VIP Allylic Amination

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Iridium-Catalyzed Synthesis of Primary Allylic Amines from Allylic Alcohols: Sulfamic Acid as Ammonia Equivalent**

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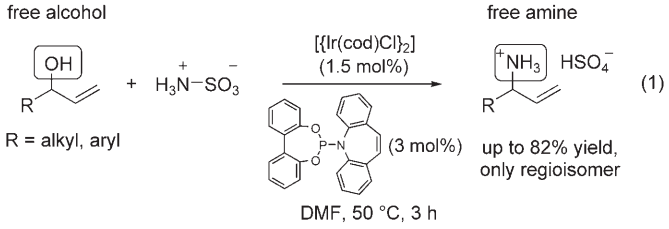
A large range of building blocks are accessible thanks to the impressive advances in homogeneous catalysis. Many reactions require the use of preactivated reactants with the exception of simple atom-transfer processes, such as epoxidation or hydrogenation. Additionally, the protected products must be subjected to further chemical steps prior to their actual application. The rapid and direct access to building blocks without additional processing being required is scarce despite the fact that such processes would be of great use.[1] We have been interested in these types of transformations for some time;[2,3] we have focused our attention on the development of nitrogen nucleophiles that would give access to unprotected primary amines.[4]

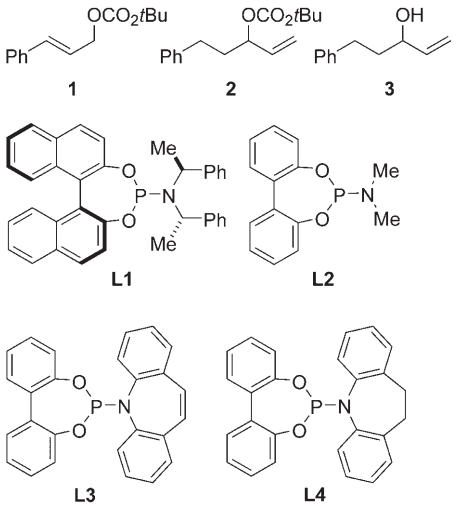
Herein we report the use of sulfamic acid (H_2NSO_3H) as an inexpensive, commercially available ammonia equivalent in allylic substitutions to afford directly allylic amines in excellent regioselectivity and synthetically useful yields.[5] The process employs a commercially available iridium catalyst precursor as well as a novel phosphoramidite–olefin ligand,[6] which can be synthesized in one step. A welcome side effect is the fact that allylic alcohols can be directly employed as the starting materials for the transformation without the need for prior activation [Eq. (1); cod = cycloocta-1,5-diene].



One of the most convenient methods for the synthesis of allylic amines is the Ir-catalyzed allylic substitution pioneered by the research groups of Takeuchi,[7] Hartwig,[8] Helmchen[9] and Alexakis.[10] However, whereas secondary and tertiary amines can be accessed in excellent yields and stereoselectivities, primary amines can only be prepared through the use of protected forms of ammonia.[11] In this respect, Helmchen and co-workers has recently reported the use of *o*-nosylamides and *N*,*N*-diacylamides in enantioselective Ir-catalyzed allylic amination reactions.[12]

To increase the practicality and atom economy[13] of the Ir-catalyzed allylic amination reaction to give primary amines, we have investigated the chemistry of sulfamic acid and specifically its capacity to serve as an ammonia equivalent. Sulfamic acid is a crystalline, inexpensive solid that has found limited applications in organic synthesis,[14] primarily as an acid catalyst.[15] However, to the best of our knowledge, sulfamic acid has never been employed as a nitrogen source in a process, despite its many potential advantages (low toxicity, non-corrosive, non-odorous, low molecular weight).

At the outset of our studies, we examined the reaction of *tert*-butyl cinnamyl carbonate (**1**) as a test substrate with sulfamic acid in the presence of a catalyst derived from the Feringa phosphoramidite ligand **L1** and Ir^I (Scheme 1).[3,16]



Scheme 1. Test substrates and ligands for the Ir-catalyzed allylic amination reaction with sulfamic acid.

However, all experiments conducted in THF, CH_2Cl_2, CH_3CN, EtOH, MeOH, or acetone were hampered by the low solubility of sulfamic acid, which led to recovery of starting material **1**. Although sulfamic acid is soluble in dipolar aprotic solvents such as *N*,*N*-dimethylformamide (DMF), dimethylacetamide (DMA), or dimethyl sulfoxide (DMSO), no conversion into the desired amine product or its derivatives (that is, secondary sulfamate) was observed.

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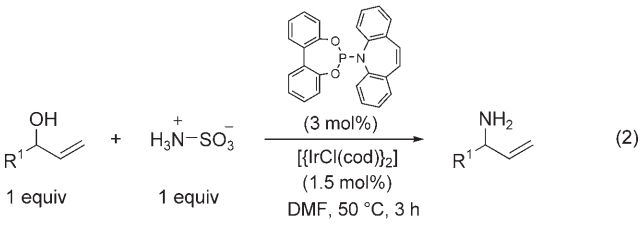
The first set of promising results were achieved with branched *tert*-butyl carbonate **2** as the substrate in DMF (15% conversion). Of greater significance, however, was the subsequent observation that alcohol **3** could be employed directly under otherwise identical conditions (15% conversion). This finding was key to the further optimization of the process. In transition-metal catalyzed allylic substitution reactions, activated allylic substrates (for example, halides, esters, carbonates, or carbamates) are usually required to facilitate the formation of the crucial allyl–metal intermediate.[17] Alternatively, reagents such as Et_3B or metal catalysts (Bi^{III}) can provide the in situ activation of a free alcohol.[18] The discovery of a process that involved the direct use of allylic alcohols was an unexpected bonus. Moreover, to the best of our knowledge, no transition-metal-mediated process in which a single reagent serves as both the ammonia source and in situ activator of a hydroxy group has been previously reported.

We further investigated the influence of various ligands. The nitrogen-based pyridylbis(oxazoline) (pybox) ligand only displayed decreased reactivity (5% conversion).[19] No amination was observed with the use of PPh_3 and $P(NMe_2)_3$ (<5% conversion) but we obtained 25% conversion with $P(OPh)_3$. Using 1.5 mol% of $[\{Ir(cod)Cl\}_2]$ and 3 mol% of the achiral phosphoramidite ligand **L2**, we achieved 30% conversion of **3** (DMF, 24 h, 23 °C).

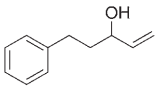
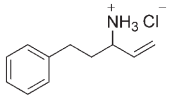
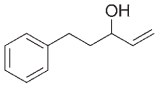
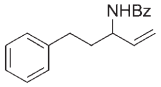
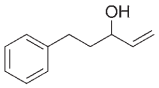
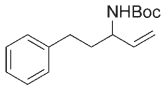
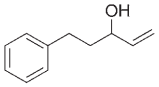
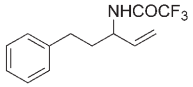
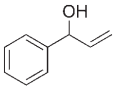
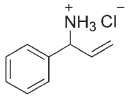
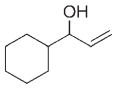
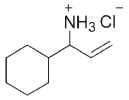
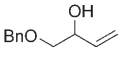
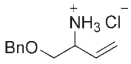
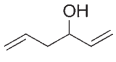
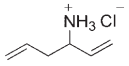
Based on our interest in alkenes as ligands in transition-metal catalysis,[20] we investigated the olefin ligand **L3** in the substitution process. Ligand **L3** can easily be synthesized from inexpensive 2,2′-biphenol, PCl_3, and 5*H*-dibenzo[*b*,*f*]azepine.[21] The reaction with this ligand was remarkably clean (>99% conversion, DMF, 24 h, 23 °C). When we used the saturated analogue, ligand **L4**, only 20% conversion of alcohol **3** was achieved.[22,23]

It is worth noting that the Ir-catalyzed transformation proceeds with complete regioselectivity.[24] Furthermore, neither di- nor triallylated amines could be observed in the unpurified reaction mixture. With the optimal conditions in hand, we investigated the scope of the reaction [Eq. (2), Table 1]. A convenient way to isolate the amine products is through the precipitation of their hydrochloride salts. However, a salient feature of the process results from the use of an ammonia equivalent, in which the amine can be subsequently protected in situ as the benzamide (entry 2, Bz = benzoyl), the Boc-carbamate (entry 3, Boc = tert-butoxycarbonyl), or the trifluoroacetamide (entry 4). In fact, the protection can facilitate the isolation of the product for certain low-molecular-weight substances produced on small scale. Various substituents are permitted in the substrate including phenyl- (entry 5), cylohexyl- (entry 6), as well as benzyloxymethyl-substituted allylic amines (entry 7, Bn = benzyl). Noteworthy is also the isolation of hexa-1,5-dien-3-amine hydrochloride (entry 8) in 75% yield without any isomerization of the double bond.



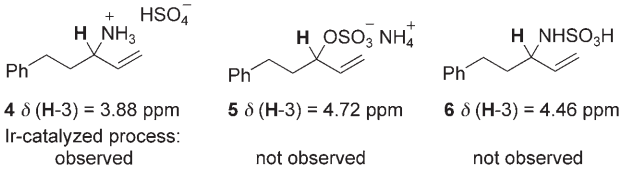
(2)

Table 1: Investigation of the substrate scope.

Entry	Substrate	Product	Yield [%][a]
1			82[b]
2			73[c]
3			71[d]
4			71[e]
5			78[b]
6			75[b]
7			71[b]
8			75[b]

[a] Yield of product isolated after purification by chromatography. Regioselectivity was >99:1 as shown and determined by ^{1}H NMR spectroscopy of the unpurified reaction mixtures. [b] Isolated as the hydrochloride salt by treatment of the purified amine with 2 M HCl in diethyl ether. [c] Treatment of the unpurified reaction mixture with Et_3N, BzCl. [d] Treatment of the unpurified reaction mixture with 0.5 M aq NaOH, Boc_2O. [e] Treatment of the unpurified reaction mixture with K_2CO_3, $(CF_3CO)_2O$. For further experimental details, see the Experimental Section and the Supporting Information.

To get further insight in this interesting process, the course of the reaction was followed using time-dependent ^{1}H NMR spectroscopy in [D_7]DMF, in which the signal corresponding to H-3 of our test alcohol **3** was monitored.[25] In analogy to the reaction on preparative scale, the NMR experiments showed the clean transformation of **3** (δ(H-3) = 4.04 ppm) into the corresponding amine **4** (δ(H-3) = 3.88 ppm) within three hours (Scheme 2). In a separate experiment, we investigated the influence of an excess of sulfamic acid (2 equiv). The desired amine **4** was generated after two hours as shown by the appearance of the corresponding signal of the amine. When the reaction was allowed to continue over 8 h, amine **4** is observed to undergo partial conversion into another product with a characteristic signal at δ = 4.46 ppm. To assign a structure for this product, we conducted additional experiments in [D_7]DMF: Treatment of alcohol **3** with two equivalents of sulfamic acid after eight hours gave quantita-



Scheme 2. Selected results from the spectroscopic experiments in [D_7]DMF.

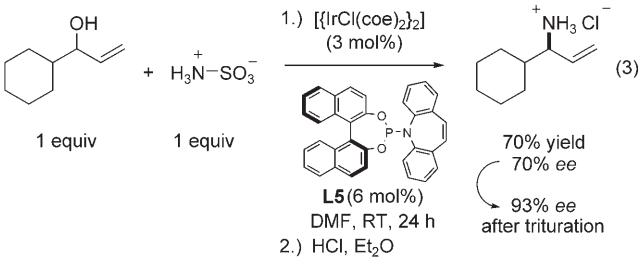
tive sulfate ester **5** (δ(H-3) = 4.72 ppm) which is consistent to what is known in the literature.[5] The more potent commercially available sulfating agent sulfur trioxide-*N*,*N*-dimethylformamide performs sulfation in an analogous way to deliver **5** already after 1 h. When amine **4** is treated under the same conditions, sulfamate **6** could be obtained along with side products after nine hours.

These spectroscopic observations allow us to make the following conclusions:

1) When an excess of sulfamic acid was employed in the Ir-catalyzed process, the amine **4** initially produced underwent partial sulfamation with the second equivalent of sulfamic acid to form **6**. This sulfamation only began after **3** had been entirely transformed into **4**.
2) Throughout the course of the Ir-catalyzed process, no signals corresponding to the sulfate ester **5** were observed. Given the long reaction time required to perform the sulfation with sulfamic acid (eight hours), it is unlikely that the sulfate ester **5** serves as activated intermediate in the Ir-catalyzed reaction.
3) The absence of signals corresponding to **6** leads us to suspect that sulfamic acid does not act as a nucleophile in the catalytic process.

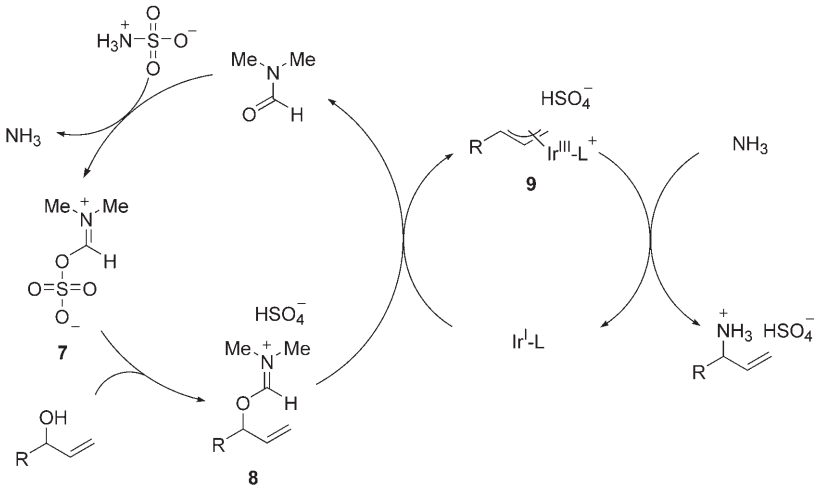
Based on these observations, we developed a working model shown in Scheme 3. It has been suggested in the literature that *N*,*N*-dimethylformamide undergoes a condensation reaction with sulfamic acid[26] to form a Vilsmeier-like intermediate **7**.[27] We speculate that this reactive intermediate is generated here, and that it subsequently reacts with the allylic alcohol to form **8**.[28] This activated species then can participate in an oxidative addition reaction with the iridium complex.[29] The resulting iridium–allyl species **9** is sufficiently electrophilic to undergo a nucleophilic attack by ammonia, thus liberating the primary protonated allylic amine product.

Our aim was to apply the unique aspects of sulfamic acid chemistry to a catalytic asymmetric process. The modular structure of phosphoramidite ligand **L3** allows the incorporation of a wide range of chiral diol backbones. For example, the integration of *(S)*-binol in place of 2,2′-biphenol resulted in the chiral ligand **L5**, which, in combination with Ir^I, can be used in the reaction of 1-cyclohexylprop-2-en-1-ol to provide *(S)*-1-cyclohexylprop-2-en-1-amine hydrochloride in 70% yield and 70% *ee*.[30] [Eq. (3); coe = cyclooctene] Although



this result is far from optimal, it represents the first example of direct generation of a primary enantiomerically enriched allylic amine from an allylic alcohol.[31]

In conclusion, we demonstrate for the first time the direct Ir-catalyzed conversion of an allylic alcohol into an allylic amine with the use of sulfamic acid. This method does not require either separate prior activation or protecting group operations and thus the process is attractive both economically and ecologically. Also, promising preliminary results towards the development of an asymmetric process have been achieved. Further mechanistic investigations as well as the fine-tuning of ligands are underway. The fact that sulfamic acid can serve as an ammonia equivalent is intriguing and may have an application in other transformations that invlove the conversion of OH into NH_2 groups.



Scheme 3. Proposed working model. L = ligand.

Experimental Section

Representative procedure: A Schlenk flask under argon was charged with [{Ir(cod)Cl}$_2$] (10.1 mg, 15 μmol, 1.5 mol%) and **L3** (12.2 mg, 30 μmol, 3 mol%). DMF (2 mL) was added and the reaction mixture was stirred at 23 °C for 15 min. The allylic alcohol (1.00 mmol, 1 equiv) was added by syringe, followed by solid sulfamic acid (97 mg, 1.00 mmol, 1 equiv). The resulting reaction mixture was heated to 50 °C. After completion of the reaction (usually 3–4 h, as monitored by TLC), the solvent was evaporated at high vacuum. The resulting brown residue was dissolved in CH_2Cl_2 (10 mL) and sat. aq $NaHCO_3$ solution (10 mL) and stirred for 10 min. The aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure to afford the crude allylic amine. The ratio of regioisomers was

determined by ^{1}H NMR analysis of the unpurified sample. The desired amine was obtained after purification of the residue by flash chromatography on basic or neutral alumina using CH_2Cl_2/MeOH as eluent. As some amines proved to be unstable and/or volatile, they were obtained through precipitation of their more-stable hydrochloride salts by addition of 2 M HCl in Et_2O.

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[31] Cinnamyl alcohol did not serve as substrate under our current reaction conditions, even when the Hartwig catalyst-activation protocol (Ir^I and **L1**) was employed; see Ref. [8d].

