Selenium Catalysis

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# Direct Oxidative Allylic and Vinylic Amination of Alkenes through Selenium Catalysis**

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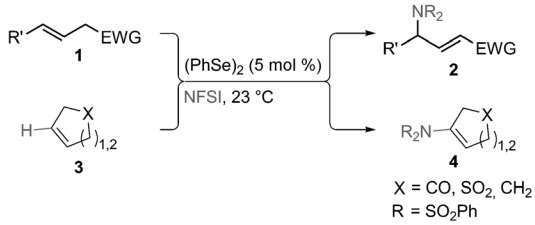
*Dedicated to Professor Erick M. Carreira on the occasion of his 50th birthday*

The fundamental importance of efficient C–N bond-forming reactions is reflected in the plethora of nitrogenated, naturally occurring and anthropogenic compounds with essential biological function.[1] Due in part to their relevance in the realm of medicinal as well as agrochemical applications,[2] numerous efforts have been dedicated to the development of novel processes for the construction of carbon–nitrogen bonds.[3] In this context, palladium-catalyzed oxidative amidations and imidations of arenes and olefins have become the subject of intensive investigations.[4] Hegedus et al. reported one of the first examples of a $Pd^{II}$-catalyzed intramolecular oxidative amination of allylic aniline derivatives using $CuCl_2$ or benzoquinone for the regeneration the $Pd^{II}$ catalyst.[5] Stahl and co-workers later documented the use of molecular oxygen as the terminal oxidant for a cognate amination reaction.[6] Recently, White and co-workers disclosed an intermolecular, oxidative allylic amination of simple olefins catalyzed by a palladium bis(sulfoxide) complex in the presence of either a chromium–salen complex[7a] or a Brønsted base[7b] co-catalyst leading to linear allylic amines.

In addition to transition-metal-catalyzed protocols, a number of iodine(III)-mediated nitrogenations of carbon–hydrogen bonds have been documented, for example aminations of aromatic $C(sp^2)$–H and benzylic $C(sp^3)$–H systems.[8] Most recently, Muñiz and co-workers described the stoichiometric use of a mixed hypervalent iodine reagent for the oxidative, allylic amination of 2-arylated propene derivatives.[9] Furthermore, Sharpless et al. reported a selenium(IV)-mediated allylic amination of alkenes by means of a hetero-Alder-ene reaction.[10] Koizumi and co-workers described the stereoselective synthesis of nonracemic allylic amines derived from selenimides by means of a [2,3]-sigmatropic rearrangement.[11] Very recently, Yeung et al. disclosed an enantioselective bromoaminocyclization of homoallylic amines using a mannitol-derived tetrahydroselenophene catalyst.[12]

Despite these remarkable achievements, to date there has been only a limited number of reports on the direct, oxidative nitrogenation of alkenes promoted by non-transition-metal catalysts. Given the increasing demand for more cost-efficient alternatives to precious metals as catalysts, main-group elements such as sulfur[13] and selenium[14] turned out to be appropriate candidates. In the course of our research program towards the development of new metal-free protocols for the catalytic and chemoselective nitrogenation of unactivated olefins we became interested in the use of organodiselanes as potent redox-active catalysts. From reports first by Sharpless et al.[15] and later by Tunge et al.[16] it is known that reactions of simple alkenes with *N*-halosuccinimides (halogen = Cl, Br) in the presence of selenium catalysts generally furnish the corresponding allylic and vinylic halides. However, cognate intermolecular Se-catalyzed processes leading to allylic or vinylic imide derivatives have, to the best of our knowledge, not been reported thus far.[17] A major difficulty associated with the design of such an imidation reaction using *N*-haloimides as the terminal oxidant is the inherent preference for halogen transfer instead of incorporation of the nitrogen entity. As a viable solution to this problem we present herein a selenium catalysis protocol for the efficient synthesis of a broad variety of allylic and vinylic imides **2** and **4**, respectively, using *N*-fluorobenzenesulfonimide (NFSI)[18] as the terminal oxidant and nitrogen source (Scheme 1).




***Scheme 1.*** Formation of allylic and vinylic amine derivatives through the selenium-catalyzed intermolecular oxidative imidation of alkenes. EWG = electron-withdrawing group.

In initial experiments benzyl pent-3-enoate (**1a**) was reacted with 1 equiv of NFSI in the presence of 5 mol% of various di(hetero)aryldiselanes in THF (0.2 M) at ambient temperature for 16 h (Table 1). While diphenyl diselane provides access to target structure **2a** in a reasonable yield of 64% (Table 1, entry 1), dipyridin-2-yl diselane and diferrocenyl diselane furnished allylic imide **2a** only in moderate yields of 55% and 48%, respectively (Table 1, entries 2 and 3). During the course of these experiments the formation of

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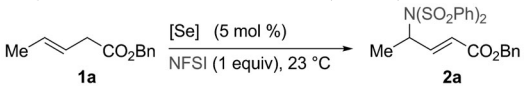
***Table 1:*** Optimization of the selenium-catalyzed allylic imidation.[a]




| Entry | Cat. | Solv. | Additive | Yield [%] |
|---|---|---|---|---|
| 1 | $(PhSe)_2$ | THF | – | 64 |
| 2 | $(2\text{-PyrSe})_2$ | THF | – | 55 |
| 3 | $(FcSe)_2$ | THF | – | 48 |
| **4** | **$(PhSe)_2$** | **THF** | **4 Å MS** | **84** |
| 5 | $(PhSe)_2$ | $Et_2O$ | 4 Å MS | 64 |
| 6 | $(PhSe)_2$ | 1,4-dioxane | 4 Å MS | 74 |
| 7 | $(PhSe)_2$ | MeCN | 4 Å MS | 60 |
| 8 | – | THF | 4 Å MS | 0 |
| 9[b] | $(PhSe)_2$ | THF | 4 Å MS | 82 |

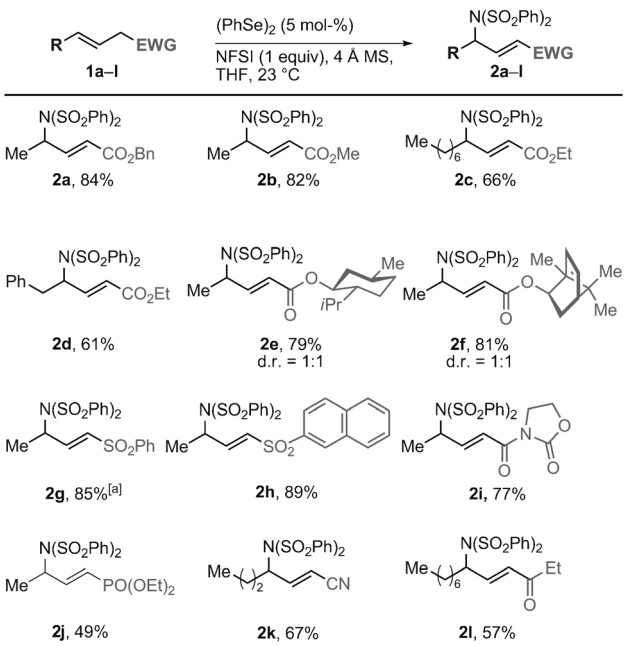
[a] Conditions: **1a** (0.27 mmol), NFSI (0.27 mmol), catalyst (5 mol%), solvent (1.35 mL), 23 °C under Ar. NFSI = *N*-fluorobenzenesulfonimide, 2-Pyr = pyridin-2-yl, Fc = ferrocenyl, MS = molecular sieves. Reaction time: 16 h. [b] 1.1 equiv of 2,6-di-*tert*-butylpyridine was added to the reaction mixture.

($E$)-benzyl 4-oxopent-2-enoate was observed as a by-product in varying amounts. This finding was attributed to the presence of adventitious water in the reaction medium. In order to sequester any residual water 4 Å molecular sieves were added to the reaction medium, which led to an improved yield of 84% under otherwise identical conditions (Table 1, entry 4). Subsequently, a variety of different solvents were screened. In general, other ethereal solvents, such as diethyl ether (64%, Table 1, entry 5) and 1,4-dioxane (74%, entry 6), led to inferior yields. When the reaction was carried out in acetonitrile, allylic imide **2a** was isolated in a reasonable yield of 60% (Table 1, entry 7).

In order to exclude the possibility of background reactivity between NFSI and the substrate, the transformation was attempted in the absence of selenium catalysts. Under these conditions no conversion was observed in the course of 16 h (Table 1, entry 8). To further exclude the possibility of Brønsted acid catalysis promoted by the coproduct HF, the reaction was carried out in the presence of 1.1 equiv of 2,6-di-*tert*-butylpyridine (Table 1, entry 9). However, even in the presence of a base, product **2a** was isolated in 82% yield. Altogether, these observations support the postulated role of the organodiselanes as the only catalytically active species in these transformations.

With an efficient set of conditions in hand, we continued our investigations with the exploration of the substrate scope (Scheme 2). Therefore, alkenes **1a–l** were synthesized and tested in the title transformation. In general, allylic imides **2a–l** were isolated in reasonable to very good yields ranging from 49–89% and with high levels of regio- and chemoselectivity.[19] In addition, the method is very tolerant towards various functional groups, such as ester, sulfone, amide, ketone, phosphonate, and nitrile moieties.

It should be pointed out that compounds **2a–f** showcase a novel and step-efficient entry to $\gamma^4$-amino acid derivatives.[20] Related structures are found in a number of biologically active cyclic peptides such as didemnins,[21] syringolins,[22] and glidobactins.[23] Due to the high potential with regard to medical applications, natural and artificial




***Scheme 2.*** Substrate scope for the selenium-catalyzed synthesis of allylic imides **2a–l**. Unless indicated otherwise, all reactions were performed as follows: **1a–l** (0.17–0.59 mmol), NFSI (1 equiv), $(PhSe)_2$ (5 mol%), THF (0.2 M), 16–20 h 23 °C. [a] Yield was determined by $^1$H NMR spectrosctopy. Imides **2c,d** and **2l** were derived from *Z*-configured alkenes.

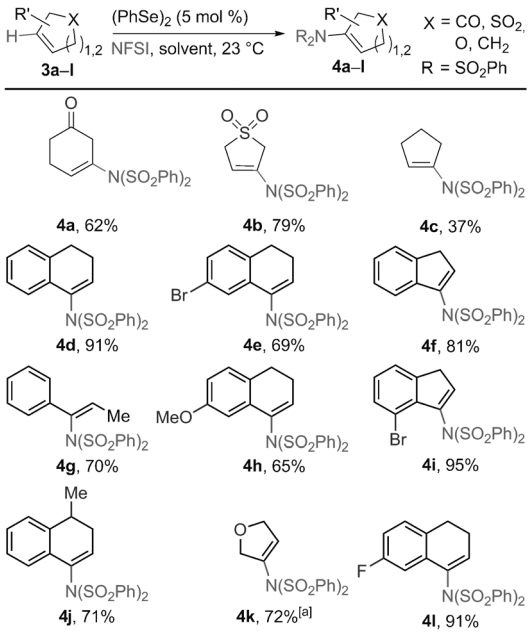
peptides containing $\gamma^4$-amino acids have recently become the subject of intensive investigations.[24] In contrast to our protocol, however, traditional methods for the construction of vinylogous amino acid motifs commonly rely on dissipative homologation reactions using phosphorus ylides.[24d]

In order to test the influence of chiral auxiliaries on the diastereoselectivity, enantiomerically enriched esters **1e** and **1f** were subjected to the standard reaction conditions. Although the corresponding imides **2e** and **2f** were obtained in high yields of 79% and 81%, respectively, each product was isolated as an equimolar mixture of diastereomers.

Next, we turned our attention to the catalytic imidation of cyclic alkenes (Scheme 3). For this purpose cyclohex-3-en-1-one (**3a**) was initially reacted with 1 equiv of NFSI under standard conditions. In contrast to expectations, the preferential formation of vinylic imide **4a** (62% yield)[25] along with its allylic isomer (27% yield)[26] was detected. An even better chemoselectivity in favor of the vinyl product **4b** was observed when sulfolene (**3b**) was used. The resulting imide **4b** was isolated in 79% yield together with 9% of its allylic isomer. Although the yield was low yields (37%), conversion of cyclopentene (**3c**) exclusively furnished imide **4c** as the only isolable product.[27] To the best of our knowledge, the formation of imides **4a–c** represents the first case of the oxidative, intermolecular C($sp^2$)–H imidation of electron-neutral alkenes promoted by an organodiselane catalyst.

In addition to the vinylic imidation of (hetero)cycloalkenes **4a–c**, this protocol proved also very fruitful for the conversion of styrene-type derivatives, such as β-methylstyrene (**3g**), indenes (**3f** and **3i**), and dihydronaphthalenes (Scheme 3). In order to obtain satisfactory yields for the latter

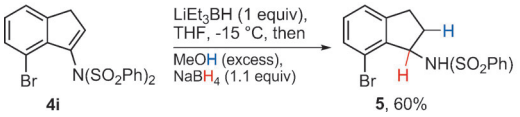



***Scheme 3.*** Substrate scope for the selenium-catalyzed synthesis of vinyl imides **4a–l**: Unless indicated otherwise, all reactions were performed as follows: **3a–l** (0.19–0.43 mmol), NFSI (1 equiv), THF (**3a–c**) or 1,4-dioxane (**3d–l**) (each 0.2 M), 16–20 h, 23 °C. [a] 5 equiv of **3k** was used and the yield of **4k** is based on NFSI.

substrates, the standard reaction conditions shown in Scheme 2 had to be altered. Thus, the use of 1,4-dioxane (0.2 M) as the solvent at room temperature in the presence of 5 mol% of the Se catalyst and 4 Å molecular sieves was identified as the best set of reaction parameters. Under these modified conditions vinyl imides **4d–l** were obtained in reasonable to excellent yields ranging from 65–95%. Both electron-deficient (e.g. **4i**, 95%; **4l**, 91%) and electon-rich (**4h**, 65%) substrates were well tolerated.

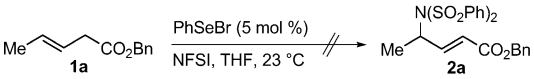
Having established a robust protocol for the C($sp^2$)–H imidation of cyclic alkenes, we eventually envisioned a one-pot sequence consisting of reductive desulfonylation/protonation followed by nucleophilic trapping of the transiently formed imine species to arrive at the corresponding functionalized sulfonamide. Such a scenario would not only demonstrate that the nitrogen group can be selectively deprotected but it would also exemplify the use of vinylimides **4** as masked enamine precursors. To prove our hypothesis, we initially screened for a number of reducing agents using compound **4i** as our test substrate. Unfortunately, neither samarium(II) iodide[28] nor sodium naphthalenide[29] provided access to the desired desulfonylation product.[30] Treatment of vinyl imide **4i** with 1 equiv of $LiEt_3BH$ in THF at −15 °C eventually furnished an unstable enamide intermediate [Eq. (1)].[31] Direct addition of methanol (100 vol% based on THF) and sodium borohydride (1.1 equiv) to the enamide-containing THF solution finally gave rise to benzylic sulfonamide **5** in 60% yield over two steps.

To elucidate the reaction mechanism of the oxidative imidation, we initially wanted to determine whether formation of the C–N bond is actually catalyzed by diphenyl



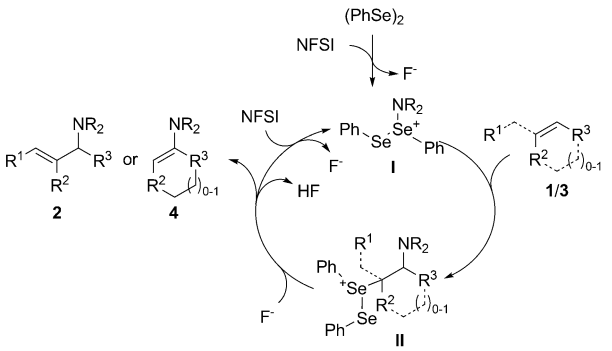

(1)

diselane or by a preformed, oxidized selenium derivative, such as $PhSeN(SO_2Ph)_2$ or PhSeF.[32] In the first experiments, alkene **1a** was reacted with 1 equiv of NFSI in THF (0.2 M) in the presence of PhSeBr (5 mol%) as the catalyst [Eq. (2)]. Under these conditions, however, no product formation was detected. According to literature precedence, PhSeBr is known to undergo addition into electron-neutral alkenes to transiently form aryl alkylselanes.[33] In combination with our own results these data suggest that NFSI is not sufficiently reactive to initiate dehydroselenylation, the key step leading to allylic imide **2a**.




(2)

To further substantiate the key role of diphenyl diselane for the oxidative imidation, we analyzed an equimolar mixture of NFSI and $(PhSe)_2$ in [$D_8$]THF by $^1$H NMR spectroscopy at ambient temperature over the course of 9 h. During that period continuous degradation of NFSI down to 9% was observed while 82% of the diselane catalyst remained intact. In a control experiment NFSI alone was found to be stable in [$D_8$]THF throughout the same time period. Next, a 5:1 mixture of NFSI and $(PhSe)_2$ was reacted under otherwise identical conditions. In the course of 16 h the diselane was completely degraded while 44% of NFSI remained intact. Importantly, no further decomposition of NFSI was detected after the disappearance of $(PhSe)_2$. From these observations we conclude that the Se–Se bond is crucial for the catalytic activity. Based on the analytical data as a whole, we postulate the following tentative catalytic cycle (Scheme 4). First, NFSI undergoes nucleophilic attack by diphenyl diselane leading to cationic species **I**. Subsequent addition to alkene **1** gives rise to cationic adduct **II**,[34] which in turn undergoes elimination to complete the catalytic cycle.[35]




***Scheme 4.*** Tentative catalytic cycle for the oxidative imidation of alkenes **1** and **3**.

In summary, we have disclosed an organodiselane-catalyzed intermolecular allylic and unprecedented vinylic imidation of unactivated alkenes using NFSI as both the terminal oxidant and the nitrogen source. It was also demonstrated that vinylimides formed by the title procedure can be used as masked enamides through chemoselective cleavage of a sulfonyl group. Furthermore, the method features a new avenue toward the synthesis of vinylogous $\gamma^4$-amino acid derivatives, a molecule class often found in protease inhibitors. Consequently, we anticipate this method to successfully complement current catalytic methods in the realm of oxidative C–N bond constructions. Efforts toward the development of an asymmetric variant of the allylic imidation are currently in progress.

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