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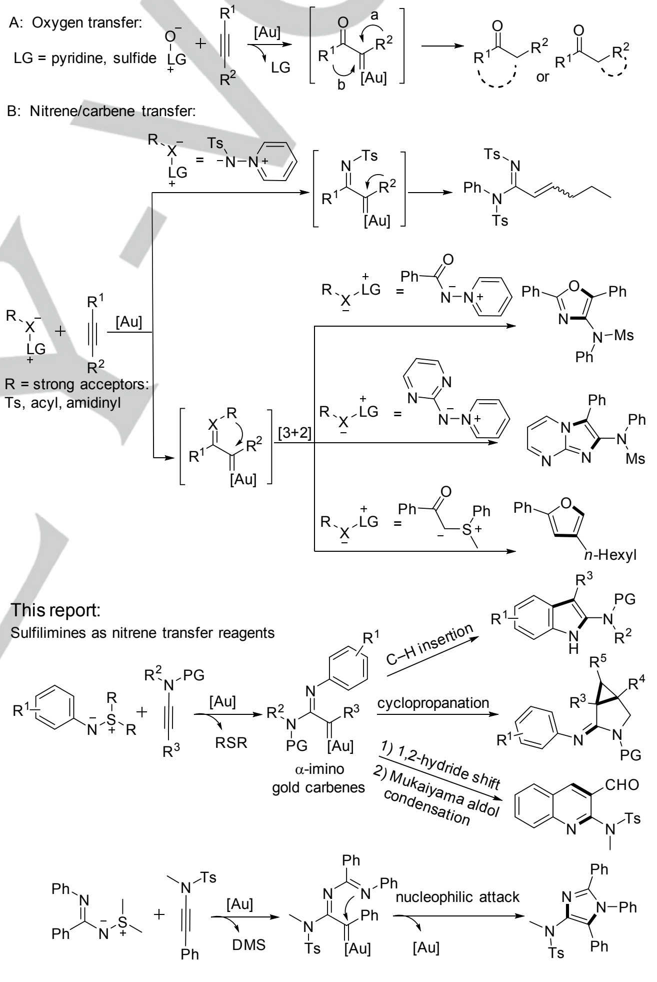
Sulfilimines as Versatile Gold Nitrene Transfer Reagents: Facile Access to Aza-Heterocyclic Diversity

Xianhai Tian,[a] Lina Song,[a] Matthias Rudolph,[a] Frank Rominger,[a] Thomas Oeser,[a] and A. Stephen K. Hashmi*[a,b]

Abstract: We herein report the unprecedented synthesis of diverse biologically important aza-heterocycles by employing sulfilimines as nitrene transfer reagents, this class of sulfur-based aza-ylides has not been successfully used for gold nitrene transfer before. This work contains an efficient generation of α-imino gold carbenes *via* N–S cleavage of sulfilimines. These gold carbenes undergo C–H insertion, cyclopropanation and nucleophilic attack to form indoles (44 examples), 3-azabicyclo[3.1.0]hexan-2-imines (24 examples) and imidazoles (3 examples). This work represents the unique gold-catalyzed reaction between alkynes and sulfur ylides, and also includes the first examples of aza-heterocycle syntheses *via* intermolecular nitrene transfer followed by cyclopropanation of the α-imino gold carbenes. Moreover, an unexpected synthesis of 4-acylquinolines (3 examples) from 2-acylphenyl sulfilimines and propargylic silyl ether derivatives by using a 1,2-hydride shift onto the α-imino gold carbene and a subsequent Mukaiyama aldol cyclization was discovered.

Over the last decade, gold catalysis[1] has been vastly utilized in the electrophilic activation of alkynes. Especially, the generation of gold carbenes from alkynes through intra- and intermolecular atom transfer processes and subsequent trapping of such carbenes has emerged as a powerful tool for efficient transformations. While *N*-oxides[2] and sulfoxides[3] were commonly employed for the formation of α-oxo gold carbenes, the intramolecular trapping of such α-oxo gold carbenes is restricted to functional groups in the substituents (Scheme 1, A). By contrast, the inter- or intramolecular nitrene transfer from nucleophilic nitrene equivalents such as pyridine-based aza-ylides,[4] azides,[5] 2*H*-azirines,[6] and isoxazole derivatives,[7] as well as carbene transfer from sulfonium ylides,[8] extend the opportunities for ring formation reactions; the generated gold carbenes can be trapped by functionalities attached to either the transfer reagents or the alkynes. Among these transfer reagents, ylides like pyridine-based aza-ylides (N^-–N^+), sulfonium ylides (C^-–S^+) have attracted considerable interests for their distinctive advantages in organic synthesis because of the functional group tolerance (Scheme 1, B), e.g. 1,2-hydride shifts[4f] or [3+2] annulations to form oxazoles,[4a] furans,[8a] and imidazo-diazines.[4c] However, to the best of our knowledge, these ylides are limited to strong acceptors (sulfonyls, acyls, amidinyls) on the anions to tune their stablity and reactivity. For the generation of α-imino gold carbenes the use of new ylides bearing an aryl group on the anions is highly challenging and of great importance, such gold carbenes can efficiently form C-C bonds by insertion into the *ortho*-C–H bonds.



Scheme 1. Previous work on atom transfer processes from ylides and envisioned α-imino gold carbene formation from sulfilimines *via* N–S bond cleavage.

Sulfur-based ylides are valuable synthetic intermediates due to their high reactivity, sulfonium ylides[9] have been investigated with great success with respect to [2+1] annulations for classic cyclopropane synthesis from alkenes, epoxide synthesis from carbonyl compounds, and aziridine synthesis from imines. Recently, even in gold chemistry, acyl-stablized sulfonium ylides were employed as gold-carbene precusors for 1,3-dipolar [3+2] annulations[8] and cyclopropanations.[10] In contrast to this, the

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study of their nitrogen analogues, sulfilimines,[11] remain comparatively underdeveloped, especially in gold chemistry. Compared with other nucleophilic nitrenes, sulfilimines feature inexpensive and easy synthesis,[12] and due to the strong polarization towards the nitrogen atom, these buliding blocks can emerge as valuable synthetic intermediates by N–S bond cleavage.[13] Nevertheless, to the best of our knowledge, this versatile and promising metal–nitrene precursor has never been successfully applied as a gold carbene precusor, although *N*-sulfonylsulfilimines were employed by Zhang et al.[4b] for the synthesis of α,β-unsaturated amidines (only 2 examples) in less than 35% yield and quite moderate *E/Z* ratios of 1.5/1 to 2/1. Inspired by previous reports[14] and in line with our interests on gold-catalyzed C–H annulations (N–O bond cleavage for nitrene transfer),[7b,d,g] we envisioned the generation of α-imino gold carbenes from sulfilimines and ynamides, which could be flexibly and divergently trapped by four types of functionalities attached to either sulfilimines or ynamides to form four different aza-heterocycles (Scheme 1).

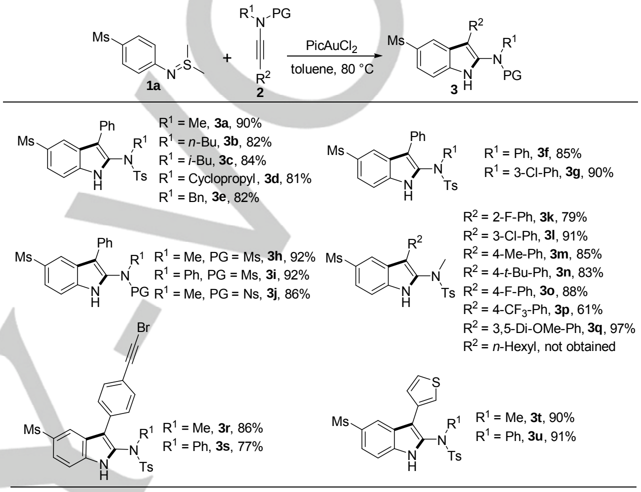
Table 1: Optimization of the reaction conditions[a]

Entry	Catalyst	Solvent	Time/h	Yield[b]
1	IPrAuCl/$AgNTf_2$	toluene	24	17%
2	$PPh_3AuCl/AgNTf_2$	toluene	24	13%
3	$NaAuCl_4$	toluene	4	77%
4	**$PicAuCl_2$**	**toluene**	**4**	**90%**
5	$PicAuCl_2$	THF	4	67%
6	$PicAuCl_2$	DCE	4	72%
7	-	toluene	4	n. d.[c]

[a] General reaction conditions: **1a** (0.3 mmol, 1.5 equiv), **2a** (0.2 mmol, 1.0 equiv), catalyst (5 mol%), solvent (2.0 mL, 0.1 M), 80 °C; [b] Isolated yield of product **3a**; [c] n. d.: not detected.

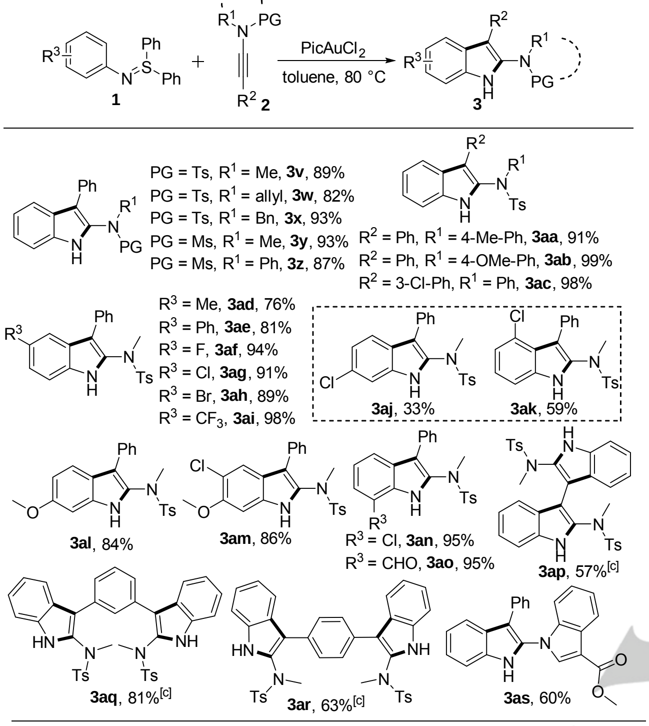
The reaction between *S*,*S*-dimethylsulfilimine **1a** and ynamide **2a** in toluene at 80 °C for 24 h with IPrAuCl/$AgNTf_2$ as catalyst was explored first, providing 2-aminoindole **3a**[15] in 17% yield (Table 1, entry 1). $PPh_3AuCl/AgNTf_2$ as catalyst did not improve the reaction (entry 2). Further screening showed that gold(III) complexes are more efficient catalysts (entry 3–4), and $PicAuCl_2$[16] delivered **3a** in 90% yield (entry 4). A short solvent optimization showed that toluene is the best solvent (entry 5–6). In the absence of any catalyst no desired product was obtained (entry 7).

Under the optimized conditions, we investigated the reaction scope. A series of ynamides bearing alkyl and aryl groups on the nitrogen atom gave the corresponding 2-aminoindoles (**3a**–**3g**) in 81-90% yield (Scheme 2). Ynamides with other protective groups like methylsulfonyl and easily cleavable 4-nitrophenylsulfonyl gave **3h**–**3j** in high yields. Ynamides bearing diverse functionalities including electron-withdrawing, electron-donating, and halogen substituents on the benzene rings delivered the desired products **3k**–**3q** in good to high yields, while an alkyl ynamide (R^2 = *n*-hexyl) reacted unselectively (detected by TLC). Substrates containing sensitive bromoethynyl motif were especially well tolerated affording products **3r** and **3s** in 86% and 77% yield. 3-(Thien-3-yl)-substituted indoles **3t**–**3u** could also be synthesized.

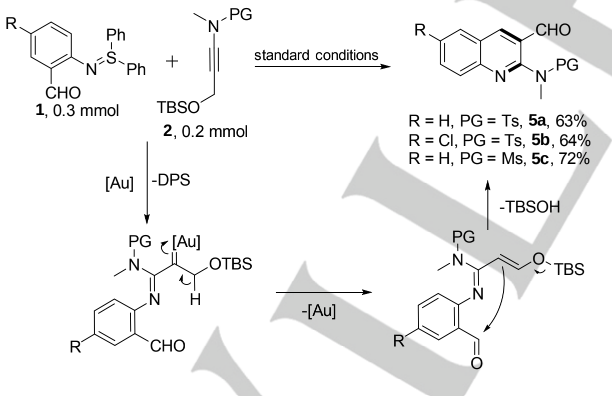


Scheme 2. Scope with respect to the ynamides[a, b]. [a] Reaction conditions: **1a** (0.3 mmol, 1.5 equiv), **2** (0.2 mmol, 1.0 equiv), $PicAuCl_2$ (3.8 mg, 5 mol%), toluene (2 mL, 0.1 M); [b] Yield of isolated product **3**.

We then tested the reactivity of *N*-phenylsulfilimines. Due to the poor stability of *S*,*S*-dimethyl-*N*-phenylsulfilimines without electron-withdrawing groups on the benzene ring, we sought to prepare diverse indoles from *S*,*S*-diphenyl-*N*-phenylsulfilimines (Scheme 3). To our delight, triphenylsulfilimine **1b** reacted efficiently with a variety of ynamides to afford an array of products **3v**–**3ac** in 82%–99% yields. Ylides **1c**–**1h** bearing methyl, phenyl, halogen and trifluoromethyl groups at the 4-positions also gave **3ad**–**3ai** in good to excellent yield. The efficiency was contrary to the electron density on the aromatic ring. 3-Substituted-phenyl sulfilimines were also found to be suitable for the synthesis of 2-aminoindoles. The substrate with a chloro substituent at 3-position could be converted in high efficiency with a poor ortho/para selectivity (**3ak**/**3aj** = 59/33, solid state molecular structure of **3ak**[15] is shown in the supporting information), while both 3-methoxy- and 4-chloro-3-methoxyphenyl sulfilimines led to single regioisomers (**3al**–**3am**) in high yields. 7-Chloroindole **3an** could be prepared from 2-chlorophenylsulfimine **1l**. For 2-acylphenylsulfilimines, 7-acylindole **3ao** was isolated in 93% yield from normal ynamide **2a**, while 4-acylquinolines **5a-c** were prepared from propargylic silyl ethers under standard conditions through a 1,2-hydride shift onto the α-imino gold carbene and sequential Mukaiyama aldol cyclization (Scheme 4). Larger molecules **3ap**–**3ar** containing two indole cores were obtained by bidirectional reactions of bis-ynamides and 3 equivalents triphenylsulfilimine **1b**. Furthermore, a non-sulfonyl-protected ynamide bearing an indole core is also suitable for this transformation (**3s**).

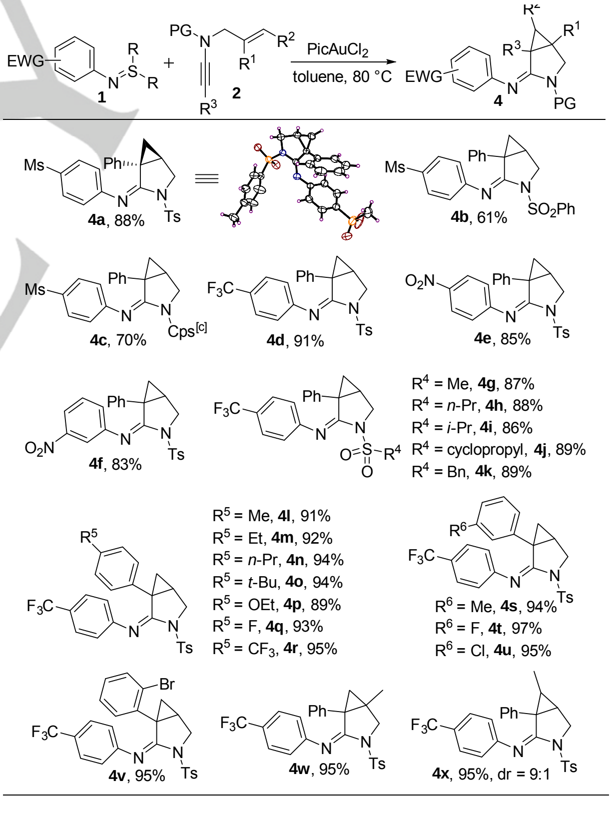


Scheme 3. Scope of sulfilimines[a, b]. [a] Reaction conditions: **1** (0.3 mmol, 1.5 equiv), **2** (0.2 mmol, 1.0 equiv), PicAuCl$_2$ (3.8 mg, 5 mol%), toluene (2 mL, 0.1 M); [b] Yield of isolated product **3**; [c] 3.0 equiv ylide **1a** was used.



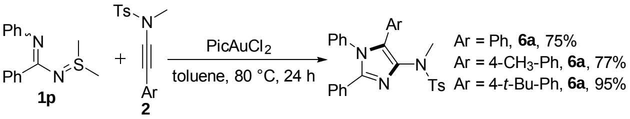
Scheme 4. Synthesis of 4-acylquinolines through gold-catalyzed cascade transformations[a]. [a] Isolated yield of **5**.

The products are not only confined to quinoline and indole derivatives. Under the same reaction conditions, by using *S*,*S*-dimethyl sulfilimine **1a** and *N*-allyl ynamide as substrates, we prepared 3-azabicyclo[3.1.0]hexan-2-imine **4a**[15] rather than the indole product, through cyclopropanation of the corresponding gold carbene (Scheme 5). Sulfilimine **1a** also reacted well with ynamides bearing either phenylsulfonyl or 4-chlorophenylsulfonyl on the nitrogen (**4b−4c**). *S*,*S*-Diphenyl-*N*-phenyl sulfilimines bearing other electron-withdrawing groups (NO$_2$, CF$_3$) at either *meta*- or *para*-positions underwent the desired cyclopropanation process to give the corresponding products in 83%-91% yield. This reaction was found to be compatible with a series of *N*-alkylsulfonyl-substituted ynamides (R^4 = Me, *n*-Pr, *i*-Pr, cyclopropyl, Bn) and the products **4g−4k** were all obtained in higher than 86% yields. Ynamides with diverse substituents (R^5 = Me, Et, *n*-Pr, *t*-Bu, Oet, F, CF$_3$) at the 4-positions of the benzene rings were also tested. As expected, these ynamides provided the corresponding cyclopropane compounds **4l−4r** in excellent yields. When R^6 was varied from an electron donating group (methyl) to an electron withdrawing group (chloro or fluoro) at 3-positions of the benzene rings, the reactions proceeded smoothly and the corresponding products **4s−4u** were achieved in excellent yields. A bromo substituent also survived in this transformation, and the target **4v** was obtained in 95% yield. Product **4w** with two vicinal quaternary carbon centers could be efficiently synthesized by the treatment of N-(2-methylallyl)ynamide (R^2 = Me) with *N*-(4-trifluoroPhenyl)sulfilimine **1h**. An internal alkene derivative gave product 6-methyl-3-azabicyclo[3.1.0]hexan-2-imine **4x** in 95% yield with a diastereomer ratio of 9:1.



Scheme 5. Synthesis of 3-azabicyclo[3.1.0]hexan-2-imines **4** [a, b]. [a] Reaction conditions: for products **4a**-**4c**, R = Me, **1a** (0.3 mmol, 1.5 equiv), **2** (0.2 mmol, 1.0 equiv), PicAuCl$_2$ (3.8 mg, 5 mol%), toluene (2 mL, 0.1 M); for products **4d**-**4x**, R = Ph, **1** (0.2 mmol, 1.0 equiv), **2** (0.24 mmol, 1.2 equiv), PicAuCl$_2$ (3.8 mg, 5 mol%), toluene (2 mL, 0.1 M); [b] Yield of isolated product **4**. [c] Cps = 4-chlorophenylsulfonyl.

To completely explore the reactivity pattern between sulfilimines and ynamides, we further attempted to probe the feasibility of imidazole synthesis from *N*-iminylsulfilimine **1p**. Fortunately, under the standard conditions, the fully-substituted imidazole derivatives **6a-c** were formed in 75-95% yields by employing the second nitrogen atom as a trapping functional group (Scheme 6).



Scheme 6. Synthesis of imidazole **6** through nucleophilic attack of the gold carbene[a,b]. [a] Reaction conditions: **1p** (0.3 mmol, 1.5 equiv), **2** (0.2 mmol, 1.0 equiv), $PicAuCl_2$ (3.8 mg, 5 mol%), toluene (2 mL, 0.1 M); [b] Yield of isolated product.

In conclusion, this successful and broad use of sulfilimines for the synthesis of biologically important amino-substituted aza-heterocycles and carbocycles via gold iminocarbene intermediates clearly demonstrates the synthetic potential of these reagents and reactions, which certainly is not limited to the specific examples in this manuscript. Future applications also will benefit from the fact that the sulfilimine reagents are cheap and readily available, a future challenge is the use of less activated alkynes.

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Keywords: sulfilimines • gold carbenes • gold catalysis • C–H annulations • cyclopropanations

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COMMUNICATION

Readily available sulfilimines were successfully applied as versatile nitrene transfer reagents. By trapping the α-imino gold carbenes that were formed with divergent functionalities, four different types of aza-heterocycles (indoles, 3-azabicyclo[3.1.0]hexan-2-imines, quinolines, and imidazoles) were prepared in high efficiency.

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