Heterocycle Synthesis

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Gold(I)-Catalyzed N-Desulfonylative Amination versus N-to-O 1,5-Sulfonyl Migration: A Versatile Approach to 1-Azabicycloalkanes

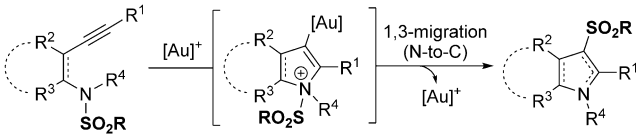
Solène Miaskiewicz, Boris Gaillard, Nicolas Kern, Jean-Marc Weibel, Patrick Pale, and Aurélien Blanc**

Abstract: *Valuable 1-azabicycloalkane derivatives have been synthesized through a novel gold(I)-catalyzed desulfonylative cyclization strategy. An ammoniumation reaction of ynones substituted at the 1-position with an N-sulfonyl azacycle took place in the presence of a gold cation by intramolecular cyclization of the disubstituted sulfonamide moiety onto the triple bond. Depending on the size of the heterocyclic ring and substitution of the substrates, two unprecedented forms of nucleophilic attack on the sulfonyl group were exploited, that is, a N-desulfonylation in the presence of an external protic O nucleophile (37–87 %, 10 examples) and a unique N-to-O 1,5-sulfonyl migration (60–98 %, 9 examples).*

Since the beginning of this century, homogeneous gold catalysis has emerged as a continuously growing field of investigation.[1] Indeed, owing to their exceptional π acidity, cationic gold(I) complexes have been used in a myriad of synthetic applications, especially in the catalytic activation of unsaturated carbon–carbon bonds for nucleophilic addition reactions.[2] Such studies have led to outstanding achievements in asymmetric catalysis[3] as well as in total synthesis.[4]

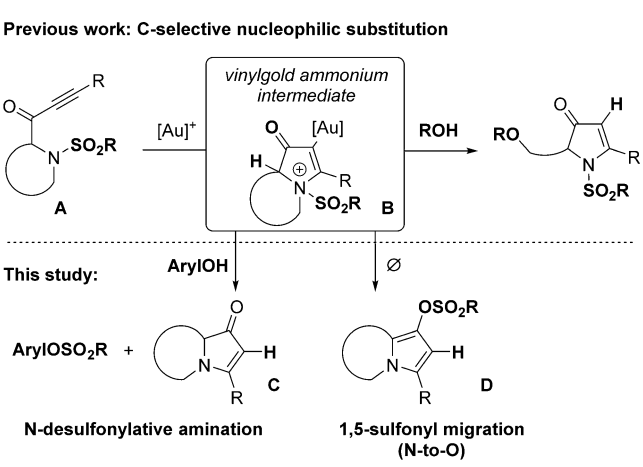
In this area, the gold-catalyzed amination of alkynes has become a very useful and common tool for the construction of elaborate heterocyclic structures containing at least one nitrogen atom.[5] The potential of these transformations has been demonstrated by their application to the synthesis of nitrogen-containing natural and biologically active products.[6] However, the amination process still demands appropriate substrate engineering. Indeed, basic amine groups often inhibit catalytic activity by strongly interacting with gold cations,[7] but also by slowing down the protodemetalation step, which is rate-limiting in many catalytic cycles.[8] To address this problem, electron-withdrawing nitrogen-protecting groups are generally used, such as the popular and robust sulfonyl groups (–SO_2R), thus inferring the need for a subsequent deprotection step. However, N-desulfonylation reactions are far from trivial and still represent a significant challenge,[9] which can hamper the transfer of interesting methodologies to real total synthesis. Indeed, strong reductive or basic conditions are typically required for N-desulfonylation,[10] and such conditions are rarely compatible with polyfunctional complex natural product targets.

The alleviation of these problems would thus offer new opportunities in total synthesis based on gold catalysis. The few known examples of gold-catalyzed intramolecular cyclization reactions of secondary sulfonamides suggest an interesting approach (Scheme 1).[11] In these reactions, sulfonyl migration from nitrogen to the gold-bound carbon atom occurs via a transient vinylgold ammonium intermediate. However, this N-desulfonylation pathway leads to compounds of limited synthetic utility owing to the formation of a C–SO_2R bond, which is difficult to cleave.[12]



Scheme 1. Known N-to-C 1,3-sulfonyl migration catalyzed by gold(I).[11]

We recently demonstrated that bicyclic vinylgold ammonium intermediates, formed by the gold activation of ynones **A** substituted at the 1-position with an *N*-sulfonyl azacycle, can be opened regioselectively by oxygenated nucleophiles. This reaction allowed the exclusive formation of pyrrolin-4-ones in high yields (Scheme 2, top).[13] On this basis, an



Scheme 2. Gold(I)-catalyzed regioselective ammonium substitution or migration with an external or internal protic nucleophile.

[*] S. Miaskiewicz, B. Gaillard, Dr. N. Kern, Prof. Dr. P. Pale, Dr. A. Blanc
Laboratoire de Synthèse, Réactivité Organiques et Catalyse
UMR 7177 associé au CNRS, Institut de Chimie
Université de Strasbourg
4 rue Blaise Pascal, 67070 Strasbourg (France)
E-mail: ppale@unistra.fr
ablanc@unistra.fr

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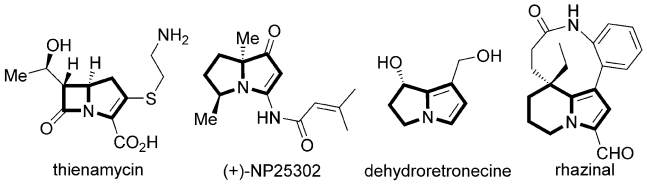
alternative pathway could be envisaged through nucleophilic attack, either inter- or intramolecularly, on the sulfonyl group on the ammonium intermediate **B**. Such a cascade would lead to the synthetically useful 1-azabicycloalkane derivatives **C** and **D** (Scheme 2, bottom).

Thus, after an initial gold-triggered ammoniumation,[14] an appropriate soft, protic, and sulfur-selective nucleophile would cleave the N–S bond and also deliver the requisite proton for demetalation, thus affording deprotected products **C** in a single operation (Scheme 2, bottom left). Besides this formal hydroamination reaction, another option could be considered in the absence of an external nucleophile. Indeed, the in situ generation of an internal O nucleophile, through a favorable keto–enol equilibrium, could lead to an N-to-O transfer of the sulfonyl group to afford vinyl sulfonate derivatives **D** (Scheme 2, bottom right).[15] Such a gold-catalyzed 1,5-sulfonyl migration would furnish powerful partners for palladium- and nickel-catalyzed cross-coupling reactions,[16] through the conversion of a weakly nucleophilic sulfonamide into an electrophilic sulfonate.

Herein, we report the successful implementation of these hypotheses in a novel step-economic gold-catalyzed strategy for the synthesis of various 1-azabicyclo[*m.n.*0]alkanes. These motifs are very important, as they are present in numerous natural products, such as carbapenem ([3.2.0]),[17] pyrrolizidine ([3.3.0]), and indolizidine ([4.3.0]) alkaloids,[18] which exhibit potent and useful biological activity (Scheme 3).

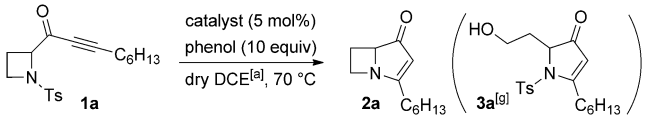


Scheme 3. Examples of naturally occurring 1-azabicyclic systems.

With this aim, we chose the readily available 1-(*N*-tosylazetidinyl) ynone **1a**[13] as a model substrate to evaluate the first strategy, that is, the N-desulfonylative cyclization reaction with phenol as a selective nucleophile. N-to-O sulfonyl migration should be minimized with this model compound because the strained azetidinium intermediate formed upon gold activation (**B** in Scheme 2) should be less prone to enolization.

Rewardingly, the simple and stable Gagosz catalyst smoothly provided the expected azabicyclic product[19] **2a** in 50% yield with 10 equivalents of phenol (Table 1, entry 1). Tuning of the ligand properties did not improve this result (Table 1, entries 2–6), whereas counterion variations had a strong effect (entries 7–9). Tetrafluoroborate emerged as the best anion and led to the best combination with tricyclohexylphosphine as the ligand. $[Cy_3PAu]BF_4$ promoted the formation of **2a** in 87% yield in only 0.5 h (Table 1, entry 10). Control experiments confirmed that the transformation did not occur in the absence of a gold catalyst, whereas silver tetrafluoroborate alone afforded a minor amount of pyrrolin-4-one[13] (**3a**) (product type in Scheme 2, top) along with degradation products (Table 1, entries 11 and 12). Phenyl 4-methylbenzenesulfonate was always produced concomitantly in these reactions, thus supporting our mechanistic hypothesis (Scheme 2).

Table 1: Screening of gold catalysts in the N-detosylative amination of **1a**.

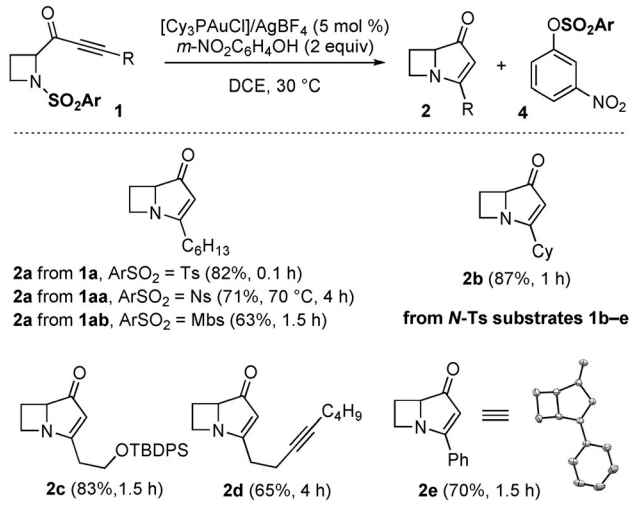


Entry	Catalyst	Time [h]	Yield [%][b,c]
1	$[Ph_3PAu]NTf_2$	5	50
2	$[(C_6F_5)_3PAu]NTf_2$	5	34
3	$[LAu]NTf_2$[d]	6	5[e]
4	$[IPrAuCl]/AgNTf_2$	24	12[e]
5	[JohnPhosAu]NTf_2	3	48
6	$[Cy_3PAu]NTf_2$	1	49
7	$[Ph_3PAuCl]/AgSbF_6$	2.5	32
8	$[Ph_3PAuCl]/AgPF_6$	1.5	49
9	$[Ph_3PAuCl]/AgBF_4$	1.5	66
10	$[Cy_3PAuCl]/AgBF_4$	0.5	87
11	–	24	–[f]
12	$AgBF_4$	5	–[g]

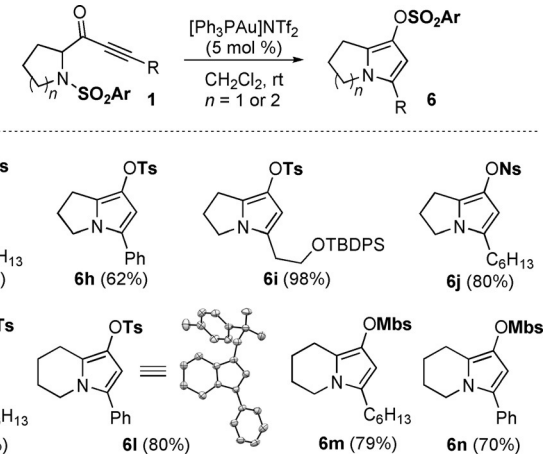
[a] DCE = 1,2-dichloroethane; $c = 0.1\ mol\,L^{-1}$. [b] Yield calculated by integration of the ^1H NMR spectrum of the crude product relative to an internal standard (dimethyl terephthalate). [c] C_6H_5OTs was observed in each reaction affording **2a**. [d] L = *tris*(2,4-di-*tert*-butylphenyl)phosphite. [e] Degradation products were observed. [f] No conversion was observed. [g] The pyrrolin-4-one **3a** was obtained in 10% yield (see the Supporting Information).[13] Cy = cyclohexyl, JohnPhos = 2-(di-*tert*-butylphosphanyl)biphenyl, Tf = trifluoromethanesulfonyl, Ts = *para*-toluenesulfonyl.

A decrease in the number of phenol equivalents as well as the temperature would make this N-desulfonylation amination synthetically more attractive. Furthermore, tuning of the nature of the phenol reagent should enable the best balance to be found between nucleophilic addition to the sulfonyl group and protodemetalation. Thus, the screening of conditions with various phenol derivatives led to optimal reaction conditions, which afforded **2a** in 81% yield with only 2 equivalents of *meta*-nitrophenol at 30 °C in the presence of 5 mol% of $[Cy_3PAuCl]/AgBF_4$ in dichloroethane (see Table S1 in the Supporting Information).

Under these conditions, we then explored the scope of this unprecedented transformation (Scheme 4). We first examined the effect of the sulfonyl group on the reaction. Substrate **1aa**, bearing a *para*-nitrobenzenesulfonyl group (Ns) on the nitrogen atom, reacted slowly under our reaction conditions. The reaction mixture had to be heated at 70 °C for 4 h for full conversion to be reached, and product **2a** was obtained in 71% yield. In contrast, compound **1ab** with a *para*-methoxybenzenesulfonyl group (Mbs) reacted well at 30 °C, but **2a** was isolated in lower yield from this reaction. Taking into account that the phenol nucleophile was especially chosen for the desulfonylation of robust tosyl derivatives (see Table S1), we next evaluated various substrates **1b–e** with the tosyl protecting group. A variety of substituents on the alkyne were well tolerated, as attested by the formation of the 1-



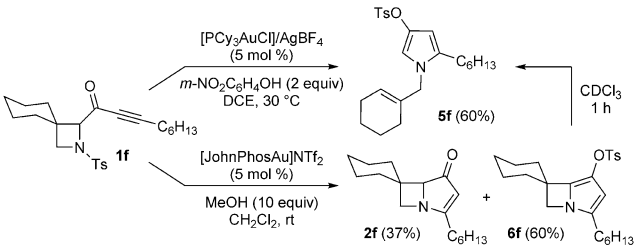
Scheme 4. Gold(I)-catalyzed N-desulfonylative amination of azetidines **1a–e** with *meta*-nitrophenol (X-ray crystal structure of **2e**).



Scheme 6. Cyclization/N-to-O 1,5-sulfonyl migration of pyrrolidine and piperidine derivatives **1g–n** (X-ray crystal structure of **6l**). TBDPS = *tert*-butyldiphenylsilyl.

azabicyclo[3.2.0]heptene derivatives **2b–e** in good to high yields (65–87%).

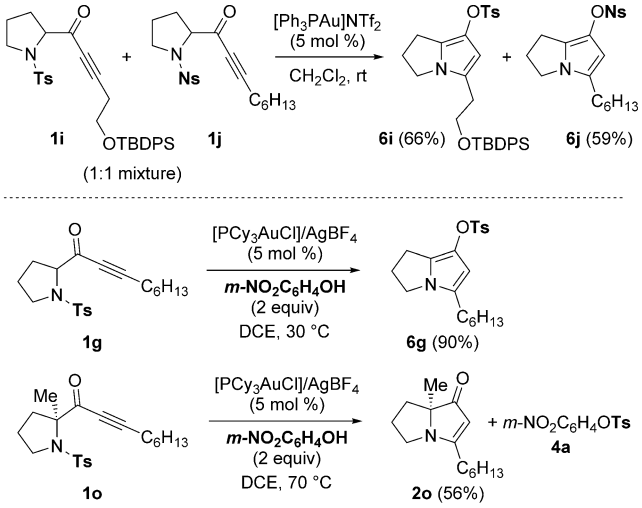
We synthesized spiroazetidine **1f** to assess the influence of *gem*-disubstitution on the azacycle (Scheme 5, top). Interestingly, pyrrole **5f** was formed as the sole product when **1f** was subjected to our reaction conditions. This product clearly arises from the postulated N-to-O sulfonyl migration (Scheme 2) followed by ring opening of the azetidine moiety upon elimination. Thus, the sterically demanding spirocyclic carbon core of **1f** seems to preclude the addition of *meta*-nitrophenol to the sulfonyl group. Indeed, the less-hindered nucleophile methanol[13] was partially able to restore the N-desulfonylation reactivity, thus affording the desired product **2f** (37%) along with **6f** (Scheme 5, bottom). The latter compound was unstable in $CDCl_3$, and rapidly evolved to **5f** through elimination.



Scheme 5. Gold(I)-catalyzed rearrangement of substituted azetidine **1f**.

We then explored the N-to-O sulfonyl migration with more flexible substrates, as they should be more prone to enolization. To our delight, various pyrrolidine and piperidine substrates **1g–n** were readily converted into the expected sulfonates **6g–n** in the presence of triphenylphosphine gold(I) triflimidate (5 mol%) in CH_2Cl_2 at room temperature without an external nucleophile (Scheme 6). Pyrrolizine[20] or indolizine[21] derivatives were obtained in high yields (62–98%) from each substrate. Structural modifications in terms of the heterocyclic ring size (Scheme 6, products **6g**,**h** versus **6k**,**l**) and the substituent on the alkyne were perfectly well tolerated (Scheme 6, products **6h**,**i**). Interestingly, other sulfonyl groups, such as Ns or Mbs, were able to migrate just as well as the Ts group, as evidenced by the formation of products **6j**,**m**,**n** in high yields.

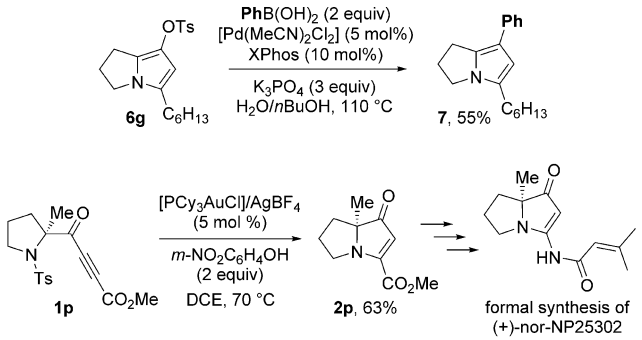
To determine the intermolecular or intramolecular nature of the N-to-O sulfonyl migration, we performed a crossover experiment by subjecting a 1:1 mixture of compounds **1i** and **1j** to our reaction conditions (Scheme 7, top). No crossover products were formed during this reaction (see the Supporting Information). This result clearly indicates that the sulfonyl migration proceeds in an intramolecular manner. To confirm the role of enolization in the N-to-O sulfonyl migration, compound **1g** and non-enolizable **1o** were treated under the N-desulfonylative amination conditions. In the presence of *meta*-nitrophenol, intermolecular N-desulfonylation did not



Scheme 7. Enolization-controlled intramolecular N-to-O sulfonyl migration versus desulfonylative cyclization.

occur with **1g**, and the tosylate **6g** was the sole product formed, without any trace of **4a** (Scheme 7). Predictably, only intermolecular N-desulfonylation occurred with **1o**, and the pyrrolizin-1-one **2o** was isolated in good yield, despite the need to heat the reaction mixture at 70 °C for full conversion to occur (Scheme 7). These results fully confirmed that enolization could be used to switch between N-desulfonylation pathways.

As mentioned above, the pyrrolyl tosylate products **6** offer a unique opportunity to reach more complex compounds through palladium- or nickel-catalyzed cross-coupling reactions. To demonstrate this possibility, we performed a Suzuki–Miyaura coupling between the dihydropyrrolizine **6g** and phenyl boronic acid. Under conditions reported for some heteroaryl tosylates,[16d] but without further optimization, these two compounds could be coupled to produce the arylated product **7** in good yield (Scheme 8, top). To further



Scheme 8. Applications of the cyclization/N-to-O 1,5-sulfonyl migration and the N-desulfonylative cyclization. XPhos = 2-dicyclohexylphosphanyl-2′,4′,6′-triisopropylbiphenyl.

illustrate the power of the gold-catalyzed N-desulfonylative amination in organic synthesis, we carried out a formal synthesis of (+)-*nor*-NP25302, a possible antileukemia agent (Scheme 8, bottom).[22] For this purpose, the enantiomerically pure pyrrolidine **1p** was prepared and treated with a gold catalyst and *meta*-nitrophenol under the conditions described above. The reaction afforded the desired pyrrolizidinone derivative **2p** in good yield.

In conclusion, we have developed two unprecedented gold(I)-catalyzed transformations that enable the efficient formation of 1-azabicycloalkane systems from readily available *N*-sulfonyl azacyclic ynone derivatives. Both transformations offer a conventient access to many biologically active molecules containing 1-azabicycloalkane motif, such as bicyclic azetidines, pyrrolizidine and indolizidine alkaloids. The gold(I)-catalyzed N-desulfonylative amination is a formal hydroamination of alkynes by sulfonamides at room temperature in the presence of *meta*-nitrophenol (2 equiv). The 1,5-migration of the sulfonyl protecting group from the nitrogen to the oxygen atom provides products suitable for postfunctionalization through transition metal-catalyzed cross-coupling reactions. The usefulness of both methodologies has been highlighted by the Suzuki–Miyaura cross-coupling of a dihydropyrrolizinyl tosylate and by a formal synthesis of (+)-*nor*-NP25302. Further investigations to extend these transformations to unactivated alkyne substrates and to apply these reactions in the total synthesis of bioactive alkaloids are ongoing in our laboratory.

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