OL | Organic Letters

Letter

Cite This: Org. Lett. XXXX, XXX, XXX−XXX

pubs.acs.org/OrgLett

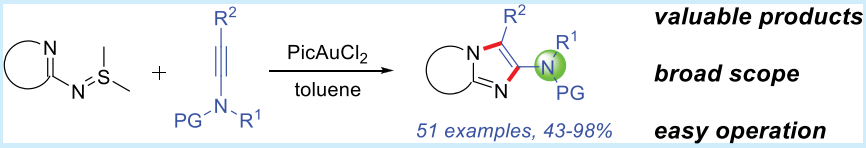
N-Pyridinyl Sulfilimines as a Source for α-Imino Gold Carbenes: Access to 2-Amino-Substituted *N*-Fused Imidazoles

Xianhai Tian,[†] Lina Song,[†] Matthias Rudolph,[†] Qian Wang,[†] Xinlong Song,[†] Frank Rominger,[†] and A. Stephen K. Hashmi*[,†,‡]

[†]Institut für Organische Chemie, Universität Heidelberg, Im Neuenheimer Feld 270, Heidelberg 69120, Germany

[‡]Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

Supporting Information



ABSTRACT: Gold-catalyzed formal 1,3-dipolar annulation between readily accessible *N*-pyridinylsulfilimines and ynamides is reported. A diverse set of imidazole derivatives is prepared from the corresponding sulfilimines and ynamides. These functionalized cyclic products can undergo further transformations to afford diverse imidazole frameworks. Moreover, in situ synthesis is feasible and shows good potential in the synthesis of nucleoside analogues.

Gold complexes have emerged as highly effective catalysts for the electrophilic activation of alkynes under homogeneous conditions.[1] In particular, gold-catalyzed reactions between ylides and alkynes can lead to bioactive compounds, and several ylidic species were applied in this type of reaction, involving O^--N^+,[2] O^--S^+,[3] N^--N^+,[4] and C^--S^+.[5] Formation of gold carbenes by intramolecular or intermolecular atom transfer processes to C−C triple bonds enables efficient transformations. Moreover, the introduction of functionality adjacent to the electrophilic gold carbene in such processes offers a wide opportunity for facile annulations to form nontrivial heterocycles. In this context, gold-catalyzed dipolar annulations between conjugated ylides, such as pyridine-*N*-aminides (N^--N^+ ylide),[4e] acyl sulfonium ylides (C^--S^+ ylide),[5a] and activated alkynes provide valuable methods for target-directed synthesis, resulting in multisubstituted oxazoles and furan derivatives.

Imidazo[1,2-*a*]pyridines[6] are keystone nitrogen-containing heterocycles highly important in widespread areas. In particular, imidazo[1,2-*a*]pyridines bearing a 2-amino group on the imidazole ring are key pharmacophores for many biologically important compounds, exhibiting a broad range of properties, including antivirus,[7] antitumor,[8] antiproliferative,[9] and smoothened antagonistic[10] activities (Figure 1). Hence, synthesis of imidazo[1,2-*a*]pyridin-2-amines is of great importance, and in the last two decades, there has been long-standing interest in the construction of N-fused imidazole frameworks. However, methods for the preparation of fused 2-amino imidazoles are rare and are based on classical multistep synthesis. Recently, Davies' group[4e] reported a gold-catalyzed [3 + 2] annulation between *N*-pyrimidinylaminide and ynamide for the synthesis of 2-amino-substituted fused imidazole. Later, Chang et al.[11] synthesized imidazo[1,2-*a*]pyridin-2-amine from 2-aminopyridine and nitrile via $SnCl_4$-promoted condensation and sequential I_2/KI-mediated oxidative cyclization. Despite these achievements, an efficient and short route to this significant compound class from readily available starting materials under mild conditions is still highly desirable.

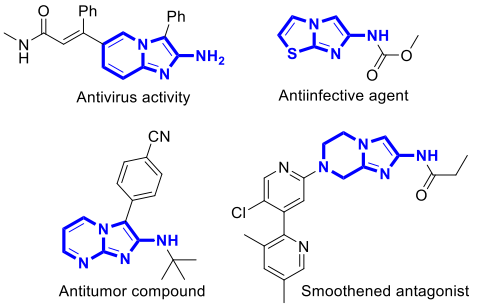


Figure 1. Bioactive compounds bearing *N*-fused 2-amino imidazole cores.

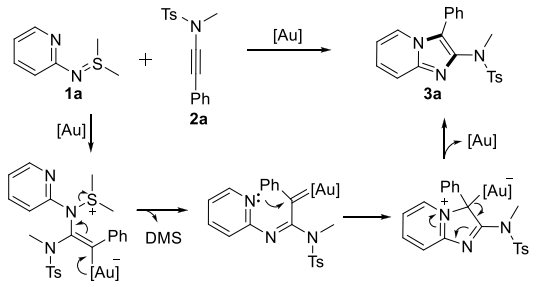
Among sulfur-containing ylides, whereas sulfonium ylides have been widely studied,[12] sulfilimines[13] are less explored. This readily available ylidic unit can serve as valuable synthetic intermediates through a cleavage of the polarized N−S bond.[14] This versatile and promising metal−nitrene precursor has been applied as a gold carbene precusor. Zhang et al.[4b] employed *N*-sulfonylsulfilimines as nitrene transfer reagents for the synthesis of α,β-unsaturated amidines (two examples). We recently developed a successful strategy for preparing diverse aza-heterocycles by utilizing *N*-phenylsulfilimines as gold carbene precusors.[15] This method contains an efficient generation of α-imino gold carbenes and subsequent divergent intramolecular trappings. Inspired by the previous studies[16] and as a continuous work on

Received: January 12, 2019

DOI: 10.1021/acs.orglett.9b00140
Org. Lett. XXXX, XXX, XXX−XXX

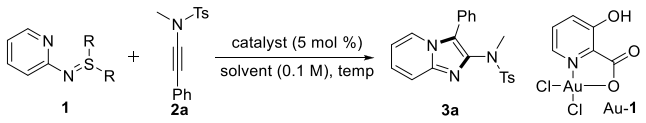
sulfilimines, we herein envisioned the construction of 2-amino-substituted imidazo[1,2-*a*]pyridine **3a** from pyridine-based sulfilimine **1a** and ynamide **2a** via a gold carbene intermediate (Scheme 1).

Scheme 1. Envisioned *α*-Imino Gold Carbene Transfer Process via N−S Bond Cleavage



Reaction between *S*,*S*-dimethyl-*N*-(pyridin-2-yl)-sulfilimine **1a** and ynamide **2a** in toluene was first tested at 80 °C by employing 5 mol % of IPrAuCl/$AgNTf_2$ as catalyst (Table 1, entry 1), resulting in imidazopyridine **3a** in 29% yield. Another gold(I) catalyst did not improve the reaction (entry 2). Gold(III) catalysts, such as $KAuBr_4$, delivered **3a** in good yield (entry 3). Among the Au(III) catalysts tested, $PicAuCl_2$[17] performed the best, affording **3a** in 95% yield. A 2 mmol scale reaction is even more efficient (entry 4). DCE and THF are also suitable solvents (entries 6 and 7). Short temperature screening (entries 8 and 9) indicated that 80 °C was the best temperature. It is worth mentioning that *S*,*S*-diphenylsulfilimine **1s** and THT-substituted sulfilimine **1r** also performed well, however, in lower yields (entries 10 and 11). In the absence of any catalyst, no desired product was achieved, obviously verifying the necessity of a gold catalyst (entry 12). Poisoning of the gold catalyst by the second product, DMS, was not observed (for the detailed investigation, see Supporting Information).

Table 1. Optimization of Reaction Conditions[a]

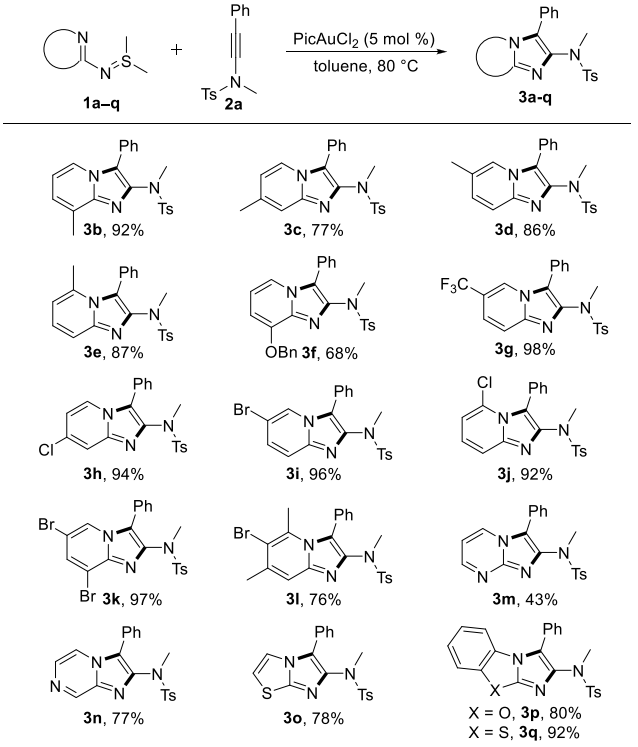


entry	RSR	catalyst	solvent	temp (°C)/ time (h)	yield[b] (%)
1	DMS[d]	IPrAuCl/$AgNTf_2$	toluene	80/24	29
2	DMS	$PPh_3AuCl/AgNTf_2$	toluene	80/24	34
3	DMS	$KAuBr_4$	toluene	80/5	77
4	**DMS**	**$PicAuCl_2$**	**toluene**	**80/4**	**95 (97)**[g]
5	DMS	Au-**1**	toluene	80/8	81
6	DMS	$PicAuCl_2$	DCE	80/9	75
7	DMS	$PicAuCl_2$	THF	80/4	87
8	DMS	$PicAuCl_2$	toluene	70/4	91
9	DMS	$PicAuCl_2$	toluene	90/4	89
10	DPS[e]	$PicAuCl_2$	toluene	100/10	61
11	THT[f]	$PicAuCl_2$	toluene	80/10	93
12	DMS		toluene	80/10	nd[c]

[a]General reaction conditions: **1** (0.3 mmol, 1.5 equiv), **2a** (0.2 mmol, 1.0 equiv), catalyst (5 mol %), solvent (2.0 mL, 0.1 M). [b]Isolated yields of product **3a**. [c]Not detected. [d]DMS: dimethylsulfide. [e]DPS: diphenylsulfide. [f]THT: tetrahydrothiophene. [g]Yield of the 2 mmol scale reaction (reaction time: 18 h).

Under the optimized reaction conditions (Table 1, entry 4), we investigated the reaction scope. As shown in Scheme 2, a series of sulfilimines bearing electron-donating groups on the pyridine ring all smoothly converted to the corresponding imidazopyridines (**3b**−**f**). Electron-deficient sulfilimines **1g**−**k**, bearing a trifluoromethyl or halogen substituent also delivered the targets **3g**−**k** in 92−98% yield. A trisubstituted ylide was also well tolerated, affording product **3l** in 76% yield, the structure of which was further confirmed by single-crystal X-ray structure analysis (Figure 2). Additionally, this reaction was elaborated to enable the synthesis of imidazo[1,2-*a*]pyrimidine **3m**, imidazo[1,2-*a*]pyrazine **3n**, imidazo[2,1-*b*]thiazole **3o**, benzo[*d*]imidazo[2,1-*b*]oxazole **3p**, and benzo[*d*]imidazo[2,1-*b*]thiazole **3q** from the corresponding sulfilimines bearing other heteroaromatic units.

Scheme 2. Scope of Sulfilimines[a,b]



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

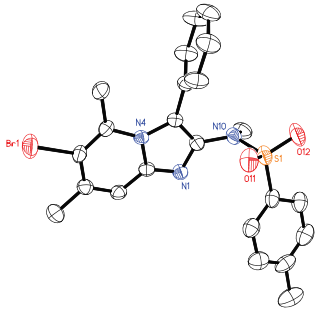
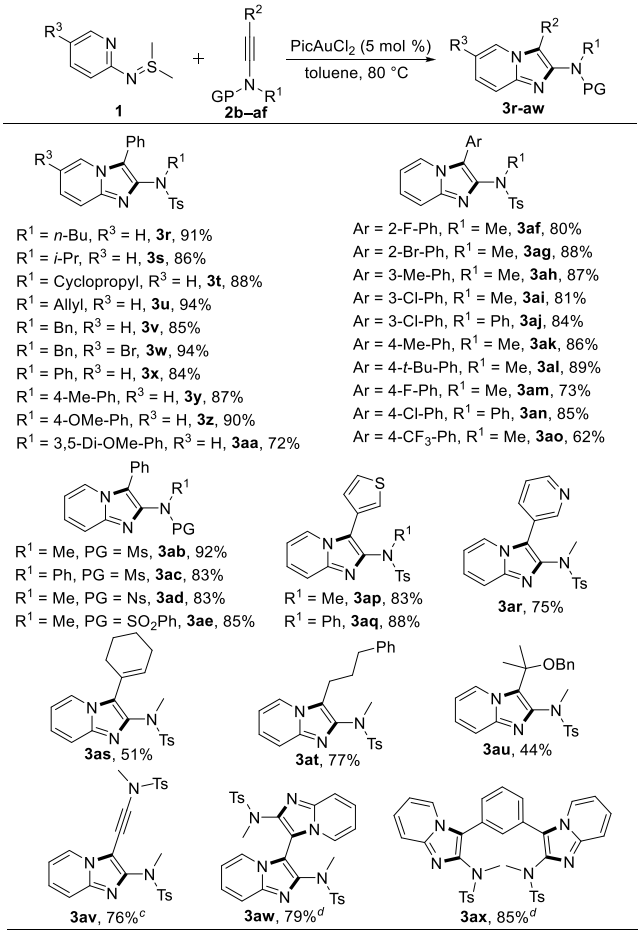


Figure 2. Solid-state molecular structure of **3l**.

DOI: 10.1021/acs.orglett.9b00140
Org. Lett. XXXX, XXX, XXX−XXX

As a next step, we tested the limitations with respect to the ynamides (Scheme 3). A wide range of *N*-Ts-substituted

Scheme 3. Scope of Ynamides[a,b]

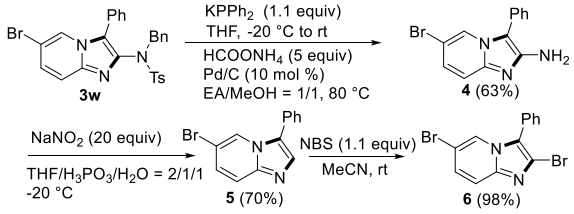


[a]Reaction conditions: **1** (0.3 mmol, 1.5 equiv), **2** (0.2 mmol, 1.0 equiv), $PicAuCl_2$ (3.8 mg, 5 mol %), toluene (2 mL, 0.1 M). [b]Isolated yields. [c]1.0 equiv of ylide **1a** was used. [d]3.0 equiv of ylide **1a** was used; reaction temperature: 85 °C.

ynamides **2b–j** with a variety of R^1 substituents, involving alkyl, allyl, benzyl, and aryl, efficiently participated in this process. For ynamides **2k–n**, containing other sulfonyl protecting groups (Ms, Ns, $PhSO_2$) on the nitrogen atom, this reaction was found to be compatible. The reaction proceeded well with various substituents in *ortho*, *meta*, and *para* positions on the benzene rings of starting ynamides **2o–x**. The efficiency correlated with the electron density on the aromatic ring. Electron-rich aryl groups gave the homologous products **3ah**, **3ak**, and **3al** in good yields, whereas the reaction was found to be less efficient with electron-withdrawing groups on the aromatic ring (**3af**, **3am**, and **3ao**). Moreover, 3-(thiophen-3-yl)-substituted (**3ap–aq**) and 3-(pyridin-3-yl)-substituted (**3ar**) imidazo[1,2-*a*]pyridines were synthesized from the corresponding heterocyclic-substituted ynamides. An ynamide with 1,3-enyne structure was also found to be suitable, albeit in 51% yield (**3as**). We then moved our focus to annulations between sulfilimines and alkyl-substituted ynamides (R^2 = alkyl). Alkyl ynamide **2ac** (R^2 = 3-phenylpropyl) reacted well, delivering the desired product **3at** in 77% yield, and no 1,2-*H*-shift product was afforded. In the absence of an α-hydrogen, ynamide **2ad** gave the target compound **3au** in 44% yield despite strong steric hindrance. Dimerized ynamide **2ae** and bis-ynamide **2af** were able to efficiently convert into products **3aw** and **3ax** containing two imidazopyridine cores by using 3.0 equiv of ylide **1a**. Imidazo[1,2-*a*]pyridine **3av**, by contrast, could be achieved by decreasing the amount of ylide **1a**.

Heterocycles with unprotected amino groups are always associated with diverse bioactivities, hence a complete deprotection strategy was required. With **3w** as an example, the sequential in situ detosyl-[18] and debenzylation processes gave free 6-bromo-3-phenylimidazo[1,2-*a*]pyridin-2-amine **4** in 63% overall yield (Scheme 4). Reductive dediazotization of **4** with sodium

Scheme 4. Important Postmodifications of 3w[a]

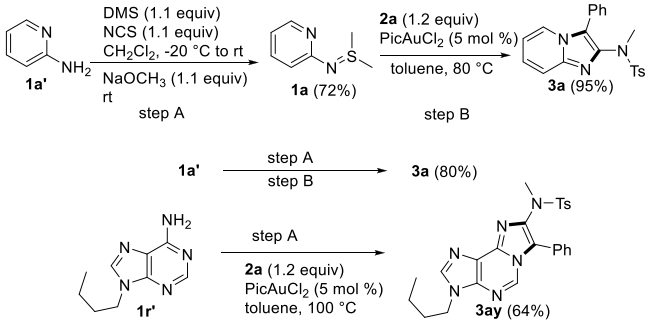


[a]Isolated yields.

nitrite in aqueous hypophosphorus acid[19] afforded 6-bromo-3-phenylimidazo[1,2-*a*]pyridine **5** in 70% yield, which can be quantitively converted into 2,6-dibromo-3-phenylimidazo[1,2-*a*]pyridine **6** via NBS-mediated bromination at the 2-position on the imidazole ring.[20] This compound could serve as a valuable precursor for cross-coupling strategies.

Saving time and energy needed for purification steps makes in situ processes important for drug and natural product synthesis. With sulfilimine **1a**, we attempted to probe the feasibility of a sequential synthesis of imidazopyridine **3a** directly from 2-aminopyridine **1a′** without purification of the intermediate **1a**. As depicted in Scheme 5, direct annulation between crude **1a** and

Scheme 5. Investigations of an in Situ Process[a]



[a]Isolated yields.

ynamide **2a** afforded product **3a** in even higher yield than the two-step reactions using pure **1a**. Further application by the in situ modification of adenine **1r′** demonstrated that this versatile protocol has great potential for the synthesis of nucleoside analogues.

In summary, *N*-pyridinylsulfilimines, as new nitrene transfer reagents, were efficiently applied for the synthesis of imidazo[1,2-*a*]pyridin-2-amines and related heterocycles via α-imino gold carbene intermediates. This method features simple reaction conditions, high efficiency, and excellent functional group compatibility. Required sulfilimines can be readily prepared

DOI: 10.1021/acs.orglett.9b00140
Org. Lett. XXXX, XXX, XXX–XXX

from commercially available, inexpensive arylamines, dimethyl sulfide, and NCS. Furthermore, in situ synthesis is available, and this in situ process showed great potential in the synthesis of nucleoside analogues. As a competing reaction, a gold-catalyzed rearrangement (see Supporting Information) of sulfilimines to offer a new approach to 3-methylthiomethyl-substituted 2-aminopyridines was discovered.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00140.

Experimental procedures and compound characterization (PDF)

Accession Codes

CCDC 1812317 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.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hashmi@hashmi.de.

ORCID

A. Stephen K. Hashmi: 0000-0002-6720-8602

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

X.T., L.S., Q.W., and X.S. are grateful to the CSC (China Scholarship Council) for a PhD fellowship.

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DOI: 10.1021/acs.orglett.9b00140
Org. Lett. XXXX, XXX, XXX−XXX