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Pd-Catalyzed Cyanoselenylation of Internal Alkynes: Access to Tetrasubstituted Selenoenol Ethers

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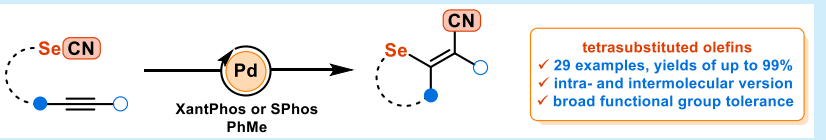


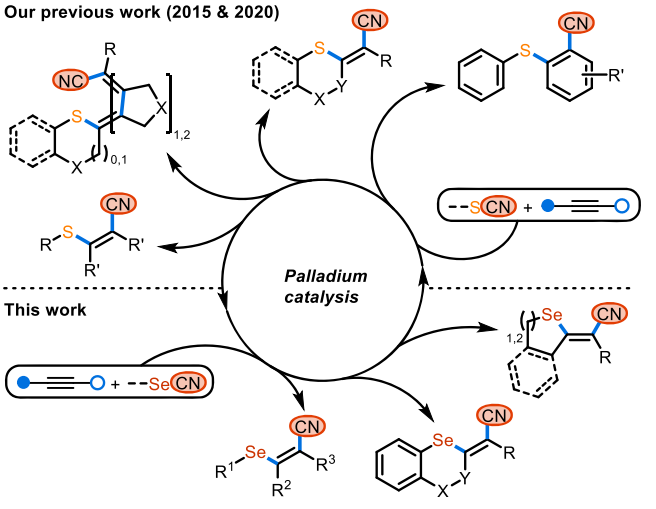
ABSTRACT: The intra- and intermolecular synthesis of selenium-substituted acyclic and heterocyclic acrylonitrile derivatives is presented. The 1,2-difunctionalization of several internal alkynes substituted not only by aliphatic and aromatic residues but also by heteroelements is realized by the Pd-catalyzed activation of aromatic and aliphatic selenocyanates. A high functional group tolerance allows straightforward access to a broad scope of tetrasubstituted olefins. X-ray studies of some products reveal noncovalent chalcogen−chalcogen interactions between oxygen and selenium.

The significance of tetrasubstituted olefins is demonstrated by their manifold applications, e.g. in functional materials[1] or in effective pharmaceuticals.[2] Chemists continue to intensify their research in this field.[3] Various methods have been developed to simplify the synthetic access to different substitution patterns.[4,5] In particular, Pd-catalyzed reactions, because of their generality and tolerance toward many functional groups, are a powerful tool to release the inherent reactivity of triple bonds.[6] For example, Larock published a regio- and stereoselective route to triphenylethylene derivatives that are parent compounds of some nonsteroidal drugs.[7] Furthermore, the synthesis of overcrowded double bonds, the essential molecular subunits in molecular switches and motors, is as important as ever. For this purpose, highly efficient cascade processes have increasingly become the method of choice.[8] Such domino reactions, as they are also called, combine economic and ecological advantages with synthetic elegance.[9] Complex skeletons are built up in a single synthetic step that involves the formation of multiple C−C bonds.[10]

In several investigations, our group has shown the tremendous power of this concept.[11] Besides classical *syn*-carbopalladations,[12] the incorporation of a formal *anti*-carbopalladation enabled the synthesis of one or more tetrasubstituted double bonds embedded in various polycyclic compounds.[13,14] Such *anti*-carbopalladations of C−C triple bonds have also been employed to access tetrasubstituted double bonds with at least one heteroatom as a substituent, as demonstrated by the preparation of a series of enol ethers[15] and enamines.[16] Nevertheless, the tetrasubstitution of an alkene with the maximum number of heterosubstituents remains underdeveloped, even though some beautiful work has been reported in recent years.[17,18]

In our earlier work, we demonstrated that Pd-catalysis is the key to conducting a cyanosulfenylation of internal alkynes, leading to highly (hetero)substituted thioenol ethers.[19] The versatility of this atom-economic addition of aromatic and aliphatic thiocyanates to internal alkynes was demonstrated by a broad range of thioacrylonitrile derivatives (Scheme 1). This process could even be extended to a cascade, leading to several

Scheme 1. Overview of Pd-Catalyzed Cyanochalcogenylation Reactions



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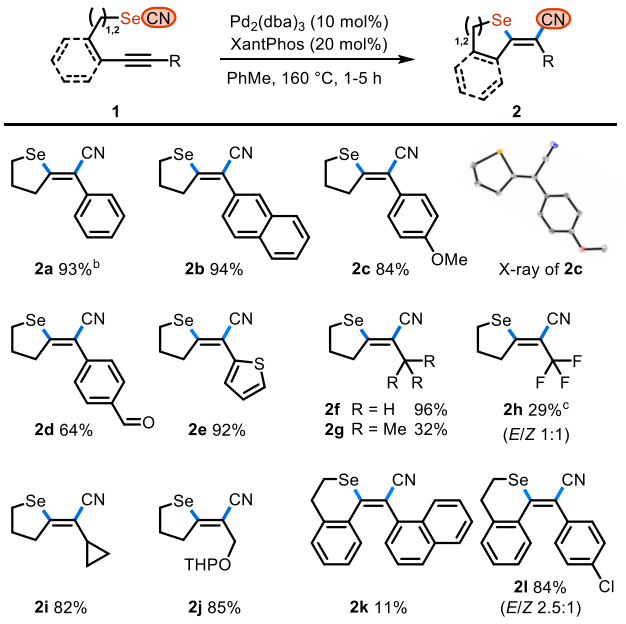
conjugated tetrasubstituted C−C double bonds, with the delivery of the cyanide as the terminating step. Based on these insights and other reports on the Pd-catalyzed activation of chalcogenocyanates,[20,21] we asked ourselves whether an extension of this reactivity to the higher homologues, the corresponding selenocyanates, might be feasible. Besides some interesting protocols for the synthesis of highly substituted vinyl selenides,[23] such an approach would easily grant access to tetrasubstituted selenoenol ethers (Scheme 1). Furthermore, this would emphasize the synthetic benefit of selenium compounds, whose importance is intensely discussed in literature.[22]

In a first series of experiments, using the catalytic systems of our previous study on the Pd-catalyzed cyanothiolation, we found that the transformation of **1a** to the tetrahydroselenophene derivative **2a** proceeded smoothly with an excellent yield of 93%. Ideal conditions include 10 mol % of $Pd_2(dba)_3$ as precatalyst and 20 mol % of XantPhos as ligand in a closed reaction vial with toluene as solvent at 160 °C.[24] Subsequently, we synthesized a variety of selenocyanates **1** tethered to alkyne moieties in order to explore the scope and limitations of this 1,2-addition process. Sterically demanding, electron-rich residues, and also electron-poor aromatic and heteroaromatic residues, at the alkyne terminus were well tolerated and afforded products **2b**−**2e** in 64−94% yield (Scheme 2), which

Scheme 2. Intramolecular Cyanoselenylation with Aliphatic Selenocyanates[a]

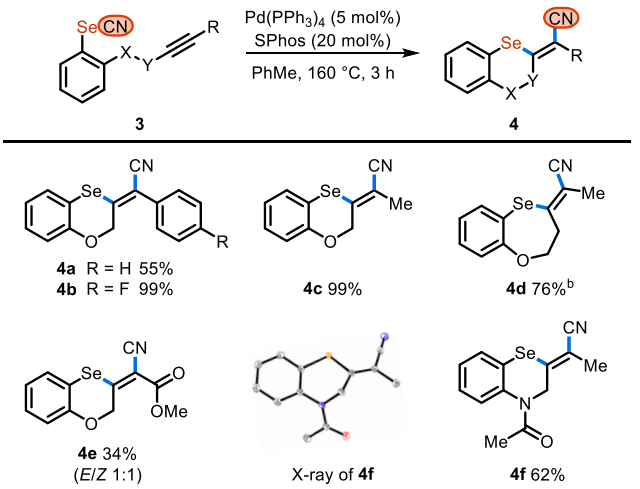


[a]General reaction conditions: substrate **1** (1.0 equiv), solvent (20 mM). Yields represent isolated compounds. [b]Large scale (1.0 mmol, 99% yield). [c]Reaction temperature: 120 °C.

is in a comparable range as for the sulfur analogues.[19] In a series with aliphatic substituents, the compounds **2f** (96%) and **2i** (82%) were obtained in excellent yields, whereas the formation of **2g** was limited by the bulkier *tert*-butyl group. The fact that the three-membered ring system stays intact demonstrates that no radical processes are involved. Product **2j**, with a THP-protected alcohol distanced by a methylene unit, was prepared successfully in 85% yield. The transformation was possible even with the strongly electron-withdrawing CF_3 group as the terminus, albeit in lower yield (**2h**, 29%). In this case, two diastereomers were found in a 1:1 ratio. Such a strong polarization leads to some extent to an isomerization of the exocyclic double bond, as we had already observed in our previous cyanosulfenylation products.[19] Furthermore, we subjected substrates with a conjugated triple bond to the reaction conditions. A naphthyl residue (**2k**) allowed the formation of the product in only 11% yield, whereas a *p*-chlorophenyl substituent provided isoselenochromene **2l** in 84% yield.

Our next goal was the transformation of aromatic selenocyanates **3** to the corresponding products **4** (Scheme 3). We realized that $Pd(PPh_3)_4$ and SPhos as ligand proved to

Scheme 3. Intramolecular Cyanoselenylation with Aromatic Selenocyanates[a]



[a]General reaction conditions: substrate **3** (1.0 equiv), solvent (20 mM). Yields represent isolated compounds. [b]Reaction time: 12 h.

be superior to the catalytic system applied for aliphatic selenocyanates. The reaction with propargylic tethers in *ortho*-position furnished the six-membered heterocycles **4a**−**4c** in good to quantitative yields. The elongation of the linker by one methylene unit allowed the synthesis of the seven-membered oxaselenepine derivative **4d** in a good yield of 76%. The conversion of a methyl propiolate led to an isomeric mixture of **4e** (34%); the *E*/*Z* isomerization is facilitated because the second acceptor in geminal position to the nitrile further weakens the double bond. The crystal structure of the (*E*)-isomer of **4e** is shown in Figure 1. Additionally, we were able to crystallize the selenazin derivative **4f**, which was obtained in a good yield of 62%.

As mentioned at the beginning, reports of tetrasubstituted double bonds functionalized with several heteroatoms are rare. Furthermore, it is often difficult to access them in a few, let alone one, synthetic step(s). Our method allows the direct and diastereoselective access to such moieties. To demonstrate this, we synthesized four examples based on the five-membered exocyclic selenoenol ether backbone (Scheme 4).

Silyl groups are predestined as a second heterosubstituent at the terminus of the alkyne unit. Using a TBS group, we generated the fully substituted olefin **6a** in a high yield of 89%. The structure was unequivocally confirmed by X-ray structure analysis. Obviously, the attachment of chalcogens such as sulfur and selenium in α-position to the alkyne paved the way

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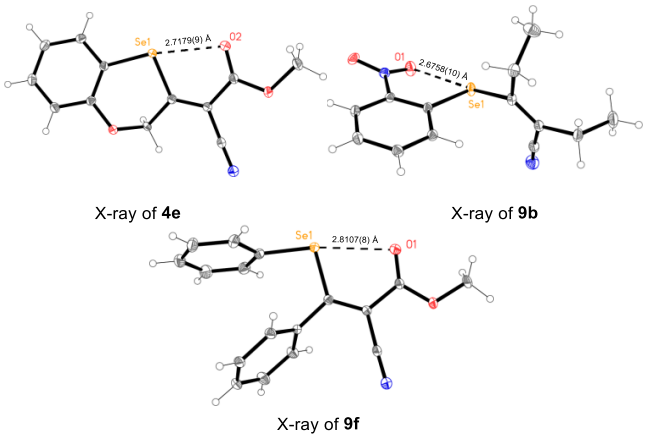
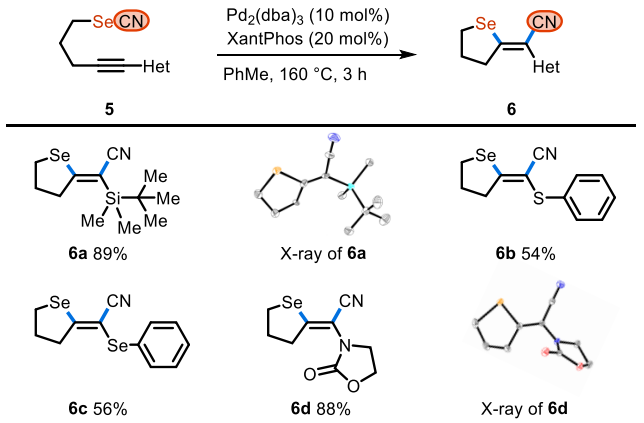


Figure 1. Noncovalent intramolecular Se···O interactions.

Scheme 4. Intramolecular Cyanoselenylation of Heterosubstituted Triple Bonds[a]

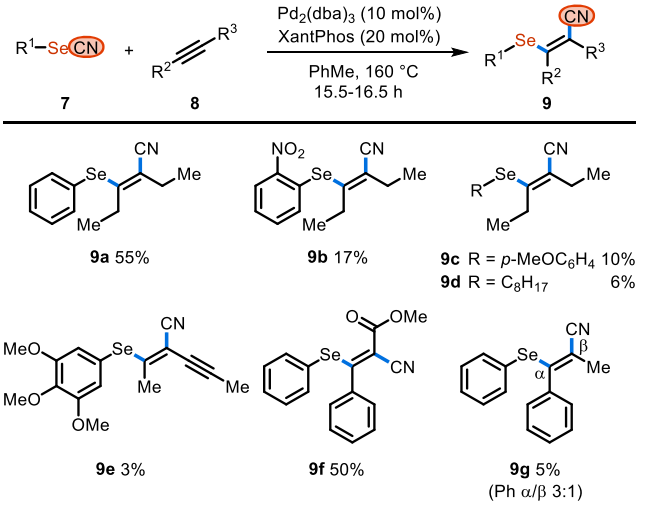


[a]General reaction conditions: substrate **5** (1.0 equiv), solvent (20 mM). Yields represent isolated compounds.

for two further examples, **6b** and **6c**, obtained in a moderate yield of 54−56%. The combination of selenium/nitrogen in *trans*-position across a double bond was realized by the synthesis of alkene **6d** starting from the corresponding ynamide. An X-ray crystal structure clearly shows the anticipated substitution pattern.

Finally, we were interested in the intermolecular reaction of a selenocyanate **7** with an internal alkyne **8** (Scheme 5). We used commercially available phenyl selenocyanate and 3-hexyne to obtain insight into this challenging transformation. Using the standard catalytic system (*cf.* Scheme 2), we observed the formation of **9a**, but only in a yield of less than 10%. To increase the yield, we had to suppress the formation of diphenyldiselenide as the major byproduct. One reason for this is the easier oxidation of selenium compared to sulfur. Disulfide formation was scarcely observed for the intermolecular cyanothiolation.[19] With 2 equiv of alkyne we were able to raise the yield of **9a** to 55%. Unluckily, these conditions did not prove suitable for the reaction of further selenocyanates (electron-poor and electron-rich aromatic, or aliphatic derivatives) with 3-hexyne. In all cases we isolated the products **9b−9d**, but in low yields ranging from 6% to 17%. Again, the respective diselenides were found to be the major products when using these starting materials. The addition of selenocyanate derivatives to unsymmetric alkynes also

Scheme 5. Intermolecular Cyanoselenylation of Symmetric and Unsymmetric Alkynes[a]



[a]General reaction conditions: substrates **7** (1.0 equiv) and **8** (2.0 equiv), solvent (100 mM). Yields represent isolated compounds.

proceeded with varying degrees of success. First, we investigated whether it is possible to use a 1,3-diyne unit for this addition. Whereas we did not observe any reaction with PhSeCN, we found traces of the desired product with the 4-methoxy derivative. Only the very electron-rich 3,4,5-trimethoxyphenyl selenocyanate eventually enabled the formation of enyne **9e**, albeit in a low, but isolable yield. In contrast, the strongly polarized acetylene carboxylic acid ester provided the push−pull-substituted acrylate **9f** in a yield of 50%; however, the expected *syn*-adduct was not obtained, but instead its *anti*-diastereomer. The configuration was determined by X-ray crystallography. The example of 1-phenyl-1-propyne shows that a nonpolarized conjugated triple bond is again difficult to convert; the corresponding product **9g** was obtained only in low yield and as a regioisomeric mixture (3:1) because of the lack of electronic and steric differentiation of the two acetylenic carbons.

In several of the X-ray crystal structures that we obtained during this study, we noticed short intramolecular Se···O contacts. Such noncovalent chalcogen−chalcogen interactions, reported in several publications, have been well studied and exploited in crystal engineering and more recently in organocatalysis.[25−27] The close Se···O contacts of the oxygen-containing selenoenol ethers **4e**, **9b**, and **9f** are shown in Figure 1; the distances range from 2.68 to 2.81 Å, which is significantly less than the sum of the van der Waals radii of oxygen and selenium (3.40 Å).[27] The angle O−Se−C ranges from 164° to 172°, demonstrating the favored directionality of this weak, but significant interaction, which might also be an additional driving force for the isomerization of the olefins (**4e** and **9f**).

In summary, we have demonstrated the versatility of Pd-catalyzed cyanoselenylation for the synthesis of tetrasubstituted olefins. This methodology allows the addition of both aromatic and aliphatic selenocyanates to diversely functionalized alkynes. The intramolecular version of this methodology is as efficient as the previously reported cyanothiolation, whereas the intermolecular reaction is rather limited. However, the transformation provides access to tetrasubstituted acyclic selenoethers and to five-, six-, and seven-membered hetero-

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cycles bearing an exocyclic double bond. In several crystal structures of oxygen-containing selenoenol ethers, short noncovalent chalcogen−chalcogen (Se···O) interactions were observed.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01582.

General experimental details and procedures; crystallographic data for **1k** (CCDC 1998935), **2c** (CCDC 1998936), *anti*-**4e** (CCDC 1998937), **4f** (CCDC 1998938), **6a** (CCDC 1998939), **6d** (CCDC 1998940), **9b** (CCDC 1998941), and **9f** (CCDC 1998942) (PDF)

Accession Codes

CCDC 1998935−1998942 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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