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# Synthesis of Aminoallenes via Selenium-π-Acid-Catalyzed Cross-Coupling of *N*-Fluorinated Sulfonimides with Simple Alkynes

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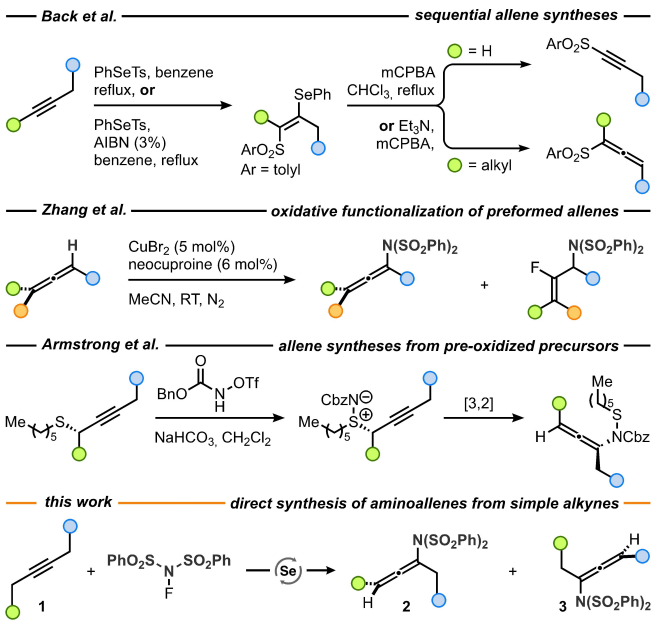
*In memory of Professor Kilian Muñiz.*

The facile synthesis of aminoallenes, accomplished by a selenium-π-acid-catalyzed cross-coupling of an *N*-fluorinated sulfonimide with simple, non-activated alkynes, is reported. Until now, aminoallenes were difficult to be accessed by customary means, inasmuch as pre-activated and, in part, intricate starting materials were necessary for their synthesis. In sharp contrast, the current study shows that ordinary internal alkynes can serve as simple and readily available precursors for the construction of the aminoallene motif. The operating reaction conditions tolerate numerous functional groups such as esters, nitriles, (silyl)ethers, acetals, and halogen substituents, furnishing the target compounds in up to 86% yield.

Allenes have been the subject of numerous scientific investigations over the past few decades, owing largely to their unique structural features and reactivity profiles.[1] For example, unlike internal alkynes, 1,3-multisubstituted allenes can exhibit axial chirality, which can be readily exploited in asymmetric synthesis.[2–4] In addition, allenes can differ significantly in the electronic constitution of their two cumulated π-bonds, depending on the substitution pattern at the termini of the propadiene subunit.[5] This specific feature is particularly prominent in allenes possessing heteroatomic residues such as oxygen or nitrogen moieties in their periphery. Given the inherent chemo- and regioselectivity that reactions of electronically differentiated allenes display,[5,6] tremendous efforts have been devoted to their synthesis from easily available resources.[1,4,7] With regard to the subclass of aminoallenes, the most common strategies involve $S_N2'$ reactions with nitrogenous nucleophiles or sigmatropic rearrangements of propargylic substrates (e.g., propargylic bromides, alcohols, and sulfides, respectively),[8] as well as prototropic isomerizations and electrophilic functionalizations of propargyl amines and enynes.[9–11] While each of these strategies has led to great success and was found to be compatible with many functional groups, an intrinsic drawback arises from the redox and step economy of these transformations (Scheme 1).[8a,d–e,9e,h,12] More precisely, in either case, the adjustment of the final oxidation state within the target molecule and the establishment of the desired skeletal connectivity takes place in more than one chemical operation. Against this background, a catalytic process that unifies an intermolecular C–N bond formation with the desired oxidation state in the target compound appears to be a strategically sound complement to the portfolio of classical




**Scheme 1.** Exemplary overview on synthetic approaches toward heterosubstituted allenes.

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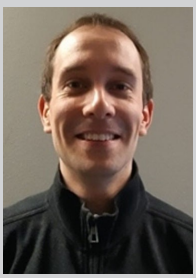
protocols. Promising candidates for the aspired title reaction are selenium-π-acids, as they have been frequently found to electrophilically activate olefinic and acetylenic π-bonds with salient chemoselectivity.[13] Typical examples include allylic alkene functionalizations such as esterifications, etherifications, nitrogenations, and halogenations.[13a–13d,13f–13l,14] With regard to alkyne functionalizations, Zhao et al. recently demonstrated the Se-catalyzed oxidation of carboxylic and phosphonic esters possessing β,γ-C–C triple bonds to give the respective α,β-ynones,[13k,15] and Liu et al. reported a visible-light mediated synthesis of oxazole acetals from *N*-propargylamides using selenium-π-acid catalysts.[16] In some earlier work by Back et al. it was shown that 1,2-selenosulfonylated alkenes, derived by radical addition of selenosulfonates to terminal alkynes, would undergo facile elimination under oxidative conditions to provide access to allenic sulfones.[17] Based on our previous mechanistic investigations on photo- and electrocatalytic allylic functionalizations of alkenes using selenium-π-acid catalysts,[14,18] we wondered whether the stepwise addition-elimination sequence described by Back et al. could be translated into a corresponding allenic amination protocol of alkynes that is merged into a single catalytic cycle. As a result of these considerations, we disclose herein the first example of a selenium-π-acid-catalyzed cross-coupling between *N*-fluorobenzenesulfonimide (NFSI) and a broad series of both functionalized and non-functionalized, electronically unbiased alkynes to furnish an extended set of aminoallenes, with NFSI acting as both the nucleophile and terminal oxidant.

At the outset of this endeavor, we decided to use 5-decyne (**1**) as the model substrate for the optimization studies (Table 1). Initially, we obtained allene **2a** in 45% yield when using 10 mol% of (*o*-anisyl-Se)$_2$ and 1.0 equiv. NFSI in toluene at 100 °C (entry 1). No reaction was observed in the absence of the diselenide (entry 2). We then proceeded by examining different solvents for the title reaction. Ethereal solvents such as THF and 1,4-dioxane gave the desired allene **2a** in yields comparable to that obtained with toluene, while TCE led to a diminished yield of only 19% (entries 3–5). Having decided to proceed with toluene as the solvent of choice, we went on to optimize the amount of NFSI required for the reaction. With 1.2 equivalents of NFSI, an increased yield of 53% was observed. However, using 3.0 equivalents led to a reduced yield of 41% (entries 6 and 7). Additionally, we hypothesized that a base could further enhance the elimination of the selenium moiety, facilitating the formation of the desired aminoallene. To substantiate our hypothesis, we individually added 1.0 equivalent of NaOAc, $K_2HPO_4$, or $Li_2CO_3$ to the reaction. The acetate was observed to impede the reaction, giving the desired product in a very low yield of 9% (entry 8). The hydrogen phosphate increased the yield to 65% and the carbonate led to an even higher yield of 68% (entries 9 and 10). Occasionally, we also observed the formation of a side-product upon full conversion of alkyne **1**, which we identified as adduct **4** (Scheme 2). To minimize the formation of this selenofunctionalized product, we decreased the catalyst loading to 2.5%, resulting in the formation of the desired product with a 77% yield (entries 11 and 12).

Prof. Alexander Breder studied chemistry at the University of Bielefeld, Germany, and received his diploma degree in 2005. Subsequently, he moved to the Swiss Federal Institute of Technology Zurich (ETH), Switzerland, where he joined the group of Prof. Erick M. Carreira. During his doctoral studies, he was working on the synthesis of marine natural products. Upon completion of his Ph.D. in 2009, he joined the group of Prof. Barry M. Trost for a postdoctorate at Stanford University, USA, where he investigated ruthenium-catalyzed domino- and consecutive reactions. In late 2011, he started his independent research career at the Georg-August-University Goettingen, Germany, where he completed his habilitation in 2017. Since April 2019, he is a Professor of Organic Chemistry at the University of Regensburg, Germany.

Dr. Felix Kraetzschmar studied chemistry at the Georg-August-University Göttingen, Germany. He obtained his Master's degree in 2014 with the thesis 'Synthesis of 1,3-Diarylpropenes for the Selenium-catalyzed Acyloxylation' in the group of Prof. Alexander Breder and continued his Ph.D. studies in the same group. In 2020, he obtained his Ph.D. degree with the thesis 'Development of Regio- and Enantioselective Transformations of Alkenes with $\lambda^3$-Iodane-Reagents and Chiral Selenium-π-Acid Catalysts'.

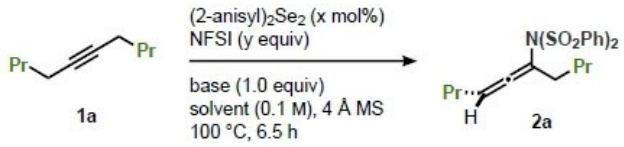
Dr. Katharina Rode studied chemistry at the Georg-August-University Göttingen, Germany. She obtained her Master's degree with a thesis on the synthesis of chiral thioamides in the group of Prof. Alexander Breder and continued her Ph.D. studies in the same group. In 2020, she completed her doctorate, during which she focused on selenium-π-acid-catalyzed functionalizations of alkenes and alkynes.



Rene Rieger studied chemistry at the Georg-August-University Göttingen, Germany. In 2016, he obtained his master's degree in chemistry with a thesis on the oxidative lactonization of alkenoic acids using dual selenium catalysis in the group of Prof. Alexander Breder. He is currently continuing his dissertation in the same group, working on selenium-catalyzed oxidative functionalizations of olefins.

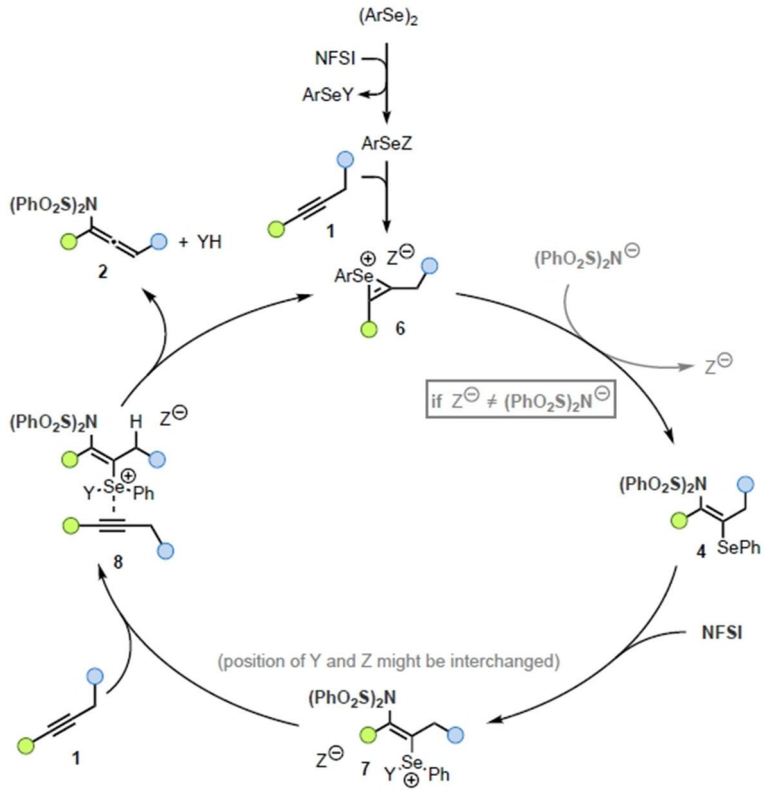
Poorva Narasimhamurthy studied chemistry at St. Joseph's College, Bangalore, India. In 2018, she obtained her Master's degree with a thesis on the functionalization of resorcinarenes in the group of Prof. Gerald Dyker, Ruhr University Bochum, Germany. She started her Ph.D. in 2018 in the group of Prof. Alexander Breder and is currently working on selenium-π-acid-catalyzed functionalizations of alkenes and alkynes

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




| Entry | x [mol %] | y (equiv) | Base | Solvent | Yield [%][a] |
|---|---|---|---|---|---|
| 1 | 10 | 1.0 | – | toluene | 45 |
| 2 | – | 1.0 | – | toluene | – |
| 3 | 10 | 1.0 | – | THF | 40 |
| 4 | 10 | 1.0 | – | 1,4-dioxane | 36 |
| 5 | 10 | 1.0 | – | TCE | 19 |
| 6 | 10 | 1.2 | – | toluene | 53 |
| 7 | 10 | 3.0 | – | toluene | 41 |
| 8 | 10 | 1.2 | NaOAc | toluene | 9 |
| 9 | 10 | 1.2 | $K_2HPO_4$ | toluene | 65 |
| 10 | 10 | 1.2 | $Li_2CO_3$ | toluene | 68 |
| 11 | 5 | 1.2 | $Li_2CO_3$ | toluene | 74 |
| **12** | **2.5** | **1.2** | **$Li_2CO_3$** | **toluene** | **77** |

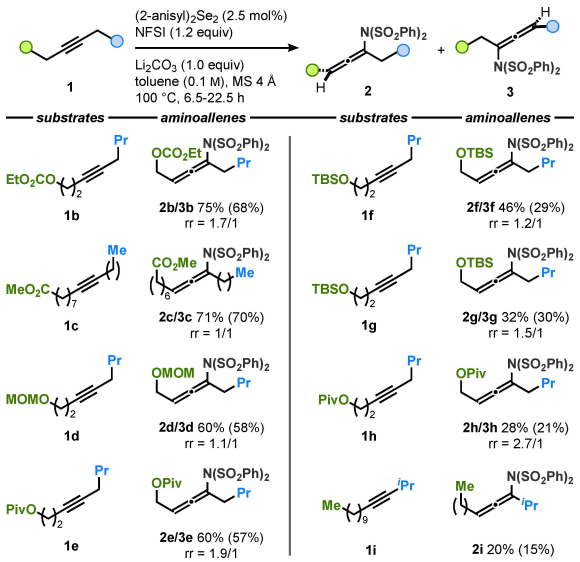
[a] Reactions were carried out on a 1.0 mmol scale. Yields were determined by $^1$H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.




**Scheme 2.** Mechanistic hypothesis on the oxidative selenium-π-acid-catalyzed synthesis of aminoallenes from simple alkynes.

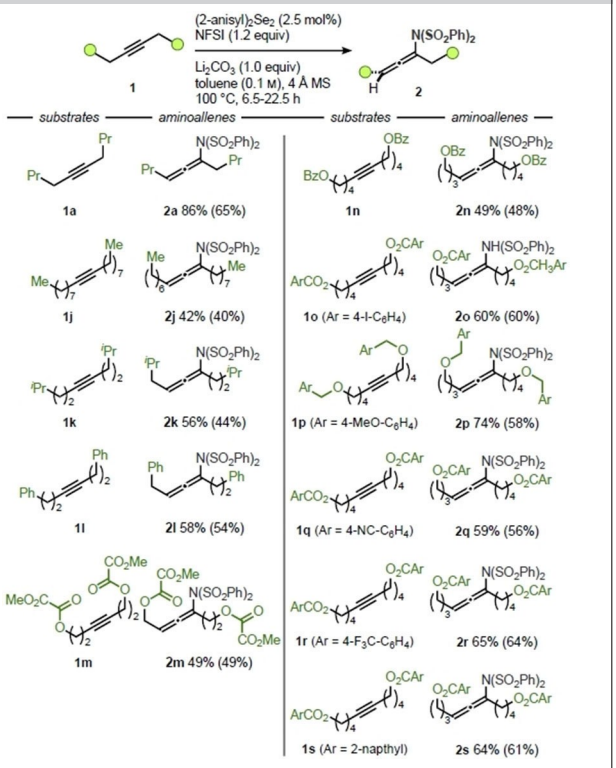
With optimized conditions in hand, we were interested in unveiling the scope and limitations of the reaction (Table 2 and Table 3). We began our investigations with unsymmetrical alkynes (Table 2) to investigate the regiochemical preference of the title reaction. With different functional groups, such as carbonate, ester, and (silyl)ether moieties, corresponding allenes **2** and **3** were obtained as regioisomeric mixtures (ratios between 1:1 to 2.7:1) in moderate to good yields ranging between 46–75% (**2b–f** and **3b–f**). In general, we observed a slight preference for the incorporation of the imide moiety in the distal position of the allene relative to any of the pre-exisiting heteroatomic functionalities. We speculate that this trend is due to electronic effects since acyloxy and carbonate residues led to slightly higher regiochemical differentiation

**Table 2.** Scope of the selenium-π-acid-catalyzed synthesis of aminoallenes using unsymmetric alkynes.[a]




[a] Reactions were carried out on a 1.0 mmol scale. Crude yields were determined by 1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard; isolated yields in parentheses; rr = regioisomeric ratio.

**Table 3.** Scope of the selenium-π-acid-catalyzed synthesis of aminoallenes using symmetric alkynes.[a]




[a] Reactions were carried out on a 1.0 mmol scale. Crude yields were determined by $^1$H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard; isolated yields in parentheses.

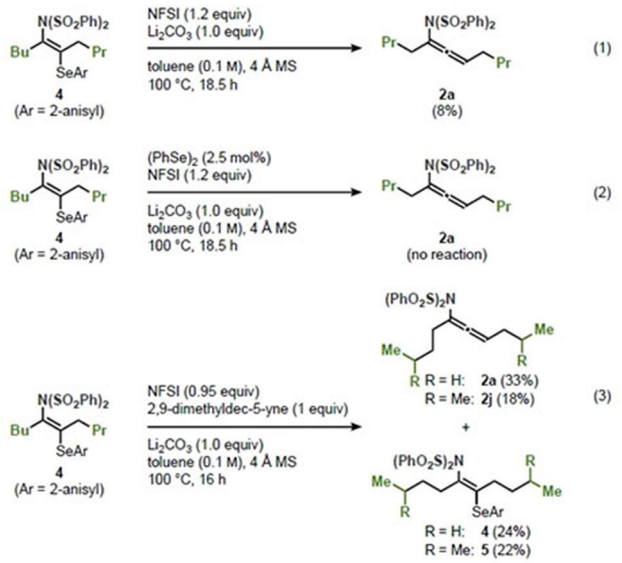
than ether residues of similar steric demand (e.g., **2e**/**3e** vs. **2f**/**3f**).

Alkynes **1g** and **1h**, which only contain a methyl group at one terminus of the respective triple bond, gave the corresponding allenes with a moderate yield of 32% (**2g**/**3g**), and 28% (**2h**/**3h**). For these products, C–N bond formation again occurred preferentially at the distal end of the newly formed allene moiety relative to the silyl ether (1.5:1) and pivalate group (2.7:1), respectively. However, in the case of secondary alkyne **1i**, regioisomer **2i** was the only product isolated, with a yield of 15%. This could be due to the greater steric hindrance from the isopropyl group, pushing the bulky selenium moiety to the less encumbered position of the alkyne and thus promoting the nucleophilic attack at the sterically more demanding position.

Motivated by these results, we shifted our attention to symmetrical acetylenes (Table 3). Alkynes with varying chain lengths, branching patterns, and substituents (**1a**, **1j**, **1k**–**1l**) gave the corresponding allenes **2a**, **2j**, and **2k**–**2l** in yields of 42–86%. Furthermore, functional groups such as esters and ethers were also found to be well-tolerated under the reaction conditions. Alkyne **1m** and PMBO-substituted alkyne **1p** gave the corresponding allenes in moderate to good yields of 49 and 74%, respectively. Substrates **1n** and **1s** possessing aromatic ester functionalities gave the corresponding allenes in moderate yields of 49 and 64%, respectively. Additionally, substrates with various substituents on the aromatic ring were also tolerated well under the reaction conditions, yielding the corresponding allenes in yields of 59 to 65% (**2o**, **2q**, and **2r**). The efficacy of the title reaction was found to be limited to internal alkynes, as no product formation was observed with terminal alkynes. A potential reason for this result might be an insufficient nucleophilicity of terminal alkynes under the title reaction conditions.

We proceeded in our study with an investigation of the reaction mechanism. To determine whether adduct **4** observed during the optimization studies was an intermediate of the catalytic cycle, we attempted to convert it into the desired product by conducting the title reaction without additional diselenide under otherwise unchanged conditions. With these deviations from the standard protocol, the desired allene was obtained in a very low yield of 8% (Equation 1). This observation is to some degree surprising as previous investigations on the allylic functionalization of alkenes had shown that selenofunctionalization intermediates analogous to compound **4** would complete the turnover upon exposure to a proper oxidant.[14a] Consequently, simple oxidation of the selenium moiety followed by its elimination does not seem to be the dominant reaction pathway. Next, we added 0.5 equivalents of $(PhSe)_2$ to a mixture of adduct **4** and 1.2 equivalents of NFSI (Equation 2). We hypothesized that the elimination event of the aryl selenium moiety may require activation by another selenium electrophile generated in situ from NFSI and $(PhSe)_2$. Unfortunately, this idea did not meet with success, as we did not observe any product formation. During our optimization studies, we observed that the reaction stagnated upon full consumption of the alkyne. Thus, we speculated that another alkyne molecule might assist as a

Lewis-base in the elimination of the selenium moiety from adduct **4** to result in the formation of the desired allene (cf. proposed Lewis-acid/Lewis-base pair **8**, Scheme 2). Correspondingly, we reacted adduct **4** with 1.0 equiv. of 2,9-dimethyldec-5-yne in the presence of NFSI (0.95 equiv). Under these conditions the reaction indeed displayed turnover, giving access to a mixture of allenes **2a** and **2k** derived from compound **4** and 2,9-dimethyldec-5-yne. In addition, we also obtained a mixture of the two aminoselenation adducts **4** and **5**, which indicated that the presence of an alkyne is pivotal for full turnover (Equation 3).[19] Although the mechanistic details are not fully understood as yet, the transfer of selenenium moieties between alkynes seems reminiscent of the transfer of chalcogenenium ions between olefins reported, i.a., by Denmark et al.[20]




Based on these observations, we propose the following catalytic cycle for the title reaction (Scheme 2). First, oxidation of the diselenide by NFSI, followed by the addition onto alkyne **1** may lead to the formation of selenirenium ion **6**,[21] which is subsequently attacked by the sulfonimide anion, forming selenoamination adduct **4**.[22] After oxidation of the selenium moiety and coordination onto another alkyne molecule, potentially leading to Lewis-adduct **8**, allene **2** and selenirenium ion **6** are formed.

In summary, we reported the first metal-free, selenium-π-acid-catalyzed synthesis of *N*-allyl sulfonimides using alkynes as starting materials and NFSI as the nucleophile and terminal oxidant. Unsymmetrical alkynes gave the corresponding regioisomeric allenes in yields of up to 75%, while symmetric alkynes gave the corresponding allenes in yields of up to 86%. Furthermore, we propose a mechanism for the desired transformation, accounting for the role played by each of the participating reagents.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** π-Acids · Amination · Homogeneous catalysis · Oxidations · Selenium

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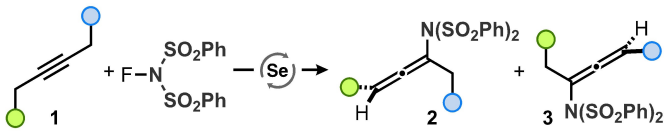
# COMMUNICATIONS

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**Synthesis of Aminoallenes via Selenium-π-Acid-Catalyzed Cross-Coupling of *N*-Fluorinated Sulfonimides with Simple Alkynes**

A step- and redox-economic route toward aminoallenes from simple alkynes and *N*-fluorobenzenesulfonimide (NFSI) was established via selenium-π-acid catalysis. This unprecedented method significantly streamlines the assembly of heterosubstituted 1,3-propadiene motifs and is characterized by a broad functional group tolerance.