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# Palladium-catalyzed hydroaminocarbonylation of alkenes with amines promoted by weak acid

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ABSTRACT

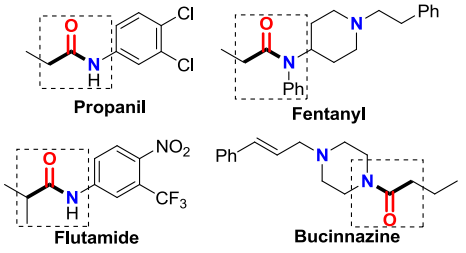
The weak acid has been identified as an efficient basicity-mask to overcome the basicity barrier imparted by aliphatic amines in the Pd-catalyzed hydroaminocarbonylation, which enables both aromatic and aliphatic amines to be applicable in the palladium-catalyzed hydroaminocarbonylation reaction. Notably, by using this protocol, the marketed herbicide of Propanil and drug of Fentanyl could be easily obtained in a one-pot manner.



## Introduction

As one of the most important fundamental structural motifs, amide has been considered as a privileged structure in natural products, pharmaceuticals, pesticides, and functional materials.[1] For instance, the core structure of Propanil (herbicide),[2] Fentanyl (potent anesthesia and analgesic drug),[3] Flutamide (antiandrogen drug),[4] and Bucinnazine (potent analgesic drug)[5] is amide (Scheme 1). Therefore, the development of sustainable and atom-economic method for the synthesis of amides continues attracting much interest in academic research and industrial chemistry.

Driven by this prevalence, various methods have been developed for the synthesis of amides in recent decades.[6,7] One of the most promising methods is hydroaminocarbonylation of simple alkenes with amines in the presence of CO, which represents an ideal and atom economic approach to amides without formation of any by-products. Various catalysts, such as Ru, Rh, Pd, Co, and Ni complexes, have been reported for this method.[8] However, to the best of our knowledge, these reported methods suffer from forcing reaction conditions and only being applicable for aromatic amines. As for the palladium-catalyzed system, the conceivable reasons for the dependence of reactivity on nature of amines might be attributed to the fact that the key Pd-hydride catalytic species only can survive under relatively acidic conditions.[8] To circumvent




**Scheme 1.** Amide-containing pesticide and pharmaceuticals.

this substrate inhibition, we developed a ternary catalyst system composed of Pd/acid/paraformaldehyde effective for the conversion with both aromatic amines and aliphatic amines, in which the paraformaldehyde was utilized to mask the basicity of aliphatic amines to facilitate producing the key active Pd–H species.[9] Inspired by this result and in connection with our interests in the carbonylation reactions,[10] we present herein a practical and efficient palladium-catalytic system for the hydroaminocarbonylation of simple alkenes with both aromatic and aliphatic amines under CO atmosphere, thus allowing the synthesis of the linear amides with high selectivity (Scheme 2). The stoichiometric amount of weak acid used in this catalytic system has been identified as an effective basicity-mask to overcome the basicity barrier imparted by the aliphatic amines and thus facilitating the hydroaminocarbonylation. Notably, in a one-pot manipulation, the Propanil and

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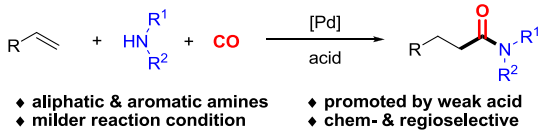


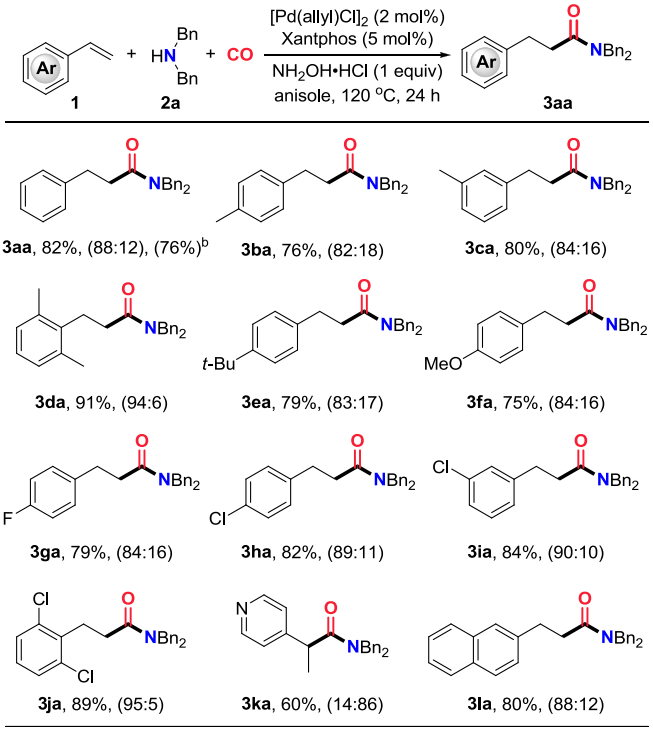

**Scheme 2.** Catalytic hydroaminocarbonylation of alkenes.

Fentanyl can be obtained in gram scale with high yields from simple ethene and corresponding amines.

## Results and discussion

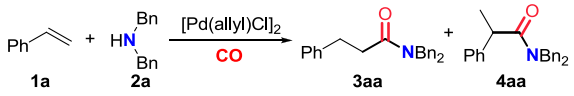
On the basis of our experience with palladium catalyzed hydroaminocarbonylation reactions, styrene (**1a**) and dibenzylamine (**2a**) were chosen as model substrates, and the reaction was performed under 10 atm of CO at 120 °C for 24 h. With DPPPen as the ligand and $[Pd(allyl)Cl]_2$ as the catalyst precursor, the reaction proceeded well in the presence of one equivalent of $NH_2OH{\cdot}HCl$ to give the desired amide in 89% yield with relatively lower regioselectivity (Table 1, entry 1). Encouraged by this result, various phosphine ligands were examined (Table 1, entries 2–9) and it was found that Xantphos was the most effective, affording 99% yield of the desired products with good regioselectivity. Next, various acids were evaluated. Only a trace amount of the product was detected when organic acids, such as $HCO_2H$, $CH_3CO_2H$, and $NH_2CH_2CO_2H$ served as additives (Table 1, entries 10–12). In addition, other acids such as TsOH, $NH_2CH_2CO_2Me{\cdot}HCl$, $NH(Me)(OMe){\cdot}HCl$, and $NEt_3{\cdot}HCl$ did not improve the reactivity and regioselectivity for this carbonylation reaction (Table 1, entries 13–17). Finally, control experiments revealed that both the palladium catalyst and acid are essential to this reaction (Table 1, entry 18).

With the optimized reaction conditions established, substrate scope of the styrenes was first investigated and the results are summarized in Scheme 3. Styrenes with various substituents on the *para*-, *meta*-, and *ortho*-positions, such as alkyl-, alkoxy-, and halogen groups, were suitable to give the corresponding products **3aa**–**3ja** in good to excellent yields with high regioselectivity. The *ortho*-substituted alkenes exert positive effect on the reactivity



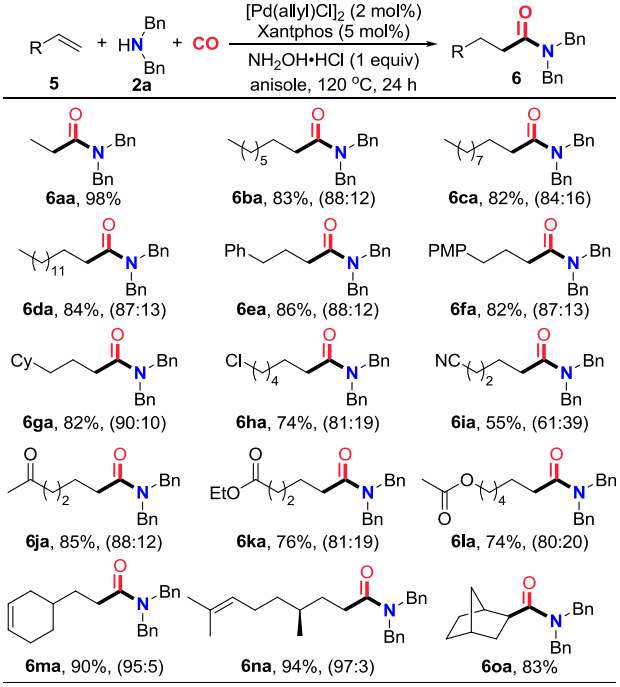

**Scheme 3.** Scope of aromatic alkenes[a]. [a]Reaction conditions: **1** (1.0 mmol), **2a** (0.5 mmol), $[Pd(allyl)Cl]_2$ (0.01 mmol), Xantphos (0.025 mmol), $NH_2OH{\cdot}HCl$ (0.5 mmol), anisole (2.0 mL), CO (10 atm), 120 °C, 24 h. Isolated of **3**; the **L/B** within parentheses were determined by GC and GC–MS analyses. [b]Gram scale.

**Table 1**
Optimization of reaction conditions[a]




| Entry | Ligand | Acid | **3 + 4** (%)[b] | **3/4**[c] |
|---|---|---|---|---|
| 1 | DPPPen | $NH_2OH{\cdot}HCl$ | 89 | 70:30 |
| 2 | DPPB | $NH_2OH{\cdot}HCl$ | <5 | — |
| 3 | DPPH | $NH_2OH{\cdot}HCl$ | 76 | 33:65 |
| 4 | BINAP | $NH_2OH{\cdot}HCl$ | <5 | — |
| 5 | DPEphos | $NH_2OH{\cdot}HCl$ | 49 | 84:16 |
| 6 | Xantphos | $NH_2OH{\cdot}HCl$ | 99 | 88:12 |
| 7 | NiXantphos | $NH_2OH{\cdot}HCl$ | 99 | 84:16 |
| 8 | *t*-BuXantphos | $NH_2OH{\cdot}HCl$ | <5 | — |
| 9 | $PPh_3$[d] | $NH_2OH{\cdot}HCl$ | <5 | — |
| 10 | Xantphos | $HCO_2H$ | 8 | 77:23 |
| 11 | Xantphos | $CH_3CO_2H$ | 7 | 72:28 |
| 12 | Xantphos | $NH_2CH_2CO_2H$ | 5 | 88:12 |
| 13 | Xantphos | TsOH | 43 | 88:12 |
| 14 | Xantphos | $NH_2SO_3H$ | 82 | 77:23 |
| 15 | Xantphos | $NH_2CH_2CO_2Me{\cdot}HCl$ | 65 | 88:12 |
| 16 | Xantphos | $NH(Me)(OMe){\cdot}HCl$ | 82 | 82:18 |
| 17 | Xantphos | $NEt_3{\cdot}HCl$ | 23 | 75:25 |
| 18 | Xantphos | — | <5 | — |

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (0.5 mmol), $[Pd(allyl)Cl]_2$ (0.01 mmol), ligand (0.025 mmol), acid (0.5 mmol), anisole (2.0 mL), CO (10 atm), 120 °C, 24 h.
[b] Yields were determined by GC analysis using *n*-cetane as the internal standard.
[c] The ratios of **3aa**:**4aa** (**L/B**) were determined by GC and GC–MS analyses.
[d] $PPh_3$ (0.05 mmol).




**Scheme 4.** Scope of aliphatic alkenes. Reaction conditions: **5** (1.0 mmol), **2a** (0.5 mmol), $[Pd(allyl)Cl]_2$ (0.01 mmol), Xantphos (0.025 mmol), $NH_2OH{\cdot}HCl$ (0.5 mmol), anisole (2.0 mL), CO (10 atm), 120 °C, 24 h. Isolated of **6**; the **L/B** within parentheses were determined by GC and GC–MS analyses.

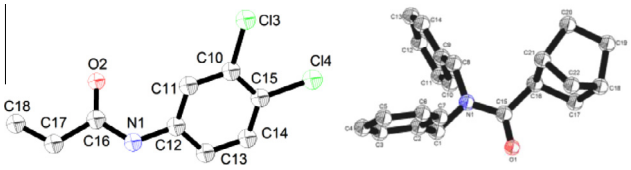
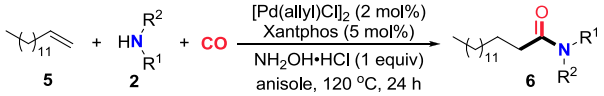



**Figure 1.** X-ray of Propanil (left) and **6oa** (right).

**Table 2**
Optimization of reaction conditions[a]




| Entry | $R^1$, $R^2$ | 6 | Yield (%) | L/B |
|---|---|---|---|---|
| 1 | $R^1 = R^2$ = Bn | **6da** | 84 | 87:13 |
| 2 | $R^1 = R^2 = (4\text{-}ClC_6H_4)CH_2$ | **6db** | 87 | 95:5 |
| 3 | $R^1 = R^2$ = *n*-Pr | **6dc** | 70 | 86:14 |
| 4 | $R^1 = R^2$ = *n*-Bu | **6dd** | 72 | 85:15 |
| 5 | $R^1$ = Bn, $R^2$ = *n*-Pr | **6de** | 70 | 83:17 |
| 6 | $R^1$, $R^2$: piperidyl | **6df** | 64 | 81:19 |
| 7 | $R^1$, $R^2$: morpholyl | **6dg** | 78 | 85:15 |
| 8 | $R^1$, $R^2$: tetrahydroisoquinolyl | **6dh** | 55 | 88:12 |
| 9 | $R^1$ = Bn, $R^2$ = H | **6di** | 73 | 90:10 |
| 10 | $R^1$ = *n*-Bu, $R^2$ = H | **6dj** | 68 | 80:20 |
| 11[b] | $R^1$ = Ph, $R^2$ = H | **6dk** | 72 | 78:22 |
| 12[b] | $R^1 = 3,4\text{-}Cl_2C_6H_3$, $R^2$ = H | **6dl** | 82 | 87:13 |

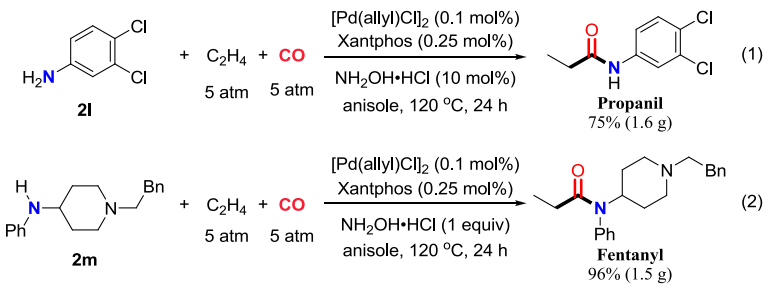
[a] Reaction conditions: **5** (1.0 mmol), **2** (0.5 mmol), $[Pd(allyl)Cl]_2$ (0.01 mmol), Xantphos (0.025 mmol), $NH_2OH{\cdot}HCl$ (0.5 mmol), anisole (2.0 mL), CO (10 atm), 120 °C, 24 h. Isolated of **6**; the **L/B** within parentheses were determined by GC and GC–MS analyses.
[b] $NH_2OH{\cdot}HCl$ (0.05 mmol).

and selectivity to afford the liner products in excellent yields with high regioselectivity (**3da** and **3ja**). It was noteworthy that the reactions with halo-substituted alkenes performed smoothly to give the corresponding amides in 79–89% yields with good regioselectivity (**3ga**–**3ja**), which could be used for further transformations. Moreover, 2-vinylnaphthalene also provided the desired liner product **3la** in a good yield under the current reaction condition. Inspired by these results, we turn our attention to the vinyl-heteroarenes. Surprisingly, when 4-vinylpyridine (**1k**) was employed as the coupling partner, the corresponding branched product **3ka** was obtained as the major product in 60% isolated yield under standard condition. Importantly, this transformation was successful for gram-scale (2.51 g) preparation, giving a comparable yield (76%) by using a much lower amount of catalyst (0.1 mol %).

To further explore the synthetic potential of this process, a series of more challenging aliphatic alkenes were subjected to this reaction under the same reaction condition (Scheme 4). To begin with, ethene was employed and the reaction performed smoothly to give the desired product in 98% yield under 5 atm of ethene. Alkyl substituted olefins with long chain **5b**–**5g** were suitable for the reaction to give products **6ba**–**6ga** in 82–84% yields. Other olefins bearing functional groups, such as chloro, ketone, nitrile, and ester, could be successfully transferred to the desired products **6ha**–**6la** in good yields. It is worth noting that the tolerance of halogens, ketone, and ester functional-group in this carbonylation reaction offers an opportunity for further transformations, which facilitates expedient synthesis of complex amides. As exemplified by reactions of 4-vinylcyclohex-1-ene (**5m**) and (+)-*β*-citronellene (**5n**), the hydroaminocarbonylation reaction took place exclusively at the terminal double bond of dienes to give the corresponding linear amides **6ma** and **6na** in excellent yields, while the internal double bond remained intact. However, the hydroaminocarbonylation of norbornene (**5o**) proceeded well under the same reaction condition to give the exo-product in 83% yield (Fig. 1, right) (determined by X-ray analysis, see Supporting information).[11]

The subsequent study was focused on substrate scope of amines. As summarized in Table 2, various amines were found to be tolerated in this carbonylation process. For example, several secondary aliphatic amines, such as dibenzylamine, dipropylamine, dibutylamine, and *N*-benzylpropan-1-amine were effective substrates to react with tetradec-1-ene smoothly to afford corresponding amides in good to excellent yields with high regioselectivity (70–87% yields). Moreover, typical cyclic amines including piperidine, morpholine, as well as 1,2,3,4-tetrahydroisoquinoline were well tolerated in this transformation, giving corresponding amides in good yields (**6df**–**6dh**), respectively. Not surprisingly, the hydroaminocarbonylation reaction with the primary aliphatic amines proceeded smoothly, offering the corresponding amides in good yields (**6di** and **6dj**). Compared to the aliphatic amines, the anilines proceed smoothly in the presence of catalytic amount of acid, producing the desired products **6dk** and **6dl** in good yields, respectively.

The practice and convenience of this novel method to amides can be readily applied in the synthesis of amide-containing herbicide and pharmaceutical. As shown in the Scheme 5, the herbicide Propanil can be effectively assembled from simple ethene, 3,4-dichloroaniline (**2l**), and CO on a gram scale in the presence of 0.1 mol % palladium catalyst and 10 mol % of weak acid. This approach represents a highly atom-economical and efficient (TON = 375) protocol for the synthesis of Propanil amide from the simple staring materials. The structure of Propanil was confirmed by single-crystal X-ray diffraction analysis (Fig. 1, left).[11] Fentanyl is a potent, synthetic opioid analgesic with a rapid onset and short duration of action, which approximately 80–100 times more potent than morphine.[3] With the newly developed catalytic system, Fentanyl was prepared in gram scale (1.5 g) by hydroaminocarbonylation of ethene with 1-phenethyl-*N*-phenyl-piperidin-4-amine (**2m**) under 5 atm of CO atmosphere in the presence of 0.1 mol % palladium catalyst. The desired pharmaceutical Fentanyl isolated in 96% yield.




**Scheme 5.** One-pot synthesis of Propanil and Fentanyl.

## Conclusions

In summary, we have successfully developed a practical palladium catalytic system for the hydroaminocarbonylation reaction of simple alkenes with both aliphatic and aromatic amines under CO atmosphere. The weak acid was found to be an effective basicity-mask to promote the desired reaction. The catalysis accommodates a diverse set of functional groups including fluoride, chloride, ketone, as well as ester functional groups. Moreover, this reaction can also be employed to one-pot synthesis of the Propanil and Fentanyl, which are important marketed herbicide and drug. Further investigations to gain a detailed mechanistic understanding of this hydroaminocarbonylation reaction and apply this strategy in other Pd–H involved catalysis are currently in progress.

## Acknowledgments

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## Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.12.031.

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11. CCDC 1426598 (Propanil) and 1426607 (**6oa**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif