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Striking AcOH Acceleration in Direct Intramolecular Allylic Amination Reactions

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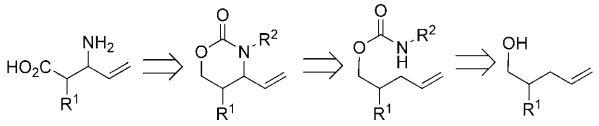
Direct functionalisation of hydrocarbons has attracted much interest for its great potential in organic synthesis.[1] These processes, by avoiding the introduction of functional groups, have atom- and step-economical advantages. In this context, allylic functionalisation of olefins[2] is an active research domain, as witnessed by recent papers on Rh-,[3] Pd-[4] and Ru-catalysed[5] allylic acyloxylations and aminations of olefins.

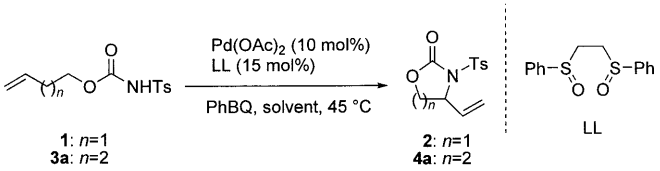
Following our interest in the synthesis of nitrogen derivatives through palladium catalysis,[6] we recently started a project aiming at developing a new method for the synthesis of β-amino acids and 1,3-amino alcohols. The target structures ensue from the cleavage of a 4-vinyl substituted 1,3-oxazinanone ring, itself accessible through direct intramolecular N-functionalisation of the allylic position of a pent-4-enyl carbamate (Scheme 1).



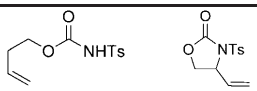
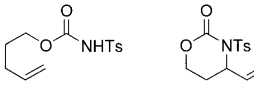
Scheme 1. Allylic C–H activation strategy toward β-aminoacids.

The strategy is inspired by the recent results reported by White on the Pd-catalysed allylic amination of but-3-enyl carbamates.[4e] In this protocol, a disulfoxide chelating ligand favours the formation of a (η^3-allyl)palladium intermediate, which is intramolecularly trapped according to a 5-*exo* process, whereas phenylbenzoquinone (PhBQ) carries out Pd re-oxidation. We selected but-3-enyl *N*-tosylcarbamate (**1**), and pent-4-enyl *N*-tosylcarbamate (**3a**) as models[7] to test the extension of White's protocol from oxazolidinones to oxazinanones (Table 1). Under White's conditions [Pd-

Table 1. From oxazolidinones to oxazinanones as targets: a preliminary screening.[a]



1: *n*=1 **3a**: *n*=2 **2**: *n*=1 **4a**: *n*=2

	Substrate	Product	Solvent	*T* [h]	Yield [%][b]
1			THF	72	73
2			CH_2Cl_2	72	79
3			AcOH	24	90
4			THF	72	77
5			CH_2Cl_2	72	95
6			AcOH	24	70

[a] **1** or **3a** (0.5 mmol), $Pd(OAc)_2$ (10 mol%), 1,2-bis(phenylsulfinyl) ethane (LL) (15 mol%), PhBQ (1.1 equiv), 45 °C. [b] Isolated yields.

$(OAc)_2$ (10 mol%), 1,2-bis(phenylsulfinyl)ethane (LL; 15 mol%), (PhBQ; 1.1 equiv), THF, 45 °C], *N*-tosyl carbamate **1** was converted into oxazolidinone **2** in 73% yield after 72 h (entry 1). Use of CH_2Cl_2 as a solvent (entry 2) increased the yield (79%). Similarly, the homologated *N*-tosylcarbamate **3a**, under the same conditions as entry 1, afforded the expected oxazinanone **4a** in 77% yield (entry 4). Again, improvement of the yield (95%) was observed on going from THF to CH_2Cl_2 (Table 1, entry 5).

Although the formal transition from oxazolidinones to oxazinones turned out to work uneventfully, we were intrigued

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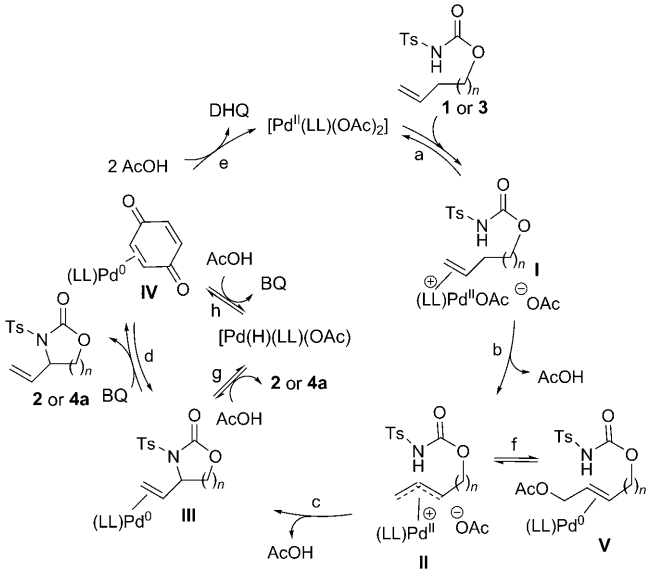
by the sluggishness of these transformations and suspected that a particularly recalcitrant step in the catalytic cycle was responsible for the slow process. The catalytic cycle (Scheme 2) starts with alkene coordination to the [Pd(LL)-



Scheme 2. Catalytic cycle of the direct intramolecular allylic amination.

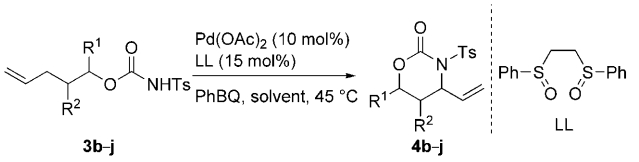
$(OAc)_2$] to give **I** (step a) followed by abstraction of one allylic hydrogen to afford the corresponding (η^3-allyl)palladium complex **II** (step b). Then, the process continues through C–N bond ring closure and formation of the Pd^0-ligated heterocycle **III** (step c). Alkene-to-benzoquinone[8,9] exchange on Pd^0 releases the final product and generates [Pd(LL)(η^2-BQ)] **IV** (step d), which is converted into dihydroquinone (DHQ) and [Pd(LL)$(OAc)_2$] (step e). Also, an equilibrium between the (η^3-allyl)palladium complex **II** and a transient species such as the [Pd^0(LL)(olefin)] complex **V** (step f) cannot be ruled out.

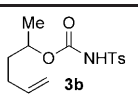
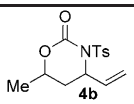
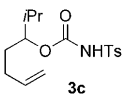
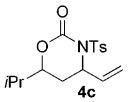
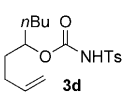
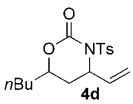
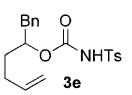
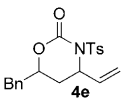
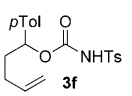
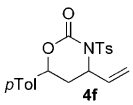
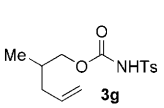
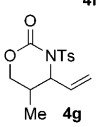
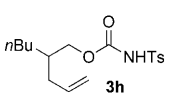
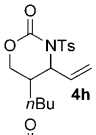
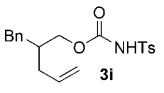
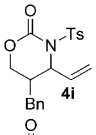
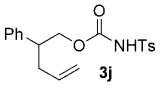
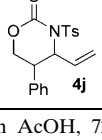
We speculated that either the allylic activation (step b) or the re-oxidation of Pd^0 (step e) could slow down the reaction. With reference to step e, Bäckvall provided convincing evidence that protic activation of benzoquinone is needed for such a redox process.[10,11] Furthermore, acetic acid has been noted to dramatically enhance the reactivity of intramolecular alkene insertions into (η^3-allyl)palladium complexes.[12–14] Finally, AcOH as the solvent may affect the equilibrium of the reversible oxidative addition of the Pd^0 complexes **III** and/or **IV** to give [Pd(H)(LL)(OAc)][15,16] (steps g and h), thereby modifying the amount of the resting state complex.

All the above considerations suggest that acetic acid may have a beneficial effect in the direct allylic amination provided that a switch toward an undesired allylic acetoxylation of the substrate (step f) is avoided.[17,18] Indeed, submission of **1** to the direct allylic amination in the presence of acetic acid as the sole solvent (Table 1, entry 3) gave oxazolidinone **2** in 90% yield in only 24 h! A marked accelerating effect was analogously observed with the homologated substrate **3a**, although in this case the yield of oxazinanone **4a** was not improved (entries 4 and 5 vs. 6).

The effect of the solvent in catalytic experiments was then investigated in more detail. To this purpose, a set of bis(homoallyl)-substituted carbamates (**3b–f**) and another of homoallyl-substituted carbamates (**3g–j**) were synthesised[7] and subjected to the direct allylic amination conditions in CH_2Cl_2 for 72 h and AcOH for 24 h. The results are reported in Table 2. Although the reactions proceeded in both solvents, only AcOH permitted total consumption of the starting substrates. Furthermore, in this solvent the reaction

Table 2. Oxazinanones **4b–j** through direct allylic amination.[a]

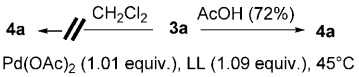


	3	4	Solvent	dr[b]	Yield [%][c]
1	 **3b**	 **4b**	AcOH	83:17	65
2			CH_2Cl_2	≥95:5	12
3	 **3c**	 **4c**	AcOH	89:11	67
4			CH_2Cl_2	74:26	10
5	 **3d**	 **4d**	AcOH	74:26	62
6			CH_2Cl_2	≥95:5	8
7	 **3e**	 **4e**	AcOH	85:15	69
8			CH_2Cl_2	60:40	87
9	 **3f**	 **4f**	AcOH	87:13	64
10			CH_2Cl_2	87:13	36
11	 **3g**	 **4g**	AcOH	67:33	54
12			CH_2Cl_2	50:50	22
13	 **3h**	 **4h**	AcOH	60:40	15
14			CH_2Cl_2	60:40	15
15	 **3i**	 **4i**	AcOH	63:37	57
16			CH_2Cl_2	60:40	35
17	 **3j**	 **4j**	AcOH	71:29	37
18			CH_2Cl_2	60:40	30

[a] Reaction times: 24 h in AcOH, 72 h in CH_2Cl_2. [b] Diastereomeric ratio determined by ^{1}H NMR spectroscopy on the crude product. The relative configuration of the major diastereoisomer was determined by NOESY experiments as *syn* for entries 1–10, whereas it could not be determined for entries 11–18. [c] Isolated yields.

times were much shorter, the yields were better, and, in the case of the bishomoallylically substituted substrates, the diastereoselectivities were enhanced. For example, **4c** was obtained in 10% yield in CH_2Cl_2 and in a more satisfactory 67% yield in AcOH (Table 2 entries 3 and 4) and **4e** as a 60:40 mixture of diastereoisomers in CH_2Cl_2 and as an 85:15 mixture in AcOH (entries 7 and 8). The diastereoselectivity of this allylic amination was found to be very dependent on the substitution pattern when run in CH_2Cl_2, ranging from $\geq$95:5 to 60:40. On the other hand, AcOH as solvent led to diastereoselectivities ranging from 89:11 to 60:40. For homoallyl-substituted substrates, the solvent effect was less dramatic, although noticeable (entries 11–18). For example, oxazinanone **4g** was obtained in 22% yield as a 50:50 mixture of diastereoisomers in CH_2Cl_2, whereas a 67:33 diastereomeric ratio was obtained in 54% yield in AcOH (entries 11 and 12). Compound **4j** was obtained as a 60:40 mixture of diastereoisomers in CH_2Cl_2 and this ratio rose to 71:29 in AcOH (entries 17 and 18).

To gain further mechanistic insight, cyclisation of **3a** was repeated in CH_2Cl_2 and in AcOH by using stoichiometric amounts of $Pd(OAc)_2$ without benzoquinone. While the former experiment led to complete recovery of the starting material, the latter test afforded cleanly the expected oxazinanone **4a** in 72% yield after 22 h at 45°C (Scheme 3).



Scheme 3. Stoichiometric conversion of **3a** into **4a**.

These results suggest that in an aprotic solvent, such as CH_2Cl_2, BQ coordination is necessary to allow the whole process to occur,[19] and prove that AcOH can enable it, even in the absence of BQ, presumably by assisting ionisation through protonation of the coordinated acetate ligands.

Steps d and e were then inspected by DFT calculations.[20] As to the former step, the oxazinanone–benzoquinone substitution (**III**→**IV**) is found to be exothermic by -8.7 kcal mol^{-1}. Then, the detailed events in step e have been monitored in terms of free energies. The [Pd^0(LL)(η^2-BQ)] complex **IV** with two hydrogen-bonded AcOH molecules (the zero-energy point **A** in Figure 1) undergoes a conjugate addition of Pd^0 to BQ through an energy barrier ($\mathbf{TS_{A-B}}$) as high as $+17.9$ kcal mol^{-1}, to give the "fleeting"[21] intermediate **B** ($+10.6$ kcal mol^{-1}). The Pd atom in complex **B** is coordinated by LL, AcO^- and BQ ligands. The last one interacts with the metal through the C atom (Pd–C = 2.19 Å) which lies α to the carbonyl and bends off the C_6 ring by about 10°. In this step the persistent hydrogen-bonding between a second AcOH molecule and BQ is crucial. Indeed, without this interaction the barrier would rise up by about 50%. Furthermore, the concerted incoming of the acetate ligand is fundamental for metal oxidation, as without it, the simply protonated BQ would stay in a likely unproductive dihapto coordination to Pd^0.[22] The electronic flow from **A** to **B** shows that the entering AcO^- ligand assists the transfer of the originally back-donated metal electron pair to the carbon atom, which formally becomes a σ-alkyl donor toward the oxidised d^8 metal. However, the rather long Pd–

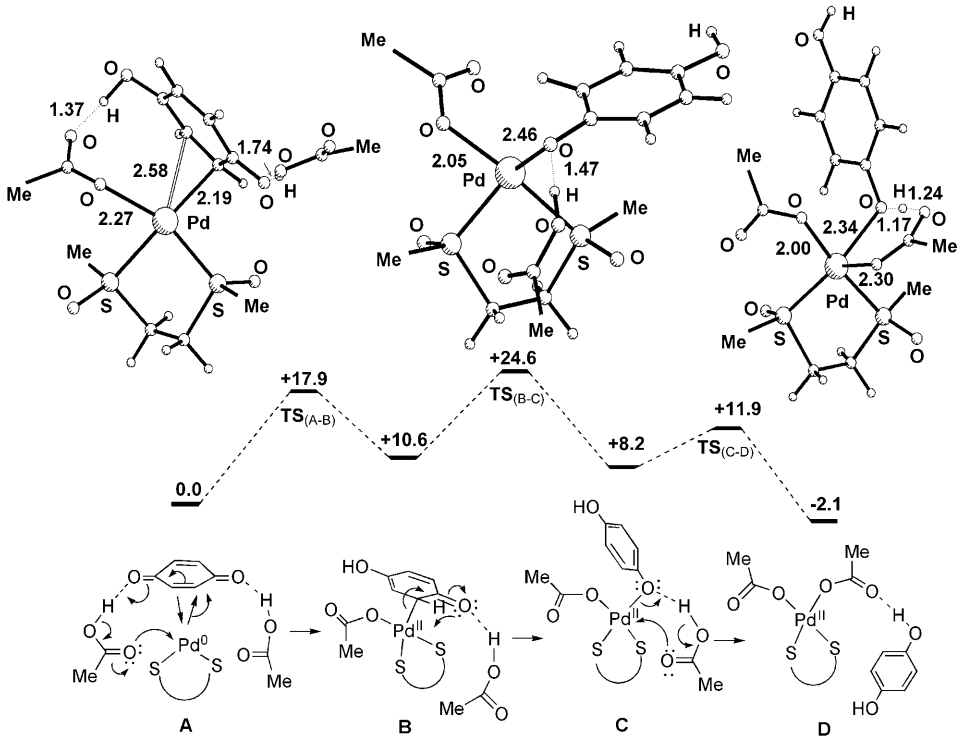


Figure 1. Structural and free energy profile with global electron flow for step e in Scheme 2. The reported ΔG values in kcal mol^{-1} are those of the PCM Model in AcOH solution. All structural details are given in the Supporting Information.

C distance (2.19 Å) and the sum of the bond angles at the coordinated α-C atom ($\Sigma = 350°$)[23] suggest for **B** an already pronounced phenoxide nature with the known η^1-coordination to Pd^{II} of its quasi-aromatic ring.[24]

Then, the phenol character is fully attained in **C**, in which the BQ carbonyl oxygen atom acts as the $2e^-$ donor. Such a major structural rearrangement requires a significant barrier ($\mathbf{TS_{B-C}} = +14.0\ kcal\,mol^{-1}$) and is favoured by $-2.4\ kcal\,mol^{-1}$ with respect to **B**. Again, the step is assisted by strong hydrogen-bonding of the second AcOH molecule (O···H is only 1.47 Å in $\mathbf{TS_{B-C}}$), as without it the barrier increases by 50%. The final step proceeds smoothly ($\mathbf{TS_{C-D}}$ $+3.7\ kcal\,mol^{-1}$) and entails the second BQ protonation with the concomitant coordination of another AcO^- ligand to reach the global minimum **D** ($-2.1\ kcal\,mol^{-1}$ lower than **A**). This minimum consists of dihydroquinone and the regenerated catalyst [Pd(LL)(OAc)$_2$], which are held together by residual hydrogen bonding. These results show that, through the entire process, the two AcOH molecules do not merely release protons and provide acetate ligands, but decisively control the redox and coordination properties of the metal.

In conclusion, we have demonstrated that a strong accelerating effect occurs in direct intramolecular allylic amination when the reaction is conducted in AcOH rather than in CH_2Cl_2 or THF.[19] Under these conditions the yields are usually much higher and diastereomeric ratios less dependent on the substitution pattern of the substrate than under neutral conditions. Stoichiometric tests and computational DFT analysis of the palladium reoxidation step provide an overview of the structural and energetic role of acetic acid in increasing the efficacy of the entire catalytic cycle.[25]

Experimental Section

Typical procedure for the synthesis of oxazinan-2-ones (4a–j): A round bottom flask under air was charged with *N*-tosylcarbamate **3a–j** (0.30 mmol, 1.0 equiv), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol, 0.1 equiv), bis-sulfoxide ligand LL (12.5 mg, 0.045 mmol, 0.15 equiv), phenylbenzoquinone (59.1 mg, 0.321 mmol, 1.07 equiv) and AcOH (0.8 mL). The reaction was allowed to stir at 45 °C for 24 h. The reaction mixture was hydrolysed and extracted with AcOEt. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification by column chromatography (Cyclohexane/AcOEt, 80/20) afforded oxazinan-2-ones (**4a–j**).

Computational details: DFT calculations, at the B3LYP level,[26] were performed with the Gaussian03 program.[27]The SDD[28] and 6–31G-(d,p)[29] basis sets applied to the Pd atom and the other elements, respectively. The nature of all the optimised structures was defined through frequency calculations. Polarisable continuum solvent (AcOH) effects were evaluated by means of PCM single-point calculations on the gas-phase-optimised structures.[30]

Acknowledgements

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Keywords: amination · C–H activation · density functional calculations · palladium · solvent effects

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[7] For the synthesis of the cyclisation precursors see the Supporting Information.

[8] For sake of simplicity, benzoquinone, instead of phenylbenzoquinone, is shown in the mechanism. However, these reactions work almost equally well with the former oxidizing agent.

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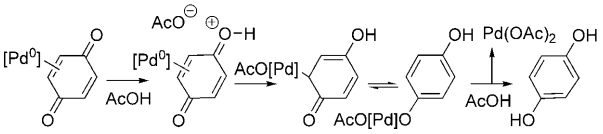
[11] In the mechanism postulated in reference [10], Pd^0 nucleophilic conjugate addition to benzoquinone is triggered through protonation by acetic acid. Subsequent aromatisation through C-to-O palladium shift, followed by ligand displacement releases $Pd(OAc)_2$. .



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[17] The Pd^{II}-catalysed allylic acetoxylation of olefins in acetic acid is a widely known process. See reference [4a], and references therein.
[18] Concerning this potential problem, the huge effective molarity associated with a five- or six-membered ring formation should override alternative intermolecular processes. Should a complex of type **V** be formed, this could re-enter the catalytic cycle through equilibration with **II**.
[19] The non-reactivity of the stoichiometric experiment in CH_2Cl_2 suggests that a further role of BQ in the catalytic experiments is activation of step a or b (e.g., by ionisation). BQ activation of step c (ref. [4c]) without activation of steps a or b seems unlikely due to the evident irreversibility of step b.
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[22] The species corresponds to the second intermediate of the sequence shown in reference [11]. The calculations show that the proton, contested between the coordinated BQ molecule and acetate anion, invariably leads to AcOH.
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