Amination Reactions

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# Bismuth-Catalyzed Direct Substitution of the Hydroxy Group in Alcohols with Sulfonamides, Carbamates, and Carboxamides**

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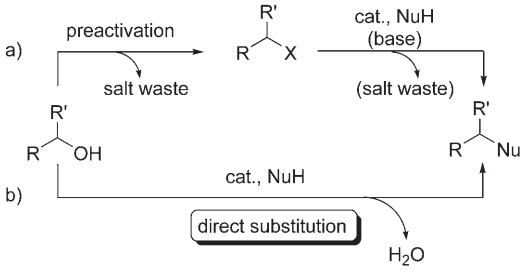
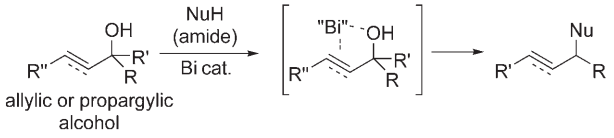
The importance of amine derivatives for the synthesis of pharmaceuticals and fine chemicals has aroused considerable interest in allylic and propargylic amination reactions.[1] Readily available allylic and propargylic alcohols are desirable substrates for the synthesis of allylic and propargylic amines. Substitution of the hydroxy group in alcohols by amine nucleophiles generally requires preactivation of the alcohols because of the poor leaving ability of the hydroxy group. Alcohols are generally transformed into the corresponding halides, carboxylates, carbonates, phosphonates, or related compounds with good leaving groups. The process inevitably produces a stoichiometric amount of salt waste. The substitution of the halides and related compounds also produces salt waste and requires a stoichiometric amount of a base (Scheme 1, path a). In this context, well-established transition-metal-catalyzed allylic aminations of allylic acetates and their derivatives have intrinsic drawbacks in terms of atom economy.[2] Therefore, the direct catalytic substitution of alcohols with amines is desirable. As no stoichiometric hydroxy-group activator is utilized, the products are produced with water as the only waste (Scheme 1, path b).




***Scheme 1.*** Substitution of the hydroxy group of an alcohol by: a) preactivation and b) direct catalytic substitution.

A number of direct allylic aminations catalyzed by late transition metals have been reported.[3,4] However, in most cases either a high reaction temperature is required or a promoter is added to enhance the leaving ability of the hydroxy group. Notable progress was made by using cationic Pd complexes with diphosphinidenecyclobutene ligands (with anilines)[4a] and a Pd complex in aqueous media (with aryl and alkyl amines).[4b] The reactions proceeded smoothly at room temperature without any additives;[4] however, the use of amides, which are less nucleophilic, is still quite rare, and a high reaction temperature is essential.[5] Nishibayashi, Hidai, Uemura, and co-workers and Toste and co-workers carried out pioneering studies on propargylic substitutions with amides in the presence of a catalytic amount of dinuclear Ru[6] and oxo-Re complexes[7] in a catalytic Nicholas reaction.[8] Good yields were observed with these systems, and a broad range of amine nucleophiles can be used; however, there remains room for improvement, as: a) 3–5 equivalents of the amine nucleophiles were required, b) the reactions were performed at a relatively high temperature (60–65 °C), and c) only secondary propargylic alcohols were used. Herein, we report that bismuth catalysis is suitable for the direct substitution of allylic, propargylic, and benzylic alcohols with sulfonamides, carbamates, and carboxamides under mild reaction conditions. A combination of commercially available $Bi(OTf)_3$ and $KPF_6$ (1–5 mol%) promoted the amination reactions at room temperature to give the products in up to 99% yield.

We reported recently the utility of bismuth catalysis[9] in the hydroamination of 1,3-dienes with amides.[10] In the hydroamination, a $Bi(OTf)_3/MPF_6$ (M = K or Cu) system not only acts as a π acid to activate 1,3-dienes, but also acts as a Lewis acid to control the position of attack of the amide nucleophile. We hypothesized that bismuth catalysis would also be suitable for the activation of allylic and propargylic alcohols, as shown in Scheme 2.[11] To test this hypothesis, the reaction of **1a** with amide **2a** was examined. $Bi(OTf)_3/KPF_6$ promoted the reaction smoothly, and **3aa** was obtained in 94% yield after 0.2 h (Table 1, entry 1). To study the efficiency of the catalyst, several control experiments were performed (Table 1, entries 2–4). $Bi(OTf)_3$ alone promoted the reaction, albeit at a lower reaction rate (Table 1, entry 2; 2 h, 76% yield). The reaction was much slower with $BiCl_3$




***Scheme 2.*** Working hypothesis for the activation of allylic and propargylic alcohols by a Bi catalyst.

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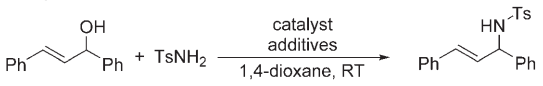
***Table 1:*** Optimization of the reaction conditions.




**1a** **2a** **3aa**

| Entry | Catalyst (mol%) | **2a** [equiv] | Additive 1 (mol%) | Additive 2 | *t* [h] | Yield [%][a] |
|---|---|---|---|---|---|---|
| 1 | $Bi(OTf)_3$ (10) | 2 | $KPF_6$ (10) | – | 0.2 | 94 |
| 2 | $Bi(OTf)_3$ (10) | 2 | – | – | 2 | 76 |
| 3 | $BiCl_3$ (10) | 2 | – | – | 12 | 70 |
| 4 | – | – | $KPF_6$ (10) | – | 12 | 0 |
| 5 | $Bi(OTf)_3$ (2) | 1.5 | $KPF_6$ (2) | – | 0.2 | 94 |
| 6 | $Bi(OTf)_3$ (2) | 1.5 | $KPF_6$ (2) | drierite[b] | 0.2 | 96 |
| 7 | $Bi(OTf)_3$ (1) | 1.5 | $KPF_6$ (1) | drierite[b] | 0.2 | 95 |

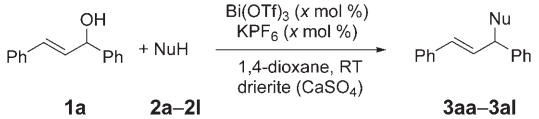
[a] Yield of the isolated product after column chromatography. [b] A quantity of 45 mg of drierite was used per 0.3 mmol of **1a**. Tf = trifluoromethanesulfonyl, Ts = *para*-toluenesulfonyl.

(Table 1, entry 3; 12 h, 70% yield).[12] $KPF_6$ alone did not afford any of the product **3aa** (Table 1, entry 4). Both $Bi(OTf)_3$ and $KPF_6$ were required for high reactivity at room temperature.[13] With the $Bi(OTf)_3/KPF_6$ system, the catalyst loading was successfully decreased to 2 mol% (Table 1, entry 5; 94% yield after 0.2 h). Compound **3aa** was obtained in 96% yield after 0.2 h in the presence of the desiccant drierite ($CaSO_4$; Table 1, entry 6).[14] Under the optimized conditions with drierite, the catalyst loading was decreased to 1 mol% without any problems (Table 1, entry 7; 0.2 h, 95% yield).

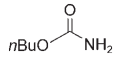
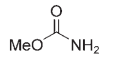
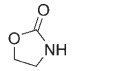
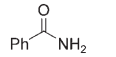
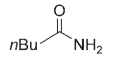
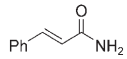
The scope of the reaction with respect to the amide substrate was examined with catalyst concentrations of 2–5 mol% (Table 2). When sulfonamides with electron-donating or electron-withdrawing substituents were used,[15] the reaction was complete within 0.2–1.5 h, and the corresponding allyl amides were obtained in high yield (Table 2, entries 1–5; 85–99%). Carbamates **2f**–**2i** were also suitable substrates and gave the desired products in 97–99% yield (Table 2, entries 6–9). With carboxamides **2j**–**2l**, the reaction rate decreased; therefore, the catalyst loading was increased for these substrates. In the presence of 5 mol% of the catalyst, carboxamide **2j** reacted smoothly, and the product was obtained in 86% yield (Table 2, entry 10; 0.6 h). Carboxamides **2k** and **2l** were much less reactive; the products **3ak** and **3al** were obtained in 88 and 95% yield, respectively, after 15 or 16 h at room temperature (Table 2, entries 11–12). The reactions of selected substrates in Table 2 were also performed in the absence of drierite. The results of these reactions, which proceeded without any difficulty, are shown in parenthesis (Table 2, entries 1, 2, 7, and 10).[14]

The scope of the reaction with respect to the alcohol substrate is summarized in Table 3. The present catalyst is also suitable for the reaction of non-benzylic allylic alcohols, such as the cyclic alcohols **1b**–**1e** (Table 3, entries 1–4; 66–96% yield) and acyclic alcohols **1f**–**1i** (Table 3, entries 5–8). The reaction of **1f** afforded **3fa** regioselectively (Table 3, entry 5; 87%). The desired products were also formed regioselectively from substrates **1g** and **1h**, with substituted aromatic rings, and the *N*-Ts indole **1i** (Table 3, entries 6–8). The reaction of **1i** proceeded smoothly with an equimolar amount of carbamate **2g** (Table 3, entry 8; 84%). With **1j** and **2e** the reaction proceeded regioselectively to afford **3je** (Table 3, entry 9), which was also obtained starting from **1k** (entry 10). Alcohol **1l** also reacted at the less hindered terminal carbon atom to give **3le** (Table 3, entry 11; 60%). The reaction of alcohol **1m** afforded **3me** as a mixture of regioisomers in a ratio of 6.7:1 (Table 3, entry 12). Diene **3ne** was obtained selectively from alcohol **1n** (Table 3, entry 13) and treatment of the tertiary alcohol **1o** with **2g** afforded the regioisomer **3og** selectively (Table 3, entry 14; *E* isomer). The results in entries 5–14 of Table 3 suggest that the amides attack selectively the sterically less hindered carbon atom of the allylic alcohol functionality. On the other hand, the propargylic alcohols **1p**–**1s** reacted regioselectively at the propargylic position (Table 3, entries 15–18).[6,7,16] Allenic products of amide attack at the triple bond were not observed for **1p**–**1s**. It is noteworthy that the desired products were obtained when the tertiary propargylic alcohols **1r** and **1s** were used. Previously reported propargylic-amination catalysts[6,7] were not applied to tertiary propargylic alcohols, possibly because of a competitive dehydration reaction to afford enynes. The addition of drierite was essential for the formation of products **3ra** and **3sf** in greater than 60% yield (Table 3, entries 17–18).[14] This Bi catalysis was also applicable to the benzylic

***Table 2:*** Direct catalytic allylic substitution of **1a** with amides **2a**–**2l**.[a]

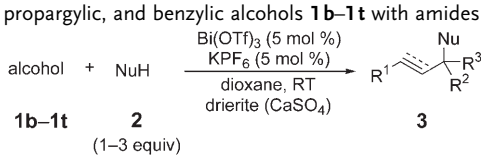



**1a** **2a–2l** (1.5 equiv) **3aa–3al**

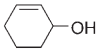
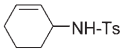
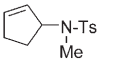
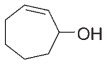
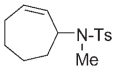
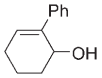
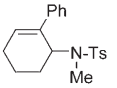
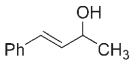
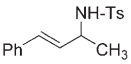
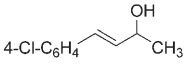
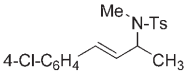
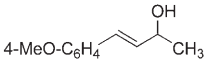
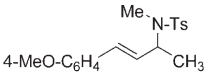
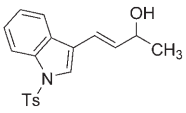
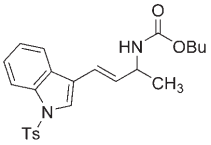
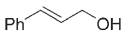
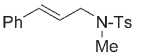
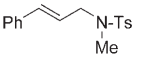
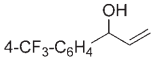
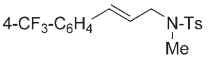
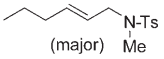
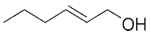
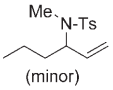
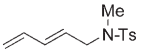
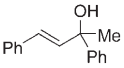
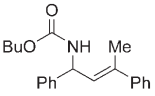
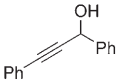
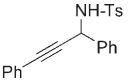
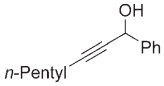
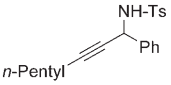
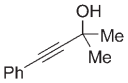
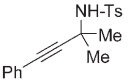
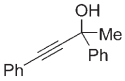
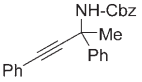
| Entry | NuH **2** | | Prod. | Cat. [mol%] | *t* [h] | Yield [%][b] |
|---|---|---|---|---|---|---|
| 1 | $TsNH_2$ | **2a** | **3aa** | 2 | 0.2 | 96 (94)[c] |
| 2 | *o*-$NsNH_2$ | **2b** | **3ab** | 2 | 0.2 | 93 (82)[c] |
| 3 | $PhSO_2NH_2$ | **2c** | **3ac** | 2 | 0.2 | 99 |
| 4 | *p*-$CF_3C_6H_4SO_2NH_2$ | **2d** | **3ad** | 2 | 0.2 | 97 |
| 5 | TsNMeH | **2e** | **3ae** | 2 | 1.5 | 85 |
| 6 | $CbzNH_2$ | **2f** | **3af** | 2 | 0.2 | 97 |
| 7 |  | **2g** | **3ag** | 2 | 0.2 | 99 (91)[c] |
| 8 |  | **2h** | **3ah** | 2 | 0.2 | 99 |
| 9 |  | **2i** | **3ai** | 2 | 0.2 | 99 |
| 10 |  | **2j** | **3aj** | 5 | 0.6 | 86 (89)[c] |
| 11 |  | **2k** | **3ak** | 5 | 15 | 88 |
| 12 |  | **2l** | **3al** | 5 | 16 | 95 |

[a] Reaction conditions: **1a** (0.3 mmol), **2** (0.45 mmol, 1.5 equiv), $Bi(OTf)_3$ (0.015 mmol, 5 mol%), $KPF_6$ (0.015 mmol, 5 mol%), drierite (45 mg), 1,4-dioxane (1.0 mL), room temperature. [b] Yield of the isolated, analytically pure compound after column chromatography. [c] The number in parenthesis is the yield of the isolated product when the reaction was performed in the absence of drierite. Cbz = carbobenzyloxy, *o*-Ns = *ortho*-nitrobenzenesulfonyl.

***Table 3:*** Direct catalytic substitution of allylic, propargylic, and benzylic alcohols **1b–1t** with amides **2**.[a]



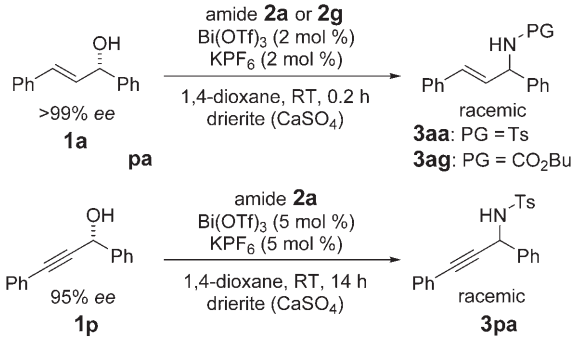

**1b–1t** **2** (1–3 equiv) **3**

| Entry | Alcohol **1** | | NuH (equiv) | Product | | *t* [h] | Yield [%][b] |
|---|---|---|---|---|---|---|---|
| 1 |  | **1b** | **2a** (2) |  | **3ba** | 2 | 96 |
| 2 |  | **1c** | **2e** (3) |  | **3ce** | 2 | 80 |
| 3 |  | **1d** | **2e** (3) |  | **3de** | 2 | 66 |
| 4 |  | **1e** | **2e** (3) |  | **3ee** | 17 | 74 |
| 5 |  | **1f** | **2a** (1.5) |  | **3fa** | 17 | 87 |
| 6 |  | **1g** | **2e** (3) |  | **3ge** | 0.2 | 99 |
| 7 |  | **1h** | **2e** (3) |  | **3he** | 0.2 | 61 |
| 8 |  | **1i** | **2g** (1) |  | **3ig** | 0.2 | 84 |
| 9 |  | **1j** | **2e** (3) |  | **3je** | 7 | 63 |
| 10 |  | **1k** | **2e** (3) |  | **3je** | 12 | 62 |
| 11 |  | **1l** | **2e** (3) |  | **3le** | 2 | 60 |
| | | | |  (major) | | | |
| 12[c] |  | **1m** | **2e** (3) |  (minor) | **3me**[d] | 1 | 55 |
| 13 |  | **1n** | **2e** (2) |  | **3ne** | 1 | 69 |
| 14 |  | **1o** | **2g** (1.5) |  | **3og** | 0.1 | 60 |
| 15 |  | **1p** | **2a** (1.5) |  | **3pa** | 18 | 82 |
| 16 |  | **1q** | **2a** (1.5) |  | **3qa** | 8 | 78 |
| 17 |  | **1r** | **2a** (2) |  | **3ra** | 4 | 63 |
| 18 |  | **1s** | **2f** (2) |  | **3sf** | 5 | 65 |
| 19 |  | **1t** | **2e** (2) |  | **3te** | 7 | 60 |

[a] Reaction conditions: **1** (0.3 mmol), **2** (0.3–0.9 mmol, 1–3 equiv), $Bi(OTf)_3$ (0.015 mmol, 5 mol%), $KPF_6$ (0.015 mmol, 5 mol%), drierite (45 mg), 1,4-dioxane (1.0 mL), room temperature (unless otherwise noted). [b] Yield of the isolated, analytically pure compound after column chromatography. [c] The reaction was performed at 40°C. [d] Major/minor = 6.7:1.

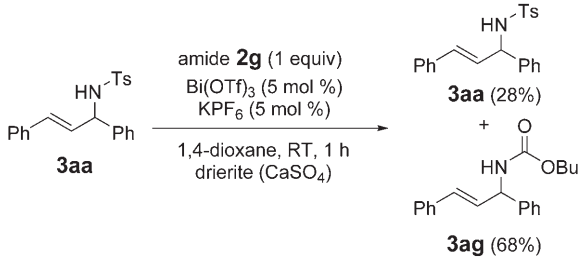
alcohol **1t**, the reaction of which with **2e** gave **3te** in 60% yield after 7 h at room temperature (Table 3, entry 19).

When the optically active alcohols **1a** and **1p** and amides **2a** and **2g** were used, only the racemic products **3aa**, **3ag**, and **3pa** were obtained (Scheme 3). This result suggests a reaction




***Scheme 3.*** Allylic and propargylic amination of the optically active alcohols **1a** and **1i**.

mechanism in which a carbenium intermediate is formed. The observed racemization could also be ascribed to the reversibility of the reaction. The result shown in Scheme 4 indicates that the reaction is reversible under the reaction conditions. When **3aa** was treated with $Bi(OTf)_3/KPF_6$ (5 mol%) and carbamate **2g** (1 equiv), a mixture of **3aa** (28%) and **3ag** (68%) was recovered after 1 h. It appears that $Bi(OTf)_3/KPF_6$ cleaved the C–N bond in **3aa**, and that **3ag** is thermodynamically more stable than **3aa**.[17,18]




***Scheme 4.*** Reversibility of the allylic amination.

In summary, we have developed a bismuth-catalyzed direct substitution of allylic, propargylic, and benzylic alcohols with sulfonamides, carbamates, and carboxamides. A combination of commercially available $Bi(OTf)_3$ and $KPF_6$ (1–5 mol%) catalyzed the reactions effectively, mostly at room temperature, to give the products in 55–99% yield. Further applications of the $Bi(OTf)_3/KPF_6$ system as well as mechanistic studies of the present reaction are under investigation.

## Experimental Section

1,4-Dioxane (1.0 mL) was added to a mixture of $Bi(OTf)_3$ (3.92 mg, 0.006 mmol), $KPF_6$ (1.11 mg, 0.006 mmol), and drierite (45 mg) in a test tube. The resulting mixture was stirred for 10 min at room temperature, then $TsNH_2$ (**2a**; 77.0 mg, 0.45 mmol) was added, followed by **1a** (63.1 mg, 0.3 mmol). The reaction mixture was stirred at 23–26 °C for 10 min. It was then diluted with diethyl ether (5 mL), and silica gel (ca. 3 g) was added. After filtration and washing with diethyl ether, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate 8:1–6:1) to give **3aa** (96%) as a colorless solid.

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[13] A combination of $Bi(OTf)_3$ and $Cu(CH_3CN)_4PF_6$ was as effective as $Bi(OTf)_3$ with $KPF_6$. $KPF_6$ was selected for the present study because $KPF_6$ is less expensive than $Cu(CH_3CN)_4PF_6$. On the basis of mechanistic studies on the $Bi(OTf)_3/MPF_6$ system in ref. [10], we speculate that $KPF_6$ is required to generate a more reactive cationic $Bi(OTf)_2{\cdot}PF_6$ species by anion exchange.

[14] Although the addition of a desiccant (drierite: $CaSO_4$) is not essential for reactive substrate combinations, such as **1a** with **2a**, the use of drierite is recommended for good reproducibility with less reactive substrates in Table 3.

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[17] We assume that the desiccant (drierite) has a positive effect on the reaction of substrates in Table 3 because of the reversibility of the reaction.

[18] The possibility that TfOH, generated from $Bi(OTf)_3$ and $H_2O$, promotes the present reaction (Tables 1–3) can not be excluded completely, even in the presence of desiccant. However, the result of the reaction in Scheme 4, in which no $H_2O$ is generated, supports the hypothesis that $Bi(OTf)_3/KPF_6$ functions as a catalyst.

  