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Copper(II) Triflate Catalyzed Allylic Arylation of Allylic Alcohols: Direct and Selective Access to *C*-Allylanilines

Ke Chen,[a, b] Houguang Jeremy Chen,[a] Jonathan Wong,[a] Jinglei Yang,[b] and Sumod A. Pullarkat*[a]

Copper(II) triflate was used as a simple and commercially available catalyst in the direct amination of allylic alcohols with anilines to provide *C*-allylanilines. A wide range of functional groups were tolerated under the reaction conditions, and the products were obtained regioselectivity without the need of an activator. A detailed mechanistic investigation was undertaken. The efficacy of this protocol was demonstrated in the conversion of the 2-allylanilines into substituted quinolines through an oxidative cycloaddition reaction.

Introduction

2-Allylanilines are simple building blocks that occupy an important place in organic synthesis, as they can provide significant amplification of molecular complexity.[1] 2-Allylanilines are traditionally prepared from *N*-allylanilines through aza-Cope rearrangement.[2] Development of protocols that circumvent the isolation of *N*-allylanilines and that allow efficient direct access to *C*-allylanilines is therefore attractive, as the products obtained are starting materials for the preparation of various bicyclic nitrogen-containing heterocycles through cyclization of the nitrogen atom onto the double bond.[1] However, the reported syntheses of *C*-allylanilines by thermal, protic acid promoted, and charge-accelerated rearrangements all have drawbacks, including harsh reaction conditions, low yields, and limited substrate scope, and are much less developed (unlike syntheses leading to their *N*-allylaniline analogues).[2c–g] Recent reports of microwave-assisted and heteropoly acid (HPA) catalyzed processes have also appeared, but these methods also suffer from similar drawbacks.[2a,b]

In reactions involving C–C bond formation by allylic substitution, malonate,[3] indole,[3,4] thiophene,[4a] pyrrole,[3,4c] benzofuran,[4a] furan,[4a,e] and benzothiophene[4a] have all been reported as common nucleophiles (Figure 1). Activated allylic alcohol derivatives such as allylic halides, carboxylates, and carbonates are common substrates in these scenarios owing to the relatively poor reactivity of their alcohols analogues. However, direct catalytic substitution involving allylic alcohols avoids the formation of stoichiometric amounts of unwanted chemical waste during the synthesis of activated substrates and is therefore more environmentally benign.[4c,5] Furthermore, the procedure produces water as the sole byproduct and hence is highly attractive, especially for large-scale synthesis. However, as a result of the aforementioned poor leaving ability of the hydroxy moiety, the direct substitution of allylic alcohols typically requires high temperatures,[6] neat conditions,[7] or considerable amounts of an activator.[8,9]

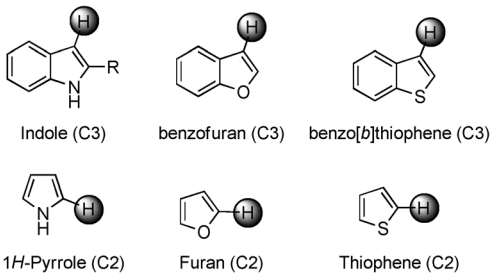

Figure 1. Nucleophiles used in reactions involving C–C bond formation by allylic substitution.

Allylic amination by employing anilines is an attractive route towards the formation of allylaniline derivatives through Ar–C or N–C bond formation. A survey of the literature revealed several reports on the transition-metal-catalyzed allylic amination of allylic alcohol derivatives such as allyl halides, carboxylates, and carbonates (and to a lesser extent alcohols themselves) with arylamines (and to a lesser extent anilines because of a buffering effect, which renders them ineffective for acid-catalyzed nucleophilic substitution reactions). However, these methods inevitably led to the predominant generation of *N*-allylanilines (Scheme 1).

For instance, metal-catalyzed allylic aminations involving anilines and alcohols (or activated alcohol derivatives) include,

[a] Dr. K. Chen, H. J. Chen, J. Wong, Dr. S. A. Pullarkat
Division of Chemistry and Biological Chemistry
School of Physical & Mathematical Sciences
Nanyang Technological University
Singapore 637371 (Singapore)
Fax: (+65) 63166984
E-mail: sumod@ntu.edu.sg

[b] Dr. K. Chen, Dr. J. Yang
Division of Aerospace Engineering
School of Mechanical and Aerospace Engineering
Nanyang Technological University
Singapore 639798 (Singapore)

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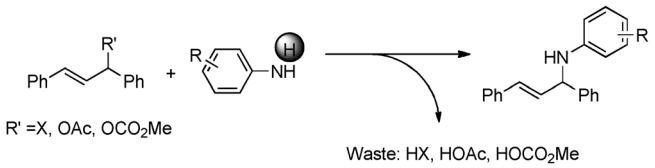
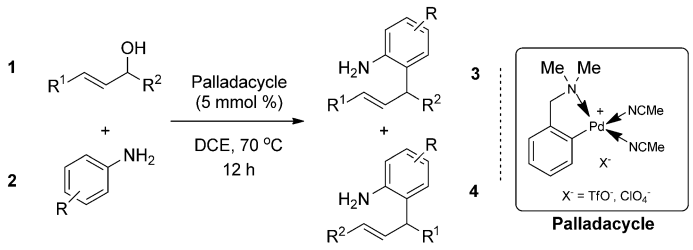


Scheme 1. Common allylic substitution reactions that lead to *N*-allylanilines.

amongst other metals, the use of palladium[6,9,10] and platinum[5b,7d,11] and to a lesser extent iron,[12] cobalt,[13] and molybdenum.[3] Notably, in all of these aforementioned protocols, the *N*-allylaniline is the predominant product formed irrespective of the catalyst employed. Although there has been reports on the $[Cu(CH_3CN)_4]PF_6$ and $CuCl_2{\cdot}2H_2O$–Cu powder catalyzed allylic amination of olefins with aryl hydroxylamines[14] and nitrosoarenes,[15] catalytic allylic amination of alcohol substrates with anilines as a route towards allylanilines has, however, not been explored hitherto.

Recently, we reported the palladacycle-catalyzed direct synthesis of 2-allylanilines from allylic alcohols (Scheme 2).[16] In line with this report on the development of a direct and "green" synthesis of *C*-allylanilines from allylic alcohols and in the context of our general interest in the development of efficient C–P, C–C, and C–N bond-formation protocols,[17] we continued our search for a significantly cheaper, more efficient, and easily accessible catalyst for this useful protocol.



Scheme 2. Palladacycle-catalyzed synthesis of *C*-allylanilines.

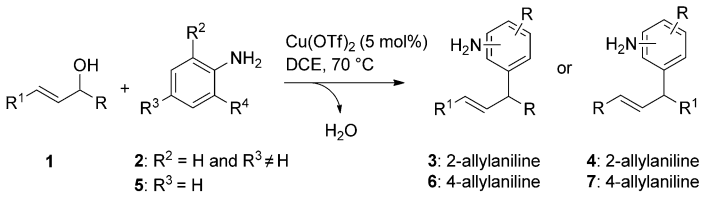
We therefore explored the application of copper catalysts in the direct synthesis of 2-allylanilines from allylic alcohols and anilines without the requirement of any additional additive or activating agent. In comparison to the palladacycle-catalyzed scenario, cheaper and more active copper(II) trifluoromethanesulfonate (triflate, $^-$OTf) promoted the allylic arylation reaction in a much shorter reaction time (3 versus 12 h) with a wider range of substrates in a more efficient manner (Scheme 3). Key mechanistic insights into the reaction mechanism were also obtained by control reactions and variable-temperature NMR (VT-NMR) spectroscopy. The potential for further transformations of the formed products is also demonstrated.

Results and Discussion

Recent literature reports have shown that copper catalysts can be efficient in various amination reaction scenarios.[18] We therefore initiated our study by screening various copper compounds for the aforementioned reaction scenario and found that $Cu(OTf)_2$ was the most effective. From the preliminary evaluation of reaction conditions with 1,3-diphenyl-2-propen-1-ol and *p*-toluidine as representative substrates, we found that the best results (90% yield) were obtained with 1,2-dichloroethane as the solvent at 70 °C over 3 h. The same reaction with the use of the palladacycle catalyst required 12 h for completion and provided the product in 85% yield under the same conditions. With the optimum conditions thus established, we proceeded to screen various substituted anilines. As shown in Table 1, the reaction showed a marked preference for the Ar–C products, namely, 2-allylanilines, over the N–C products, *N*-allylanilines, if the *para* position of the aniline was blocked by a substituent.

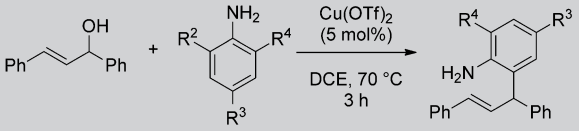
A previous report in which proton- and metal-exchanged montmorillonites were used as catalysts stated that if an electron-donating substituent such as a methoxy group was present at the *para* position of the aniline, the *C*-allylaniline was formed as the major product (93% yield).[19] However, that reaction required 150 °C and over 24 h to reach completion, and upon extending the substrate scope to include electron-withdrawing groups (e.g., 4-chloro-substituted anilines), the *N*-allylaniline was obtained as the major product, thus exhibiting lack of product selectivity (in our case, **3af** was isolated in 90% yield). For substrates such as 4-hydroxyaniline bearing both NH_2 and OH functionalities, the reaction preferred to occur selectively at the *ortho* position of the NH_2 group (**3ad**, Table 1). This result is consistent with the relative donor ability of the NH_2 and OH groups and the directing effect they consequently impart during such allylic arylation scenarios. Similar products were obtained upon screening of anilines with functional groups such as MeO and PhO. These donating groups are known to enhance the reactivity of the aniline towards allyl arylation. As expected, their allylic arylation generated the C–C bond products selectively in good to high yields.

We then proceeded to extend the substrate scope to anilines devoid of any *para* substituents. This class of substrate was not studied in our previous report in which a palladacycle catalyst was used and has also never been reported in other studies involving the formation of *C*-allylanilines. Employing

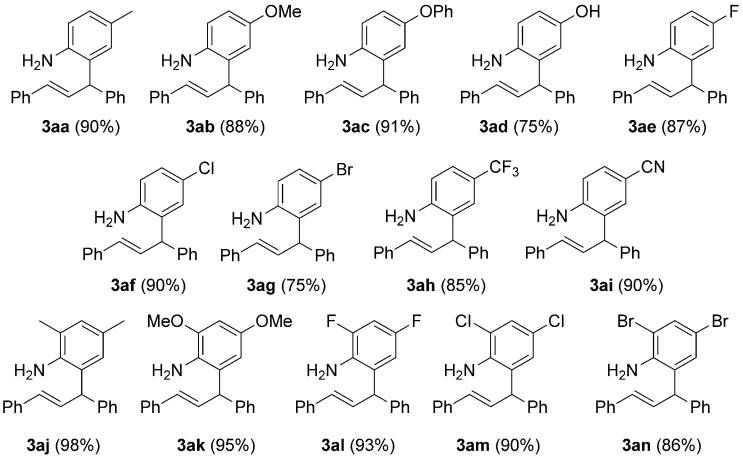


Scheme 3. $Cu(OTf)_2$-catalyzed allylic arylation of allylic alcohols.

Table 1. Cu-catalyzed allylic arylation of allylic alcohols with various anilines.[a]



1 2: R^2 = H and $R^3 \neq$ H 3



[a] All reactions were performed at 70 °C for 3 h with the allylic alcohol (0.5 mmol) and the amine (0.75 mmol). Yield of the isolated product is given in parentheses.

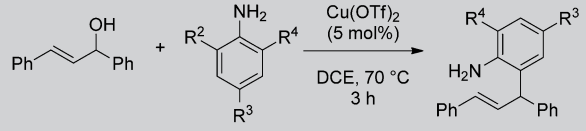
the new protocol, *C*-allylaniline products, that is, 4-allylanilines, were selectively generated (Table 2). If the *para* position and one of the two *ortho* positions were simultaneously available, 4-allylanilines were still preferentially formed instead of 2-allylanilines (**6aa**–**al**, Table 2) irrespective of the electronic nature of the *ortho* substituent. Notably, anilines with nitro, chloro, and methyl substituents at the *ortho* position were previously employed as substrates in the direct amination of allylic alcohols by using Pt(cod)Cl_2–diphosphine[5b,11c] and $MoO_2(acac)_2$ catalytic systems (cod = 1,5-cyclooctadiene, acac = acetylacetonate).[3] However, in such instances they gave the corresponding *N*-allylanilines as the main products.

Reactions involving anilines bearing electron-withdrawing functional groups such as CF_3 and CN (present at either the *para* or *ortho* position) also selectively gave the C–C products, that is, 2-allylanilines or 4-allylanilines, respectively (**3ah** and **3ai**, Table 1; **6af** and **6ag**, Table 2). This study thus extends the direct arylation protocol to include *ortho*-substituted anilines, which were conspicuously absent from all previous reports involving the synthesis of *C*-allylanilines.

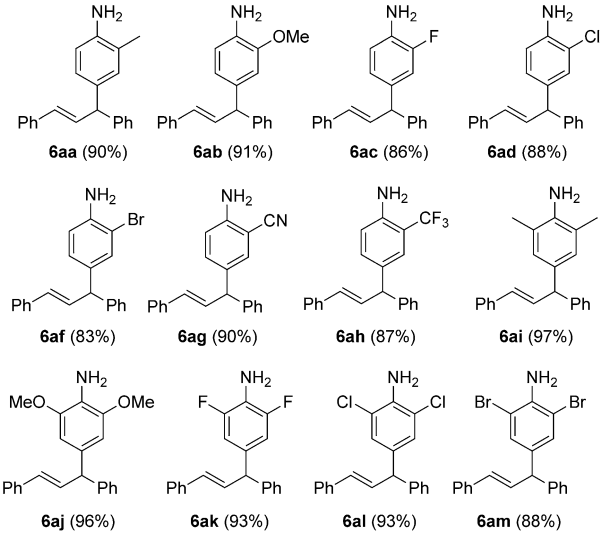
Subsequent to screening anilines, we also evaluated the applicability of this method to various allylic alcohol substrates (Table 3). Better reactivity and higher yields were obtained for allylic alcohols in which the R′ group was aryl or *t*Bu (Table 3, Entries 7, 9, 10, and 12). However, reactions in which relatively less activated alkyl-substituted allylic alcohols (Table 3, Entries 1–6 and 8) were used required higher reaction temperatures or longer reaction times to obtain better yields of the products. These results are consistent with the fact that alkyl-substituted allylic alcohols are known to be more prone to side reactions. The steric hindrance offered by the allylic alcohols and anilines also has a profound influence on the product regioselectivity. The less-hindered position on the allylic alcohol substrate is preferred by the incoming aniline for formation of the C–C bond. Furthermore, in the case of anilines in which the *para* position is blocked by substituents, the reaction showed significantly better regioselectivity with respect to the allylic alcohol owing to the steric hindrance offered by the incoming aniline nucleophile. Consequently, in the case of anilines in which the *para* position is vacant, this regioselectivity preference was not prominent (Table 3, Entries 1 and 3).

To obtain mechanistic insight, a set of reactions including one that was closely monitored by VT-NMR spectroscopy were subsequently performed. A stepwise reaction was performed between allylic alcohol **1a**/**1b** and 2,4-di-

Table 2. Cu-catalyzed allylic arylation of allylic alcohols with various anilines.[a]

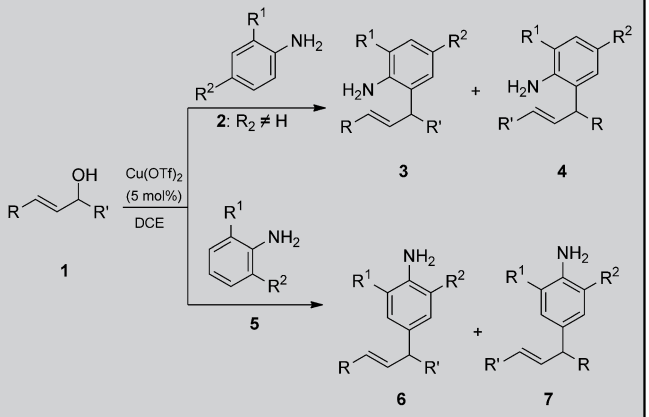


1a 5: R^3 = H 6



[a] All reactions were performed at 70 °C for 3 h with the allylic alcohol (0.5 mmol) and the amine (0.75 mmol). Yield of the isolated product is given in parentheses.

Table 3. Cu-catalyzed allylic arylation of various allylic alcohols with anilines.[a]



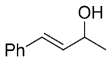
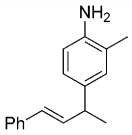
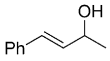
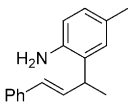
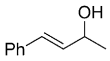
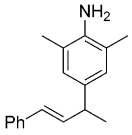
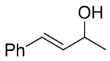
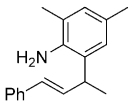
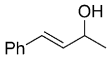
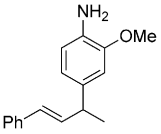
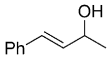
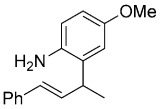
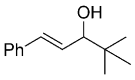
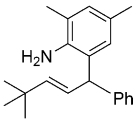
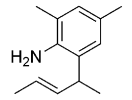
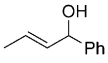
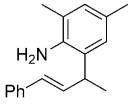
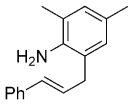
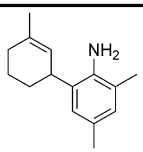
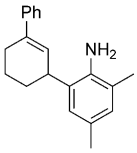
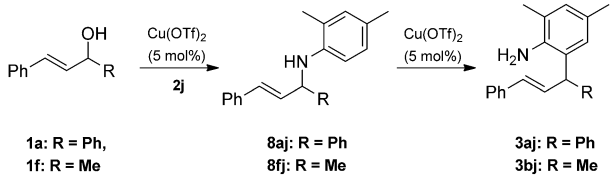
Entry	Allylic alcohol		Product, yield[b] [%]	
1[c]		**1b**		**6ba**, 65[d]
2[c]		**1b**		**3ba**, 79
3[c]		**1b**		**6bj**, 59[e]
4[c]		**1b**		**3bj**, 85
5[c]		**1b**		**6bb**, 73
6[c]		**1b**		**3bb**, 74
7		**1c**		**4cj**, 75
8[f]		**1d**		**3dj**, 60
9		**1e**		**4ej**, 85
10		**1f**		**4fj**, 71

Table 3. (Continued)

Entry	Allylic alcohol		Product, yield[b] [%]	
11		**1g**		**4gj**, 72
12		**1h**		**4hj**, 82

[a] Unless otherwise indicated, the reaction was performed at 70 °C with the allylic alcohol (0.5 mmol) and the amine (0.75 mmol). [b] Yield of the isolated product. [c] Reaction was performed at 90 °C for 6 h. [d] Ratio of **6ba**/**7ba** = 5:1 and the total yield of (**6ba**/**7ba**) was 78%. [e] Ratio of **6bj**/**7bj** = 2.2:1 and the total yield of (**6bj**/**7bj**) was 85%. [f] Reaction was performed at 90 °C for 12 h.



Scheme 4. Stepwise reaction conducted to elucidate the reaction pathway.

methylaniline (**2j**) in the presence of $Cu(OTf)_2$ (5 mol%), as shown in Scheme 4. The results revealed that initially formed kinetically favored product **8aj**/**8bj** subsequently gave rise to thermodynamically favored product **3aj**/**3bj** upon heating.

To confirm the above hypothesis, the reaction between allylic alcohol **1a** and 2,4-dimethylaniline (**2j**) was monitored by VT-NMR spectroscopy (Figure 2, see also the Supporting Information). In the ^{1}H NMR spectra of allylic alcohol **1a**, *N*-allylaniline **8aj**, and *C*-allylaniline **3aj** in [D_4]-1,2-dichloroethane, the resonance for the α-C*H* proton is distinct and appears at $\delta =$ 5.39, 5.14, and 4.85 ppm, respectively, at room temperature and at $\delta = 5.40$, 5.18, and 4.92 ppm, respectively, at 80 °C. These signals provide a good spectroscopic handle to monitor the progress of the reaction. Only the resonance signal due to α-C*H* of allylic alcohol **1a** was observed immediately after the NMR sample tube containing the reaction mixture was introduced into the magnet maintained at 80 °C (Figure 2, 0 min). As expected, the signal of the α-C*H* proton of C–N product **8aj** was observed 5 min after the start of the VT-NMR spectroscopy experiment. This indicated that the kinetically favored

C–N product was initially formed. After 10 min, the characteristic resonance for the α-C*H* proton of C–N product **8aj** and that of C–C product **3aj** were observed simultaneously. Subsequently, the concentration of thermodynamically favored C–C product **3aj** increased as the reaction progressed. After 50 min, allylic alcohol **1a** and C–N product **8aj** were com-

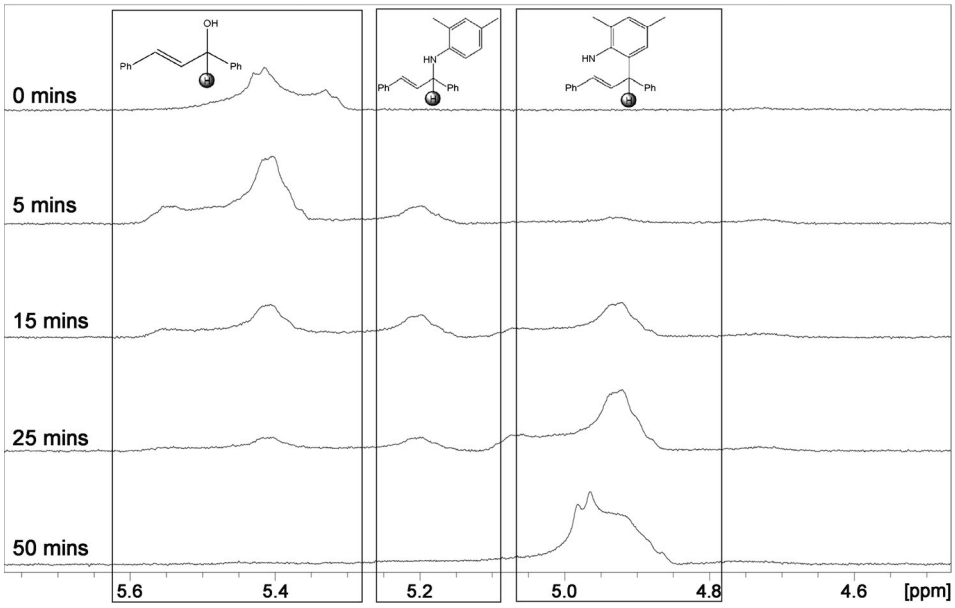
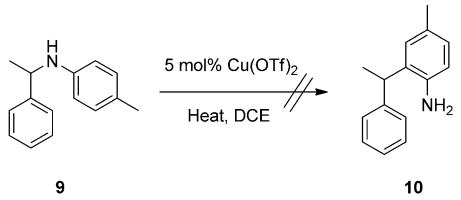


Figure 2. ^{1}H NMR spectra at 80 °C showing the gradual appearance and subsequent change in the concentrations of the C–N and C–C products with reaction time (see the Supporting Information for more detailed spectra, including the initial and final spectra at RT).

pletely converted into C–C product **3aj**, as determined by the complete disappearance of the signals for **1a** and **8aj** and the appearance of the signal for **3aj** only (see the Supporting Information for detailed spectra). After cooling of the magnet to room temperature, the ^{1}H NMR spectrum showed that the reaction was clean, and only the signals for C–C product **3aj** and an excess amount of 2,4-dimethylaniline were observed.

To further understand how the kinetically favored C–N product was converted into the thermodynamically favored C–C product, several monitored experiments were conducted. A control experiment for the Hofmann–Martius rearrangement step was set up with **9**, and rearrangement product **10** was not obtained under the optimum reaction conditions used for the catalysis or at elevated temperatures and longer reaction times (Scheme 5). This result confirmed unambiguously that $Cu(OTf)_2$ cannot promote the Hofmann–Martius rearrangement under the optimum conditions employed.

Additionally, a mixture of **3aj** and **3ak** was observed upon treatment of **8aj** with aniline **2k** (1 equiv.) under the optimum reaction conditions (Scheme 6). This result indicated that C–N cleavage was involved in the conversion of *N*-allylaniline into the *C*-allylaniline. Therefore, the reaction proceeded by further allylation in the conversion of kinetically favored product

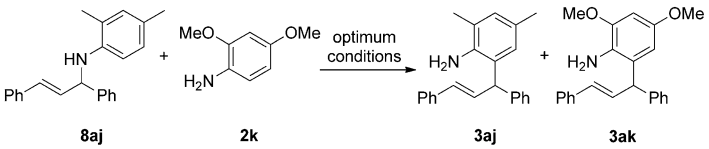


Scheme 5. Control experiment to study a possible Hofmann–Martius rearrangement.

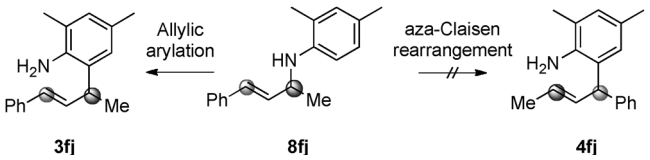
8aj into thermodynamically favored product **3aj** rather than an aza-Cope rearrangement or Hofmann–Martius sequence.

Another control experiment with **8bj** was conducted under the optimum conditions, and **3bj** was obtained as the major product instead of **4bj** (Scheme 7). This result further confirmed that the transition of **8bj** into **3bj** does not occur through an aza-Cope rearrangement, as **4bj** should be the sole product if the reaction proceeded though this route.

Finally, the synthetic utility of the obtained 2-allylaniline products was illustrated by a simple transformation. The 2-allylanilines were readily converted under mild conditions into substituted quinolines through an



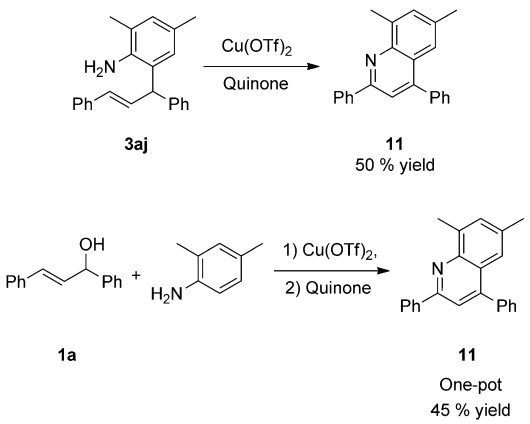
Scheme 6. Control experiment that illustrates allylic arylation.



Scheme 7. Control experiment to confirm the allylic arylation sequence.

oxidative cycloaddition reaction (Scheme 8). This cycloaddition therefore provides a new route towards the synthesis of multisubstituted quinolines of biological importance. Additionally, the one-pot synthesis of a quinoline derivative from an allylic alcohol and aniline was also demonstrated, as shown in Scheme 8. These reaction conditions, however, were not optimized with respect to the cyclization step, and therefore, the products were obtained in only moderate yields.

The utility of 2-allylanilines in the synthesis of biologically relevant heterocycles was previously demonstrated by other groups. Some notable examples include the use of *C*-allylanilines in the efficient Pd-catalyzed synthesis of *N*-aryl-2-benzylindolines by Wolfe et al.,[1k] as well as in the enantioselective synthesis of 2,5-dihydrobenzo[*b*]azepine derivatives by an allylic amination/ring-closing metathesis sequence by You et al.[1a] A significant number of highly efficient reaction protocols per-



Scheme 8. Synthetic utility of 2-allylanilines.

formed with the use of *C*-allylanilines and their derivatives have been explored by Chemler et al.[20,21] These include enantioselective intramolecular alkene aminooxygenation,[20] enantioselective alkyl Heck-type coupling cascades,[22] enantioselective indoline synthesis through alkene hydroamination,[21] intramolecular diamination towards the synthesis of 2,5-disubstituted pyrrolidines,[1e] and intramolecular carboamination of unactivated olefins towards the synthesis of pyrrolidine and piperidine derivatives.[1h]

Conclusions

In summary, we have demonstrated the use of a simple and commercially available catalyst, copper(II) triflate, for the direct and selective synthesis of *C*-allylanilines in good to high yields by direct allylic amination from relevant allylic alcohols and anilines. A wide range of functional groups were tolerated under the reaction conditions, and the products were obtained regioselectivity without the need of an activator. A detailed mechanistic investigation was undertaken, which included control experiments and VT-NMR spectroscopy analysis. The efficacy of this protocol in providing subsequent access to substituted quinolines was also demonstrated. The development of an asymmetric variant is currently being pursued in our laboratory.

Keywords: allylic compounds · amination · arylation · copper · regioselectivity

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