Diastereo- and Enantioselective Palladium-Catalyzed Cycloadditions of 5-Vinyloxazolidine-2,4-diones with Electrophilic Imines

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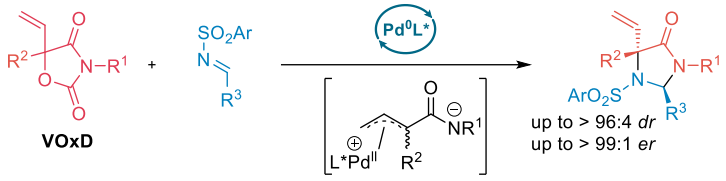
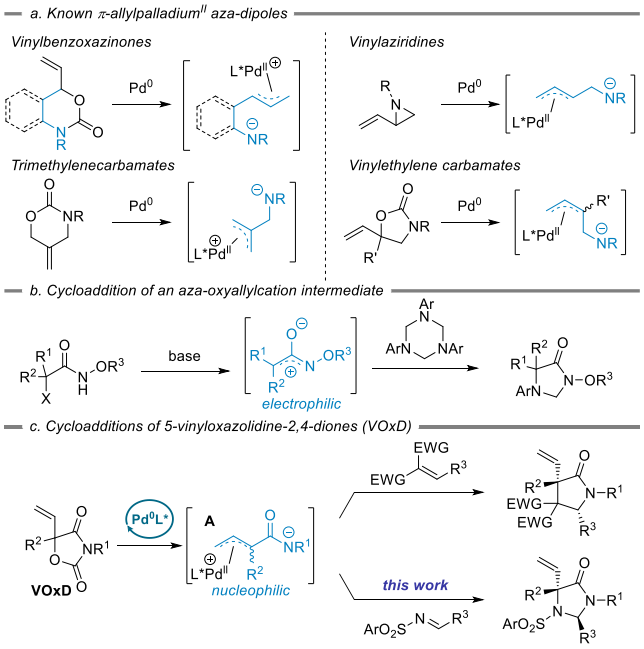
Supporting Information Placeholder



ABSTRACT: Despite the importance of the 4-imidazolidinone scaffold in bioactive compounds or organocatalysts, methodologies to access these nitrogenated heterocycles remain scarce. This manuscript describes a novel preparation of 4-imidazolidinones *via* a diastereo- and enantioselective (3+2) cycloaddition between 5-vinyloxazolidine-2,4-diones (VOxD) and electrophilic imines under palladium catalysis. This work supports the synthetic potential of VOxD as promising equivalents of the C–C(=O)–N synthon.

When devising a synthetic pathway towards valuable heterocycles, cycloadditions are an efficient strategy as these reactions allow the formation of two σ-bonds in a single step.[1] With the opportunity to control the stereochemical outcome of the transformation by careful tuning of the ligands, transition-metal catalyzed cycloaddition has notably attracted considerable attention.[2] Among this field, cycloadditions of π-allylpalladium(II) zwitterionic intermediates have proved to be an efficient tool to access a wide variety of stereodefined heterocycles.[3] Pioneering work using trimethylenemethane precursors[4] and vinylcyclopropanes[5] paved the way for significant progress in this area over the past decade and a wide variety of dipolar intermediates could be reached from different precursors. These transient species are generally formed after a decarboxylative oxidative addition of a Pd^0 catalyst, releasing an electrophilic π-allylmetal moiety connected to a nucleophilic atom. Because of the relevance of *N*-heterocycles in medicinal chemistry, the development of nitrogenated intermediates is of high interest and has been notably highlighted by Tunge's work on the cycloadditions of benzoxazinones.[6] The reactivity of vinylaziridines,[7] vinyl ethylene carbamates[8] or trimethylenecarbamates[9] has also been exploited to access decorated *N*-heterocycles in a stereodefined fashion (Scheme 1a). Recently, novel 5-vinyloxazilidine-2,4-diones (VOxD) have been reported by Guo and our group.[10] This new starting material can act as an efficient synthetic precursor of the C–C(=O)–N synthon in the presence of electrophilic alkenes to furnish enantioenriched γ-lactams *via* the zwitterionic intermediate **A** acting as the nucleophilic partner. We surmised that this new substrate could have a broad interest in synthetic organic chemistry and decided to interrogate its reactivity with other cycloaddition partners.

Scheme 1. Background and summary of this work.



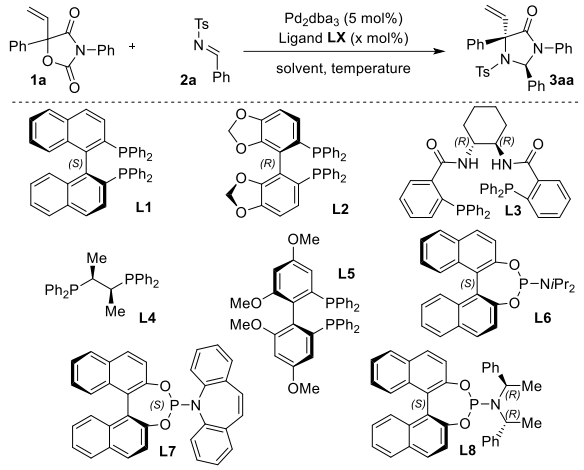
In this context, we explored the preparation of enantioenriched 4-imidazolidinones, an interesting structure encountered in bioactive natural and synthetic compounds.[11] This heterocycle has also been widely popularized by MacMillan as potent organocatalysts for a wide array of transformations.[12]

Strategies to access 4-imidazolidinones are still scarce[13,14] a,d they are often prepared by condensation of an aldehyde or

ketone with an aminoamide derived from the chiral pool.[15] Recently, a (3+2) cycloaddition of an electrophilic aza-oxyallylcation intermediate with nucleophilic 1,3,5-triazines (imine equivalents) has also been reported but this method could not be extended to an asymmetric version (Scheme 1b).[16] In this manuscript, we report a Pd^0-catalyzed diastereo- and enantioselective (3+2) cycloaddition of VOxD with electrophilic imines for the preparation of 4-imidazolidinones (Scheme 1c).

We performed our optimization study using VOxD **1a** and electrophilic *N*-tosylimine **2a** as test-substrates for this reaction. In the presence of (*S*)-BINAP **L1** and Pd_2dba_3 (THF, rt), a very low yield of the expected cycloadduct was observed (Table 1, Entry 1). We were glad to isolate **3aa** in a moderate yield (40%) but promising diastereo- and enantioselectivity (80:20 *er*) when the temperature was risen to 70 °C (Table 1, Entry 2). We then screened various families of ligand and noted that (*R*)-SEGPHOS **L2** allowed the rise of enantiomeric ratio (10:90 *er*) while Trost ligand **L3** showed no reactivity. (*S,S*)-Chiraphos **L4** and (*S*)-Garphos **L5** led to good reactivity but poor yields and enantioselectivities (Table 1, Entries 3 to 6).

Table 1. Optimization Study.[a]



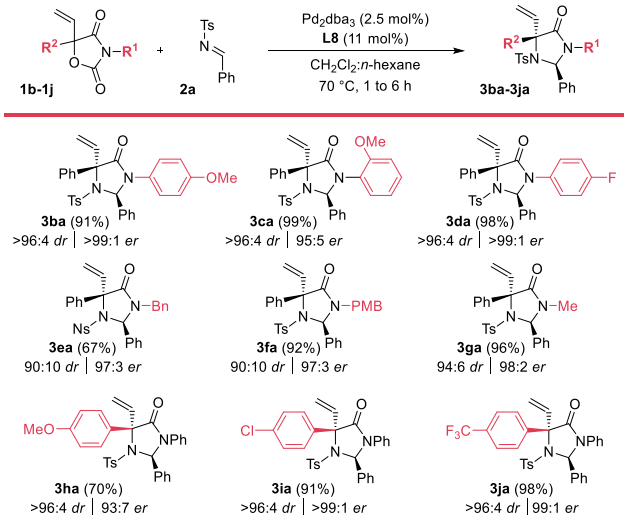
Entry	Ligand (x)	Solvent	t	T (°C)	Yield[c]	*dr*[d]	*er*[e]
1[b]	**L1** (12)	THF	48 h	rt	8[h]	-	-
2[b]	**L1** (12)	THF	24 h	70	40	80:20	81:19
3[b]	**L2** (12)	THF	24 h	70	53	81:19	10:90
4[b]	**L3** (12)	THF	48 h	70	0	-	-
5[b]	**L4** (12)	THF	16 h	70	27	88:12	61:39
6[b]	**L5** (12)	THF	16 h	70	14	75:25	75:25
7[b]	**L6** (22)	THF	48 h	70	55	>96:	95:5
8	**L6** (22)	THF	16 h	70	77	>96:	96:4
9	**L6** (22)	Toluene	16 h	70	89	>96:	96:4
10	**L6** (22)	DCM	48 h	50	93	>96:	98:2
11	**L7** (22)	DCM	48 h	50	51	>96:	95:5
12	**L8** (22)	DCM	48 h	50	84	>96:	>99:1
13	**L8** (22)	DCM:*n*-Hex[f]	4 h	70	99	>96:	>99:1
14[g]	**L8** (11)	DCM:*n*-Hex[f]	5 h	70	99	>96:	>99:1

[a]Reaction conditions: **1a** (0.075 mmol), **2a** (0.050 mmol), Pd_2dba_3 (5 mol%), ligand **LX** (x mol%) in solvent (0.5 mL, 0.1M). [b]**1a** (0.05 mmol) and **2a** (0.075 mmol). [c]Isolated yields. [d]Determined by ^1H NMR analysis of the crude product. [e]Determined by chiral HPLC analysis. [f]1:1. [g]Pd_2dba_3 (2.5 mol%)

However, we then identified electron-rich phosphoramidite **L6** as a suitable ligand for this transformation as imidazolidinone **3aa** was formed as a single diastereomer with good enantioselectivity (95:5 *er*) but still in a moderate yield of 55% (Table 1, Entry 7). The conversion was enhanced when vinyloxazolidine-2,4-dione **1a** was used as the excess reagent (Table 1, Entry 8) without much influence on the stereocontrol. Similar results were obtained in toluene (Table 1, Entry 9) but the enantioselectivity was improved using CH_2Cl_2 as the solvent (Table 1, Entry 10). Other sterically hindered phosphoramidites were then tested out. Ligand **L7** bearing an azepine moiety led to disappointing results with a drop in yield and enantioselectivity (Table 1, Entry 11) but the highly hindered phosphoramidite ligand **L8** furnished the desired product as a single diasteroisomer with excellent enantioselectivity (>99:1 *er*, Table 1, Entry 12) after a rather sluggish transformation (48 h, 84%). A quantitative and faster reaction (4 h) was observed when working at 70 °C in a CH_2Cl_2:*n*-hexane (1:1) mixture, without deterioration of the diastereo- and enantioselectivity (Table 1, Entry 13). Finally, the catalyst loading was lowered to 2.5 mol% without affecting the rate, yield or stereoselectivity of this transformation (Table 1, Entry 14).

With the optimized conditions in hand, we then turned our attention to the evaluation of the reaction's scope and began with the reactivity of the nucleophilic cycloaddition partner. Prepared from various primary amines,[17] an array of VOxD bearing different R^1 substituents on the nitrogen atom were initially tested with imine **2a**. An electron-enriched *p*-methoxyphenyl substituent (**3ba**) was tolerated and the steric hindrance brought by the methoxy group at the *ortho* position also led to the expected cycloadduct **3ca** as a single diastereomer with only a slight drop of enantiocontrol (95:5 *er*). The reaction tolerates an electron-withdrawing fluorine atom in *para* position and proceeded with great diastereo- and enantioselectivity (**3da**). Benzyl and *p*-methoxybenzyl substituted VOxD **1e** (90:10 *dr*, 97:3 *er*) and **1f** (90:10 *dr*, 97:3 *er*), respectively, were readily converted to the expected heterocycles in good yields albeit with a slight drop of diastereo- and enantioselectivity.

Scheme 2. Scope of the VOxD partner

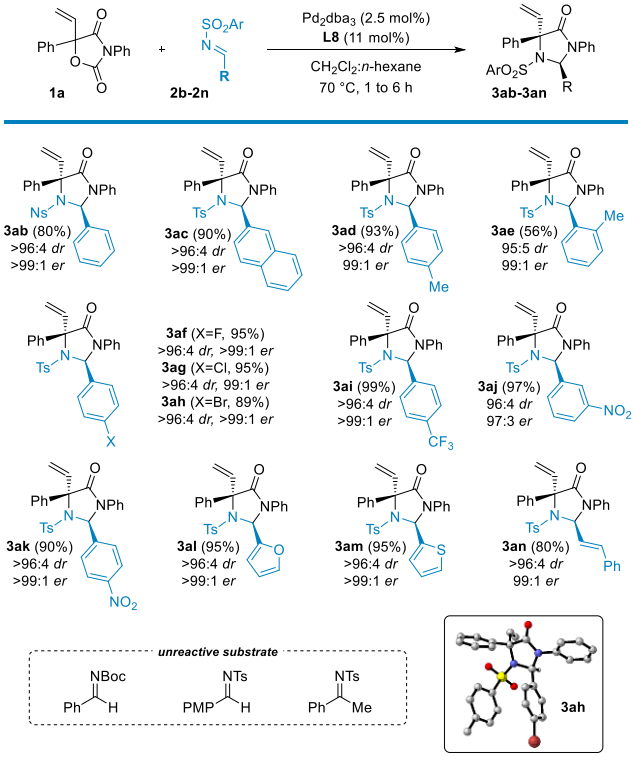


[a] Reaction conditions: **1a**-**1j** (0.30 mmol), **2a** (0.20 mmol), Pd_2dba_3 (2.5 mol%), **L8** (11 mol%), CH_2Cl_2:*n*-hexane (2 mL, 0.1M), 70 °C.

A similar observation was made for the preparation of the *N*-methyl imidazolidinone **3ga** (96%, 97:3 *dr*, 98:2 *er*). Finally the influence of the allylic aryl group R^2 was questioned. While an electron-rich *para*-methoxyphenyl group led to the 4-imidazolidinone **3ha** (70%) with a lower enantioselectivity (93:7 *er*), the presence of an inductive attractor substituent allowed us to isolate cycloadducts **3ia** (*p*-Cl) and **3ja** (*p*-CF_3) in excellent yields, diastereo- and enantioselectivities.

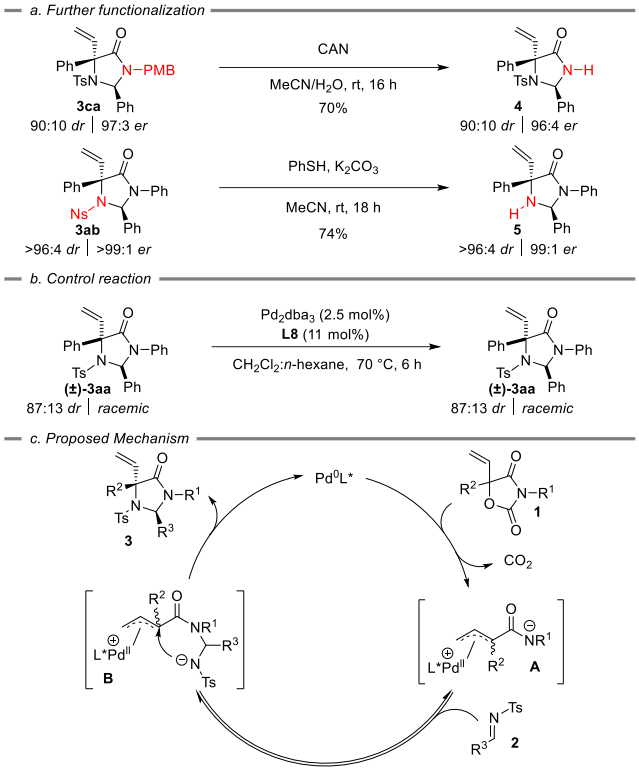
Subsequently, we examined the scope of the electrophilic aldimine using VOxD **1a** as the nucleophilic cycloaddition partner. To our delight, the transformation of *para*-nitrobenzenesulfonyl imine **2b** furnished the expected 4-imidazolidinone **3ab** (80%) as a single diastereo- and enantiomer. At this stage, a limitation to our cycloaddition strategy emerged as less-activated *N*-Boc imines could not be converted to the corresponding cycloadduct. The substitution on the phenyl ring of the aromatic imine was then examined and heterocycle **3ac** (90%) bearing a 2-naphthyl group was prepared. An inductive donor methyl group was successfully installed at the *para* position (**3ad**, 93%). The steric hindrance brought by an *ortho*-methyl substituent resulted in a drop of the yield but imidazolidinone **3ae** (56%) was still isolated with excellent stereocontrol. However, no reactivity was observed when of a more electron-rich sulfonyl imine, derived from *p*-anisaldehyde, was treated under the same reaction conditions. Halogen atoms are also tolerated on the aryl ring: 4-imidazolidinones **3af**, **3ag** and **3ah** substituted at the *para* position by a fluorine, a chlorine and a bromine atom, respectively, were all isolated as single diastereomers in excellent yields and enantiocontrol. An X-ray diffraction analysis of the brominated adduct **3ah** allowed us to determine the absolute configuration of the two newly formed stereocenters.[18]

Scheme 3. Scope of the imine partner.[a]



[a] Reaction conditions: **1a** (0.30 mmol), **2b**-**2n** (0.20 mmol), Pd_2dba_3 (2.5 mol%), **L8** (11 mol%), CH_2Cl_2:*n*-hexane (2 mL, 0.1M), 70 °C.

Scheme 4. Further synthetic transformations and mechanistic considerations.



Electron-deficient *N*-sulfonyl aromatic imines were also suitable substrates for this transformation and imidazolidinone **3ai** (99%) substituted by a *p*-trifluoromethylphenyl group was then prepared with excellent diastereo- and enantiocontrol. Stronger electron-withdrawing nitro groups were installed on the same aryl ring. Both aldimines derived from 3-nitro (**2j**, 97%) and 4-nitrobenzaldehyde (**2k**, 90%) were readily converted to the corresponding heterocycles with excellent stereocontrol. Imidazolidinones **3al** (95%) and **3am** (95%) substituted by heterocyclic 2-furyl and 2-thiophenyl groups, respectively, were also prepared as single diastereomers with excellent enantioselectivity (>99:1 *er*) in both cases. A cinnamyl group (**3an**, 80%) could be installed in place of the aryl moiety with a similar high diastereo- and enantioselectivity. Finally, this strategy was limited to the preparation of imidazolidinones bearing a single substituent at position 2 as ketimines derived from acetophenone or cyclohexanone could not be converted under the usual reaction conditions.

Among the various functional groups tolerated by this methodology, the 4-nosyl (4-Ns) and *para*-methoxybenzyl (PMB) are of interest due to their ease of removal. Hence, **3ca** could be deprotected under oxidative conditions (ceric ammonium nitrate, $MeCN/H_2O$) in good yield and the free amide **4** (70%) was isolated with preservation of stereoselectivity (90:10 *dr*, 96:4 *er*). Upon treatment with potassium thiophenolate, the 4-nosyl group of **3ab** was cleaved to furnish the corresponding secondary amine **5** (74%) without deterioration of the stereomeric ratios (Scheme 4a).

To account for the formation of these heterocycles, a proposed mechanism could start from the ring-opening of VOxD **1** by oxidative addition with a Pd^0 catalyst. After decarboxylation, the

nucleophilic π-allylpalladium(II) zwitterionic intermediate **A** would add reversibly to the electrophilic sulfonimine to form key zwitterionic intermediate **B**. Finally, the anionic nitrogen would add the electrophilic π-allyl moiety during the cyclization step to furnish **3**. When racemic 4-imidazolidinone **(±)-3aa** (87:13 *dr*) was treated under the usual conditions, no evolution of the enantiomeric ratio was observed, suggesting that the last cyclization step is irreversible (Scheme 4b). The observed stereoselectivity could arise from a control by the ligand of both the attack to the imine (**A** to **B**) and the cyclization step (**B** to **3**). However, the first formed stereocenter is far away from the chiral ligand and a more plausible mechanism would involve a DYKAT process where the attack to the imine is reversible while the ring-closure would be the stereodetermining step (Scheme 4c).[19]

In conclusion we have developed a diastereo- and enantioselective methodology towards 4-imidazolidinone heterocycles as (3+2) cycloadducts between vinyloxazolidine-2,4-diones (VOxD) and sulfonimines. Our report confirms the synthetic potential of VOxD as a useful equivalent of the C–(C=O)–N synthon.

ASSOCIATED CONTENT

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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(17) See Supporting Information for details.

(18) XRD analysis of **3ah**: 2268074. The absolution configuration of the other cycloadducts were determined by inference.

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