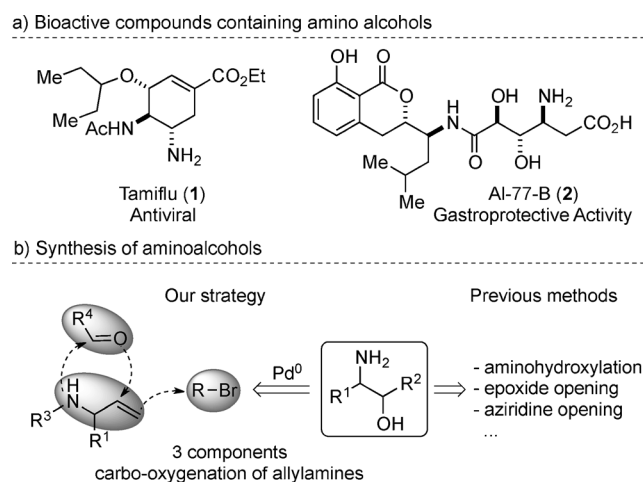


Palladium-Catalyzed Vicinal Amino Alcohols Synthesis from Allyl Amines by In Situ Tether Formation and Carboetherification**

Ugo Orcel and Jerome Waser*

Abstract: Vicinal amino alcohols are important structural motifs of bioactive compounds. Reported herein is an efficient method for their synthesis based on the palladium-catalyzed oxy-alkynylation, oxy-arylation, or oxy-vinylation of allylic amines. High regio- and stereoselectivity were ensured through the in situ formation of a hemiaminal tether using the cheap commercially available trifluoroacetaldehyde in its hemiacetal form. The obtained compounds are important building blocks, which can be orthogonally deprotected to give either free alcohols, amines, or terminal alkynes.

Vicinal amino alcohols are highly important structural motifs found in bioactive compounds such as the drug Tamiflu (**1**) or the natural product AI-77-B (**2**; Scheme 1a). They have also been broadly applied as chiral ligands and auxiliaries. Therefore, there is a strong interest in the development of new methods to access them. Two of the most common synthetic approaches are the ring-opening of epoxides or aziridines and the metal-catalyzed aminohydroxylation of alkenes (Scheme 1b).



Scheme 1. Importance and synthesis of vicinal amino alcohols.

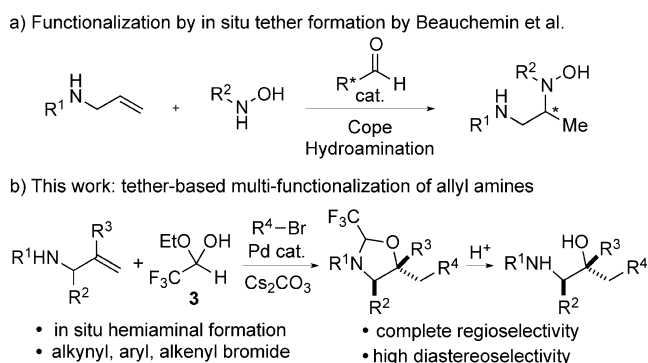
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[**] EPFL and F. Hoffmann-La Roche Ltd are acknowledged for financial support. We thank Dr. Tanguy Saget from the Laboratory of Asymmetric Catalysis and Synthesis at EPFL for helpful discussions and Alfa Aesar and Johnson Matthey for a gift of PdCl₂.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201500636>.

me 1b).^[2] Although straightforward, these methods are often plagued by regioselectivity issues.^[2b] The use of tethers has emerged as a viable strategy to achieve better selectivity and reactivity in organic synthesis.^[3] However, this method often lacks efficiency as extra steps are required for tether introduction and removal. Regarding the synthesis of vicinal amino alcohols, allyl amines are particularly attractive starting materials: numerous methods are available for their synthesis and the high nucleophilicity of nitrogen atom should allow the in situ formation of a hemiaminal tether by reaction with an aldehyde. Amino alcohol synthesis could be accompanied by the introduction of a second functional group onto the alkene, thus allowing a maximal increase in molecular complexity (Scheme 1b). The formation of a valuable C–C bond would be especially interesting, yet more challenging than the introduction of a second heteroatom.^[4] Concerning the multifunctionalization of unactivated olefins, palladium catalysis has been highly successful in the last decades,^[5] but has not yet been applied to the outlined strategy.^[6]

Precedence for the projected in situ formation of a hemiaminal tether using allyl amines and aldehydes can be found in the elegant metal-free approach developed by Beauchemin and co-workers for the Cope-type hydroamination of allylic amines (Scheme 2a).^[7] However, the use of an aldehyde as



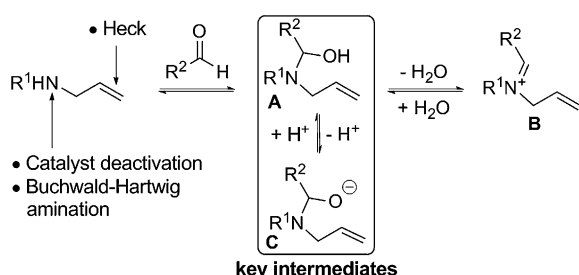
Scheme 2. The tether strategy for allyl amine functionalization.

a tether has never been reported for the palladium-catalyzed multifunctionalization of olefins. Even in the broader field of palladium catalysis, the potential of this approach has only been scarcely explored. Menche and co-workers developed an elegant synthesis of 1,3-diols through a domino acetal-formation/Tsuji–Trost reaction starting from homoallylic alcohols.^[8] Hiemstra and co-workers, and more recently Stahl and co-workers, reported the use of hemiaminals for the Wacker cyclization reaction starting from allyl amines and

alcohols, but the diastereoselectivity was low for the former and an additional step was needed to install the tether for both methods.^[9]

Based on this precedence and our interest in olefin oxy- and aminoalkynylation,^[10] we demonstrate herein that tri-fluoroacetaldehyde, used as its cheap hemiacetal form **3**, enables the palladium-catalyzed carbo-oxygenation of allyl amines through a one-pot tethered process (Scheme 2b). In this transformation, amino alcohols are successfully formed with the concomitant introduction of alkynyl, aryl, and vinyl groups. This versatile strategy combines key advantages of both intramolecular and intermolecular reactions: high reactivity, stereo-, regio-, and diastereoselectivity, as well as the use of simple starting materials.

To develop a one-pot tethered synthesis of amino alcohols starting from allyl amines, it is first important to analyze the key parameters for success of this challenging process (Scheme 3). First, the allyl amine starting materials could



Scheme 3. Speculative analysis for the tether-formation step.

react directly with palladium, thus leading to catalyst deactivation or side reactions such as Heck coupling and Buchwald–Hartwig type C–N bond formation. To avoid these pitfalls, formation of the hemiaminal intermediate **A** should be both fast and thermodynamically favored. Second, formation of a reactive iminium intermediate **B** should be avoided, as it can lead to unproductive amination with the allyl amine. Basic conditions should be better suited in this respect, as formation of the iminium is usually acid catalyzed. This would furthermore facilitate olefin functionalization by a faster *syn* oxypalladation on intermediate **C**. Indeed, we had shown in our previous work that basic conditions were necessary for the oxyalkynylation of olefins using a palladium(0) catalyst.^[10c,d] However, hemiaminal formation is usually performed under slightly acidic conditions.

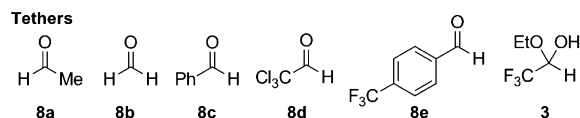
With these challenges in mind, we started our studies by examining the reaction of benzyl allyl amine (**4a**) with triisopropylsilyl ethynyl bromide (**5a**) in the presence of different bases and aldehydes (**8**) under the reaction conditions optimized for the intramolecular oxyalkynylation reaction [Pd⁰ catalyst,^[11] DPE-Phos (**7a**) as ligand, toluene, 60 °C; Table 1].^[10c] No product could be observed when using reported tether precursors such as acetaldehyde (**8a**) or formaldehyde (**8b**; entries 1 and 2).^[8,9] A small amount (about 5 % yield) of the desired product **9** could be obtained only with benzaldehyde (**8c**; entry 3). We speculated that this failure was due to the inefficient formation of the hemiaminal

Table 1: Optimization of the tethered oxyalkynylation.^[a]

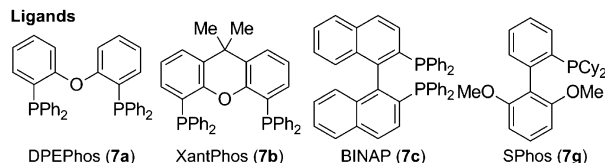
$\text{BnHN-CH}_2\text{-CH=CH}_2 \quad \text{4a} \quad 1.0 \text{ equiv}$ $\xrightarrow[\text{toluene (0.2 M), 60 }^\circ\text{C, 15 h}]{\text{Br-C}\equiv\text{C-SiPr}_3 \text{ (5a), 1.3 equiv tether (5.0 equiv) [Pd(Cp)cinnamyl] (6, 4 mol\%) ligand 7 (6 mol\%), base (1.3 equiv)}}$ $\text{Bn-CH(OH)-CH}_2\text{-CH}_2\text{-C}\equiv\text{C-SiPr}_3 \quad \text{9}$				
Entry	Tether (equiv)	Ligand	Base	Yield [%] ^[b]
1	8a (5.0)	DPEPhos (7a)	Cs ₂ CO ₃	< 1
2	8b (5.0)	DPEPhos (7a)	Cs ₂ CO ₃	< 1
3	8c (5.0)	DPEPhos (7a)	Cs ₂ CO ₃	5
4	8d (5.0)	DPEPhos (7a)	Cs ₂ CO ₃	5
5	8e (5.0)	DPEPhos (7a)	Cs ₂ CO ₃	25
6	3 (5.0)	DPEPhos (7a)	Cs ₂ CO ₃	92 ^[c]
7	3 (1.0)	DPEPhos (7a)	Cs ₂ CO ₃	71
8	3 (5.0)	DPEPhos (7a)	K ₂ CO ₃	76
9	3 (5.0)	DPEPhos (7a)	NaOtBu	8
10	3 (5.0)	XantPhos (7b)	Cs ₂ CO ₃	8
11	3 (1.5)	XantPhos (7b)	Cs ₂ CO ₃	59
12	3 (5.0)	binap (7c)	Cs ₂ CO ₃	6
13 ^[d]	3 (5.0)	PPh ₃ (7d)	Cs ₂ CO ₃	< 5
14 ^[d]	3 (1.5)	(2-Furyl) ₃ P (7e)	Cs ₂ CO ₃	93
15 ^[d]	3 (1.5)	(4-CF ₃ C ₆ H ₄) ₃ P (7f)	Cs ₂ CO ₃	82
16 ^[e]	3 (1.5)	SPhos (7g)	Cs ₂ CO ₃	40

[a] Reactions were carried out on a 0.10 mmol scale. [b] Yields were calculated from ¹H NMR spectra by using trimethoxybenzene as internal standard. [c] Yield of isolated product on 0.30 mmol scale. [d] 12 mol % of ligand was used. [e] 8 mol % of ligand was used. Cp = cyclopentadienyl.

Tethers



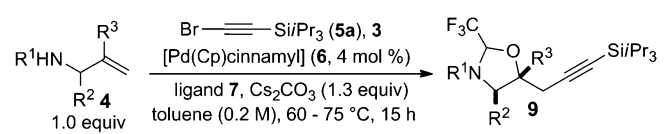
Ligands



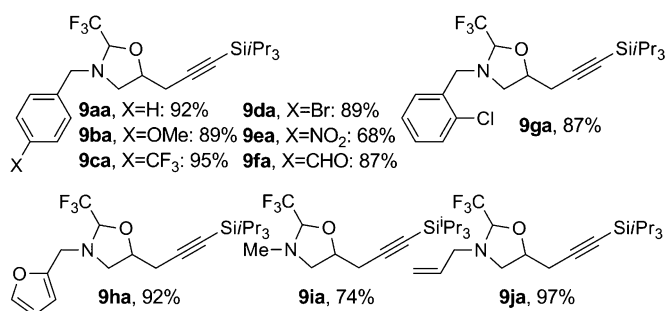
under the basic reaction conditions. To accelerate the formation of this key intermediate, more-electron-deficient aldehydes were then examined (entries 4–6). With chloral (**8d**) and *para*-trifluoromethylbenzaldehyde (**8e**), **9** could indeed be obtained in 5 and 25 % yield, respectively (entries 4 and 5). Finally, the best result was obtained with the commercial hemiacetal form **3** of trifluoroacetaldehyde,^[12] and the oxyalkynylation product **9aa** could be isolated in 92 % yield after optimization of the reaction conditions (entry 6).^[13] The best results were obtained using five equivalents of **3**. Nevertheless, **9aa** could still be isolated in 71 % yield when only 1.1 equivalents of **3** were used (entry 7). The base played also a critical role in the success of the reaction, as both potassium carbonate (entry 8) and sodium *tert*-butoxide (entry 9) gave inferior results. The product **9aa** was obtained with low diastereoselectivity (< 2:1 d.r.) under all the reaction conditions tested, but this is inconsequential when considering that the trifluoromethyl stereocenter is not present in the final amino alcohol product.^[14]

The phosphine ligand had also a strong effect on the outcome of the reaction. Other biphosphine ligands gave **9aa**

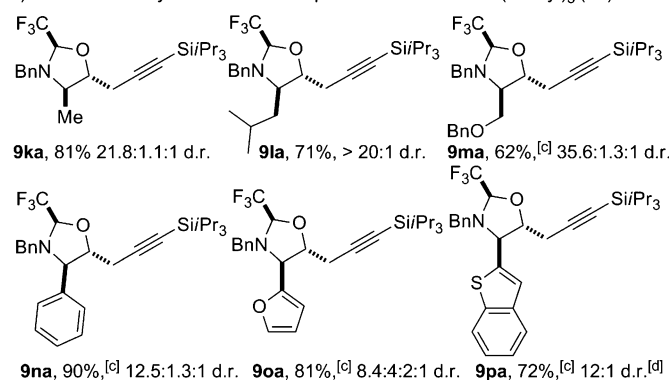
in lower yields (Table 1, entries 10–12). Interestingly, with XantPhos (**7b**) a better yield was obtained when only 1.5 equivalents of **3** were used (entry 11). Finally, the results obtained with monophosphine ligands were highly dependent of their structure. Whereas nearly no product formation was observed with triphenylphosphine (**7d**; entry 13), good results were obtained with less electron-rich aryl phosphines (entries 14 and 15). In particular tris(2-furyl)phosphine (**7e**) gave **9aa** in 93% yield (entry 14). The more sterically hindered electron-rich SPhos ligand (**7g**) led to the formation of **9aa** in only 40% yield (entry 16). From the screening of ligands, two optimum conditions emerged with either DPE-Phos (**7a**) or tris(2-furyl)phosphine (**7e**) as ligands (entries 6 and 14). As more reproducible results were obtained on preparative scale using **7a** as the ligand, it was used to examine the scope of the reaction (Scheme 4).^[15]



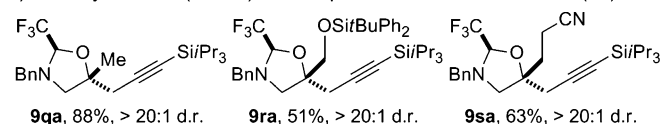
a) N-substituted allyl amines:^{[a],[b]} 4.5 equiv **3** and 6 mol % DPEPhos (**7a**)



b) α -Branched allyl amines:^[a] 3.0 equiv **3** and 12 mol % P(2-furyl)₃ (**7e**)



c) Methylallyl amines ($R^3 \neq H$):^[a] 1.5 equiv **3** and 6 mol % XantPhos (**7b**)



Scheme 4. Scope of allyl amines in the tethered-oxyalkynylation reaction. [a] Reactions were carried out on a 0.30 mmol scale. Yield of isolated products. [b] The d.r. value was lower than 2:1. [c] With 8 mol % **6** and 24 mol % P(2-furyl)₃ (**7e**). [d] The d.r. value was enriched from 4:1 to 12:1 during column chromatography.

We started by investigating the functional-group tolerance of the oxyalkynylation by modifying the benzyl group on the allyl amine (Scheme 4a). The reaction was successful in the presence of an ether, trifluoromethyl, bromo, and nitro group, as well as an aldehyde (**9ba–fa**). It is particularly interesting to see that an aryl bromide group can be tolerated. This tolerance clearly indicated a higher reactivity of the alkynyl bromide towards oxidative addition. Oxazolines bearing an *ortho*-chlorobenzyl group or a furan heterocycle were obtained in 87 and 92% yield, respectively (**9ga** and **9ha**). Finally, the reaction was also successful for a simple methyl (**9ia**) or allyl (**9ja**) substituent. In contrast, only traces of product were observed when anilines or amides/carbamates were used as starting materials.^[13]

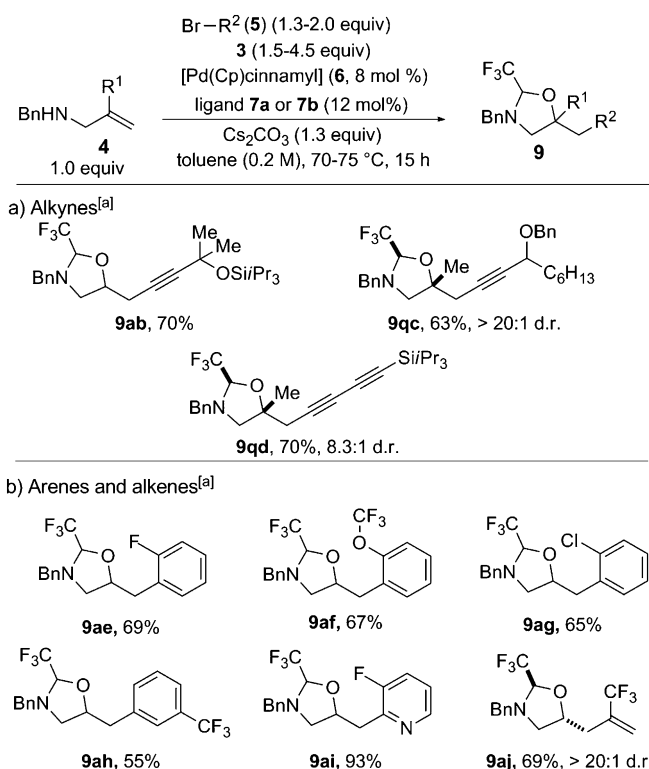
We then turned to the use of amines bearing a substituent at the allylic position (Scheme 4b). This class of starting materials is especially interesting, as the existing stereocenter could be expected to control the formation of the C–O bond and more functionalized products are obtained. Unfortunately, only very low yields were observed when using diphosphines as ligands. In this case, **7e** was the ligand of choice, and the oxazoline **9ka**, derived from the methyl-substituted allyl amine **9k**, was obtained in 81% yield as a major diastereoisomer. With larger alkyl substituents, a nearly perfect diastereoselectivity was observed (**9la** and **9ma**). Aryl substituents could also be used: the phenyl-substituted oxazoline **9na** was obtained in 90% and more than 12:1 d.r., whereas the heterocycle-substituted products **9oa** and **9pa** were formed in good yields but lower diastereoselectivity.

Substitution of the olefin of the allyl amine was examined next (Scheme 4c). 1,2-disubstituted olefins could not be used in the reaction. In contrast, the formation of tertiary ethers was possible when using **7b** as the ligand. The reaction was successful in the case of a simple methyl group (**9qa**) and also for more functionalized alkyl chains (**9ra** and **9sa**).

Up to now, only triisopropylsilyl ethynyl bromide (**5a**) had been used as a partner for the multifunctionalization reaction. This choice was based on the excellent properties of this substrate in oxyalkynylation reactions^[10c] and also its synthetic versatility as a precursor of terminal alkynes. Nevertheless, the use of functionalized alkynes would give a more convergent access into molecular complexity. Good yields could also be obtained with alkynes derived from tertiary or secondary propargylic alcohols (**9ab** and **9qc**) and diynes (**9qd**) (Scheme 5a).

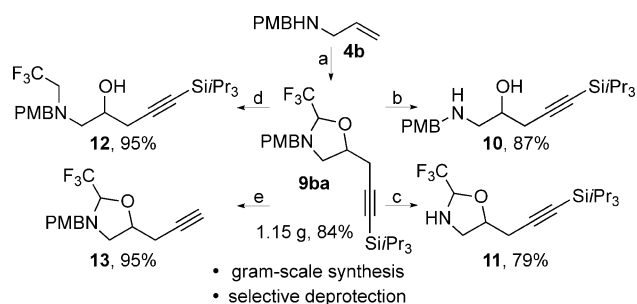
We finally extended the developed strategy to oxyarylation (Scheme 5b).^[16] The reaction was successful provided that aryl bromides slightly activated by an electron-withdrawing group were used. Benzene bromides bearing either a trifluoromethyl, fluoro, trifluoromethoxy, or chlorine group gave the oxyarylation products **9ae–h** in 55–69% yield. The oxazoline **9ai** bearing a pyridine heterocycle could be obtained in 93% yield. Finally, oxyalkenylation was also successful and gave the trifluoromethyl-substituted alkene **9aj** in 69% yield.

The obtained building blocks are highly useful, as they contain three orthogonally protected functional groups (an alcohol, an amine, and an alkyne). To demonstrate this



Scheme 5. Scope of electrophiles in the tethered-oxyfunctionalization reaction. [a] Reactions were carried out on a 0.30 mmol scale. Yield of isolated products. The d.r. value was lower than 3:1, unless otherwise noted.

synthetic potential, **9ba** was synthesized on gram scale (2.51 mmol, 1.15 g, 84 %) and subjected to selective deprotection (Scheme 6). The hemiaminal tether could be readily removed, thus affording the aminoalcohol **10** in 87 % yield. Access to the amine **11** was possible by DDQ-promoted PMB cleavage. Reductive opening of the hemiaminal yielded the trifluoroethylamine **12** in excellent yield, while TIPS removal afforded the terminal alkyne **13**, which could be additionally functionalized.



Scheme 6. Scale-up and orthogonal deprotections. Reaction conditions: a) 4.5 equiv **5a**, 1.3 equiv **3a**, 4 mol % **6**, 6 mol % **7a**, 1.3 equiv Cs_2CO_3 in toluene at 60 °C; b) *p*-toluenesulfonic acid, THF/MeOH (9:1), 60 °C; c) DDQ, $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ (24:1); d) DIBAL-H, toluene, –78 to –25 °C; e) TBAF, THF. DIBAL-H = diisobutylaluminum hydride, DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, PMB = *para*-methoxybenzyl, TBAF = tetra-*n*-butylammonium fluoride, THF = tetrahydrofuran.

In conclusion, we have developed the first palladium-catalyzed, tethered carbo-etherification of allylamines for the synthesis of vicinal amino alcohols. The use of the hemiacetal of trifluoroacetaldehyde for in situ tether formation was key to enable high yield, and regio- and diastereoselectivity under mild reaction conditions. The reaction proceeded with broad scope and high functional-group tolerance. The versatility of our method was highlighted by the possibility to introduce alkynyl, aryl, and vinyl groups onto the alkene. Free alcohols, amines, or terminal alkynes could be obtained orthogonally in one step from the synthesized products. Future work will focus on the development of an asymmetric version of the transformation and the extension to other classes of tethers.

Keywords: alcohols · alkenes · heterocycles · palladium · synthetic methods

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 5250–5254
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Received: January 22, 2015

Published online: February 26, 2015