



Palladium-catalyzed base- and solvent-controlled chemoselective allylation of amino acids with allylic carbonates

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ABSTRACT

The utilization of readily available amino acids, which is not only an oxygen nucleophile but also a nitrogen nucleophile, in palladium-catalyzed allylic substitution is realized under mild conditions. The chemoselectivity and multiple allylation are controlled by adjusting the reaction conditions. This represents the first example of this convenient access to valuable *N,O*-diallylated amino acids. Under the title conditions, a range of amino acids (α -, β -, γ -) and dipeptides can be readily converted in to the corresponding allylic products with excellent yields (67 examples, up to 99% yield) as well as good functional group tolerance.

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Amino acids represent a ubiquitous motif found in natural products and pharmaceuticals [1,2]. They have been involved in a variety of chemical transformations, especially for the synthesis of artificial amino acids, short peptides and polypeptides with specific biological activities, semi-synthetic antibiotics, new herbicide, and insecticide [3–9]. In most cases, these bifunctional substrates have to be protected, either at the amino or at the carboxylic end to ensure selective transformations. For example, amino acid esters have been already widely used in α -allylation due to the *O*-protection of the carboxylic group as an easily removable protecting group. In recent years, transition-metal-catalyzed enantioselective α -allylation of amino acid ester derivatives has received increasing attention because of the exceptional importance of α,α -disubstituted α -amino acids in biological processes; this has been demonstrated by the development of novel nucleophiles (*N*-unprotected and *N,N*-disubstituted amino acid esters, aldimine esters, ketimine esters, etc.) [10–15], electrophiles (allylic substrates, vinyl-cyclopropanes, 1,3-dienes, etc.) [16–19], and even highly efficient catalytic systems (Scheme 1a) [20–22]. However, despite the notable impressive progress achieved in this area of α -allylation,

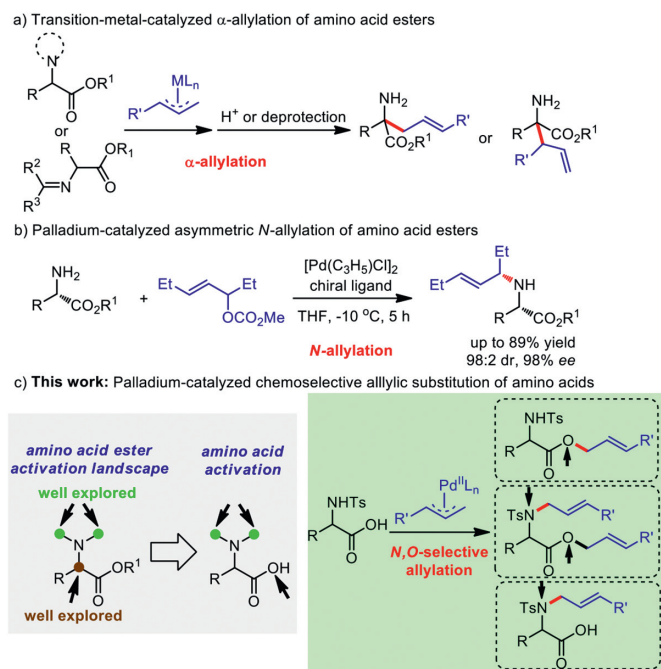
we were surprised to learn that only few examples have been reported for the asymmetric *N*-allylation of amino acid esters [23–29]. As shown in Scheme 1b, Schmalz and co-workers disclosed the stereocontrolled palladium-catalyzed *N*-allylation of amino acid esters, giving the corresponding *N*-allylation products with excellent enantio- and diastereoselectivity [28,29]. Although the solubility and selectivity increase *via* the *O*-protection of the carboxylic group on amino acid, protection may also cause some problems, e.g., increasing the number of synthetic steps and difficulty in deprotecting unstable compounds. Therefore, the development of the direct functionalization of amino acids is greatly required in organic synthesis.

As a matter of fact, compared to amino acid ester as a nucleophile, amino acid contains either N or O reactive sites, which is not only an oxygen nucleophile but also a nitrogen nucleophile (Scheme 1c). Thus, transition-metal-catalyzed *N,O*-selective allylic substitution of amino acids remains a challenge [30–33]. The major challenge in *N,O*-selective allylation is to control the competition between a nitrogen nucleophile and an oxygen nucleophile on amino acid. What is more, there is still only a very limited number of reports documented in the literature that a carboxy group serves as the nucleophile to afford allyl esters [34–45], probably because of the high reactivity of the resulting allylic esters with metal catalysts. Therefore, we were challenged to develop an efficient methodology for such reactions.

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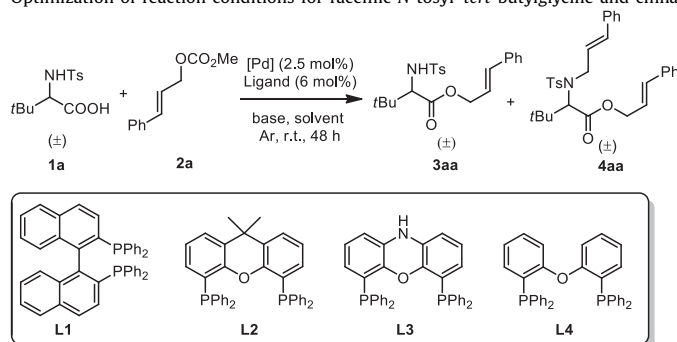
Scheme 1. Development of allylic substitution of amino acid esters and amino acids.

Herein we report the first palladium-catalyzed chemoselective allylic substitution with amino acids as *N*- and *O*-nucleophiles (Scheme 1c). In this context, chemoselectivity for the allylation can be exclusively driven by adjusting the bases and solvents. This new strategy would provide a general and efficient approach to valuable allylated amino acid derivatives.

Our investigation into Pd-catalyzed selective allylic esterifications and aminations began with the evaluation of ligands for coupling racemic *N*-tosyl-*tert*-butylglycine **1a** and (*E*)-cinnamyl methyl carbonate **2a**. Initially, this reaction was conducted in the presence of 2.5 mol% of Pd(PPh₃)₂Cl₂ and 6 mol% of ligand **L1** (BINAP). The *N,O*-diallylated product **4aa** was generated in 35% yield (Table 1, entry 1). To our delight, replacing BINAP with ligand **L2** (Xantphos) gave a substantially improved reaction efficiency (Table 1, entry 2, 86%). Encouraged by this result, a series of phosphine ligands with different bite angles and electronic natures were screened to identify ligands that would improve the reaction activity and selectivity (Table 1, entries 3 and 4, and Table S1 in Supporting information). As a result, Xantphos still turned out to be far superior. These couplings were all screened using Xantphos as the ligand of choice on palladium, which revealed that only Pd(PPh₃)Cl₂ was suitable (Table 1, entries 5–7 and Table S1). Further screening of the reaction conditions revealed that CH₃CN served as the best solvent compared with DCM, 1,4-dioxane, DMF, toluene, EtOAc, THF, DMSO, NMP or CH₃OH (Table 1, entries 8–11 and Table S2 in Supporting information). Increasing the amount of catalyst loading and carbonate reagent led to a higher (94%) yield of **4aa** (Table 1, entry 12).

Table 1

Optimization of reaction conditions for racemic *N*-tosyl-*tert*-butylglycine and cinnamyl methyl carbonate **2a** as substrates.^a



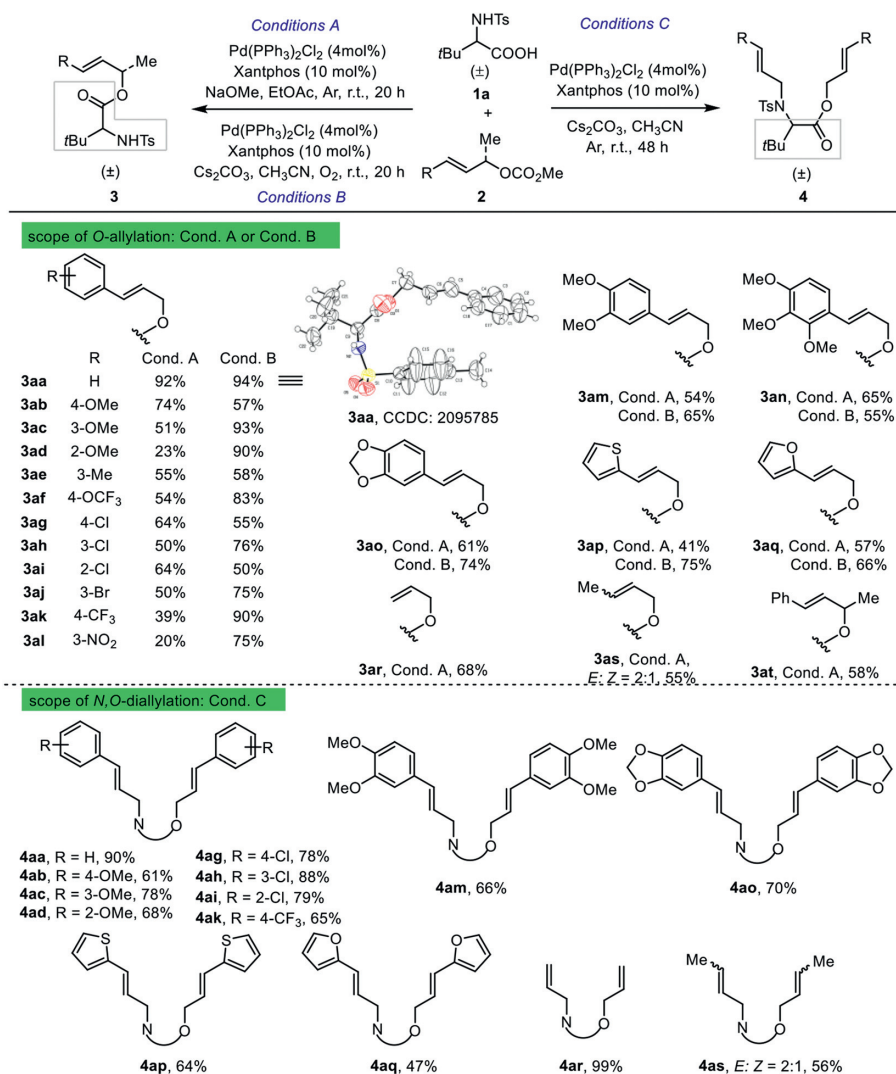
| Entry | 1a/2a | [Pd] | Ligand | Base | Solvent | Yield of 3aa (%) | Yield of 4aa (%) |
|-------------------|--------------|--|-----------|---------------------------------|--------------------|-------------------------|-------------------------|
| 1 | 1/2 | Pd(PPh ₃) ₂ Cl ₂ | L1 | Cs ₂ CO ₃ | CH ₃ CN | – | 35 |
| 2 | 1/2 | Pd(PPh ₃) ₂ Cl ₂ | L2 | Cs ₂ CO ₃ | CH ₃ CN | – | 86 |
| 3 | 1/2 | Pd(PPh ₃) ₂ Cl ₂ | L3 | Cs ₂ CO ₃ | CH ₃ CN | – | 20 |
| 4 | 1/2 | Pd(PPh ₃) ₂ Cl ₂ | L4 | Cs ₂ CO ₃ | CH ₃ CN | – | 30 |
| 5 | 1/2 | Pd(OAc) ₂ | L2 | Cs ₂ CO ₃ | CH ₃ CN | – | 54 |
| 6 | 1/2 | Pd(dba) ₂ | L2 | Cs ₂ CO ₃ | CH ₃ CN | – | 36 |
| 7 | 1/2 | Pd(COD)Cl ₂ | L2 | Cs ₂ CO ₃ | CH ₃ CN | – | 44 |
| 8 | 1/2 | Pd(PPh ₃) ₂ Cl ₂ | L2 | Cs ₂ CO ₃ | DCM | – | 43 |
| 9 | 1/2 | Pd(PPh ₃) ₂ Cl ₂ | L2 | Cs ₂ CO ₃ | 1,4-dioxane | – | 63 |
| 10 | 1/2 | Pd(PPh ₃) ₂ Cl ₂ | L2 | Cs ₂ CO ₃ | DMF | – | 30 |
| 11 | 1/2 | Pd(PPh ₃) ₂ Cl ₂ | L2 | Cs ₂ CO ₃ | EtOAc | 13 | 87 |
| 12 ^b | 1/2.2 | Pd(PPh ₃) ₂ Cl ₂ | L2 | Cs ₂ CO ₃ | CH ₃ CN | – | 94 |
| 13 ^{b,c} | 1/2.2 | Pd(PPh ₃) ₂ Cl ₂ | L2 | Cs ₂ CO ₃ | EtOAc | 78 | 10 |
| 14 ^{b,d} | 1/2.2 | Pd(PPh ₃) ₂ Cl ₂ | L2 | Cs ₂ CO ₃ | EtOAc | 55 | – |
| 15 ^{b,d} | 1/2.2 | Pd(PPh ₃) ₂ Cl ₂ | L2 | Cs ₂ CO ₃ | CH ₃ CN | 99 | – |
| 16 | 1/2 | Pd(PPh ₃) ₂ Cl ₂ | L2 | K ₂ CO ₃ | EtOAc | 20 | – |
| 17 | 1/2 | Pd(PPh ₃) ₂ Cl ₂ | L2 | NaOtBu | EtOAc | 39 | 41 |
| 18 | 1/2 | Pd(PPh ₃) ₂ Cl ₂ | L2 | NaOMe | EtOAc | 73 | – |
| 19 ^b | 1/1.5 | Pd(PPh ₃) ₂ Cl ₂ | L2 | NaOMe | EtOAc | 94 | – |

^a Condition: **1a** (0.1 mmol), **2a** (0.2 mmol), [Pd] (2.5 mol%), ligand (6 mol%), base (0.05 mmol), solvent (1 mL). Yields were determined by ¹H NMR spectroscopy of the crude reaction mixture with 1,2-dibromomethane as internal standard.

^b Pd(PPh₃)₂Cl₂ (4 mol%), and **L2** (10 mol%) were used.

^c Under an atmosphere of ambient air.

^d Under an atmosphere of ambient O₂.

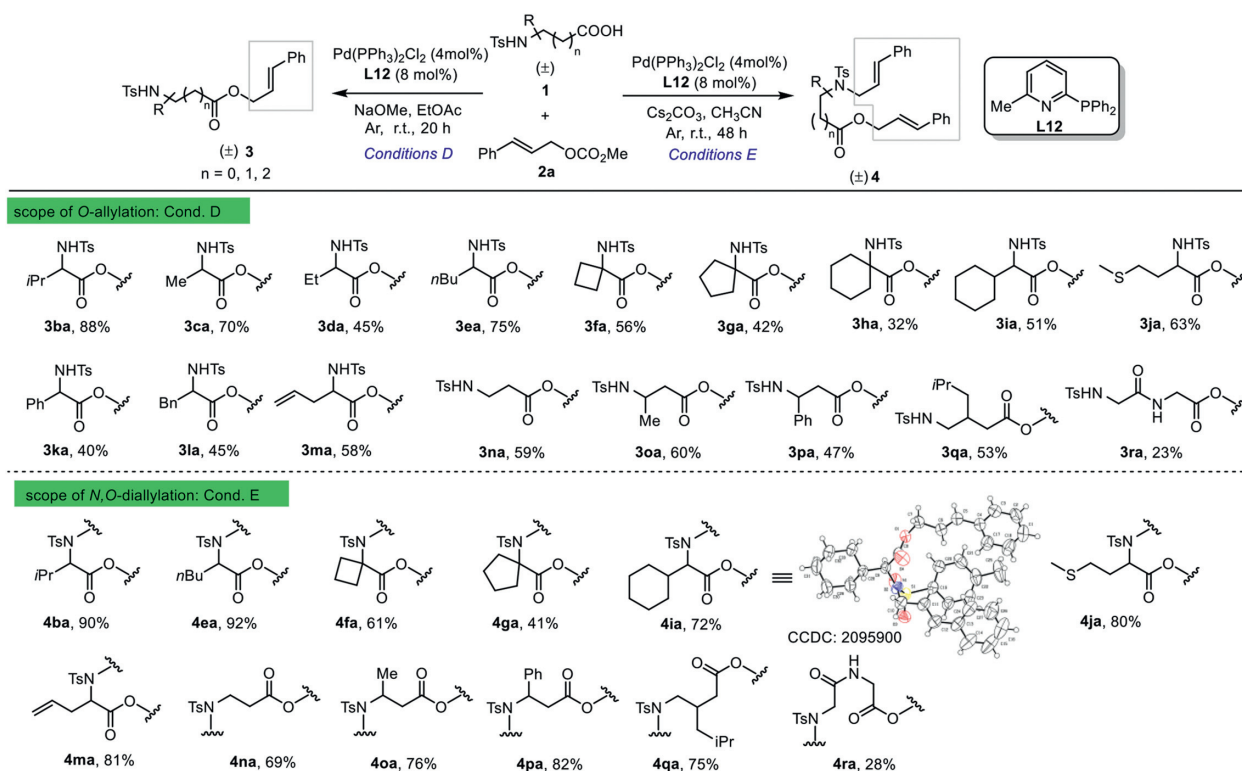


Scheme 2. Scope of the allylic methyl carbonate coupling partner with racemic *tert*-butylglycine. For reaction conditions of *O*-allylation see entries 19 and 15 in Table 1; *N,O*-diallylation see entry 12 in Table 1.

Interestingly, this reaction performed in EtOAc gave the allylic esterification product **3aa**, though with only a 13% yield, which suggested that the selective allylation of *N*-nucleophile or *O*-nucleophile on *tert*-butylglycine was possible by controlling the reaction conditions (Table 1, entry 11). Indeed, conducting the reaction under an atmosphere of air or oxygen led to a remarkable increase in yield of the desired *O*-allylated product **3aa** (Table 1, entries 13 and 14, 78% and 55%). Gratifyingly, using CH₃CN as the reaction medium, conversion of *N*-Ts *tert*-butylglycine **1a** with carbonate **2a** under an O₂ atmosphere resulted in an outstanding yield (entry 15, O₂, **3aa**, 99% vs. entry 12, Ar, **4aa**, 94%). As a Pd-catalyzed allylic C–H acetoxylation [46–48], the beneficial effect of molecular oxygen on the *O*-allylation reflects its ability to enhance the rate by trapping the putative Pd(0)-alkene species and promote C–O reductive elimination from π -allyl-Pd(II) complexes. More importantly, a peroxo-Pd^{II} intermediate could be detected by ESI-HRMS under an atmosphere of ambient O₂ (Fig. S2 in Supporting information for details), which indicated that molecular oxygen may just kill the catalyst in time to prevent the *N*-allylation. Finally, a variety of organic and inorganic bases were screened and NaOMe proved to be the best one for the *O*-allylation product **3aa** (Table 1, entries 16–19 and Table S3 in Supporting information). These findings clearly showcase that (a) the allylic substitution

favors the *O*-nucleophile more than the *N*-nucleophile on amino acids [49] and (b) *N*-allylic alkylation of amino acids could be suppressed when NaOMe and EtOAc were used as the base and solvent or under an O₂ atmosphere. When the Ts group was changed to Ac or H, poor results were delivered and only trace amounts of **3aa** were obtained.

With the optimal conditions established, we first reacted a representative set of allylic carbonates **2** with *N*-tosyl-*tert*-butylglycine **1a** to explore the generality of this reaction. It is noteworthy that *O*-allylic alkylation of *tert*-butylglycine was executed under the reaction conditions presented in entry 15 (Conditions B) or 19 (Conditions A) of Table 1. As summarized in Scheme 2, this transformation demonstrated a broad scope with respect to the allylic carbonate reaction partner under both reaction conditions and the corresponding *O*-allylated products **3aa–3at** were obtained with excellent chemoselectivity of up to 94%. The molecular structure of **3aa** was unambiguously confirmed by X-ray crystallographic analysis (CCDC: 2095785). An array of cinnamyl carbonates **2b–2k** bearing either an electron-donating (e.g., MeO, Me, OCF₃) or an electron-withdrawing (e.g., Cl, Br, CF₃) group at the phenyl ring were all suitable for the reaction, and afforded the desired allylic esters **3ab–3ak** in 58%–93% yields. Notably, the *m*-nitro-substituted carbonate was also tolerated and furnished the



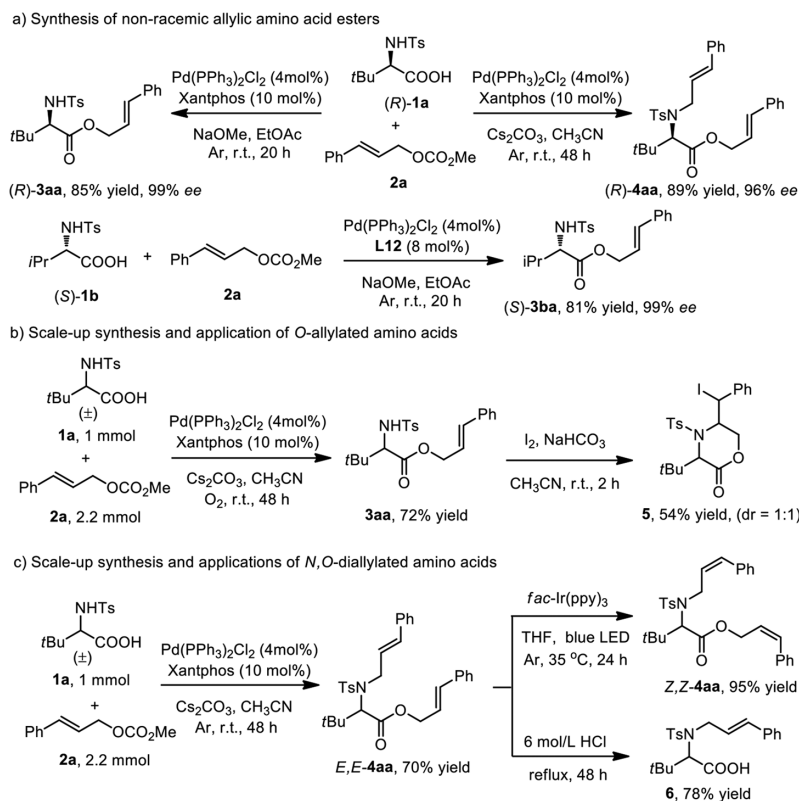
Scheme 3. Scope of the racemic amino acid coupling partner with cinnamyl methyl carbonate. For reaction conditions of O-allylation see Table S5, entry 11 and N,O-diallylation see Table S5, entry 13.

corresponding product **3al** in 75% yield. The presence of *para* (**3ab**, **3af**, **3ag**, and **3ak**), *meta* (**3ac**, **3ae**, **3ah**, **3aj**, and **3al**), or *ortho* (**3ad** and **3ai**) substitutions on the aryl group proved to be feasible. Furthermore, the substrates **2m–2o** with 3,4-di-MeO groups or a bulky fused aryl ring on the phenyl also worked well in this reaction and gave the desired allylic esters **3am–3ao** in 65–74% yields. Importantly, the reactions of 2-thienyl-, 2-furyl-substituted substrates **2p** and **2q** all proceeded smoothly to provide the products **3ap–3aq** in 66% and 75% yields, respectively. Meanwhile, we were pleased to find that our method can also be applied to alkyl carbonates (**3ar** and **3as**, 68% and 55%). Remarkably, 1,3-disubstituted allyl carbonate **2t** reacted smoothly toward the corresponding O-allylic product **3at** in 58% yield. It is interesting to note that in most cases these two conditions could be complemented each other toward the O-allylic substitution of *tert*-butylglycine. Subsequently, we focused on the simultaneous construction of C–O and C–N bonds under optimal conditions of N,O-diallylic substitutions (Table 1, entry 12, Conditions C). The allylation reactions of the carbonates with alkoxy, halogen, trifluoromethyl, and 1,3-benzodioxole groups were successful, producing densely functionalized N,O-diallylated products **4aa–4ao** in 61–90% yields. What is more, heterocyclic aromatic substrates could also react smoothly with *tert*-butylglycine **1a** to give the expected products **4ap** and **4aq** in 64% and 47% yields, respectively. In addition, the reaction using 3-alkyl-allyl carbonate provided **4as** in moderate yield.

Encouraged by these results, we turned our attention to the investigation of the amino acids scope (Table S5 in Supporting information). Frustratingly, it was found that the optimized protocol of the O-allylation (Table 1, entry 19, Conditions A) proved to be ineffective for the N-Ts valine and a poor yield of the desired allylic ester **3ba** was obtained (Table S5, entry 1, 28%). To enhance the activity and selectivity of this reaction, some key factors affecting the performance of this transformation are explored. The best reaction conditions were found with a simple pyridyl-derived

phosphine **L12** as a ligand when reducing the amount of the base (Table S5, entries 11 and 13). To probe the applicability of the developed protocol, the cinnamyl methyl carbonate **2a** was reacted with a set of racemic N-Ts-protected α -amino acids **1**. The results summarized in Scheme 3 show that outstanding chemoselectivities and isolated yields were observed in most cases, independent of the amino acid sidechain. A series of valuable O-allylated and N,O-diallylated amino acid derivatives were finally gained in moderate to good yields (**3ba–3ma**, 32%–88%; **4ba**, **4ea–4ga**, **4ia**, **4ja**, **4ma**, 41%–92%). The molecular structure of N,O-diallylated product **4ia** was established by X-ray crystallographic analysis. Notably, this transformation was found to be compatible with a series of β - and γ -amino acids with excellent selectivity for O-allylation and N,O-diallylation (**3na–3qa**, 47%–60%; **4na–4qa**, 69%–82%). Besides, dipeptide also gave the corresponding products **3ra** and **4ra**.

To further demonstrate the potential applications of this protocol, methyl carbonate **2a** was reacted with non-racemic amino acids such as N-Ts-D-*tert*-butylglycine and N-Ts-L-valine, upon which the desired non-racemic allylic amino acid esters (*R*)-**3aa**, (*R*)-**4aa**, and (*S*)-**3ba** were isolated in high yields and without any detectable loss of absolute stereochemical information (Scheme 4a). Furthermore, the N,O-selective allylic reactions could be easily performed on 1 mmol scale (Schemes 4b and c, 72% and 70%). The application of these allylic amino acids generated by this method is demonstrated in Scheme 4. For example, further transformation of **3aa** was realized by treatment with I₂ and NaHCO₃ in CH₃CN, providing the synthetically valuable morpholin-2-one **5** in 54% yield with 1:1 dr (Scheme 4b). Interestingly, product *E,E*-**4aa** could undergo an isomerization [50], using our previously reported method of a photocatalytic *E* to *Z* isomerization [51] to deliver the *Z,Z*-isomer in high yield (Scheme 4c, *Z,Z*-**4aa**, 95%). More importantly, product **4aa** could also be conveniently transformed into N-allylated amino acid **6** with a good yield upon acidic hydrolysis (Scheme 4c, 78%). So far, three N,O-selective allylation products (O-



Scheme 4. Scale-up synthesis and synthetic applications.

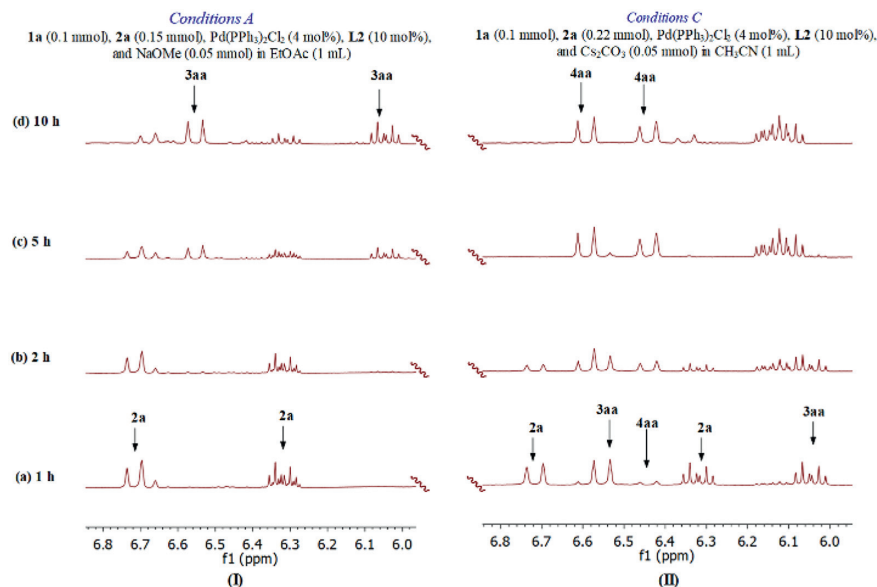
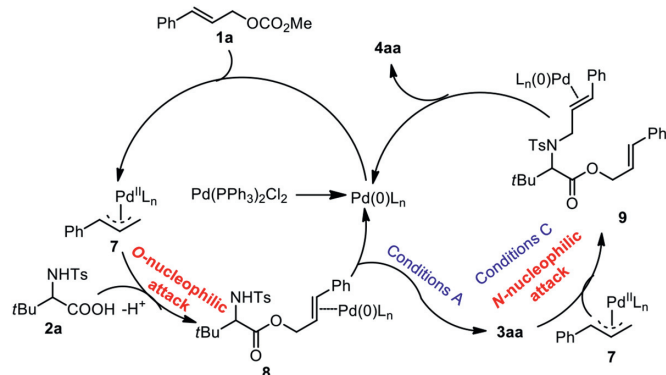


Fig. 1. ¹H NMR Spectra (CDCl₃, 400 MHz): I: performed from **1a** (0.1 mmol), **2a** (0.15 mmol), Pd(PPh₃)₂Cl₂ (4 mol%), **L2** (10 mol%), and NaOMe (0.05 mmol) in EtOAc (1 mL) at room temperature; II: **1a** (0.1 mmol), **2a** (0.22 mmol), Pd(PPh₃)₂Cl₂ (4 mol%), XantPhos (10 mol%), and Cs₂CO₃ (0.05 mmol) in CH₃CN (1 mL) at room temperature.

allylated, *N*-allylated, and *N,O*-diallylated) were obtained through the base and solvent-controlled *N,O*-selective allylation of amino acids. This method provides a new way for the selective modification of amino acids.

To gain insight into the reaction pathway, we examined the reaction processes of *O*-allylic and *N,O*-diallylic substitutions by ¹H NMR spectroscopy of the crude reaction mixtures (Fig. 1 and Fig. S1 in Supporting information). As illustrated in Fig. 1, the ¹H NMR spectra of reaction time clearly show the formation of the desired

products **3aa** and **4aa** under the optimized reaction conditions. The reaction of **1a** with **2a** gave the *O*-allylated amino acid **3aa** under the conditions A after 5 h, and the ¹H NMR spectrum showed two doublets at δ 6.53, *J* = 15.8 Hz and δ 5.18, *J* = 10.8 Hz, and doublet of triplet at δ 6.02, *J* = 15.9, 6.7 Hz (Fig. 1, I-c). The product **4aa** was not observed even extending the allylation time to 48 h. It is important to note that a mixture of **1a** and **2a** followed by Pd-catalyzed allylation under the conditions C after 1 h afforded **3aa** in a good yield, along with a trace amount of **4aa** (Fig. 1, II-a). As



Scheme 5. Proposed mechanism for Pd-catalyzed selective allylic esterification and amination of amino acids.

the reaction progress, *N,O*-diallylated amino acid **4aa** content increased, while *O*-allylated product **3aa** content in the reaction mixture decreased gradually (Fig. 1, II-b-d). These results indicate that the transformation of **3aa** into **4aa** could be crucial for the *N,O*-diallylic substitution. In addition, as the effect of molecular oxygen, the conversion of **3aa** into **4aa** was suppressed in the presence of water (Table S4 in Supporting information).

On the basis of these results, a plausible mechanism for the Pd-catalyzed chemoselective allylation of amino acids is shown in Scheme 5. Similar to other allylic substitutions, oxidative addition of an allylic carbonate (**1a**) to Pd(0) gives a Pd- π -allyl species **7**. Subsequently, the intermediate **7** underwent esterification with amino acid **1a** to form the desired product **3aa** and Pd(0). The *O*-allylation generated product **3aa** which underwent *N*-allylation via the *N*-nucleophilic attack to the intermediate **7**, thus forming a new C–N bond and the final *N,O*-diallylated product **4aa**. When NaOMe and EtOAc are used as the base and solvent, or conducting the reaction under an O₂ atmosphere or with extra water, the catalytic cycle of *N*-allylation is interrupted and the intermediate **9** is not formed during this catalysis.

In conclusion, we have developed the first example of Pd-catalyzed chemoselective allylic alkylation of amino acids with allylic carbonates. The protocol provides a general and efficient approach to various important *O*-allylated, *N*-allylated, and *N,O*-diallylated amino acid derivatives. The simplicity and availability of the amino acid nucleophile, the mild reaction conditions, and the broad scope of the allylic carbonates are the attributes of the present system. We anticipate additional applications of this strategy for catalytic asymmetric carbon–oxygen and carbon–nitrogen bond formations.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ccl.2022.02.029.

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