

# Regioselective Synthesis of Multifunctional Allylic Amines; Access to Ambiphilic Aziridine Scaffolds

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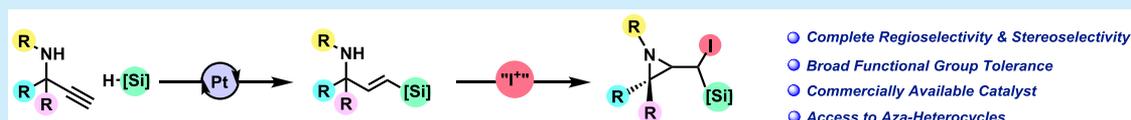
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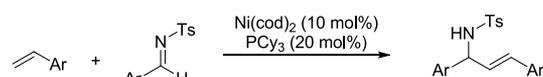


**ABSTRACT:** We describe, for the first time, a highly regioselective hydrosilylation of propargylic amines. The reaction utilizes a PtCl<sub>2</sub>/XantPhos catalyst system to deliver hydrosilanes across the alkyne to afford multifunctional allylic amines in high yields. The reaction is tolerant to a wide variety of functional groups and provides high value intermediates with two distinct functional handles. The synthetic applicability of the reaction has been shown through the synthesis of diverse ambiphilic aziridines.

Allylic amines are found in both natural products and pharmaceutical compounds alike.<sup>1</sup> Furthermore, they are widely used as high value building blocks in synthetic organic chemistry.<sup>2</sup> As such, their synthesis has attracted sustained interest from the organic chemistry community. Carbon–carbon coupling reactions between activated imines and unsaturated moieties has seen rapid improvement over the past two decades with notable examples from Zhou,<sup>3</sup> Krische,<sup>4</sup> Shibasaki,<sup>5</sup> and others<sup>6</sup> (Scheme 1). Direct amination has also been shown to be successful in this area, with the Tsuji–Trost reaction proving particularly useful in the arena of total synthesis.<sup>7</sup> Further examples from Rovis,<sup>8</sup> Kobayashi,<sup>9</sup> and Hartwig<sup>10</sup> show that very selective reactions can be developed, providing these useful building blocks with complete control of stereoselectivity.

## Scheme 1. Synthesis of Allylic Amines

### a) Hydroalkenylation of Imines (Zhou)



### b) Reductive Coupling of Alkynes & Imines (Krische)



### c) Hydrosilylation of Propargylic Amines (This Work)

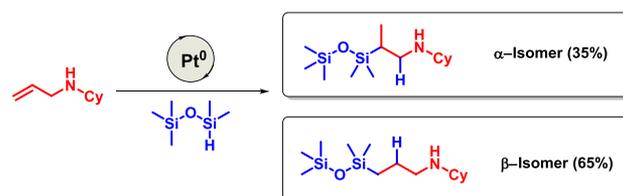
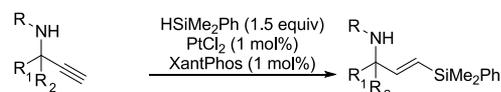


Figure 1. Previous attempts.

Entry	Loading (mol %)	Ligand	Temp (°C)	α:β	Conv. (%)
1	1	-	50	1:7	>99
2	1	DavePhos	50	1:10	>99
3	1	XPhos	50	1:20	>99
4	1	SPhos	50	1:14	>99
5	1	tBuXPhos	50	1:10	>99
6	1	CyJohnPhos	50	1:12	>99
7	1	JohnPhos	50	1:9	>99
8	1	XantPhos	50	>1:99	>99
9	-	Xantphos	50	n.d	n.r

Figure 2. Optimization study.

Although these reactions provide the desired allylic amine in high yields and good stereoselectivity, their functional group variability is relatively small. Additionally, many of the reactions described provide terminal olefins, which potentially

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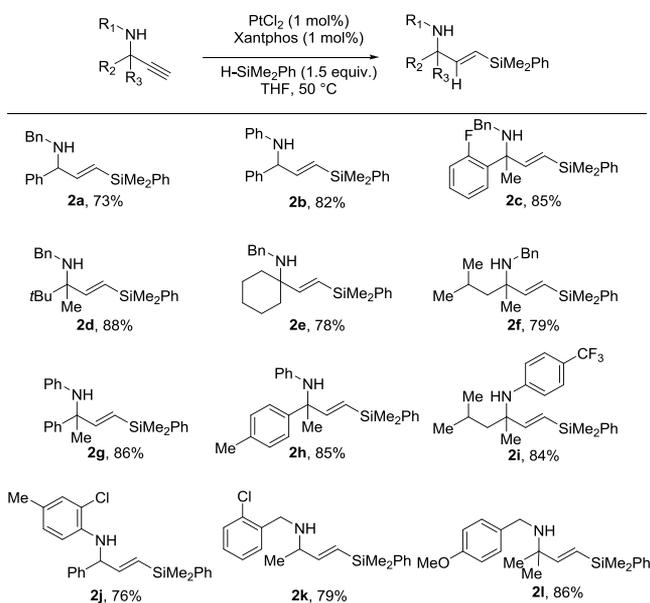


Figure 3. Aryl and benzyl derivatives.

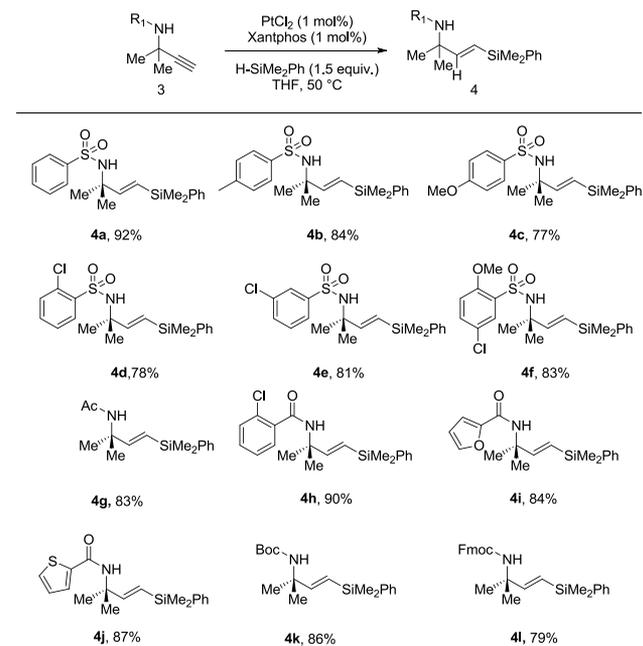
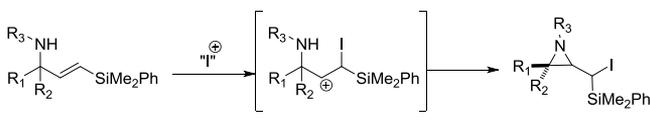


Figure 4. Sulfonamide, amide, and carbamate derivatives.

## Scheme 2. Synthetic Strategy toward Ambiphilic Aziridines



limits their use in complex target synthesis. This issue has been somewhat overcome in the past decade, with elegant examples described by White<sup>11</sup> and Meek.<sup>12</sup> Although advances have been made, the need to develop new methods to produce multifunctional allylic amines remains high. In particular, there is a strong desire to produce these moieties bearing multiple and complementary functional handles from readily available starting materials.

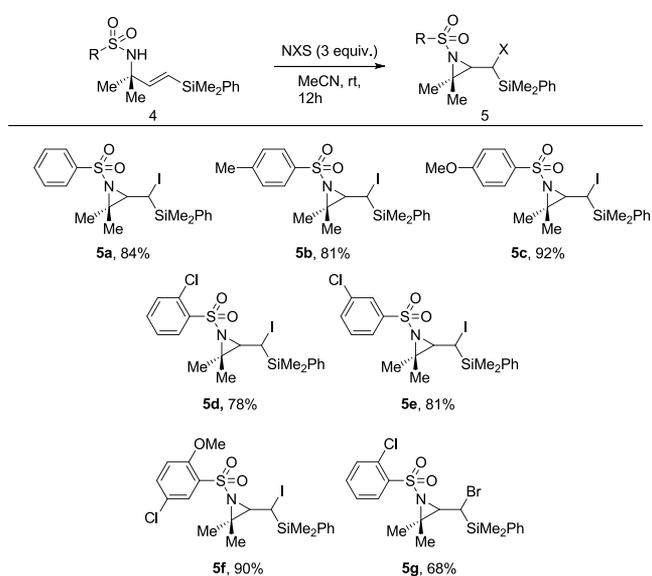
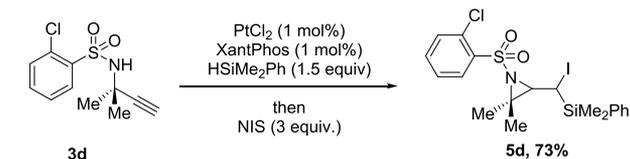
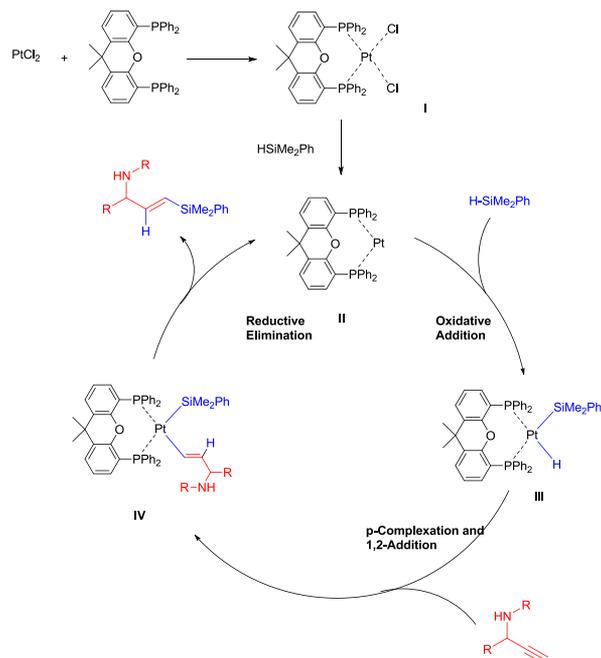


Figure 5. Ambiphilic aziridine scope.

## Scheme 3. Telescoped Synthesis of Functionalized Aziridines



## Scheme 4. Proposed Reaction Mechanism



As part of ongoing research within our group, we required ready access to a range of allylic amines bearing pendant organosilicon functional groups to allow for the synthesis of aziridine scaffolds. Aziridines are important nitrogen-containing heterocycles that have been shown to have wide-ranging biological activities and uses in medicinal chemistry.<sup>13</sup> Furthermore, their importance to synthetic organic chemistry

as synthetic intermediates has resulted in considerable effort to develop synthetic methodology to access them.<sup>14</sup> These methodologies often rely on the Corey–Chaykovsky reaction<sup>15</sup> or the use of functionalized diazo compounds.<sup>16</sup>

A survey of the literature revealed that the established methods described above would be unsuited to this purpose, and indeed, this proved true in practice. We therefore decided that an alternative to C–C coupling was required, as well as allowing the use of more readily available starting materials. To this end, we have developed the first hydrosilylation reaction of propargylic amines to afford a single regioisomer in high yields.

Platinum-catalyzed hydrosilylation reactions were first described in the 1950s,<sup>17</sup> with the disclosure of hexachloroplatinic acid.<sup>18</sup> Since then, the field has matured, with the development of more sophisticated catalytic systems being disclosed.<sup>19</sup> Of these, platinum is still widely used, due to its  $\pi$ -Lewis acidity and functional group tolerance. As a result of the increased cocoordinative ability of nitrogen, platinum-catalyzed hydrosilylation of amine-containing moieties is scarcely reported in the literature. Speier disclosed the attempted hydrosilylation of allyl amines, resulting in the formation of an isomeric mixture of silanes (Figure 1).<sup>20</sup>

Given that the poisoning of hexachloroplatinic acid by amine and amide moieties is documented, this is not particularly surprising. Endo demonstrated the relationship between the ratio of nitrogen donors to platinum centers and the retardation effect on catalyst efficiency.<sup>21</sup> When studying the hydrosilylation of *N*-allylamines, Chechelska-Noworyta found that it was necessary to decrease the nucleophilicity of the nitrogen through either steric or electronic factors. Without tuning these factors, the regioselectivity drops to approximately 2:1  $\beta$ : $\alpha$ .<sup>22</sup> Furthermore, Pregosin and co-workers have shown that both aliphatic and aromatic amines preferentially displace olefinic ligands in the complex formed between PtCl<sub>2</sub> and styrene.<sup>23</sup> These investigations show that this transformation is nontrivial in nature and represents an unmet need within the synthetic community.<sup>24</sup> As mentioned, we required a robust method to produce these important allylic amine intermediates with a range of pendant functional groups. **1a** was chosen as a model substrate, as it does not deactivate the amine moiety toward the aforementioned metal complexation.

We began our investigation by treating **1a** with dimethylphenylsilane in the presence of PtCl<sub>2</sub> as catalyst (Figure 2). Unsurprisingly, this provided an inseparable mixture of products, with the desired  $\beta$ -isomer being formed preferentially. We then began a survey of monodentate phosphine ligands, which improved the selectivity profile of the reaction. Although improved, the undesired  $\alpha$  isomer was still produced in non-negligible quantities, with the best result observed when using XPhos in a 1:2 ratio relative to the catalyst.<sup>25</sup> We reasoned that the monodentate ligand was being displaced by the amine during the reaction, and reducing the impact of the bulky ligands on selectivity. We therefore switched our focus to bidentate ligands and found that Xantphos (Figure 1, entry 8) was unique in its ability to provide full conversion and complete control (>99:1) of regiochemistry, providing the desired  $\beta$ -isomer as the sole product. Further exploration of solvent, temperature, and catalyst loading resulted in a less efficient reaction.

With these conditions in hand, we turned our attention to probing the substrate scope of the reaction (Figure 3). The reaction was tolerant to secondary (**2a**, **2b**, **2j**, **2k**) propargyl amines, providing the desired product in high yield as a single

regioisomer. Symmetrical (**2e**) and unsymmetrical propargyl amines (**2c**, **2d**, **2f**) also worked well, producing allyl amines with multiple points of derivatization. The reaction also tolerated diverse electronics, with electron-donating (**2g**, **2h**) and -withdrawing (**2i**) as well as mixed (**2j**) aryl groups all working well. Furthermore, electron-withdrawing (**2k**) and -donating amines (**2l**) proceeded smoothly.

As we envisaged this methodology to be used in in-house medicinal chemistry programs, we wanted to explore the effect that sulfonamides, amides, and carbamates had on the reaction. We were initially concerned that the extra points of interaction would compete for the active metal species; however, our concerns were, thankfully, misplaced.

As shown in Figure 4, sulfonamides bearing weakly (**4b**) and strongly (**4c**) electron-donating and electron-withdrawing groups (**4c**, **4d**) were all well tolerated, producing fragments with multiple functional handles. Mixed electronics (**4f**) were also successful in the reaction, providing the allyl amine in high yield. In a similar vein, amides also worked very well, with the vinyl silanes produced in excellent yield throughout. Aliphatic (**4g**), aryl (**4h**), and heteroaromatic (**4i**, **4j**) amides all proceeded in a straightforward manner, affording a single regioisomer in each case. Finally, we explored the use of well-established carbamate protecting groups. Both Boc (**4k**) and Fmoc (**4l**) proceeded smoothly, providing scaffolds with complementary deprotection strategies.

As noted, ready access to multifunctional aziridines was a key goal in this research. We reasoned that an alternative approach to these heterocycles could be realized, using the well-established  $\beta$ -silicon effect to our advantage.<sup>26</sup> In particular, we wanted to explore if an iodination triggered ring closure could be used to access ambiphilic substrates (Scheme 2).

We therefore subjected **4a** to *N*-Iodosuccinamide (NIS) at room temperature, and saw complete conversion to the product after 12 h. Delighted that our hypothesis was proved correct, we explored the reaction further. As shown (Figure 5), a range of aziridines can be produced in high yields including electron-donating (**5a–c**) and -withdrawing (**5d**, **5e**) as well as mixed (**5f**) electronics. When **2a** or **4g** was subjected to same reaction conditions, an inseparable mixture of products was formed, presumably due to competing migrations and alternative cyclization modes as reported by Taguchi.<sup>27</sup> Pleasingly, when **4x** was treated with *N*-Bromosuccinamide (NBS), the halogenation–aziridination reaction was also effective, affording **5g** in 68% yield.

Finally, we wanted to explore if the aziridine product could be obtained in a telescoped fashion (Scheme 3).<sup>28</sup> This has the benefit of reducing the number of chromatography operations, as well as increasing the overall economy and efficiency of the process. To this end, we subjected **3e** to the hydrosilylation conditions followed by NIS. This strategy proved successful, and the aziridine product (**6e**) was obtained in 73% over the two steps.

Based on previous studies of the reactivity of platinum–phosphine complexes, in addition to the highly studied Chalk–Harrod hydrosilylation mechanism<sup>25a</sup> and the stereo- and regiochemical outcome of the transformation, we propose the following reaction mechanism (Scheme 4). Initially, Pt(II) complex (**I**) is formed via complexation of XantPhos to PtCl<sub>2</sub> to form *cis*-Pt(XantPhos)Cl<sub>2</sub>. This complex has been previously isolated and fully characterized, and the <sup>31</sup>P NMR spectra of the complex formed under our reaction conditions

are in agreement with the data previously reported.<sup>29</sup> Silane-mediated reduction<sup>23</sup> of this complex generates the Pt(0) species (II), with the generation of dihydrogen. This intermediate then undergoes oxidative addition into the silicon–hydride bond to yield the 16-electron Pt(II) species (III). Alkyne coordination to III then allows for a 1,2-*syn*-hydroplatination via migratory insertion, with the hydride being delivered to the more electropositive terminus of the alkyne to furnish IV. Subsequent reductive elimination regenerates the initial Pt(0) species and affords the vinyl silane as a single regio- and stereoisomer.

In conclusion, we have developed the first regioselective hydrosilylation of propargylic amines to provide stereochemically defined allylic amines. We have shown the catalyst system to be tolerant to a range of important functional groups including benzyl, amide, sulfonamide, and carbamate. Furthermore, we have shown the synthetic utility of these allylic amines, producing multifunctional aziridines via an operationally simple iodination–cyclization protocol.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.1c01398>.

Experimental procedures along with characterization data and copies of <sup>1</sup>H and <sup>13</sup>C spectra (PDF)

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### Notes

The authors declare no competing financial interest.

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