

Alkyne Aminopalladation/Heck and Suzuki Cascades: An Approach to Tetrasubstituted Enamines

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Abstract: Alkyne aminopalladation reactions starting from tosylamides are reported. The emerging vinylic Pd species are converted either in an intramolecular Heck reaction with olefinic units or in an intermolecular Suzuki reaction by using boronic acids exhibiting broad functional group tolerance. Tetra(hetero)substituted tosylated enamines are obtained in a simple one-pot process.

The dual functionalization of internal alkynes is an important method of generating tetrasubstituted double bonds.^[1,2,3] For this purpose, either special reagents^[4] have been designed or transition metal catalysts, especially those based on Pd, have been used. In many cases a carbopalladation of a $\text{C}\equiv\text{C}$ triple bond has been used, leading to a vinyl-Pd species.^[5] Such intermediates are able to react in various ways: the most common is the further reaction with either an alkyne or an alkene or via a metalated species. In the latter case, the sequence is terminated by a cross-coupling, whereas in the former case the cascade continues. Such carbopalladation cascades using $\text{C}\equiv\text{C}$ triple bonds have been developed by many groups during recent decades.^[6] These transformations have paved the way to unusual molecular architectures such as helicenes,^[2,3,7] fenestranes,^[8] highly substituted cyclooctatetraenes^[9] and molecular switches;^[10] natural products^[11] have also proved accessible in a quick and facile fashion.

Whereas the majority of these Pd-catalyzed cascades commence with a carbopalladation step of a π -system, much less is known about heteropalladation cascades. In 2020, we

discovered methods for the thio- and selenopalladation of internal alkynes.^[12] In recent years, the groups of Bower^[13] and Watson^[14] have exploited aminopalladation reactions of alkenes (aza-Heck reactions), based on an original report by Narasaka^[15] (Scheme 1, top). This elegant work has led to the facile synthesis of, for example, pyrrolidines and complex lactams.^[16] The key to generating a reactive N–Pd species was the decoration of the nitrogen with a pentafluorobenzoyl ester ($\text{O}^{\text{F}}\text{Bz}$). Originally used on oximes, this special group was later also successfully employed as a substituent of tosyl amides.^[17] The unusual oxidative addition of the palladium into the nitrogen-oxygen bond had already been proposed by Narasaka, but had never been proved. Later, Hartwig^[18] and Stahl^[19] were able to isolate this intermediate in similar systems.

Because of our great interest in Pd-catalyzed cascades with alkynes, we wondered the question whether similar cascades starting with tosylamide could be performed with alkynes. Tetrasubstituted double bonds of the enamine type would be formed. (Bis)heterosubstituted alkynes as starting materials would lead to highly heterosubstituted olefin units. As terminating processes, we chose either Heck or Suzuki cross-coupling reactions (Scheme 1).

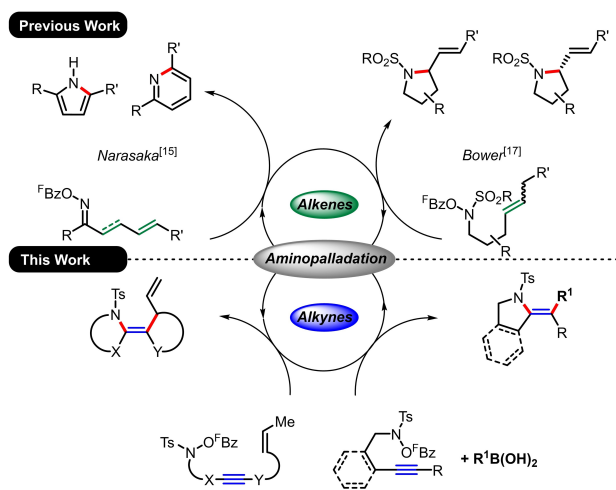
As previous reports on aza-Heck reactions have revealed, $\text{P}(\text{3,5}(\text{CF}_3)_2(\text{C}_6\text{H}_3))_3$, with its electron-withdrawing aryl moieties, is a crucial ligand to allow oxidative addition into the N–O bond. Thus, we started our optimization of the anticipated sequence with this ligand and with $\text{Pd}_2(\text{dba})_3$ as a Pd^0 source. Employing substrate **1a** in our initial conditions using 2 equivalents of

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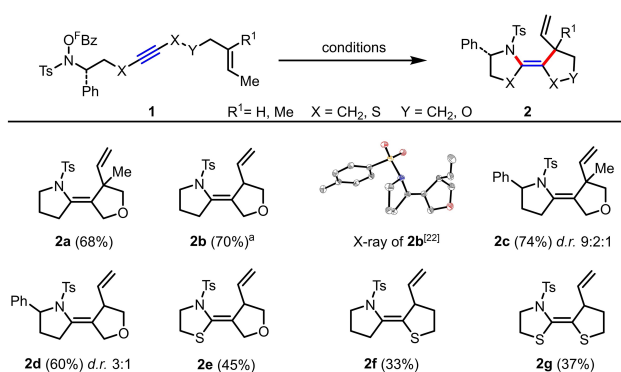
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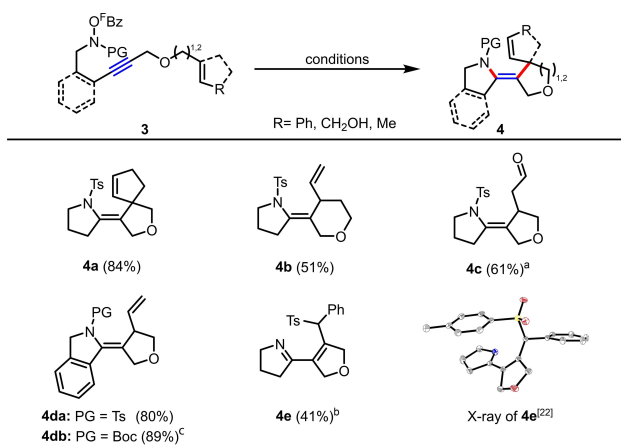
Scheme 1. Alkene carboamination and our work with alkyne carboaminations.

Cs_2CO_3 as base in toluene at 100°C resulted in a 28% yield of the desired product. Unfortunately, we also observed 45% of the corresponding nitrile as a byproduct. Switching to triethylamine as base increased the yield of **2a** to 68% and completely suppressed the byproduct formation. Further optimization proved that the addition of H_2O resulted in a cleaner reaction without decreasing the yield. DMF or DMA did not allow the reaction to proceed, in contrast to previous studies of similar systems (for details see the Supporting Information).

With optimized reaction conditions in hand, we started investigating the scope (Scheme 2) with the less sterically demanding substrate **1b**. We were pleased to see that **2b** was synthesized in 70% yield and with complete regioselectivity leading to the terminal double bond. We demonstrated the reliability of the cascade in larger scale reactions by performing this reaction on a 1.0 mmol scale (69%) and verified the molecular structure by X-ray crystallography. Phenyl substitu-



Scheme 2. Alkyne carboamination/Heck coupling cascade of enynes **1**. Reaction conditions: 80 μmol scale, $\text{Pd}_2(\text{dba})_3$ (10 mol%), $\text{P}(\text{3,5}(\text{CF}_3)_2\text{C}_6\text{H}_3)_3$ (25 mol%), Et_3N (2.00 equiv.) and H_2O (2.50 equiv.), PhMe (0.025 M), $100\text{--}120^\circ\text{C}$, 1–2 h. [a] 1.0 mmol scale: 69% yield. Ellipsoid probability of 50%.

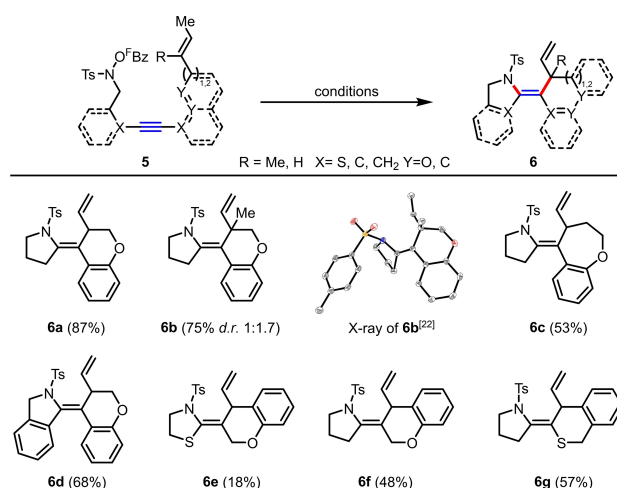


Scheme 3. Alkyne carboamination/Heck coupling cascade of enynes **3**. Reaction conditions: 80 μmol scale, $\text{Pd}_2(\text{dba})_3$ (10 mol%), $\text{P}(\text{3,5}(\text{CF}_3)_2\text{C}_6\text{H}_3)_3$ (25 mol%), Et_3N (2.00 equiv.) and H_2O (2.50 equiv.), PhMe (0.025 M), $100\text{--}120^\circ\text{C}$, 1–2 h. [a] Oxidation of the hydroxy group was achieved by β -hydride elimination. [b] 168 μmol , $\text{Pd}_2(\text{dba})_3$ (5 mol%), $\text{P}(\text{3,5}(\text{CF}_3)_2\text{C}_6\text{H}_3)_3$ (25 mol%), Et_3N (25 mol%) in THF (0.1 M), 110°C , 16 h. Ellipsoid probability of 50%. [c] $\text{Pd}(\text{P}(\text{3,5}(\text{CF}_3)_2\text{C}_6\text{H}_3)_3)_2$ (10 mol%), Et_2NH (2.00 equiv.), 1,4-dioxane (0.025 M), 130°C , 2 h.

ents in α -position to the tosylamide were tolerated; the transformation delivered products **2c** and **2d** in 60–74% yield. Introducing divalent sulfur in α -position to the triple bond decreased the yields significantly, probably because of poisoning of the Pd catalyst.

To further expand the scope, we utilized an internal cyclic double bond to form spirocyclic compound **4a** in very good yield of 84% (Scheme 3). Ring expansion to a six-membered ring **4b** was possible in a yield of 51% to obtain a tetrahydropyran moiety. We were pleased to see that the introduction of a terminal hydroxy group resulted in an oxidation during the terminating β -hydride elimination, giving aldehyde **4c** in a yield of 61%. Isoindoline system **4da** was generated in 80% yield. By slightly changing the reaction conditions, we were also able to perform the cascade with a Boc-protected nitrogen to obtain **4db** in 89% yield. Employing a cinnamyl group, we observed an unexpected 1,5-shift of the tosyl group into the benzylic position resulting in the corresponding imine **4e** in 41% yield. We were also able to prove the outcome of this rearrangement by X-ray crystallography.

As already observed for **4d**, an aryl moiety directly attached to the triple bond increases the yield, and chromane **6a** was accessed in 87% yield (Scheme 4). We assume that the rigid aromatic ring brings the terminal double bond into closer proximity to the triple bond, so that the coordination is facilitated. Employing the more sterically demanding substrate with the additional methyl group, we obtained product **6b** in 75% yield. The NMR data showed a double signal set of the desired product with an intensity of 1:1.7. Crystal structure analysis showed a disorder involving alternative positions of the ring nitrogen atom, and thus we suggest that a stereocenter on the nitrogen has been formed. Because of the rigidity of the system and steric bulk in α -position to the double bond, the nitrogen is unable to invert, creating a second stereocenter. Formation of seven-membered ring system **6c** was made



Scheme 4. Alkyne carboamination/Heck coupling cascade of enynes **5** leading to chromane derivatives **6**. Reaction conditions: 80 μmol scale, $\text{Pd}_2(\text{dba})_3$ (10 mol%), $\text{P}(\text{3,5}(\text{CF}_3)_2\text{C}_6\text{H}_3)_3$ (25 mol%), Et_3N (2.00 equiv.) and H_2O (2.50 equiv.), PhMe (0.025 M), $100\text{--}140^\circ\text{C}$, 1 h. Ellipsoid probability of 50%.

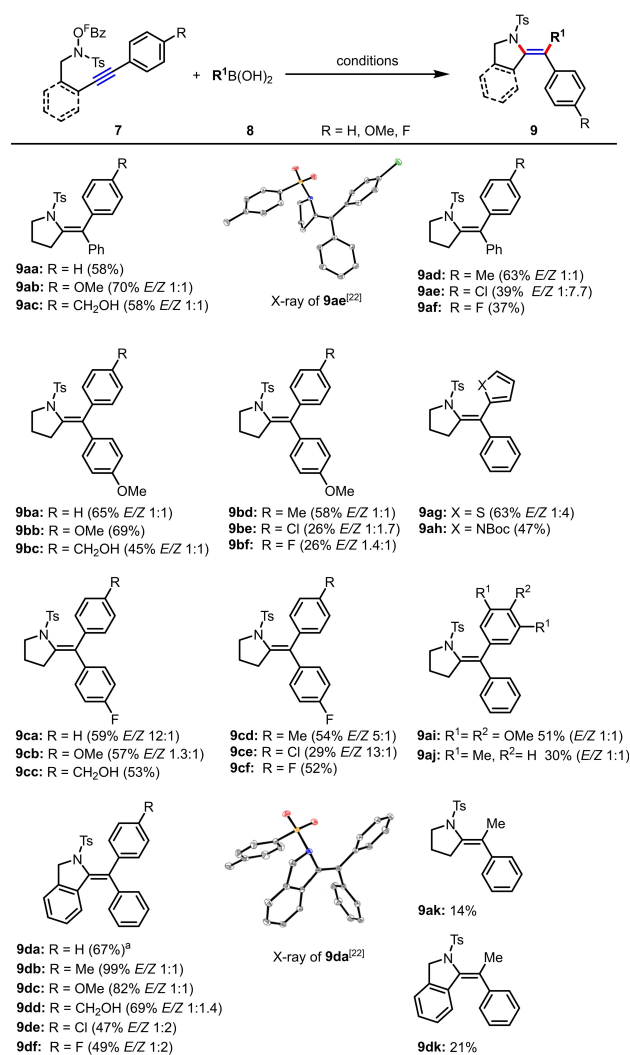
possible by a simple elongation of the aliphatic chain. By introducing a second aryl ring in a tolane-type precursor **5d** we were able to form isoindoline-substituted chromanone system **6d** in 68% yield. Expanding the chromanone and thioisochromanone scope, we achieved yields between 57 and 18% (**6e–6g**).

To demonstrate the versatility of this alkyne carboamination, we turned our attention to other terminating processes. As cheap, commercially available reagents with low toxicity we chose boronic acids **8** for an intermolecular Suzuki-type cross-coupling; corresponding boronic acid esters did not work at all and the use of Molander's salts resulted in significantly lower yield. Thus, we prepared precursor **7** in a simple three-step synthesis.

Upon screening for the optimal reaction conditions, we realized that toluene as solvent in cooperation with Cs_2CO_3 as base, $\text{Pd}_2(\text{dba})_3$ as Pd^0 source and $\text{P}(3,5(\text{CF}_3)_2(\text{C}_6\text{H}_3))_3$ as ligand is prone to form inseparable mixtures of the desired product and byproducts. By using 1,4-dioxane as the solvent and AgF as the fluoride source we were able to suppress by-product formation completely (for details see the Supporting Information). Unfortunately, dba was often unseparable from these products by column chromatography. In the literature we found the superstable Pd^0 source $\text{Pd}(\text{P}(3,5(\text{CF}_3)_2(\text{C}_6\text{H}_3))_3)_2$, which already bears the necessary ligand in a ready-made compound and simplifies both the reagent handling and purification.^[20]

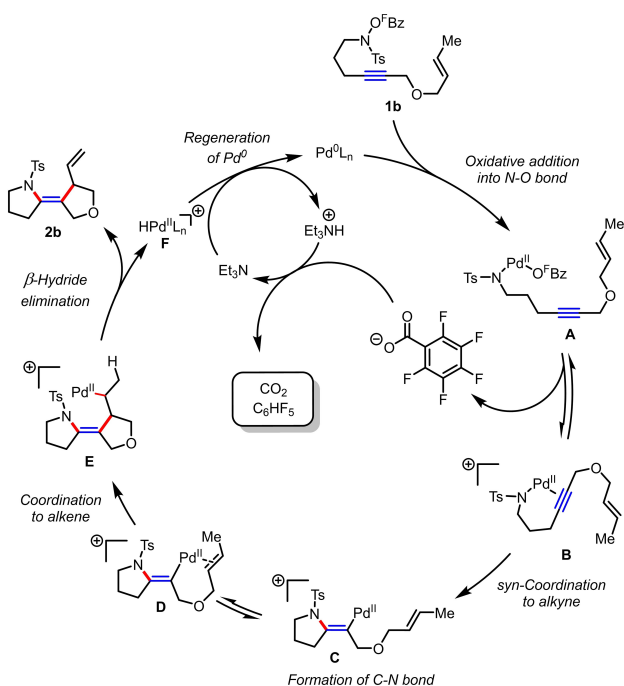
With the optimized conditions in hand, we examined the scope of the reaction (Scheme 5). We observed that electron-rich boronic acids gave better yields (of **9ab**, **9ad**) than halogen-substituted boronic acids delivering **9ae** and **9af**. Similar effects held true with respect to the electronic properties of the substrates. The electron-rich, methoxy-bearing substrate **7b** was generally higher yielding than fluorine-containing substrate **7c**. We were pleased to be able to use a boronic acid containing a hydroxy group without significantly decreasing the yield (**9ac**, **9bc**, **9cc**, **9dd**, 45–69%). As we observed in our carboamination/Heck cascade, the tolane-type substrate **7d** furnished products **9da–9df** with the highest yields. Heteroaromatic rings such as thiophene gave the corresponding product **9ag** in 63% yield (*E/Z* ratio 1:4) whereas the rather bulky NBoc-protected pyrrole led to **9ah** in 47% yield (as a single isomer). We also tried to introduce alkyl boronic acids into the cascade. However, with methyl boronic acid as the only working alkyl boronic acid, we observed heavily decreased yields of 21 and 14%, respectively. By conducting a 1.0-mmol-scale experiment using the tolane-type precursor **7d** and the electron-neutral phenyl boronic acids with a reduced amount of 5% of the palladium catalyst, we proved the reliability of our reaction on larger scales, obtaining a yield of 74% and thus exceeding the 67% reached in a 0.1-mmol experiment. Furthermore, we observed that with increasing electron density of the two aryl systems, the double bond starts to isomerize up to an *E/Z* ratio of 1:1. Both the steric bulk and the electronic properties decrease the double bond character and allow the system to isomerize.

Based on our observations in this project and the investigations of the mechanism by Bower et al., we propose for the



Scheme 5. Intermolecular carboamination/Suzuki cross-coupling cascade. Reaction conditions: 100 μmol scale, $\text{Pd}(\text{P}(3,5(\text{CF}_3)_2(\text{C}_6\text{H}_3))_3)_2$ (10 mol%), AgF (1.20 equiv.), $\text{R}^1\text{B}(\text{OH})_2$ (2.50 equiv.), 1,4-dioxane (0.025 M), 100 °C, 0.5–1.5 h. [a] The yield for 1.0 mmol scale with 5 mol% of Pd catalyst was 74%. Ellipsoid probability of 50%.

carboamination/Heck cascade the catalytic cycle depicted in Scheme 6. The oxidative addition of the Pd^0 into the N–O bond forms intermediate **A**. The decarboxylation of the pentafluorobenzoate, which is mediated by triethylamine, allows the palladium to coordinate to the triple bond in a *syn* fashion (**B**). After carbon–nitrogen bond formation, the palladium is now located at the second carbon of the former triple bond (**C**). From here, the palladium is able to coordinate to the adjacent double bond (**D**), a prerequisite for the formation of a carbon–carbon bond (**E**). By a terminating β -hydride elimination, product **2b** and palladium hydride (**F**) are released. The Pd^0 is then regenerated by triethylamine and reenters the cycle. For the termination by the Suzuki reaction we propose a similar cycle up to intermediate **C**. To enable a Suzuki-type reaction, a Pd fluoride complex forms, which then undergoes transmetalation with the boronic acid.^[21] After reductive elimination of the



Scheme 6. Proposed mechanism for the carboamination/Heck cascade.

palladium and concomitant C–C bond formation, the Pd⁰ species is able to reenter the catalytic cycle.

In conclusion, we have presented a carboamination of internal alkyne units by using tosylamides. The emerging Pd vinyl species, obtained after C–N bond formation, is either converted by a Heck reaction by using an olefinic moiety or transformed in a Suzuki cross-coupling by using boronic acids. In both cases, tetrasubstituted enamines are formed. If α - or α,α' -heterosubstituted triple bonds are used, tetrasubstituted double bonds containing up to three heteroatoms are obtained. In both cases, a broad scope is established, and the transformations lead to a variety of complex tetrasubstituted olefin units. Further investigations to expand such alkyne carboamination cascades to other termination processes are underway in our laboratory.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: alkynes · carboamination · cascades · Pd catalysis · tetrasubstituted olefins

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