ChemPubSoc Europe

DOI: 10.1002/chem.201601260

CHEMISTRY A European Journal Full Paper

Palladium Catalysis

Palladium-Catalyzed Aminocarbonylation of Allylic Alcohols

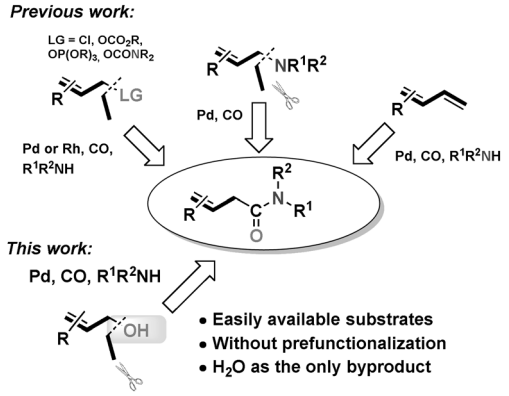
Haoquan Li, Helfried Neumann, and Matthias Beller*[a]

Abstract: A benign and efficient palladium-catalyzed aminocarbonylation reaction of allylic alcohols is presented. The generality of this novel process is demonstrated by the synthesis of β,γ-unsaturated amides including aliphatic, cinnamyl, and terpene derivatives. The choice of ligand is crucial for optimal carbonylation processes: Whereas in most cases the combination of $PdCl_2$ with Xantphos (**L6**) gave best results, sterically hindered substrates performed better in the presence of simple triphenylphosphine (**L10**), and primary anilines gave the best results using cataCXium® PCy (**L8**). The reactivity of the respective catalyst system is significantly enhanced by addition of small amounts of water. Mechanistic studies and control experiments revealed a tandem allylic alcohol amination/C–N bond carbonylation reaction sequence.

Introduction

Allylic alcohols represent sustainable and versatile building blocks in organic synthesis.[1] Among the various allylic substrates, allylic alcohols are the most common and easily accessed from renewable resources and bulk chemicals. In fact, many of these substrates are commercially available or can be conveniently synthesized by numerous methodologies.[2] Furthermore, naturally occurring terpenes such as phytol, geraniol, nerol, farnesol, etc., are broadly used in the fragrance industry and have also found various applications in organic synthesis. For example, the industrial manufacturing of vitamin E and vitamin K1 are based on allylic alcohols.[3]

Due to its specialized structure, investigations for novel transformations of allylic alcohols have attracted significant attention from both academic and industrial researchers.[4] In this respect, carbonylation reactions of allylic substrates constitute versatile tools for the synthesis of β,γ-unsaturated carboxylic derivatives using abundant CO.[5] More specifically, β,γ-unsaturated amides are highly useful synthetic intermediates in organic synthesis, and are typically synthesized from the corresponding activated allylic compounds by cyanation/hydration reactions,[6] or alternatively, from α,β-unsaturated acid chlorides by the Arndt–Eistert reaction and subsequent amidation.[7] Recently, we reported an atom-economic aminocarbonylation reaction of dienes using a palladium/1,2-bis(di-*tert*-butyl-phosphinomethyl)benzene (dtbpx) catalyst system to give β,γ-unsaturated amides (Scheme 1).[8] Nevertheless, the instability of most dienes, the gaseous nature of butadiene, and the availability of 1,3-dienes constitute major limitations and thus prompted us to look for more practical and general methodologies.



Scheme 1. Synthesis of β,γ-unsaturated amides: comparison of previous and current work.

Compared to the direct functionalization of allylic alcohols, the palladium-catalyzed carbonylation of activated allylic compounds such as allyl halides,[9] allyl carbonates,[10] phosphonates,[11] and carbamates[12] have been known since the 1990s.[13] In all these procedures, a significant amount of waste is inevitably generated not only during the prefunctionalization step, but also during the reaction process. On the other hand, palladium-catalyzed carbonylations of allylamines[13b,14] have also been studied, but suffer from the limited availability of the starting materials (Scheme 1). In comparison, the direct aminocarbonylation of allylic alcohols constitutes an ideal choice regarding availability and stability. Such carbonylations are challenging due to the poor leaving group ability of the hydroxyl group.[15] Hence, for direct use of allylic alcohols in carbonylation reactions, acidic additives such as Lewis acids,[16]

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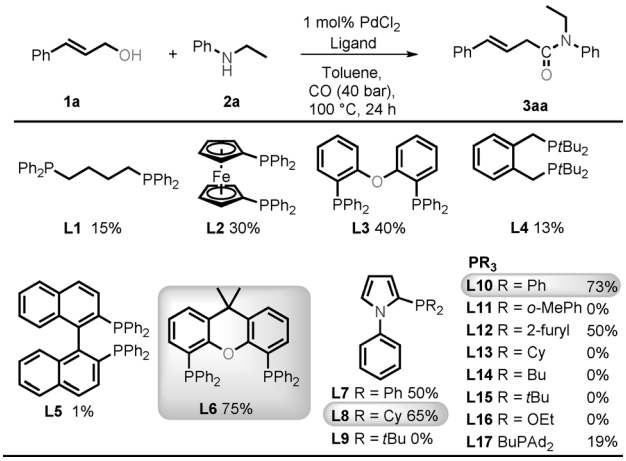
Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/chem.201601260.

Brønsted acid,[17] or CO_2[18] are essential. Unfortunately, these promotors are often deactivated in the presence of basic amines, such as those used in aminocarbonylation. In continuation of our long-standing interest in carbonylation reactions, we report here a palladium-catalyzed aminocarbonylation of allylic alcohols for the first time.[19]

Results and Discussion

At the beginning of our study, the carbonylation of cinnamyl alcohol (**1a**, 1 mmol) with *N*-ethylaniline (**2a**, 1 mmol) was chosen as the model reaction (Scheme 2). In the presence of $PdCl_2$ (1 mol%) as the catalyst precursor, 17 different phosphine ligands (4 mol% for monodentate ligands and 2 mol% for bidentate ligands) were tested without any co-catalyst (see Scheme 2). Applying commercially bidentate ligands such as dppb **L1** (bite angle 94°), dppf **L2** (bite angle 99°), DPEphos **L3** (bite angle 104°; DPEphos = bis-[2-(diphenylphosphino)phenyl]ether)), and dtbpx **L4**, all of which have been proven to promote a variety of carbonylation reactions, only low yields (15–40%) of the desired product **3aa** were obtained. In addition, with BINAP **L5** (bite angle 93°), only 1% of the product could be observed.[20] To our delight, in the presence of Xantphos **L6** (bite angle 108°), a good yield of 75% was obtained. From these results, we conclude that a larger bite angle seems to be beneficial for this reaction.[21] Next, *N*-phenylpyrrole-type ligands **L7**–**L9** were tested considering their activity in a variety of coupling reactions.[22] Among these ligands, the cyclohexyl-substituted derivative **L8** (cataCXium® PCy) gave the best result (65% yield). As expected, a variety of standard monodentate ligands (**L11**–**L17**) gave no or low conversion. However, to our delight, even simple and inexpensive PPh_3 **L10** gave a very good result (73% yield), although undesired palladium black is observed after the reaction. Based on all these results, the commercially available ligand Xantphos **L6** was finally chosen for the following studies.

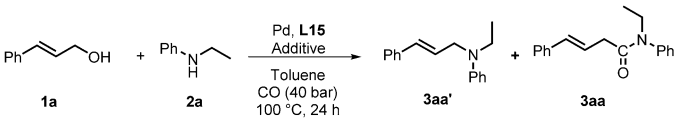


Scheme 2. Palladium-catalyzed aminocarbonylation of allylic alcohol: ligand screening. Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), ligand (**L1**–**L6** 2 mol%, **L7**–**L17** 4 mol%), toluene (2 mL), CO (40 bar), 100 °C, 24 h; yield determined by GC analysis with isooctane as the internal standard.

To improve the reactivity of the catalyst system, we investigated the additive effect. For example, when decreasing the catalyst loading to 0.5 mol%, only 19% yield of **3aa** was observed (Table 1, entries 2–3), with the amination product **3aa'** as a major byproduct. Despite the presence of the amine, the addition of a catalytic amount of trifluoroacetic acid (TFA), methanesulfonic acid (MSA), or hydrochloric acid (HCl) improved the yield significantly in each case (entries 4–6, respectively). More surprisingly, when we added water (10 μL), which is a side product during the reaction, an improved yield was also obtained (80%, entry 7). Furthermore, fine tuning the amount of **1a** to 1.5 equiv led to quantitative yield of the desired amide (entry 8). Even with 0.25 mol% palladium loading, an excellent yield was obtained after 48 h (92% yield, entries 9 and 10). However, further decreasing the catalyst loading to 0.1 mol% gave only traces of **3aa**.

To gain more insight into the mechanism of this aminocarbonylation reaction of allylic alcohols, several control experiments were conducted (Tables 2 and 3). Under CO atmosphere, using a halide-free palladium catalyst ($Pd_2(dba)_3$ as the precursor; dba = dibenzylideneacetone), and Xantphos as the ligand in the presence of water as the additive, 31% of **3aa'** was observed as the main product, and no carbonylation to **3aa** occurred (Table 2, entry 1). However, using the same catalyst and adding 5 mol% of HCl, 77% yield of amide **3aa** was observed (entry 2). Interestingly, the addition of a catalytic amount of allyl chloride (0.5 mol%) also leads to a good yield of **3aa**, which is explained by the formation of catalytically active allyl-palladium species through oxidative addition. In contrast, adding 10 mol% of NaOH into the reaction mixture, **3aa'** and **3aa** were not observed (entry 4). All these control experiments clearly demonstrate that the

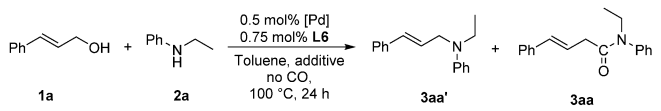
Table 1. Palladium-catalyzed aminocarbonylation of allylic alcohol: Influence of additives.[a]



Entry	Pd [mol%]	Ligand [mol%]	Additive	Yield **3aa** [%]
1	$PdCl_2$ (1)	**L6** (2)	–	75
2	$PdCl_2$ (1)	**L6** (1.5)	–	75
3	$PdCl_2$ (0.5)	**L6** (0.75)	–	19
4	$PdCl_2$ (0.5)	**L6** (0.75)	TFA (3 mol%)	75
5	$PdCl_2$ (0.5)	**L6** (0.75)	MSA (3 mol%)	84
6	$PdCl_2$ (0.5)	**L6** (0.75)	HCl (3 mol%)	87
7	$PdCl_2$ (0.5)	**L6** (0.75)	H_2O (10 μL)	80
8	$PdCl_2$ (0.5)	**L6** (0.75)	H_2O (10 μL)	95[b]
9	$PdCl_2$ (0.25)	**L6** (0.375)	H_2O (10 μL)	25[b] 92[b,c]
10	$PdCl_2$ (0.1)	**L6** (0.15)	H_2O (10 μL)	trace[b,c]

[a] General conditions: **1a** (1 mmol), **2a**(1 mmol), $PdCl_2$, **L6**, toluene (2 mL), 100 °C, 24 h, CO (40 bar). [b] **1a** (1.5 mmol). [c] 48 h.

Table 2. Palladium-catalyzed aminocarbonylation of cinnamyl alcohol **1a**: Control experiments.[a]



1a 2a 3aa' 3aa

Entry	Pd	CO [bar]	Additive	3aa' [%]	3aa [%]
1	$Pd_2(dba)_3$	40	H_2O (10 μL)	31	0
2	$Pd_2(dba)_3$	40	HCl (5 mol%)	0	77
3	$Pd_2(dba)_3$	40	allyl chloride (0.5 mol%) H_2O (10 μL)	0	80
4	$PdCl_2$	40	NaOH (10 mol%)	0	0
5	$Pd_2(dba)_3$	–	None	15	–
6	$Pd_2(dba)_3$	–	H_2O (10 μL)	10	–
7	$Pd_2(dba)_3$	–	HCl (5 mol%)	64	–
8	$PdCl_2$	–	H_2O (10 μL)	90	–
9	$PdCl_2$	–	Et_2NH (1 equiv)	0	–

[a] Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), [Pd] (0.005 mmol, 0.5 mol%), **L6** (0.0075 mmol, 0.75 mol%), CO (40 bar), 100 °C, 24 h.

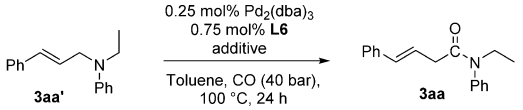
presence of halide or acid is crucial for the promotion of the carbonylation process.

To clarify the role of the halide additive further, reaction of **1a** with **2a** was performed in the absence of CO atmosphere (Table 2, entries 5–9). Without any additive, only 15% of **3aa'** was formed by palladium-catalyzed allylic substitution reaction (entry 5). A slightly lower yield of **3aa'** was also observed in the presence of additional water (entry 6). However, addition of 5 mol% of HCl (in Et_2O solution) significantly increased the yield of **3aa'** to 64% (entry 7). In comparison, the combination of $PdCl_2$ as the catalyst precursor and 10 μL of water gave 90% yield of the amine after 24 h (entry 8). In contrast, in the presence of 1 equivalent of basic diethylamine, the reactivity was completely inhibited and only the starting material was recovered (entry 9). In conclusion, acid (HCl) or in situ generated HCl significantly improved the amination reaction of the allylic alcohol, whereas addition of basic amines inhibited the reaction.

To compare the reactivity of cinnamyl alcohol and the corresponding amine, the carbonylation of **3aa'** using $Pd_2(dba)_3$ without any additive was investigated. Indeed, the reaction proceeded and 11% yield of **3aa** could be observed (Table 3, entry 1). Interestingly, only a slightly increased yield (25%, entry 2) was obtained by adding 5 mol% of HCl into the reaction media. Surprisingly, by further adding 10 μL of water, the byproduct of the amination reaction of the allylic alcohol, the yield of **3aa** increased considerably to 93% (entry 3). In this case, in the presence of halide, water is not only promoting the amination step, but also promoting the carbonylation step.

Furthermore, the progress of the reaction was monitored by analysis of samples taken from the reaction mixture. After an induction period of around 100 min, which could probably be explained by the in situ generation of Pd^0 and HCl by the water–gas shift reaction, **1a** and **2a** were quickly consumed and transformed into the amination product **3aa'** in around 200 min (see Figure 1). At the same time, less than 10% of the final product **3aa** was formed. Afterwards, the formation of

Table 3. Palladium-catalyzed aminocarbonylation of **3aa'**.[a]



3aa' 3aa

Entry	Additive	3aa [%][b]
1	None	11
2	HCl (5 mol%)	25
3	HCl (5 mol%), H_2O (10 μL)	93

[a] Reaction conditions: **3aa'** (1 mmol), $Pd_2(dba)_3$ (0.0025 mmol, 0.25 mol%), **L6** (0.0075 mmol, 0.75 mol%), CO (40 bar), 100 °C, 24 h; [b] Yield determined by GC with isooctane as an internal standard.

3aa seemed to be accelerated probably due to the decrease of **2a** concentration and also the increase of concentration of **3aa'**. Together, the formation and consumption of **3aa'** reached an equilibrium and stayed still for around 200 min at approximately 40% yield. Then, the concentration of **3aa'** started to decrease along with an increase in yield of **3aa**.

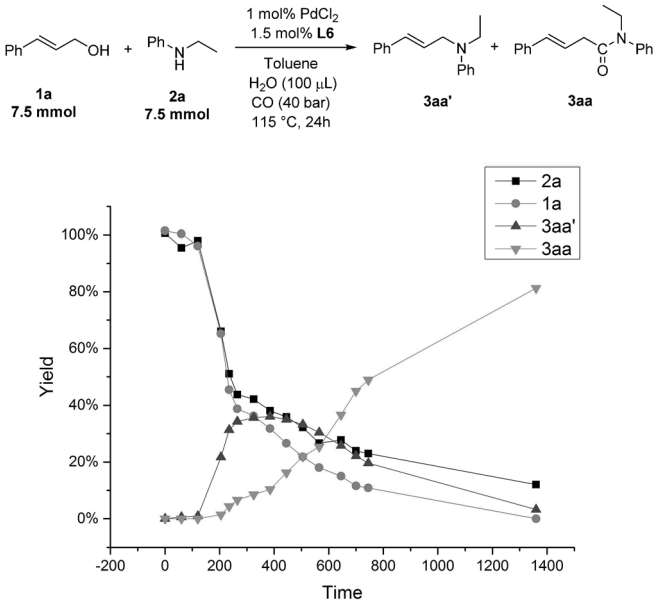
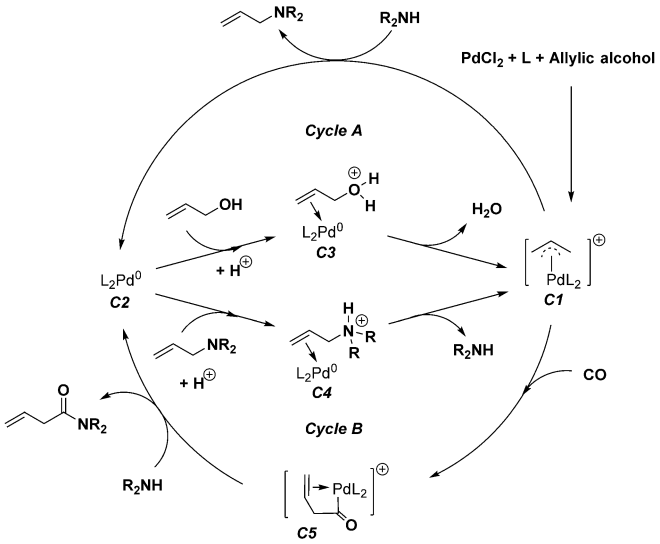


Figure 1. Reaction profile of the palladium-catalyzed aminocarbonylation of allylic alcohol.

Based on the previous mechanistic understandings of palladium-catalyzed Tsuji–Trost-type reactions, we suggest this reaction follows the mechanistic pathway as depicted in Scheme 3. Basically, this reaction involves two catalytic cycles, the amination of the allylic alcohol (*Cycle A*) and the carbonylation of the allylic amine (*Cycle B*), both of which are closely related to each other. At the beginning, the catalytically active allyl palladium species ***C1*** is generated by the reaction of $PdCl_2$ with the allylic alcohol **1a**.[23] At this stage, both CO coordination/insertion and the nucleophilic attack of amine to allyl palladium species are possible, steps which seem to be controlled by the

concentration of free amine. At the beginning stage of the reaction, the concentration of free amine is high, and thus the aminolysis of the allyl-palladium species is faster, which generates allylic amine and regenerates the Pd^0 species ***C2***. The activation of allylic alcohol and allyl amine are promoted by the in situ generated or added acid and regenerate ***C1*** (*Cycle A*). Likewise, the other cycle starts from the oxidative addition of allyl amine to Pd^0 ***C2***, which is assisted by acid and water. With progress of the reaction, CO insertion to ***C1*** will generate acyl-palladium species ***C5***. Finally, the aminolysis of the acyl-palladium species affords the desired carbonylation product and regenerates ***C2*** (*Cycle B*).



Scheme 3. Palladium-catalyzed aminocarbonylation of allylic alcohols: proposed reaction pathway.

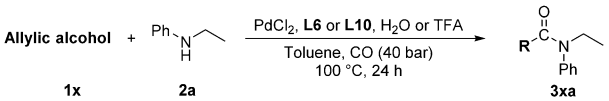
In order to explore the scope of this novel reaction, a variety of allylic alcohols were tested (Table 4). 1-Phenylprop-2-en-1-ol (**1 b**) as a substrate yielded the linear product **3 ba** in high yield (95%, entry 1). This clearly indicates that the reaction goes via an allyl-palladium complex as the reaction intermediate. Starting from the parent allyl alcohol **1 c** (3 equiv) the carbonylation process led to 92% yield of **3 ca** (entry 2). However, using sterically more hindered β-methallyl alcohol (**1 d**) under standard conditions (*condition A*), no desired product was observed. Gratifyingly, employing less hindered **L 10** as ligand under slightly modified conditions (with 5 mol% TFA as additive, see *condition B*), the corresponding product **3 da** could be obtained in 40% yield (entry 3). On the other hand, a good yield was obtained with crotyl alcohol (**1 e**) (84% yield, *E/Z* = 76/24, entry 4). As expected, but-3-en-2-ol (**1 f**) as the substrate gave the identical product (i.e., **3 ea** = **3 fa**) in 87% isolated yield (entry 5). Another example of a 1-substituted allyl alcohol **1 g** also gave the linear product **3 ga**, as the final product, in 84% isolated yield (entry 6). Similar to **1 d**, the di-substituted alcohol **1 h** did not afford the desired product using Xantphos even with TFA as additive. However, using PPh_3 **L 10** as the ligand, 53% isolated yield was obtained at 100 °C (entry 7). A further increase in the reaction temperature to 120 °C yielded the product in 83%. Moreover, cyclic allyl alcohols, such as cyclohex-2-enol (**1 i**), reacted smoothly under condition B (51% isolated yield of **3 ia**, entry 8).

To highlight the application potential of our developed method, several industrially relevant, advanced building blocks were carbonylated. For example, starting from **1 j**, which constitutes an intermediate from the bulk telomerization of 1,3-butadiene to 1-octene, **3 ja** was obtained in 62% isolated yield (*E/Z* = 80/20, Table 4, entry 9).[24] Moreover, renewables such as geraniol (**1 k**), nerol (**1 l**), and linalool (**1 m**), which are used in the perfume and fragrance industry, gave quantitative yield of the desired amides (*E/Z* = 67/33, 62/38, and 62/38, respectively, entries 10–12). Noticeably, in all these cases the internal C=C bond remained intact under such reaction conditions. Furthermore, acyclic diterpene alcohols, for example phytol and isophytol, were successfully transformed into the corresponding amides in very good yields (95 and 90% yield, respectively, *E/Z* = 68/32, entries 13 and 14). Farnesol (**1 p**), an example of an acyclic sesquiterpene, afforded 88% yield of the corresponding amide (a mixture of four isomers, ratio 15:20:24:41, entry 15). To note, homofarnesylic acid amide (**3 pa**) can be used for the synthesis of (±)-ambroxan, which is used as amber-like perfume material, through an acid-catalyzed cyclization reaction.[7a]

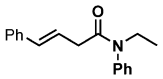
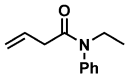
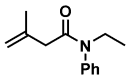
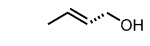
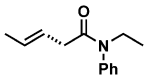
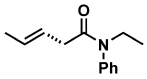
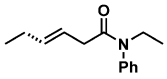
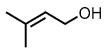
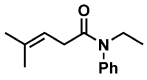
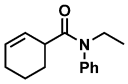
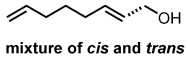
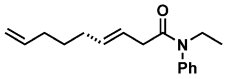
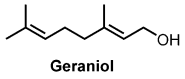
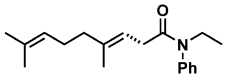
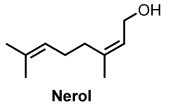
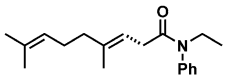
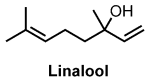
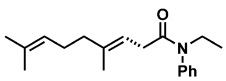
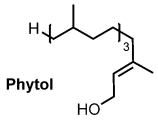
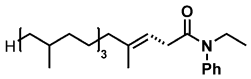
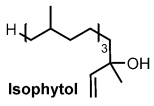
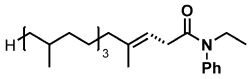
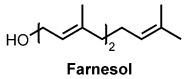
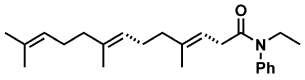
To investigate the influence of electronic effects and the functional group tolerance of this method, different *N*-substituted anilines were reacted with **1 a** (Scheme 4). With 4-methoxy-*N*-methylaniline as the substrate, **3 ab** was obtained in 89% yield. Using anilines with simple electron-withdrawing groups (F and Cl substituents), the corresponding products **3 ac** and **3 ad** were obtained also in good yield (90 and 81%, respectively). Reaction of the cyclic indoline led to the corresponding **3 ae** in 65% isolated yield. More sterically demanding amines such as *N*-cyclohexylaniline, *N*-benzyl-4-methoxyaniline, and *N*-methyl-2-(trifluoromethyl)aniline were all well tolerated under these conditions (92, 83, and 90% yield, respectively). Finally, 10,11-dihydro-5H-dibenzo[b,f]azepine was tested and afforded **3 ai** in 69% yield.

In general, *N*-alkylation reactions of primary amines are more challenging because mono- and dialkylation reactions could take place at the same time. Nevertheless, in the reaction of aniline and our model substrate cinnamyl alcohol, monoalkylation prevailed, leading to **4 aa**. However, 1,3-diphenylpyrrolidin-2-one was observed as a side product, which derives from the competitive intramolecular carbonylation reaction at the benzylic position of *N*-cinnamylaniline. By carefully selecting an appropriate ligand (4 mol% cataCXium® PCy **L 8**) **4 aa** was obtained in 63% isolated yield (Scheme 5). Less-activated aliphatic allylic alcohols without benzylic stabilization do not undergo this cyclization reaction. Hence, starting from isobutenol (**1 d**) and aniline, **4 da** was isolated in 72% yield after 48 h heating. With crotyl alcohol (*E/Z* mixture, **1 e**) as the substrate, **4 ea** was selectively obtained (85% yield). Furthermore, good yields were also obtained when using prenol (**1 h**), geraniol (**1 k**), or 2-cyclohexen-1-ol (**1 i**) as the substrate (91, 72, and 89% isolated yield for **4 ha**, **4 ka**, and **4 ia**, respectively). Again,

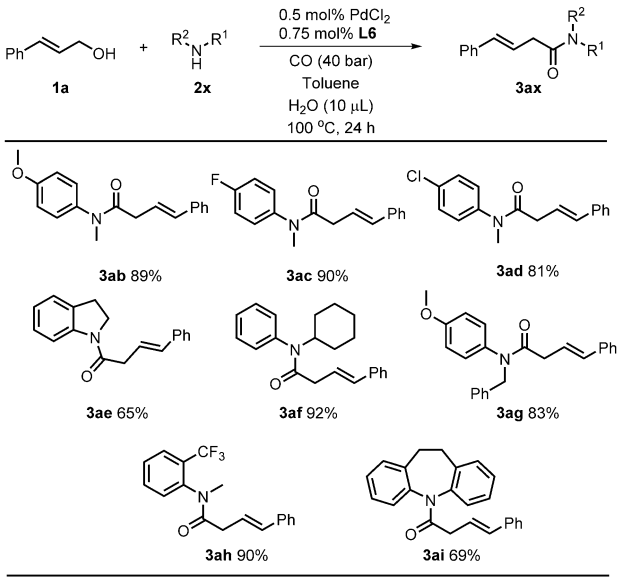
Table 4. Palladium-catalyzed aminocarbonylation of allylic alcohols: substrate scope.[a]



1x 2a 3xa

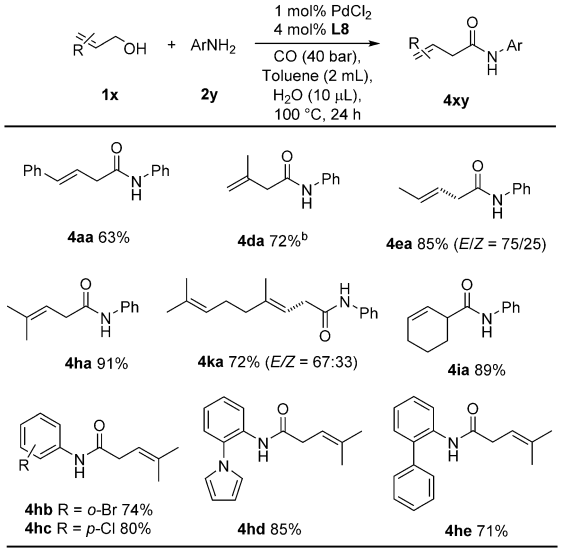
Entry	Allylic alcohol		Ligand	Additive	Product		Yield [%][e]
1		**1 b**	Xantphos	H_2O (10 μL)		**3 ba**	95[b]
2		**1 c**	Xantphos	H_2O (10 μL)		**3 ca**	92[b,d]
3		**1 d**	PPh_3	TFA (5 mol%)		**3 da**	40[b]
4	 mixture of *cis* and *trans*	**1 e**	Xantphos	H_2O (10 μL)		**3 ea**	84 (*E*/*Z* = 76/24)[b]
5		**1 f**	Xantphos	H_2O (10 μL)		**3 fa**	87 (*E*/*Z* = 76/24)[b]
6		**1 g**	Xantphos	H_2O (10 μL)		**3 ga**	84 (*E*/*Z* = 82/18)[b]
7		**1 h**	PPh_3	TFA (5 mol%)		**3 ha**	53[b] 83[c]
8		**1 i**	PPh_3	TFA (5 mol%)		**3 ia**	51[c]
9	 mixture of *cis* and *trans*	**1 ij**	Xantphos	TFA (5 mol%)		**3 ja**	62 (*E*/*Z* = 80/20)[b]
10	 Geraniol	**1 ik**	PPh_3	TFA (5 mol%)		**3 ka**	95 (*E*/*Z* = 67/33)[c]
11	 Nerol	**1 l**	PPh_3	TFA (5 mol%)		**3 la**	95 (*E*/*Z* = 62/38)[c]
12	 Linalool	**1 m**	PPh_3	TFA (5 mol%)		**3 ma**	95 (*E*/*Z* = 62/38)[c]
13	 Phytol	**1 n**	PPh_3	TFA (5 mol%)		**3 na**	95 (*E*/*Z* = 68/32)[c]
14	 Isophytol	**1 o**	PPh_3	TFA (5 mol%)		**3 oa**	90 (*E*/*Z* = 68/32)[c]
15	 Farnesol (mixture of isomers)	**1 p**	PPh_3	TFA (5 mol%)		**3 pa**	88[c]

[a] Condition A: **1** (1.5 mmol), **2** (1 mmol), $PdCl_2$ (0.5 mol%, 0.005 mmol), **L6** (0.75 mol% 0.0075 mmol), or Condition B: **1** (1.5 mmol), **2** (1 mmol), $PdCl_2$ (0.5 mol%, 0.005 mmol), **L10** (2 mol%, 0.02 mol%) in toluene (2 mL), CO (40 bar) for 24 h. [b] 100 °C. [c] 120 °C. [d] **1** (3 mmol). [e] Yield of the isolated products, *E*/*Z* ratio determined by gas chromatography.



Scheme 4. Palladium-catalyzed aminocarbonylation of allylic alcohols: scope of secondary amines. Reaction conditions: **1** (1.5 mmol), **2** (1 mmol), $PdCl_2$ (0.5 mol%, 0.005 mmol), **L6** (0.75 mol%, 0.0075 mmol), H_2O (10 μL) in toluene (2 mL), CO (40 bar), 100 °C for 24 h, yields of isolated product shown.

this method is shown to be general to different aniline derivatives. Starting from 3-methylbut-2-en-1-ol (**1h**), anilines bearing *ortho*-Br and *para*-Cl substituents were transformed to the corresponding β,γ-unsaturated amides with good yields (74 and 80% isolated yields, respectively). More sterically hindered 2-(1H-pyrrol-1-yl)- and 2-phenyl-anilines were also well tolerated and afforded selectively the corresponding β,γ-unsaturated amides **4hd** and **4he** in 85 and 71% yield, respectively.



Scheme 5. Palladium-catalyzed aminocarbonylation reactions with primary anilines. Reaction conditions: **1** (1.1 mmol), **2** (1 mmol), $PdCl_2$ (1 mol%, 0.01 mmol), **L8** (4 mol%, 0.04 mmol), H_2O (10 μL) in toluene (2 mL), CO (40 bar), 100 °C for 24 h, yields of isolated product shown. [a] 48 h

Conclusion

In conclusion, for the first time, a palladium-catalyzed direct aminocarbonylation reaction of allylic alcohols has been achieved. Notably, the reactivity of the catalyst system is significantly improved by adding water (or acid) as an additive. Starting from easily available allylic alcohols and aromatic amines, a variety of β,γ-unsaturated amides could be synthesized in high yields under mild reaction conditions with good functional group tolerance (34 examples, 40–95% yield). Mechanistic studies by performing control experiments reveal the important role of halides in this reaction. We expect that this newly developed catalytic method will inspire synthetic chemists to apply more carbonylation reactions in fine chemical and pharmaceuticals syntheses.

Acknowledgements

The Federal Ministry of Education and Research (BMBF) and Evonik Industries are gratefully acknowledged for their general support. We would like to thank the analytical department of LIKAT for support. The supportive discussions with Dr. Qiang Liu, Dr. Raffaella Ferraccioli, and Jie Liu are gratefully acknowledged.

Keywords: allylic · amide · carbonylation · homogeneous catalysis · palladium

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Received: March 16, 2016
Published online on ■■ ■■, 0000

FULL PAPER

Palladium Catalysis

*H. Li, H. Neumann, M. Beller**

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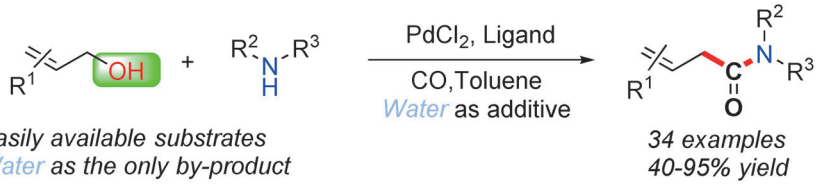
Palladium-Catalyzed Aminocarbonylation of Allylic Alcohols



Amino-zing carbonylation! A palladium-catalyzed direct aminocarbonylation reaction of allylic alcohols is achieved. Starting from easily available allylic alcohols and aromatic amines, a variety of β,γ-unsaturated amides could be synthesized in high yields under mild reaction conditions (34 examples, 40–95% yield).