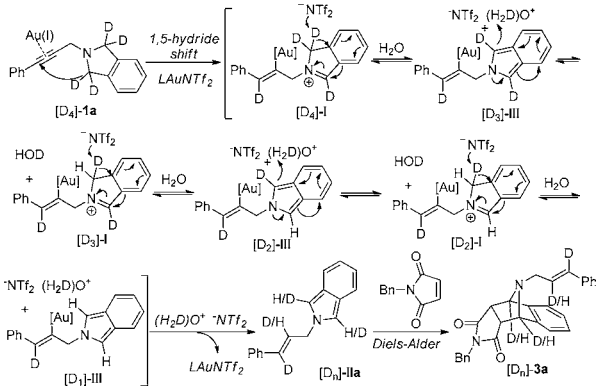
In addition to showing excellent generality for the arylalkynylisoindolines **1**, the protocol could also be amenable to a wide scope of dienophiles **2** (Scheme 2). The use of *N*-methylmaleimide (**2b**) as a dienophile furnished the corresponding product **4a**[16] in an 85% yield with perfect *endo*-selectivity, while **4b** was isolated in an 84% yield with a 15/1 diastereomeric ratio in favor of *endo*-product when *N*-phenylmaleimide (**2c**) was used. The cascade reaction with dimethyl fumarate (**2d**) also proceeded cleanly to give **4c** as a single diastereomer, whereas a 1/1 *endo*/*exo*-mixture of **4d** was created from a similar reaction with dimethyl maleate (**2e**). However, benzylidene malononitrile (**2f**) showed less reactivity to afford the desired product **4e** in a lower yield (52%). In contrast, the use of dimethyl acetylenedicarboxylate (**2g**) as a dienophile at 60 °C was unable to generate the desired polycyclic product although the [1,5]-hydride transfer indeed occurred, presumably because the dimethyl acetylenedicarboxylate is highly active and undergoes some unidentified reactions. Alternatively, after **1a** was initially transformed into isoindole catalyzed by *t*-BuXPhosAuNTf$_2$ in DCE at 60 °C under N_2 for 3 h, the solution was cooled down to 20 °C and treated with dimethyl acetylenedicarboxylate (**2g**) to enable the generation of the desired product **4f** in an 81% yield.

To get insight into reaction mechanism, some deuterium labeling experiments were performed (Scheme 3). The exposure of deuterated [D_4]-**1a** to the optimal conditions led to [D_4]-**3a** in 88% yield with a 100% deuterium at vinyl carbon *a* (eq 3), indicating the clean occurrence of [1,5]-hydride transfer. Surprisingly, a significant deuterium loss was observed at carbon *c* (D^3), and only 38% deuterium was found at vinyl carbon *b*, which we presumed might arise from protonation of the intermediate with residual water. Indeed, the addition of 3 equiv of water led to an even more significant deuterium loss at carbon-*c* (D^3, 75% vs 35%) and much less deuterium at vinyl carbon-*b* (D^2, 38% vs 9%) while the deuterium at vinyl carbon-*a* remained 100% (eq 4). As a comparison, a similar reaction of [D_4]-**1a** conducted in the presence of D_2O led to [D_4]-**3a** with a considerable improvement in carbon *b* and *c* (eq 5). Moreover, when the cascade reaction of **1a** was conducted with D_2O (3.0

Scheme 3. Deuterium-Labeling Experiments



Scheme 4. Proposed Mechanism



equiv) under the otherwise identical conditions, a [D_3]-**3a** was isolated in an 84% yield, with 25% and 63% deuterium content for the carbon *b* and *c*, but no deuterium was observed at carbon *a* (eq 6). These facts clearly demonstrated that the external water participated in the protonation of the isoindole and vinylgold parts of the key intermediate generated from the gold catalyzed [1,5]-hydride shift step.

On the basis of the deuterium-labeling experiments, a plausible mechanism was proposed (Scheme 4). Initially, a [1,5]-hydride shift of [D_4]-**1a** occurred under the promotion of gold(I) to generate an intermediate [D_4]-**I**, which subsequently underwent reversible protonation and deprotonation reaction sequences with external water (or D_2O) under the assistance of the resultant bis((trifluoromethyl)sulfonyl)amide (Tf_2N^-),[17] leading to the formation of equilibrium mixture of various deuterated *N*-cinnamylisoindole [D_n]-**IIa** by protodemetalation of corresponding vinylgold species [D_n]-**III**. Finally, the Diels−Alder reaction of [D_n]-**IIa** with the *N*-benzylmaleimide would occur to afford [D_n]-**3a** with various deuterium ratios at the deuteratable carbons.

In conclusion, we have demonstrated that the gold(I) appears to be an efficient catalyst for the hydride shift of sp^3 C−H onto the unactivated carbon−carbon triple bond in the context of the

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substrate to enable alkynylisoindolines to act as latent dienes capable of participating in an intermolecular Diels–Alder reaction with various dienophiles. This protocol provides an atom-economical synthesis of structurally complex polycyclic products in high yields from easily accessible molecules by redox-economical functionalization of sp^3 C–H bonds under mild conditions. The deuterium-labeling experiments indicate that the reaction involves a [1,5]-hydride shift onto the gold-activated alkyne to generate a *N*-cinnamylisoindole, which undergoes the subsequent Diels–Alder reaction.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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