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# Gold(I)-Catalyzed Reactions between *N*-(*o*-Alkynylphenyl)imines and Vinyldiazo Ketones to Form 3-(Furan-2-ylmethyl)-1*H*-indoles via Postulated Azallyl Gold and Allylic Cation Intermediates

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Cite This: *Org. Lett.* 2021, 23, 1378−1382

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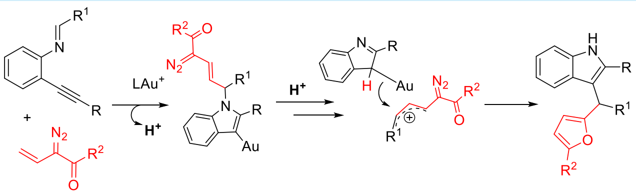
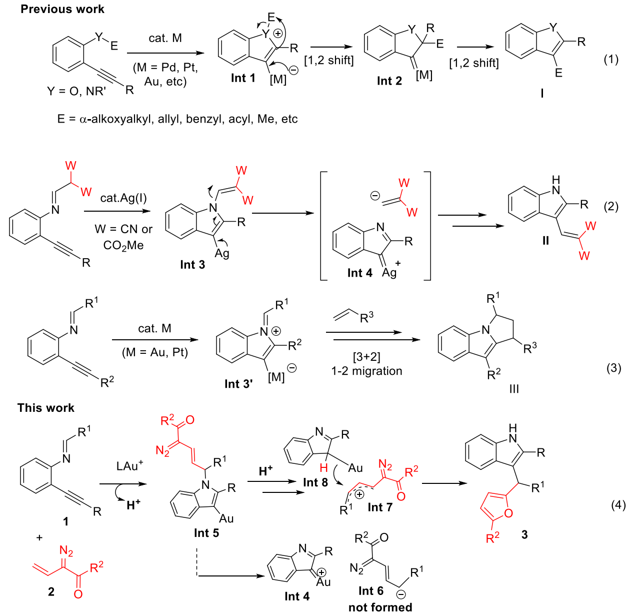
**ABSTRACT:** This work describes gold-catalyzed additions of vinyldiazo ketones to *N*-(*o*-alkynylphenyl)imines to yield 3-(furan-2-ylmethyl)-1*H*-indoles involving skeletal rearrangement; these new catalytic reactions are applicable to a wide range of substrates. We postulate a new mechanism involving an initial addition of diazo ketones to azomethine ylide intermediates to yield gold-containing *N*-alkylated indole intermediates that undergo proton-induced 1,3-group migrations, generating azallyl gold and allylic cation pairs.



Substituted indoles form the core skeletons of a wide range of pharmaceuticals and naturally occurring alkaloids.[1] To date, numerous synthetic approaches have been developed to generate this ring system via transition-metal catalysis.[2] In Scheme 1, transition-metal-catalyzed 1,3-migratory cycloisomerization of *o*-alkynylaryl ethers and *N*,*N*-disubstituted anilines provides a powerful approach to the synthesis of 2,3-disubstituted benzofurans and indoles (eq 1).[3] The transformations involve initial formation of alkenylmetal (Pd, Pt, Rh, Ir, Au, Cu, Co, In) intermediates that subsequently undergo consecutive 1,2-migrations over a broad range of functionalities, including $\alpha$-alkoxyalkyl,[4] allyl,[5] benzyl,[6] acyl,[7] methyl,[8] sulfonyl,[9] and boryl groups,[10] before proceeding to 2,3-disubtituted indole derivatives (**I**). In contrast with a consecutive 1,2-migration in eq 1, Oh reported ion pair intermediates **Int-4** in the Ag(I)-catalyzed cycloisomerization of *N*-(*o*-alkynylphenyl)imines to enable 1,3-vinyl migrations. In this mechanism, vinyl anions **Int-4** were greatly stabilized with two electron-withdrawing groups (eq 2).[11] With other *N*-(*o*-alkynylphenyl)imines, Iwasawa recently reported the formation of azomethine ylides **Int-3′** from *N*-(*o*-alkynylphenyl)imines, which reacted well with alkene in catalytic [3 + 2]-cycloadditions (eq 3).[12] We sought new reactivity of these azomethine ylides **Int-3′**. Herein, we report gold-catalyzed synthesis of 3-(furan-2-ylmethyl)-1*H*-indoles from the reactions of azomethine ylides (**Int-3′**) with vinyldiazo ketones. Instead of an expected [3 + 2]-cycloaddition, we observed an initial addition of vinyldiazo ketones to azomethine ylides (**Int-3′**) to yield addition intermediates (**Int-5**) and a proton. We note that a consecutive 1,2-migration in eq 1 requires a positive charge on the heteroatoms Y (Y = O, NR) to enable 1,2-migrations, thus inapplicable to our new system. The ion pair intermediates in eq 2 fail to work with our catalysis because the expected allylic anions **Int-6** are unlikely

**Scheme 1. Reactions on Metal-Containing Indole Intermediates**



**Received:** January 6, 2021
**Published:** February 9, 2021

https://dx.doi.org/10.1021/acs.orglett.1c00038

to survive in the presence of $H^+$. As a concerted 1,3-migration is thermally forbidden, in this work, we propose formation of new intermediate pairs involving allylic cations **Int-7** and azallyl gold species **Int-8** after a protonation of key intermediates **Int-5**.

The significance of this catalysis is that indole-containing triarylmethane derivatives are easily available (**IV-1** to **IV-6**, Figure 1).[13] Indole derivatives **IV-1** and **IV-2** are demonstrated to be an anticancer scaffold[13a] and an antibacterial agent, respectively.[13b] Compounds **IV-3** and **IV-4** are aromatase an inhibitor[13c] and an anti-inflammatory agent, respectively.[13d] Species **IV-5** has been used as an antitubercular agent.[13e] Compound **IV-6** has been tested as a antiobesity drug.[13f]

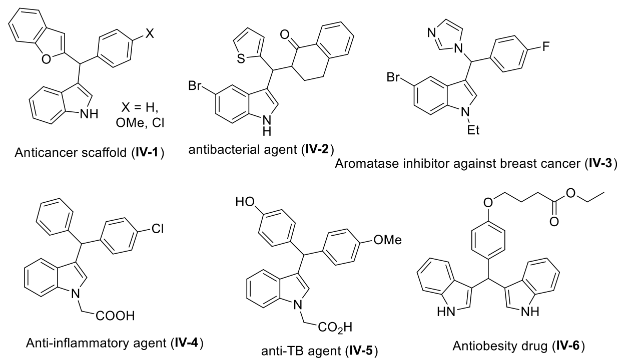
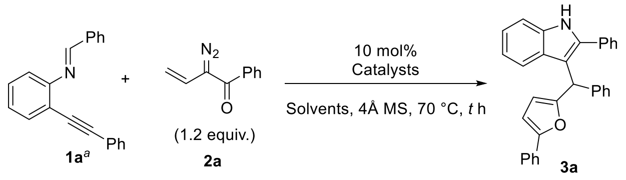


**Figure 1.** Representative bioactive molecules.

We optimized the reactions of (*E*)-1-phenyl-*N*-(2-(phenylethynyl)phenyl)methanimine **1a** with vinyldiazo ketone **2a** using different gold catalysts, and the findings are summarized in Table 1. Our initial IPrAuCl/AgOTf (10 mol %) evaluation in DCE at 70 °C (3 h) afforded an indole derivative **3a** in 81% (entry 1). With LAuCl/AgOTf (L = P($t$-Bu)$_2$($o$-biphenyl)) (10 mol %), the yield of product **3a** was increased to 84% yield (entry 2). Other gold phosphine catalysts such as L′AuCl/AgOTf (L′ = (PhO)$_3$P and PPh$_3$) produced compound **3a** in 75 and 83% yields, respectively (entries 3 and 4). Alternative halide scavengers such as LAuCl/X (X = AgNTf$_2$, AgSbF$_6$, and NaBARF) gave compounds **3a** in 63, 0, and 0% yields, respectively, with AgSbF$_6$ and NaBARF giving a complicated mixture of products (entries 5–7). The ligating ability of $^-NTf_2$ seems to be crucial. For LAuCl/AgOTf (L = P($t$-Bu)$_2$($o$-biphenyl)), the desired product **3a** yields were as follows (entries 8–10): THF (29%), toluene (76%), and $CH_3CN$ (0%). AgOTf alone was completely inactive (entry 11). $AuCl_3$ and $PtCl_2$ gave a complicated mixture of products (entries 12 and 13). The structure of compound **3a** was inferred from X-ray diffraction of its relative structure **4c** (see Table 3, entry 3). An overall review of Table 1 suggests that gold catalysts containing electron-rich ligand and basic counteranions are more appropriate for this new catalysis, probably due to an enhanced stabilization of gold carbenes.

### Table 1. Optimization of the Reaction Conditions

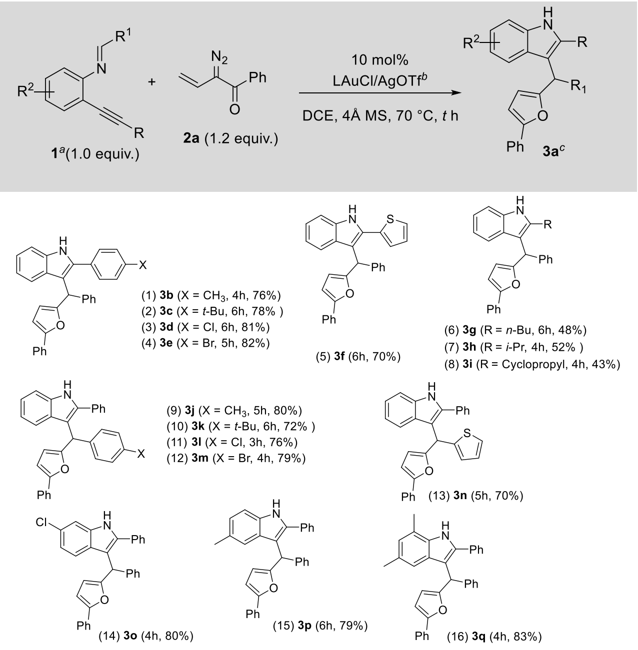


| entry | catalyst | solvent | $t$ (h) | yield[b] (**3a**) |
|---|---|---|---|---|
| 1 | IPrAuCl/AgOTf[c] | DCE | 3 | 81 |
| 2 | LAuCl/AgOTf[d] | DCE | 2 | 84 |
| 3 | (PhO)$_3$PAuCl/AgOTf | DCE | 5 | 75 |
| 4 | PPh$_3$AuCl/AgOTf | DCE | 2 | 83 |
| 5 | LAuCl/AgNTf$_2$ | DCE | 4 | 63 |
| 6 | LAuCl/AgSbF$_6$ | DCE | 6 | |
| 7 | LAuCl/NaBARF | DCE | 5 | |
| 8 | LAuCl/AgOTf | THF | 6 | 29 |
| 9 | LAuCl/AgOTf | toluene | 3 | 76 |
| 10 | LAuCl/AgOTf | CH3CN | 6 | |
| 11 | AgOTf | DCE | 6 | |
| 12 | AuCl$_3$ | DCE | 5 | |
| 13 | PtCl$_2$ | DCE | 5 | |

[a] [**1a**] = 0.1 M. [b] Product yields are reported after separation from a silica column. [c] IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidine, [d] L = P($t$-Bu)2($o$-biphenyl), DCE = 1,2-dichloroethane, THF = tetrahydofuran.

We assessed the scope of these catalytic reactions of various *N*-(*o*-alkynylphenyl)imines **1** with vinyldiazo ketone **2a**; the findings are summarized in Table 2. For certain alkyne substrates **1b–1e** with 4-substituted species of phenylalkyne (R = 4-XC$_6$H$_4$; X = CH$_3$, $t$-butyl, Cl, and Br), their subsequent products **3b–3e** were obtained in 76–82% yields (entries 1–4). For their 2-thienyl substituted analogue **1f**, its corresponding product **3f** was produced in 70% yield (entry 5). We also prepared alkylalkyne substrates **1g–1i** (R = $n$-butyl, isopropyl, and cyclopropyl), rendering the desired products **3g–3i** in 43–52% yields (entries 6–8). We tested the reactions on substrates **1j–1m**, bearing 4-substituted phenyl imines (R$^1$ = 4-XC$_6$H$_4$; X = CH$_3$, $t$-butyl, Cl, and Br), further providing the desired products **3j–3m** in 72–80% yields (entries 9–12). 2-

### Table 2. Scope of the Reaction with Various *N*-(*o*-Alkynylphenyl)imines

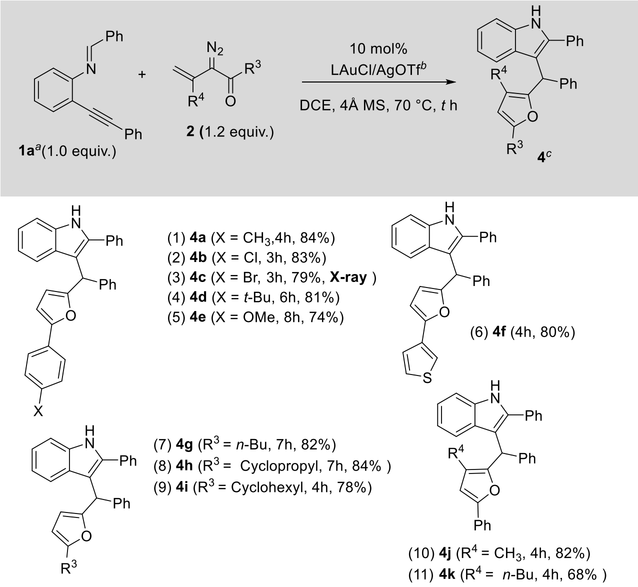


[a] [**1**] = 0.1 M. [b] L = P($t$-Bu)2($o$-biphenyl). [c] Product yields are reported after separation from a silica column, Tf = trifluoromethanesulfonyl.

https://dx.doi.org/10.1021/acs.orglett.1c00038
Org. Lett. 2021, 23, 1378−1382

Thienylalkyne analogue **1n** afforded its resulting product **3n** in 70% yield (entry 13). For starting substrates **1o**−**1q**, variations of the $R^2$ substituents at their bridged benzenes still maintained high catalytic efficiency, yielding the desired products in 79−83% yields (entries 14−16).

### Table 3. Scope of the Reaction with Various Vinyldiazo Ketones



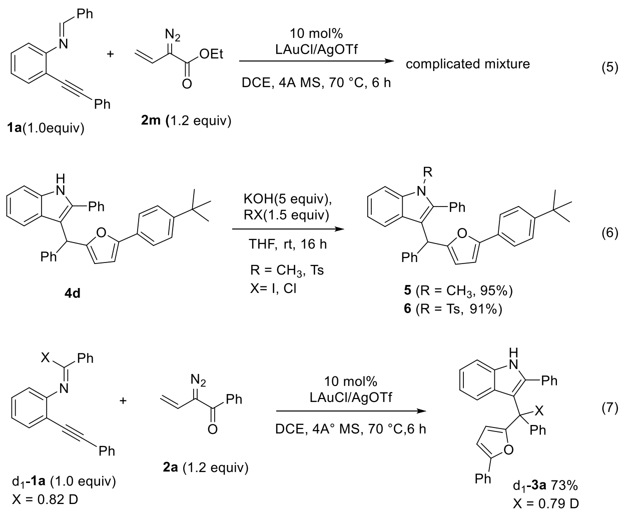
(1) **4a** (X = $CH_3$,4h, 84%)
(2) **4b** (X = Cl, 3h, 83%)
(3) **4c** (X = Br, 3h, 79%, **X-ray** )
(4) **4d** (X = *t*-Bu, 6h, 81%)
(5) **4e** (X = OMe, 8h, 74%)
(6) **4f** (4h, 80%)
(7) **4g** ($R^3$ = *n*-Bu, 7h, 82%)
(8) **4h** ($R^3$ = Cyclopropyl, 7h, 84% )
(9) **4i** ($R^3$ = Cyclohexyl, 4h, 78%)
(10) **4j** ($R^4$ = $CH_3$, 4h, 82%)
(11) **4k** ($R^4$ = *n*-Bu, 4h, 68% )

[a] [**1a**] = 0.1 M. [b] L = P(*t*-Bu)2(*o*-biphenyl). [c] Product yields are reported after separation from a silica column, Tf = trifluoromethanesulfonyl.

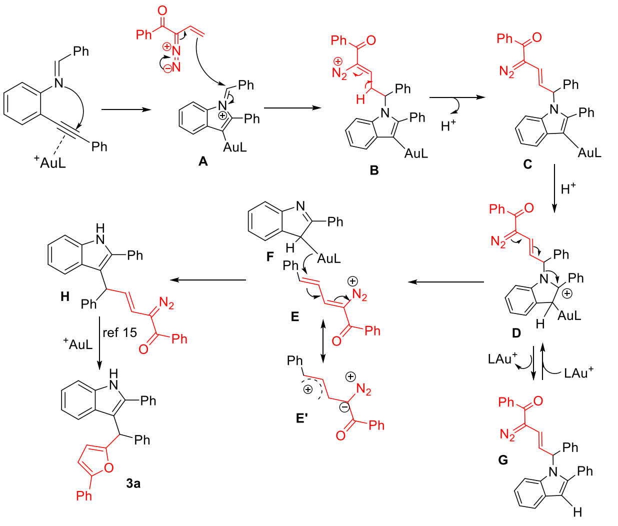
We assessed the substrate scope using various vinyldiazo ketones **2** in this catalytic sequence; the yields of products are summarized in Table 3. We prepared the species of vinyldiazo **2b**−**2f** bearing distinct 4-phenyl ketones ($R^3$ = 4-$XC_6H_4$; X = $CH_3$, Cl, Br, *t*-butyl, and OMe), and their resulting products **4a**−**4e** were obtained in 74−84% yields (entries 1−5). X-ray diffraction of compound **4c** confirms our proposed structure. Again, 3-thienyl ketone species **2g** produced the expected product **4f** in 80% yield (entry 6). This new catalysis was further compatible with $\alpha$-diazo alkylketones **2h**−**2j** ($R^3$ = *n*-butyl, cyclopropyl, and cyclohexyl), rendering the desired products **4g**−**4i** in 78−84% (entries 7−9). We also checked the reactions on 2-substituted vinyldiazo ketones **2k**−**2l** ($R^4$ = Me and *n*-butyl), producing compounds **4j** and **4k** in 82 and 68% yields, respectively (entries 10 and 11).

Scheme 2 shows mechanistic investigations and chemical functionalizations of one representative compound **4d**. We performed an additional experiment between (*E*)-1-phenyl-*N*-(2-(phenylethynyl)phenyl)methanimine **1a** and vinyldiazo ester **2m** using optimized conditions, which give a complicated mixture of product (eq 5); this reaction requires an $\alpha$-diazo ketone to activate the reaction. Methylation and tosylation of species **4d** with MeI/KOH and TsCl/KOH afforded *N*-methylated or *N*-tosylated products **5**−**6** in 95% and 91% yields respectively (eq 6). We performed a deuterium-labeling experiment to elucidate the mechanisms of formation of indole derivatives **3**. We prepared a sample $d_1$-**1a** containing X = 0.82 deuterium content at the imine proton, which afforded compound $d_1$-**3a** comprising X = 0.79 D at the methane carbon, indicating a formal 1,3-benzyl migration (eq 7).

### Scheme 2. Mechanistic Investigations and Chemical Functionalization of 4d



### Scheme 3. A Plausible Reaction Mechanism



We postulated a mechanism in Scheme 3. The gold catalyst is expected to form azomethine ylides **A** via an initial cyclization of *N*-(*o*-alkynylphenyl)imine reagents. A nucleophilic attack of diazo ketone **2a** to azomethine ylides **A** will form intermediate **B**, which is prone to loss of a proton, further leading to formation of gold containing *N*-substituted indoles **C**. Protonations of indoles are well-known at the C(3)-carbon[14] rather than on the nitrogen atom. Accordingly, species **C** undergo protonation to form C(2)-benzyl carbocations **D**. As the vinyldiazo moiety of species **D** is electron-rich and highly nucleophilic, this electronic effect leads to a cleavage of the C−N bond of species **D**, yielding azallylgold **F** and bezylic cation **E** that further stabilized its resonance form **E′**. Although an elimination of $LAu^+$ from intermediates **D** to yield indole species **G** is also likely to occur, we believe that this process is reversible to enable a complete transformation of species **D** into **E**. A recombination of reactive species **E** and **F** produces indole species **H**, of which the vinyldiazo ketone can be transformed into a furan ring according to our previous work.[15]

In summary, this work reports gold-catalyzed reactions of *N*-(*o*-alkynylphenyl)imines and vinyldiazo ketones[16] to form 3-(furan-2-ylmethyl)-1*H*-indole products over a wide scope of substrates. We postulate an initial gold-catalyzed cyclization of *N*-(*o*-alkynylphenyl)imines to form azomethine ylides that are subsequently attacked by vinyldiazo ketones to form gold-containing *N*-substituted indoles and a proton. Further protonation of these key indole intermediates likely forms a pair of intermediates such as azallyl gold and allylic cations to enable 1,3-formal group migrations.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00038.

> Experimental procedures, characterization data, crystallography data, and $^1$H NMR and $^{13}$C NMR spectra for representative compounds (PDF)

### Accession Codes

CCDC 2049435 contains 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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### Author Contributions

☐A.S.K.R. and A.S.N. contributed equally.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors thank the Ministry of Science and Technology (MOST 107-3017-F-007-002) and the Ministry of Education (MOE 106N506CE1), Taiwan, for supporting this work.

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https://dx.doi.org/10.1021/acs.orglett.1c00038