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Fungicide-inspired precursors of π-allylpalladium intermediates for palladium-catalyzed decarboxylative cycloadditions†

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Inspired by a fungicide, we designed 5-vinyloxazolidine-2,4-diones as new precursors of π-allylpalladium zwitterionic intermediates and developed palladium-catalyzed asymmetric (5 + 3) cycloaddition with azomethine imines and (3 + 2) cycloaddition with 1,1-dicyanoalkenes. Both reactions proceeded smoothly under mild reaction conditions to produce various chiral heterocyclic compounds in high yields with excellent enantioselectivities. These results revealed that 5-vinyloxazolidine-2,4-diones were a type of suitable precursor for palladium catalysis and will find extensive applications in Pd-catalyzed reactions such as cycloaddition and allylic alkylation.

Introduction

Palladium-catalyzed decarboxylative cycloaddition reactions have been intensely studied in the past decade and become one of the most powerful and versatile tools in the selective construction of structurally diverse carbo- and heterocyclic compounds.[1] These reactions proceed *via* π-allylpalladium intermediates *in situ* generated from decarboxylation of precursors. Due to the crucial role of π-allylpalladium intermediates in these transformations, the design and use of new precursors are extremely important for development of palladium-catalyzed cycloadditions and always attract much attention of synthetic chemists. A variety of precursors with diverse structures have been invented to realize numerous useful cycloaddition reactions. On the basis of their structures, these precursors can be categorized as vinyl cyclic carbonates,[2] methylidene cyclic carbonates,[3] vinyl cyclic carbamates,[4] methylidene cyclic carbamates,[5] vinyl lactones,[6] methylidene lactones[7] and acyclic carbonates.[8] Among them, cyclic carbamates[4–5] and lactones[6,7] were usually used for synthesis of functionalized nitrogen heterocycles and carbocycles. In the structures of these typical precursors, an electron-withdrawing group was often needed and linked with an atom at the α-position of the carbonyl in the ring (Scheme 1a). It could assist decarboxylation in the presence of a palladium catalyst to generate a zwitterionic π-allylpalladium intermediate. However, the electron-withdrawing group could not be fused into the ring of the cycloaddition products and is only present as a substituent attached to the ring. The related cycloaddition reactions lack atom economy in terms of ring formation. Obviously, a cyclic precursor having an electron-withdrawing group in the ring will overcome this problem. Nevertheless, such an atom economical cyclic precursor for Pd-catalyzed cycloaddition reactions has not yet been reported to date. During our studies on new pesticides, we found that a fungicide, vinclozolin,[9] provides a wonderful template for design of new precursors (Scheme 1b). Vinclozolin marketed by the BASF was a dicarboximide fungicide that had been widely used in Europe and the United States to protect grapes, fruits, vegetables, hops, ornamental plants, and grass from fungal damage.[9] As indicated in Scheme 1b, vinclozolin can be considered an analogue of vinyl cyclic carbamates, in which the carbonyl plays a role as an electron-withdrawing group, and may decarboxylate in the presence of palladium catalysts to form reactive intermediates to react with various reaction partners. On the basis of its structural features, we designed some new precursors such as cyclic carbonates, carbamates and lactones (Scheme 1b). As our initial discovery, we synthesized various 5-vinyloxazolidine-2,4-diones, which are readily available and are easily modified as required. These precursors produce π-allylpalladium intermediates in the presence of palladium catalysts, which may function as three or five-membered synthons for cycloaddition reactions (Scheme 1b). Herein, we present Pd-catalyzed (5 + 3) and (3 + 2) cycloaddition reactions of 5-vinyloxazolidine-2,4-diones.

Results and discussion

The reaction of 5-vinyloxazolidine-2,4-dione **1e** and azomethine imine **2a** was chosen for screening reaction conditions (Table 1). When a combination of 5 mol% of $Pd_2dba_3 \cdot CHCl_3$

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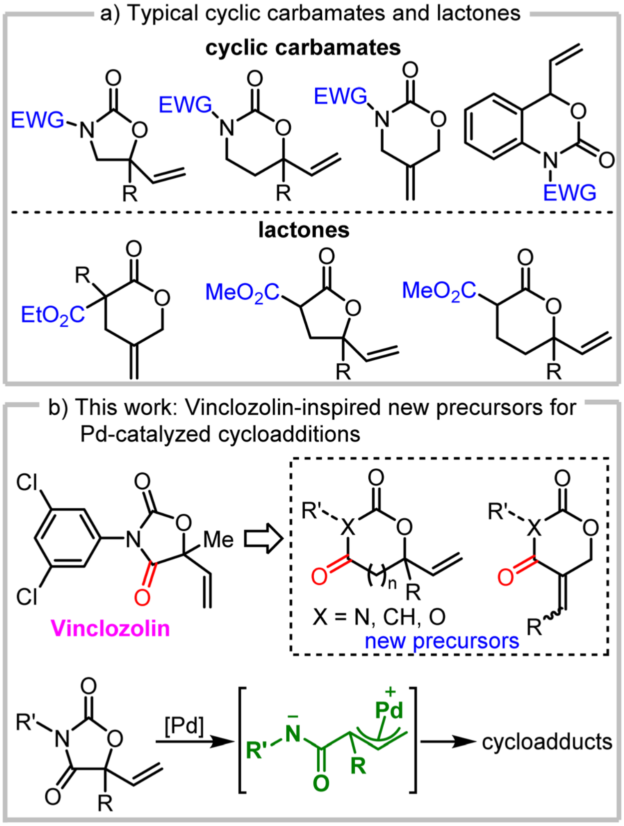
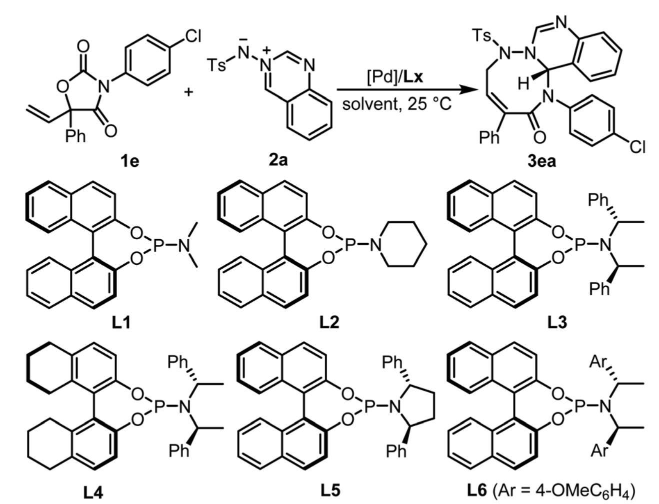


Scheme 1 Typical precursors and vinclozolin-inspired new precursors for palladium-catalyzed cycloadditions.

and 20 mol% of phosphoramidite **L1** was used, the reaction proceeded smoothly in CH_2Cl_2 (DCM) at 25 °C to afford the (5 + 3) cycloaddition product **3ea** in 99% yield, albeit with 65% ee (entry 1). In the case of the piperidine-substituted ligand **L2**, the reaction enantiocontrol was increased to 81% ee (entry 2). Pleasingly, the employment of chiral ligand **L3** resulted in an amazing 92% ee with 91% yield (entry 3). Encouraged by the promising result, more axially chiral phosphoramidite ligands were examined in the presence of $Pd_2dba_3\cdot CHCl_3$ (entries 4–6). The reaction utilizing chiral ligand **L4** worked with lower enantiomeric excess (entry 4). The cyclic amine-derived chiral ligand **L5** displayed weak enantiocontrol, affording the product in 87% yield with poor 23% ee (entry 5). The chiral ligand **L6**, which has an electron-rich methoxy group on the benzene ring, did very well in both yield and enantioselectivity (entry 6). Its catalytic results were comparable to that of chiral ligand **L3**. Some solvents such as toluene, $CHCl_3$, MeCN, DCE (1,2-dichloroethane) and 1,4-dioxane were next screened at 25 °C (entries 7–11). This investigation led to the finding that DCM is optimal for the process in terms of reactivity and enantioselectivity, giving the desired product **3ea** in 91% yield with 92% ee (entry 3 *vs.* entries 7–11). When the reaction was performed at 0 °C under otherwise identical reaction conditions, the yield of the product **3ea** decreased to 81% yield, but the ee value stayed at 92% (entry 12). Further decreasing the temperature to −10 °C almost shut down the reaction (entry 13).

Table 1 Optimization of reaction conditions for Pd-catalyzed (5 + 3) cycloaddition[a]



Entry	Ligand	Solvent	*t* (h)	Yield[b] (%)	ee[c] (%)
1	**L1**	DCM	12	99	65
2	**L2**	DCM	12	96	81
3	**L3**	DCM	12	91	92
4	**L4**	DCM	12	84	83
5	**L5**	DCM	12	87	23
6	**L6**	DCM	12	90	89
7	**L3**	Toluene	12	96	87
8	**L3**	$CHCl_3$	12	Messy	—
9	**L3**	MeCN	12	97	84
10	**L3**	DCE	12	91	90
11	**L3**	Dioxane	12	97	86
12[d]	**L3**	DCM	48	81	92
13[e]	**L3**	DCM	72	Trace	—
14[f]	**L3**	DCM	12	47	90

[a] Unless otherwise indicated, all reactions were performed with **1e** (0.12 mmol), **2a** (0.1 mmol), $Pd_2dba_3\cdot CHCl_3$ (5 mol%), and ligand (20 mol%) in solvent (1.0 mL) at 25 °C under an argon atmosphere. [b] Isolated yields. [c] Determined by chiral HPLC analysis. [d] 0 °C. [e] −10 °C. [f] $Pd_2dba_3\cdot CHCl_3$ (2.5 mol%) and **L3** (10 mol%) were used.

Decreasing the catalyst loading to 2.5 mol% of $Pd_2dba_3\cdot CHCl_3$ and 10 mol% of **L3** led to a significant decrease in the yield (entry 14). On the basis of the above experimental results, the optimal reaction conditions were determined to be the use of $Pd_2dba_3\cdot CHCl_3$ (5.0 mol%) and **L3** (20.0 mol%) as the catalysts at 25 °C in DCM.

With the optimized reaction conditions in hand (Table 1, entry 3), the variation of substituents on nitrogen atoms in the substrates 5-vinyloxazolidine-2,4-diones **1** were investigated in the (5 + 3) cycloaddition of azomethine imine **2a**, and the results are summarized in Table 2. The 5-vinyloxazolidine-2,4-diones **1** bearing electron-withdrawing groups such as F, Cl, Br and CF_3 groups on the benzene ring produced the products **3ba–3ga** with high yields and excellent enantioselectivities (entries 2–7). In general, the 5-vinyloxazolidine-2,4-diones **1** having electron-donating substituents on the benzene ring of the Ar group were

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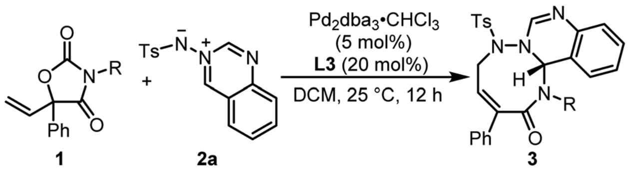
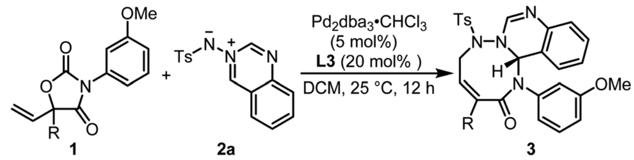
Table 2 The scope of 5-vinyloxazolidine-2,4-diones **1** in Pd-catalyzed (5 + 3) cycloaddition[a]



Entry	R	3	Yield[b] (%)	ee[c] (%)
1	Ph	**3aa**	96	90
2	3-FC_6H_4	**3ba**	80	90
3	4-FC_6H_4	**3ca**	89	91
4	3-ClC_6H_4	**3da**	77	91
5	4-ClC_6H_4	**3ea**	91	92
6	4-BrC_6H_4	**3fa**	76	91
7	4-$CF_3C_6H_4$	**3ga**	71	90
8	3-MeC_6H_4	**3ha**	94	92
9	4-MeC_6H_4	**3ia**	94	90
10	3,5-$Me_2C_6H_3$	**3ja**	95	91
11	3-$OMeC_6H_4$	**3ka**	88	93
12	4-$OMeC_6H_4$	**3la**	86	90
13	4-$OCF_3C_6H_4$	**3ma**	65	90

[a] Unless otherwise indicated, all reactions were performed with **1** (0.12 mmol), **2a** (0.1 mmol), $Pd_2dba_3 \cdot CHCl_3$ (5 mol%) and **L3** (20 mol%) in DCM (1.0 mL) at 25 °C under an argon atmosphere. [b] Isolated yields. [c] Determined by chiral HPLC analysis.

Table 3 The scope of 5-vinyloxazolidine-2,4-diones **1** in Pd-catalyzed (5 + 3) cycloaddition[a]



Entry	R	3	Yield[b] (%)	ee[c] (%)
1	Ph	**3ka**	88	93
2	2-FC_6H_4	**3na**	60	96
3	4-FC_6H_4	**3oa**	95	93
4	3-ClC_6H_4	**3pa**	91	92
5	4-ClC_6H_4	**3qa**	86	96
6	3,4-$Cl_2C_6H_3$	**3ra**	91	95
7	3-BrC_6H_4	**3sa**	83	94
8	4-BrC_6H_4	**3ta**	93	94
9	3-MeC_6H_4	**3ua**	89	92
10	4-MeC_6H_4	**3va**	93	93
11	4-^{i}PrC_6H_4	**3wa**	85	90
12	4-CyC_6H_4	**3xa**	95	88
13	4-^{t}BuC_6H_4	**3ya**	82	90
14	2-Naphthyl	**3za**	96	94
15	3-Thienyl	**3z′a**	91	90

[a] Unless otherwise indicated, all reactions were performed with **1** (0.12 mmol), **2a** (0.1 mmol), $Pd_2dba_3 \cdot CHCl_3$ (5 mol%) and **L3** (20 mol%) in DCM (1.0 mL) at 25 °C under an argon atmosphere. [b] Isolated yields. [c] Determined by chiral HPLC analysis.

also tolerable, affording the desired products in 65–95% yields and 90–93% ee (entries 8–13). The substrate 3,5-dimethylphenyl-substituted **1j** performed the reaction well to afford the product **3ja** in high yield with excellent enantioselectivity (entry 10). Moreover, 4-trifluoromethoxyphenyl-substituted 5-vinyl-oxazolidine-2,4-dione **1m** gave the desired product in 65% yield and 90% ee (entry 13). The absolute configuration of the products was assigned through X-ray crystallographic analysis of the product **3ea.**[10]

Following exploration of the variation of substituents on nitrogen atoms in 5-vinyloxazolidine-2,4-diones **1**, we explored the scope of substituents at the α-position of carbonyl in the same substrates **1** (Table 3). A wide range of aryl substituted 5-vinyloxazolidine-2,4-diones **1** having different electronic and steric properties were well-tolerated, providing various chiral eight-membered heterocyclic compounds (**3ka**, **3na–3z′a**) in high yields with excellent enantioselectivities (entries 1–15). The *o*-fluoro-substituted substrate **1n** displayed good reactivity and enantioselectivity, affording the eight-membered heterocyclic product in 60% yield with 96% ee (entry 2). The disubstituted substrate **1r** having two chlorine atoms worked well too, delivering the corresponding product **3ra** in 91% yield with 95% ee (entry 6). Moreover, 5-vinyloxazolidine-2,4-dione having a 2-naphthyl group reacted smoothly to afford the product in 96% yield and 94% ee (entry 14). Lastly, the heteroaryl-substituted 5-vinyloxazolidine-2,4-dione proved to be a viable precursor of allylpalladium intermediates, giving the corresponding product **3z′a** in 91% yield with 90% ee (entry 15). In addition, 1 mmol (299 mg) of azomethine imine **2a** was reacted with the substrate **1q** for 12 h under the optimal reaction conditions to give the product **3qa** in 96% yield with 95% ee. Furthermore, two alkyl-substituted 5-vinyloxazolidine-2,4-diones such as 3-(3,5-dichlorophenyl)-5-methyl-5-vinyloxazolidine-2,4-dione (vinclozolin) and 3-(4-methoxyphenyl)-5-methyl-5-vinyloxazolidine-2,4-dione were also tried in the current reaction. Unfortunately, both substrates resulted in messy systems under standard reaction conditions and no desired product was observed.

We moved on to evaluate the scope of azomethine imines **2** (Table 4). Several azomethine imines having different substituents or protection groups were examined and the desired products (**3qb–3qi**) were obtained in 66–97% yield with 92–97% ee (entries 1–8). Specifically, the 6-fluoro and 7-bromo-substituted azomethine imines were compatible substrates, providing the corresponding products (**3qb** and **3qc**) in high yields with excellent enantioselectivities (entries 1 and 2). The azomethine imines **2** bearing electron-donating groups such as 6-OMe and 7-OMe exhibited similar reactivities and enantioselectivities as the substrates having electron-withdrawing groups delivered the desired products (**3qd** and **3qe**) (entries 3 and 4). Notably, several other azomethine imines with different sulphonyl protecting groups displayed nearly identically excellent reactivities and enantioselectivities (**3qf–3qi**, 91–97% yields, 94–97% ee) (entries 5–8).

To further investigate the application of 5-vinyloxazolidine-2,4-diones in Pd-catalyzed cycloadditions, we used electron-

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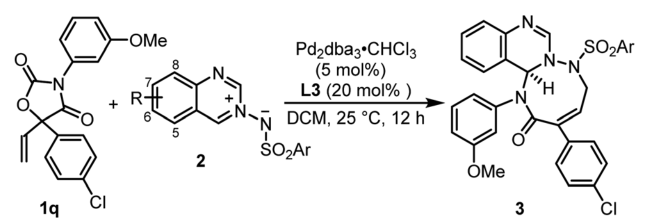
Table 4 The scope of azomethine imines **2** in Pd-catalyzed (5 + 3) cycloaddition[a]

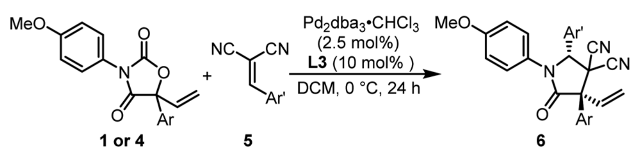


Entry	R	Ar	3	Yield[b] (%)	ee[c] (%)
1	6-F	4-MeC_6H_4	**3qb**	84	96
2	7-Br	4-MeC_6H_4	**3qc**	66	93
3	6-OMe	4-MeC_6H_4	**3qd**	91	92
4	7-OMe	4-MeC_6H_4	**3qe**	69	94
5	H	Ph	**3qf**	97	94
6	H	2,4,6-$Me_3C_6H_2$	**3qg**	91	96
7	H	4-$^tBuC_6H_4$	**3qh**	91	97
8	H	4-$OMeC_6H_4$	**3qi**	93	96

[a] Unless otherwise indicated, all reactions were performed with **1q** (0.12 mmol), **2** (0.1 mmol), $Pd_2dba_3 \cdot CHCl_3$ (5 mol%) and **L3** (20 mol%) in DCM (1.0 mL) at 25 °C under an argon atmosphere. [b] Isolated yields. [c] Determined by chiral HPLC analysis.

deficient olefins as reaction partners to explore new reactions. To our delight, as indicated in Table 5, Pd-catalyzed (3 + 2) cycloaddition of 5-vinyloxazolidine-2,4-diones with trisubstituted olefins was successfully realized. These 5-vinyloxazolidine-2,4-diones **1** or **4** bearing electron-donating or withdrawing groups on the aromatic Ar group were reacted with benzalmalononitrile **5**, affording the corresponding products **6** in 79–97% yield with 91–95% ee (entries 1–6). Under the optimized reaction conditions, 1,1-dicyanoalkenes having either an electron-donating group such as methyl or electron-withdrawing group such as fluoro on the aromatic Ar group displayed good reactivity, delivering the expected products **6ab** and **6ac** in high yields with excellent enantioselectivities (entries 7 and 8). The 1,1-dicyanoalkene **5d** bearing a furan-2-yl group was well accommodated, giving the product in 75% yield with 97% ee (entry 9). The scaled-up reaction was also practicable. The reaction of the alkene **5a** (1 mmol, 154 mg) with 5-vinyloxazolidine-2,4-dione **4a** proceeded smoothly to give the pyrrolidin-2-one derivative **6aa** in 95% yield with 95% ee. The absolute configuration of the products was determined through X-ray crystallographic analysis of the product **6aa**.[10]

Table 5 Pd-catalyzed (3 + 2) cycloaddition with 1,1-dicyanoalkenes[a]

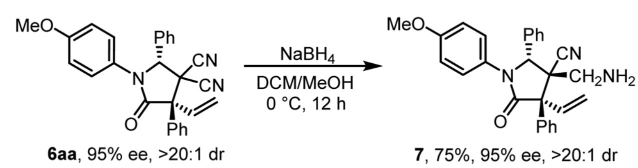


Entry	Ar	Ar′ in 5	6	Yield[b] (%)	ee[c] (%)
1	Ph	Ph	**6aa**	95	95
2	4-ClC_6H_4	Ph	**6ba**	91	91
3	4-BrC_6H_4	Ph	**6ca**	89	91
4	4-MeC_6H_4	Ph	**6da**	79	95
5	2-Naphthyl	Ph	**6ea**	95	92
6	3-Thienyl	Ph	**6fa**	97	92
7	Ph	4-FC_6H_4	**6ab**	82	94
8	Ph	4-MeC_6H_4	**6ac**	86	95
9	Ph	2-Furanyl	**6ad**	75	97

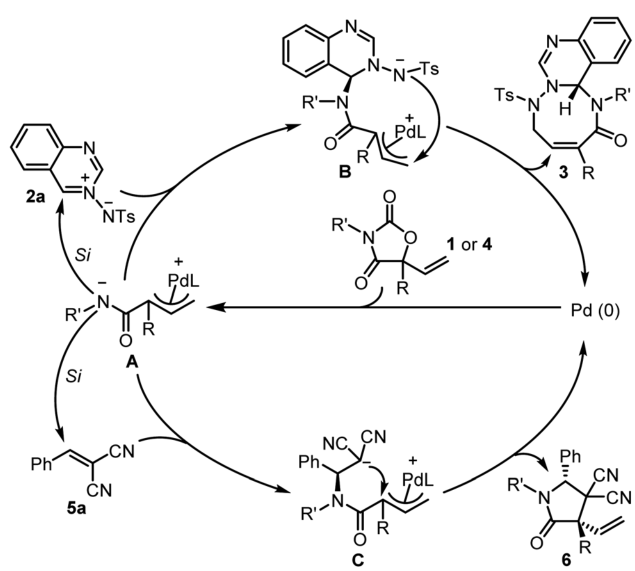
[a] Unless otherwise indicated, all reactions were performed with **1l** or **4** (0.15 mmol), 5 (0.10 mmol), $Pd_2dba_3 \cdot CHCl_3$ (2.5 mol%) and **L3** (10 mol%) in DCM (1.0 mL) at 0 °C under an argon atmosphere. [b] Isolated yields. >20 : 1 dr, determined by ^1H NMR analysis. [c] Determined by chiral HPLC analysis.

Following evaluation of the substrate scope, we carried out further transformation of the product **6aa** (Scheme 2). One of the two cyano groups was reduced to an aminomethyl group with $NaBH_4$ in the mixed solvent (DCM : MeOH = 1 : 1) at 0 °C, thus generating the compound **7** containing three consecutive chiral centers without loss of ee. In the compound **6aa**, the cyano group above the pyrrolidinone ring is situated in a less crowded environment than the one below the ring and thus is more easily reduced, leading to high yield of the monoreduction product. The absolute configuration of the derivative **7** was assigned by X-ray crystallographic analysis.[10]

The reaction mechanisms were proposed as shown in Scheme 3. In the presence of a Pd catalyst, 5-vinyloxazolidine-2,4-dione **1** undergoes a decarboxylation ring-opening reaction



Scheme 2 Further transformation.



Scheme 3 The proposed reaction mechanisms.

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to afford the zwitterionic intermediate **A**, which attacked the azomethine imine **2a** from the *Si* face to give the intermediate **B**. Subsequent intramolecular annulation led to a (5 + 3) annulation product **3**. While internal attack on the π-allyl intermediate could result in (3 + 3) cycloaddition to afford a six-membered heterocycle, steric hindrance from the substrate (*i.e.*, the NT group and tertiary carbon center) might play a significant role in switching the regioselectivity of this process. A terminal attack on the π-allyl intermediate would instead result in a (5 + 3) cycloaddition (Scheme 3). With the use of 1,1-dicyanoalkene **5a** as the electrophilic reagent, the reaction underwent a (3 + 2) annulation to give the five-membered heterocyclic product **6** (Scheme 3), which was easier to form in comparison with the seven-membered cyclic product from a (5 + 2) annulation pathway.

Conclusions

In conclusion, inspired by a fungicide, we designed new precursors of π-allylpalladium zwitterionic intermediates and demonstrated that 5-vinyloxazolidine-2,4-diones were a type of suitable precursor for Pd-catalyzed cycloaddition reactions. With the use of these precursors, we developed Pd-catalyzed asymmetric (5 + 3) cycloaddition with azomethine imines, providing an efficient access to challenging chiral eight-membered heterocyclic compounds in high yields with excellent enantioselectivities. Moreover, we also achieved palladium-catalyzed asymmetric (3 + 2) cycloaddition of 5-vinyloxazolidine-2,4-diones with 1,1-dicyanoalkenes, giving pyrrolidin-2-one derivatives in high yields with excellent diastereoselectivities and enantioselectivities. These results indicated that allylpalladium zwitterionic intermediates from 5-vinyloxazolidine-2,4-diones are versatile reactive intermediates for cycloaddition and allylation reactions and will find extensive application in metal-catalyzed reactions. Further studies on application of 5-vinyloxazolidine-2,4-diones and other new precursors are currently underway in our laboratory.

Author contributions

H. G. conceived and directed the project. K. L. performed reaction experiments and synthesis of substrates. S. Z., W. W. and J. D. performed synthesis of substrates and some data collection. S. Y. and Y. W. helped with the crystallographic data analysis. H. G. and K. L. wrote the manuscript. All authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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