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Synthesis of 2-Aminoindoles through Gold-Catalyzed C−H Annulations of Sulfilimines with *N*-Arylynamides

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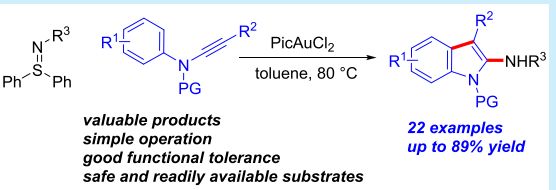
Supporting Information

ABSTRACT: A new gold-catalyzed C−H annulation of sulfilimines with *N*-phenylynamides is presented. As key intermediates of this operationally simple reaction, the in situ generated α-imino gold carbenes insert into the ortho C−H bonds of the phenyl groups to afford 2-aminoindoles bearing a variety of substitution patterns in high selectivities. This reaction offers a facile approach to biologically important 2-aminoindoles by using inexpensive and readily available starting materials.



The indole core, an extraordinarily important structural component, is present in many natural products and synthetic medicinal compounds.[1] 2-Aminoindoles are among the most important of these substrates in pharmaceutical chemistry.[2,3] Beyond the diverse bioactivities shown by prominent examples (Figure 1), the 2-aminoindole unit can act as a planar aromatic structure and interact with a protein target by virtue of the two adjacent hydrogen-bond donors.[4]

Consequently, the development of methodologies toward 2-aminoindoles is highly desirable. Traditional methods include palladium-catalyzed aminations of 2-haloindoles,[5] cross-coupling cascade reactions,[6] multistep reactions,[7] and a recent base-promoted [4 + 1] cycloaddition of *o*-aminobenzyl chlorides with isocyanides.[8] These protocols, however, require strong bases, high temperatures, harsh substrates, or give specialized products bearing only special substituents at the 3-positions of the indole cores. Recently, gold-catalyzed conversion of ynamides offers new alternatives to highly regioselective routes to these compounds. Skrydstrup et al. synthesized 2-aminoindoles through a gold(I)-catalyzed hydroamination of ynamides with 2-iodoanilines and a subsequent palladium-catalyzed cross-coupling reaction (Figure 1).[9] Ye's group[10] developed a gold-catalyzed reaction of the potentially explosive benzyl azides and *N*-phenylynamides for the synthesis of 2-aminoindoles. Hashmi et al. prepared 2-aminoindoles from anthranils and ynamides with the restriction of an acyl group at the 7-position of the indole framework.[11a] Given these advances and drawbacks, a general, facile method using safe and readily accessible substrates is still challenging and of great importance.

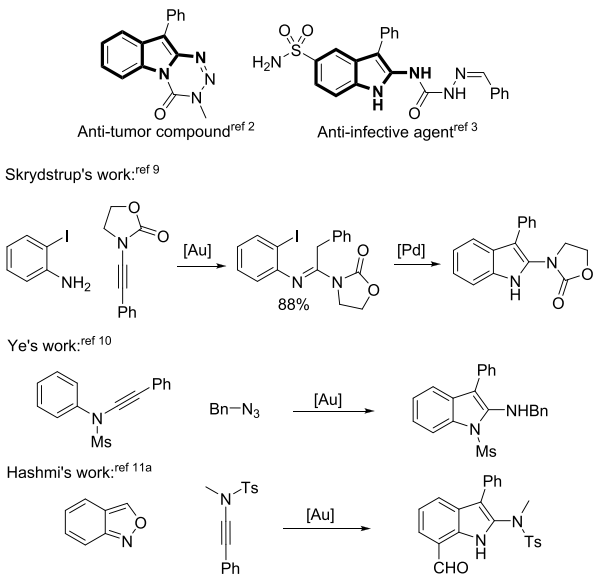


Figure 1. Representative bioactive 2-aminoindoles and syntheses of 2-aminoindoles by means of gold catalysis.

Gold catalysis[12] involving alkyne activation and subsequent oxygen,[13] carbene,[14] as well as nitrene transfer[15] reactions represents one of the most concise and promising complexity-generating strategies. Aza-heterocycles with labile N−X bonds (X = C, N, O) including 2*H*-arizines,[16] pyrido[1,2-*b*]-indazole,s[17] and isoxazole derivatives[18] as gold nitrene transfer reagents facilitate the syntheses of heterocycles (Scheme 1A), whereas the ring-opening in situ generated α-imino gold carbenes are mostly trapped by a limited number of functionalities, mainly originating from the nitrene transfer reagents. By comparison, ylides and ylide-like reagents such as azides,[19] pyridium aza-ylides,[20] sulfonium ylides,[14] and sulfilimines[21] have propelled the rapid development of efficient transformations because of the diversity of trapping functionalities on the anions (Scheme 1B). While conjugated ylides

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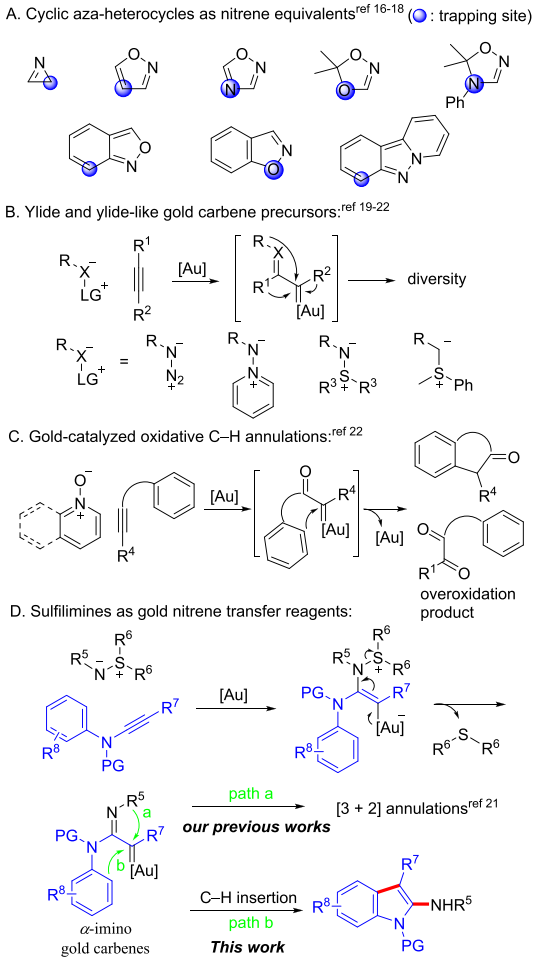
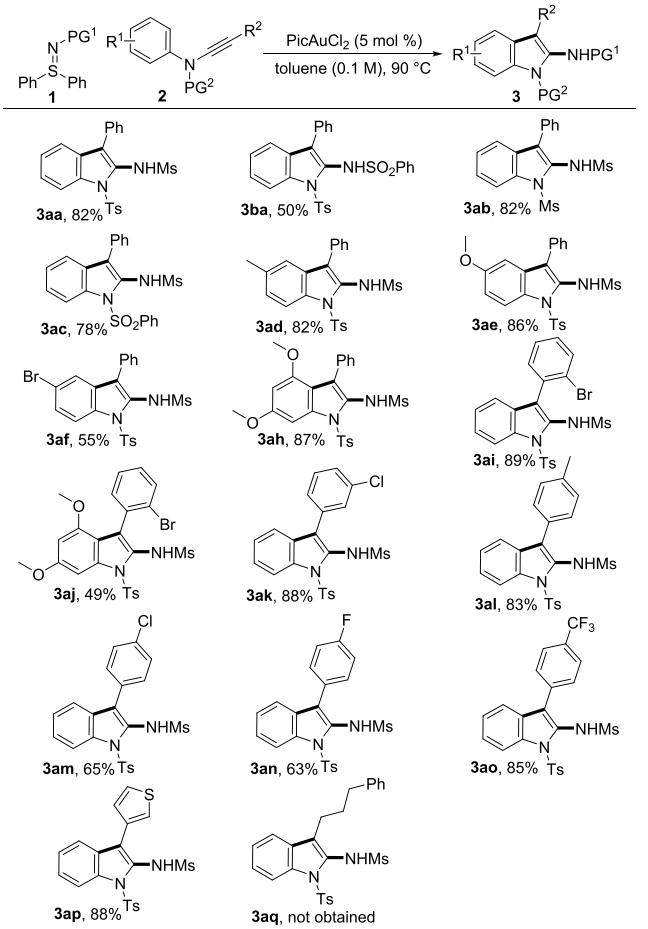
Scheme 1. Gold-catalyzed reactions involving carbene intermediates



always undergo [3 + 2] dipolar annulations, with non-conjugated groups on the anions the generated gold carbenes can be intramolecularly trapped by the functional groups within the alkynes. An intramolecular C−H insertion reaction for the synthesis of bicyclic systems can be expected by introduction of an aromatic group to the alkyne moiety. Unlike oxidative cyclization[22] reactions using *N*-oxides, with the main drawback of overoxidation to form a diketone product (Scheme 1C), gold-catalyzed annulations of *N*-arylynamides and benzyl azides efficiently delivered 2-aminoindoles.[10] Azides, however, are potentially hazardous and poisonous. Moreover, nitrogen as a leaving group creates the danger of explosive decomposition in the scale-up of reactions, which limits the synthetic applicability of this method. To this end, a readily available and safe reagent with a mild leaving group is highly desirable. We recently reported [3 + 2] annulations of sulfilimines with ynamides for the syntheses of 2-amino-indoles,[21a] 4-aminoimidazoles,[21a] fused 2-aminoimidazoles,[21b] and 4-aminooxazles[21c] by installing different functional groups (aryls, heteroaryls, iminyls, and acyls) on the nitrogen anions of sulfilimines (Scheme 1D, path a). We now envisioned a new synthetic approach to 2-aminoindoles (Scheme 1D, path b). The generated α-imino gold carbenes insert into the ortho C−H bonds of the preinstalled aryl groups, providing *N*,*N*′-disubstituted 2-aminoindoles. As nonexplosive waste, the released sulfides showed no poisoning of the gold catalyst.

We began our investigation by employing *N*-sulfonylsulfilimines **1** as a nitrene source. As shown in Scheme 2, under the same reaction conditions ($PicAuCl_2$, 80 °C, toluene) as in our previous reports,[21] *N*-methylsulfonyl-protected sulfilimine **1a** reacted efficiently with *N*-phenylynamide **2a** and the desired product **3aa** (single-crystal X-ray structure analysis, see Figure 2) was obtained in 82% yield. This reaction was compatible

Scheme 2. Reaction Scope[a,b]



[a]Reaction conditions: **1** (0.3 mmol, 1.5 equiv), **2** (0.2 mmol, 1.0 equiv), $PicAuCl_2$ (3.8 mg, 5 mol %), toluene (2.0 mL, 0.1 M). [b]Isolated yields.

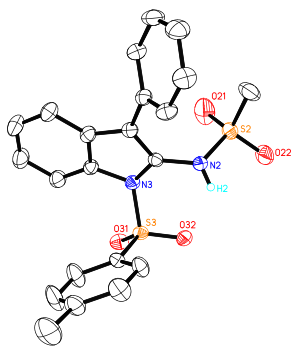


Figure 2. Solid-state molecular structure of **3aa**.

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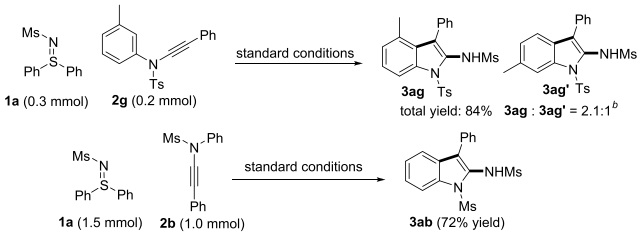
with *N*-phenylsulfonyl-substituted sulfilimine **1b**, giving indole **3ba** in 50% yield. Ynamides **2b,c** with other protecting groups (Ms, SO_2Ph) on the nitrogen atoms were also converted to products **3ab,ac** in good yield. With either electron-rich or electron-deficient aryl groups on the nitrogen atoms, ynamides **2d−f** were suitable substrates to undergo the desired transformation. 3-Methylphenyl ynamide **2g** afforded a mixture of 4-methylindole **3ag** and 6-methylindole **3ag′** with a ratio of 2.1:1 in 84% combined yield (Scheme 3). This C−H

Scheme 3. Test of a 3-Methylphenyl Ynamide 2g and a Millimole-Scale Reaction[a]



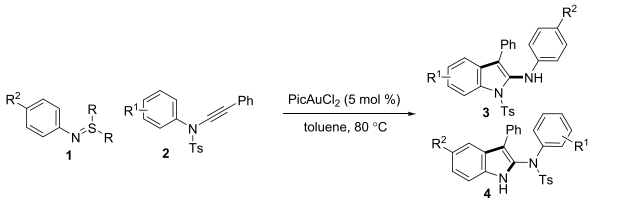
[a]Isolated yields. [b]The ratio of **3ag**/**3ag′** was determined by ^{1}H NMR.

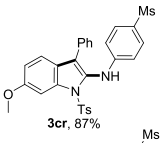
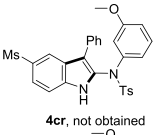
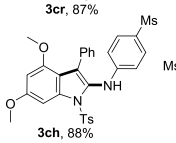
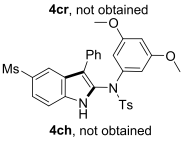
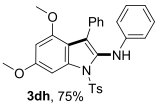
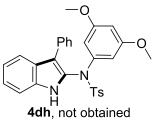
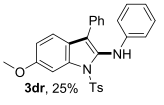
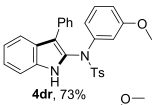
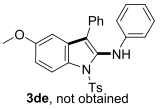
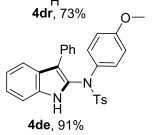
annulation reaction even tolerates an electron-rich dimethoxyphenyl ynamide, providing **3ah** in 87% yield. When R^2 was varied from an electron-poor aryl group (either a phenyl halide or a trifluoromethylbenzene) to an electron-rich group (*p*-methylbenzene) within the ynamides, the reactions proceeded smoothly and the corresponding products **3ai−ao** were prepared in 49−89% yield. The high-quality success with a thiophene-containing ynamide is notable. Unfortunately, an alkyl ynamide reacted sluggishly and unselectively, and the target indole **3aq** was not obtained. Furthermore, the reaction of **3ab** (Scheme 3) could conveniently be conducted on a mmole scale.

The reaction scope was further extended to *N*-arylsulfilimines (Scheme 4). The *α*-imino gold carbenes from such ylides could lead to two types of indole products by competitive C−H insertions. *N*-Phenyl ylides **1c,d** and *N*-phenyl ynamides with a methoxy group at the *meta*-position were examined. Gratifyingly, the treatment of *S*,*S*-dimethylsulfilimine **1c** with the 3-methoxyphenyl-substituted ynamide **2r** delivered *N*-phenyl-1-tosyl-1*H*-indol-2-amines **3cr** in 87% yield through a regioselective C−H annulation (Scheme 4). A 3,5-dimethoxyphenylynamide **2h** also showed excellent efficiency for the preparation of product **3ch**. Clearly, the gold carbenes prefer to insert into the *ortho*-C−H bonds of the more electron-rich phenyl group. By reacting with triphenylsulfilimine **1d**, 3-methoxyphenylynamide **2r** gave divergent products **4dr** (73% yield) and **3dr** (25% yield), while 3,5-dimethoxyphenyl-derived ynamide **2h** afforded a single product **3dh** in 75% yield. Notably, the reaction between sulfilimine **1d** and 4-methoxyphenylynamide **2e** yielded **4de** as a single product. These results demonstrate that the different electronic properties of the two nitrogen atoms (the imino nitrogen atom and the amide nitrogen atom) also have a significant influence on the C−H insertion processes.

In conclusion, we have described a new gold(III)-catalyzed C−H annulation of sulfilimines and *N*-phenylynamides for the synthesis of 2-aminoindoles. The reaction involves *α*-imino gold carbene intermediates. The current report features readily available substrates, mild conditions, and good substrate tolerance. Dimethyl (or diphenyl) sulfide as a safe leaving

Scheme 4. Synthesis of 2-Aminoindoles 3 or 4 through Competitive C−H Annulations



entry	ylide **1**	ynamide **2**	product **3**	product **4**
1	**1c**: R = Me, R^2 = Ms	**2r**: R^1 = 3-MeO	 **3cr**, 87%	 **4cr**, not obtained
2	**1c**: R = Me, R^2 = Ms	**2h**: R^1 = 3,5-diMeO	 **3ch**, 88%	 **4ch**, not obtained
3	**1d**: R = Ph, R^2 = H	**2h**: R^1 = 3,5-diMeO	 **3dh**, 75%	 **4dh**, not obtained
4	**1d**: R = Ph, R^2 = H	**2r**: R^1 = 3-MeO	 **3dr**, 25%	 **4dr**, 73%
5	**1d**: R = Ph, R^2 = H	**2e**: R^1 = 4-OMe	 **3de**, not obtained	 **4de**, 91%

[a]Reaction conditions: **1** (0.3 mmol, 1.5 equiv), **2** (0.2 mmol, 1.0 equiv), $PicAuCl_2$ (3.8 mg, 5 mol %), and toluene (2.0 mL, 0.1 M). [a]Isolated yields of products **3** and **4**.

group makes this method a practical and safely scalable alternative for synthesizing these biologically important heterocyclic compounds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b01501.

Experimental procedures and compound characterization (PDF)

Accession Codes

CCDC 1861977 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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Notes

The authors declare no competing financial interest.

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