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Palladium-Catalyzed Asymmetric [8+2] Dipolar Cycloadditions of Vinyl Carbamates and Photogenerated Ketenes

Qun-Liang Zhang[a], Qin Xiong[b], Miao-Miao Li[a], Wei Xiong[a], Bing Shi[a], Yu Lan*[b,c], Liang-Qiu Lu*[a,d], and Wen-Jing Xiao[a]

Abstract: Higher-order cycloadditions, particularly [8+2] cycloadditions, are a straightforward and efficient strategy for constructing significant medium-sized architectures. Typically, configuration-restrained conjugated systems are utilized as 8π-components for higher-order concerted cycloadditions. However, for this reason, 10-membered monocyclic skeletons have never been constructed via the catalytic asymmetric [8+2] cycloaddition with high peri- and stereoselectivity. Here, beyond traditional concerted processes, we accomplish an enantioselective [8+2] dipolar cycloaddition via the merger of visible light activation and asymmetric palladium catalysis. This protocol provides a new route to 10-membered monocyclic architectures bearing chiral quaternary stereocenters with high chemo-, peri-, and enantioselectivity. The success of this strategy relied on the facile in-situ generation of Pd-containing 1,8-dipoles and their enantioselective trapping by ketene dipolarophiles, which were formed in situ via a photo-Wolff rearrangement.

Over the past six decades, the importance of higher-order cycloadditions for the construction of medium-sized heterocyclic skeletons has been demonstrated.[1] In this context, since the first work from Doering and Wiley in 1960,[2] a variety of [8+2] cycloadditions have been developed.[3] These transformations usually require configuration-restrained, conjugated 8π-components[4-6] to reduce the reaction complexity and entropic barriers, i.e., to disfavour intramolecular cyclizations and facilitate the periselectivity. Thus, only polycyclic products containing 10-membered units can be obtained with the previous strategies. In addition to chemo- and periselectivity, good enantiocontrol remains a formidable challenge in asymmetric [8+2] cycloadditions. Recently, impressive breakthroughs were achieved by using reactants bearing cycloheptatriene units.[4,7] For example, in 2013, the group of Feng[4a] reported the first Lewis acid-catalyzed enantioselective [8+2] cycloaddition of azaheptafulvenes with alkylidene malonates, producing cycloheptatriene-fused pyrroles in high yields and enantioselectivities (Figure 1A). In 2017, Jørgensen and coworkers[4b] disclosed the first organocatalytic asymmetric [8+2] cycloaddition of electron-deficient heptafulvenes with 2-cycloalkenones, affording polycyclic cycloadducts in moderate yields and high stereoselectivities (Figure 1B). Despite these great advances, the development of new concepts and catalysis systems beyond concerted cycloadditions and the construction of 10-membered monocyclic skeletons are still highly desirable.[1b]

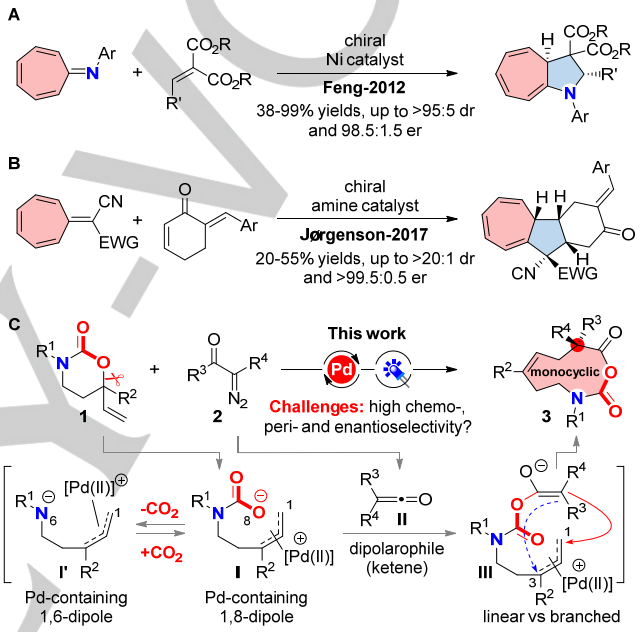

Figure 1. Design plan of catalytic asymmetric [8+2] dipolar cycloadditions.

Based on the pioneering works of Trost[8a] and Tsuji,[8b] dipolar cycloadditions built upon Pd-catalyzed allylic alkylations have been established as a powerful tool for carbo- and heterocycle synthesis.[9] In this field, vinyl carbamates were always utilized as versatile precursors for Pd-containing reactive dipoles through the oxidative addition of a Pd(0) catalyst followed by the release of carbon dioxide (CO_2) from the resulting zwitterionic intermediate.[10] Based on the continued interest in transition-metal-catalyzed dipolar cycloaddition (TMCDC) reactions,[10d,11] we wondered whether the CO_2 unit could be retained,[12] thus providing a promising opportunity for higher-order dipolar cycloadditions. As proposed in Figure 1C, vinyl carbamates **1** were in situ converted to Pd-containing 1,8-dipoles **I** by reacting with suitable Pd(0) catalysts, and reactive ketene dipolarophiles **II**[13] were generated through photo-Wolff rearrangements upon exposure of *α*-diazoketone **2** to visible light.[11c,11e,14] Then, the nucleophilic addition of the carbonate anions to the ketenes and the subsequent intramolecular allylation of the enolate intermediates would result in desired 10-membered monocyclic product **3**. Though reasonable in principle, there are three selectivity issues making the proposed pathway challenging: 1) the intramolecular cyclization of intermediate **I** or its decarboxylative

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variant **I'** would compete with the designed intermolecular cycloaddition; 2) a periselectivity issue exists during the intermolecular addition to ketene **II** depending on the release of CO_2 or not, and the intramolecular allylation step of **III** (linear versus branched selectivity); 3) the enantioselective formation of chiral quaternary stereocenters will also be difficult.[15]

Initially, considering the electronic effect of the amine on the stability of the carbamate, tosyl (Ts)- and 4-MeO-benzyl (PMB)-substituted vinyl carbamates **1a'** and **1a** were prepared and tested in the Pd-catalyzed higher-order dipolar cycloaddition with prepared ketene **IIa** as the dipolarophile and racemic Monophos **L1** as the ligand. The first reaction only provided an inseparable mixture of 6- and 8-membered cycloadducts **4aa'** and **5aa'**, neither of which had retained the CO_2 unit (Figure 2A). To our delight, the second reaction did indeed deliver desired 10-membered monocyclic compound **3aa** (as the racemate) in a good yield (Figure 2B).

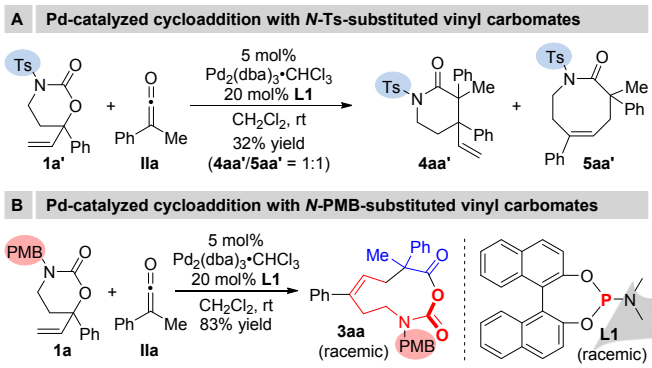

Figure 2. Preliminary trials on the desirgned reaction. dba: dibenzylideneacetone.

Encouraged by the above result, the asymmetric version was explored by applying chiral P,S ligands that were developed in our group. As illustrated in Figure 3A, chiral ligand **L2** bearing a biphenyl phosphoramidite unit, which had a good performance in our previous asymmetric [4+2] dipolar cycloadditions of vinyl benzoxazinones and ketenes,[11c] can also promote this asymmetric higher-order cycloaddition in a good efficiency and enantioselectivity (**L2**: 95% yield, 14:86 er). The use of 3,3'-modified BINOL-derived P,S ligands **L3** and **L4**, which gave the best results in our recently reported Pd-catalyzed asymmetric [4+2] cycloadditions[11f] and Cu-catalyzed asymmetric [3+2] cycloadditions,[11d] could not provide better results on the enantioselectivity (**L3**: 86% yield, 86:14 er; **L4**: 74% yield, 80:20 er). Next, these chiral P,S ligands were modified to further improve the stereoselectivity. Changing the substituent on the nitrogen atom did not affect the enantiocontrol (**L5**: 88% yield, 87:13 er), and removing the substituents on the 3,3'-positions of the BINOL skeleton or two phenyl groups of the diphenylethyl skeleton decreased the enantioselectivities (**L6**: 84% yield, 28:72 er; **L7**: 60% yield, 24:76 er). To our surprise, reversing the relative configurations of the BINOL and diphenylethyl skeletons produced chiral cycloadduct **3aa** in an excellent yield and enantioselectivity (**L8**: 99% yield, 96:4 er). Comparing the enantio-inductions of chiral ligands **L1** and **L6**-**L8**, we concluded that both the chirality of the BINOL and the diphenylethyl skeleton contribute significantly to the stereoselectivity of the reaction, and the match between these two different chiral factors is important for high level of enantiocontrol. Many other standard ligands that are widely used in TMCDC reactions were evaluated, but no better results were observed. For example, when chiral monophosphoramidite ligands (Figure 3B, **L1'**, **L9**-**L11**) were used, cycloadduct **3aa** was generally obtained with much lower yields and er values; when other standard bidentate ligands, such as Trost ligand **L12** or Paltz ligand **L13**, were utilized, no reaction occurred. Under the above reaction conditions, replacing ketene **IIa** with *α*-diazoketone **2a** under the irradiation of 6 W blue LEDs was feasible, and the reaction provided the same product in 49% NMR yield and 96:4 er (Figure 3C, all-in procedure). Later, a simple modification of the operation remarkably improved the yield with the same enantioselectivity (Figure 3C, stepwise, one-pot procedure: 99% NMR yield and 97% isolated yield, 96:4 er).

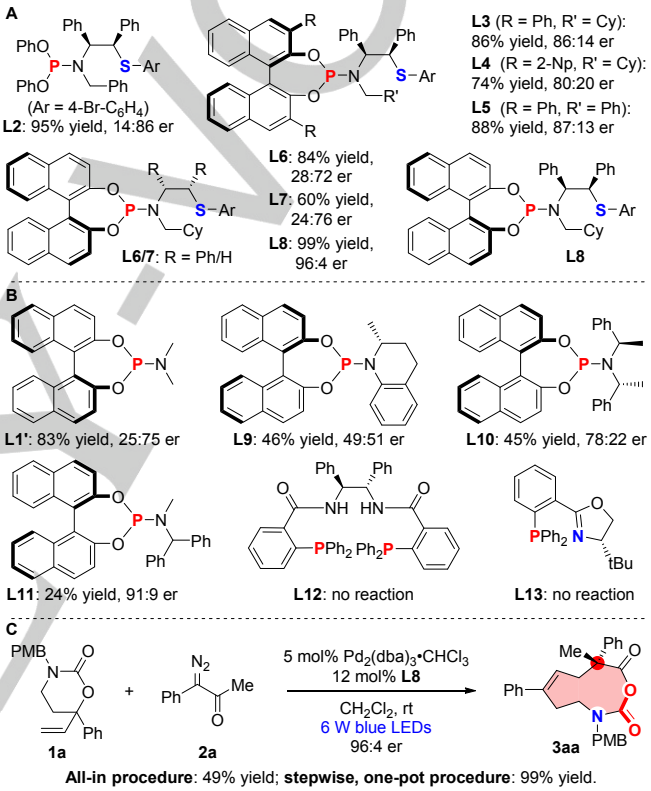

Figure 3. The effect of chiral ligands and procedures on the Pd-catalyzed asymmetric [8+2] cycloaddition.

With the optimal conditions in hand, the generality of this catalytic asymmetric [8+2] dipolar cycloaddition was explored. As highlighted in Table 1, a wide range of vinyl carbamates bearing different aryl groups could readily participate in this higher-order dipolar cycloaddition. For example, variation of the electronic (i.e., H, MeO, F, and Cl) or steric (i.e., *t*-Bu and Ph) effect of aryl ring at the *para*-position were tolerated in the catalytic system, affording the corresponding products in high yields and er values (Table 1, entries 1-6, **3aa**-**3fa**: 88-97% yields and 96:4-97:3 er). Specifically, vinyl carbamates with sensitive aryl groups, such as 4-styrenyl, which is prone to polymerization, were suitable for this cycloaddition (Table 1, entry 7, **3ga**: 90% yield and 95:5 er). Furthermore, variation of the substitution pattern, for example, 3-OMe- and 3,5-diMe-substituted phenyl groups as well as *β*-naphthyl and 3,4-benzodioxolane-fused systems, was proven compatible, delivering the desired cycloadducts with good reaction efficiencies and high levels of

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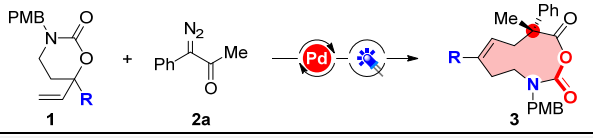
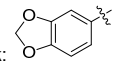
enantiocontrol (Table 1, entries 8-11, **3ha**-**3ka**: 87-93% yields and 95:5-97:3 er). Vinyl carbamate **1l** bearing a heteroaryl moiety, 2-thienyl, was suitable for this reaction, too. Corresponding cycloadduct **3la** was afforded in 86% yield and 94:6 er (Table 1, entry 12). The success of this asymmetric [8+2] cycloaddition could be further extended to substrate **1m** bearing an unsaturated vinyl group, albeit with a slightly decreased reaction efficiency and enantioselectivity (Table 1, entry 13, **3ma**:71% yield and 87:13 er). Notably, 2-aryl or alkyl-substituted vinyl carbamates are not currently applicable in this higher-order cycloaddition.

Table 1: Scope of the Vinyl Carbomate Partners[a]

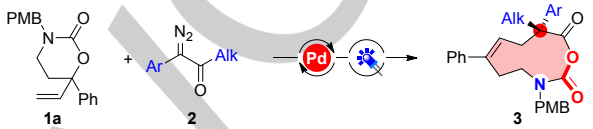


entry	1: R	3	yield (%)[b]	Er[c]
1	**1a**: Ph	**3aa**	97	96:4
2	**1b**: 4-MeO-C_6H_4	**3ba**	95	97:3
3	**1c**: 4-F-C_6H_4	**3ca**	94	96:4
4	**1d**: 4-Cl-C_6H_4	**3da**	91	96:4
5	**1e**: 4-*t*-Bu-C_6H_4	**3ea**	97	96:4
6	**1f**: 4-Ph-C_6H_4	**3fa**	88	96:4
7	**1g**: 4-Vinyl-C_6H_4	**3ga**	90	95:5
8	**1h**: 3-MeO-C_6H_4	**3ha**	93	97:3
9	**1i**: 3,5-2Me-C_6H_3	**3ia**	90	95:5
10	**1j**: *β*-Naphthyl	**3ja**	87	97:3
11	**1k**: 	**3ka**	89	97:3
12	**1l**: 2-Thienyl	**3la**	86	94:6
13	**1m**: Vinyl	**3ma**	71	87:13

[a]Conditions: irradiate **2a** (0.6 mmol) in 1.5 mL of CH_2Cl_2 with 6 W blue LEDs at rt for 5 hours, then transfer the generated ketene solution to a mixture of **1** (0.3 mmol), $Pd_2(dba)_3$•$CHCl_3$ (5 mol%) and chiral ligand **L8** (12 mol%) in CH_2Cl_2 (1.5 mL) and stir at rt for another 10 hours. [b]Isolated yields. [c]Determined by chiral HPLC analysis.

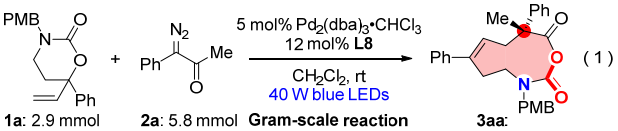
Next, the variation of *α*-diazoketones was studied under the standard reaction conditions. As shown in Table 2, the introduction of electronically different substituents at the 4-position of the phenyl ring was compatible with this catalytic asymmetric [8+2] cycloaddition, producing enantioenriched 10-membered monocyclic compounds in moderate to high yields with high enantioselectivities (Table 2, entries 1-7, **3ab**-**3ah**: 72-91% yields and 94:6-97:3 er values). Notably, the structure and absolute configuration of 10-memered product **3ah** were unambiguously established by single-crystal X-ray diffraction; the structures of other cycloadducts were assigned by analogy.[17] Moreover, *α*-diazoketones bearing 3-substituted aryl moieties (Table 2, entries 8-10) or a *β*-naphthyl group (Table 2, entry 11) were found to be suitable feedstock for this asymmetric cycloaddition, affording medium-sized cycloadducts in 70-92% yields and with ≥95:5 er values. In addition to methyl, *α*-diazoketones with other alkyl groups, such as ethyl, *n*-butyl, and benzyl ether-containing propyl groups, were examined, and they led to corresponding cycloadducts **3am**-**3ao** in 54-94% yields and 95:5-96:4 er values. While, *α*-diazoketones bearing alkenyl functional group and 2-aryl group, cannot participate in this transformation, and it is not yet clear why. To show the utility of the present methodology, a gram-scale reaction was performed with substrates **1a** and **2a** under the standard conditions. Desired product **3aa** can be obtained in 81% isolated yield with 96:4 er (Eq. 1). Additionally, the treatment of compound **3aa** with trace *N*-methylpiperidine under solvent-free conditions at 180 °C for 30 mins produced 8-membered monocycle **5aa** in a moderate yield with retention of the optical purity (Eq. 2).[18]

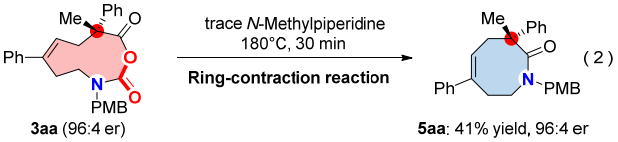
Table 2: Scope of the α-Diazoketone Partners[a]



entry	2: Ar, Alk	3	yield(%)[b]	Er[c]
1	**2b**: 4-Me-C_6H_4, Me	**3ab**	91	95:5
2	**2c**: 4-F-C_6H_4, Me	**3ac**	91	95:5
3[d]	**2d**: 4-Cl-C_6H_4, Me	**3ad**	81	96:4
4[d]	**2e**: 4-Br-C_6H_4, Me	**3ae**	72	95:5
5[d]	**2f**: 4-CO_2Me-C_6H_4, Me	**3af**	89	97:3
6[d]	**2g**: 4-CF_3-C_6H_4, Me	**3ag**	72	96:4
7	**2h**: 4-Ph-C_6H_4, Me	**3ah**	90	94:6
8	**2i**: 3-MeO-C_6H_4, Me	**3ai**	92	97:3
9[d]	**2j**: 3-F-C_6H_4, Me	**3aj**	70	96:4
10[d]	**2k**: 3-Cl-C_6H_4, Me	**3ak**	74	96:4
11	**2l**: *β*-Naphthyl, Me	**3al**	90	95:5
12	**2m**: Ph, Et	**3am**	94	96:4
13	**2n**: Ph, *n*-Bu	**3an**	79	95:5
14	**2o**: Ph, BnO(CH_2)$_3$	**3ao**	54	96:4

[a-c]The same with Table 1. [d]Reaction conditions B (all-in operation): mix $Pd_2(dba)_3$•$CHCl_3$ (5 mol%) and chiral ligand **L3** (12 mol%) in 1-chlorobutane/1,2-dichloroethane (3 mL, 1:1) and stir at rt for 30 min, then introduce **1a** (0.3 mmol) and **2** (0.6 mmol) and stir for another 10 hours under the irradiation of 6 W blue LEDs; others are the same with reaction conditions A.





Furthermore, preliminary density functional theory (DFT) calculations were performed to elucidate the origin of the observed chemo- and periselectivity.[16] A simplified variant of optimal ligand **L8** (Ph and Cy groups were replaced with Me groups) was used for the cycloadditions of both vinyl carbamate **1a** (PMB) and **1a'** (Ts). As shown in Figures S2 and S3 in Supporting Information, the oxidative addition of the Pd catalyst to substrates **1a** and **1a'** is the rate-determined step in each reaction (for **1a**, ΔG = 25.3 kcal/mol; for **1a'**, ΔG = 21.5 kcal/mol). Furthermore, compared with the nucleophilic addition to the ketene dipolarophile, it is much more difficult for resulting zwitterionic intermediate **PMP-II** to release CO_2 (for addition, ΔG = 12.5 kcal/mol; for CO_2 release, ΔG = 17.9 kcal/mol), while in the case of **Ts-II,** the opposite trend was observed by analyzing the difference in the activation energies. As illustrated Figure S4, comparisons of bond order (BO) and bond length (BL) confirmed that it is more difficult to break the C-N bond to release CO_2 from **PMP-II** ($BO_{C\text{-}N}$ = 1.1954; $BL_{C\text{-}N}$ = 1.44 Å) than from **Ts-II** ($BO_{C\text{-}N}$ = 0.5844; $BL_{C\text{-}N}$ = 1.50 Å). In the case of substrate **1a**, two possibilities for the intramolecular allylic alkylation of the adduct of **PMP-II** with ketene **2a** were investigated: the linear selectivity leading to the 10-membered cyclic product seems to be favored over the branched selectivity leading to the 8-membered cyclic product based on their activation energies (ΔG = 5.3 kcal/mol vs 9.0 kcal/mol). These DFT results were in accordance with the experimentally observed chemo- and periselectivity of these higher-order cycloadditions of **1a** and **1a'**.

In conclusion, we have successfully developed the first Pd-catalyzed asymmetric [8+2] dipolar cycloaddition of vinyl carbamates with photogenerated ketenes. This transformation provides a mild and highly selective protocol for accessing a wide range of enantioenriched 10-membered monocyclic compounds with chiral quaternary stereocenters. Moreover, preliminary DFT calculations were performed to rationalize the high chemo- and periselectivity. Although further analysis of the stereochemical outcome is ongoing, this catalytic asymmetric [8+2] dipolar cycloaddition provides a new platform for the higher-order cycloaddition and enantioselective construction of medium-sized monocyclic architectures.

Acknowledgements

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Keywords: [8+2] cycloaddition • medium-sized ring • palladium catalysis • visible light

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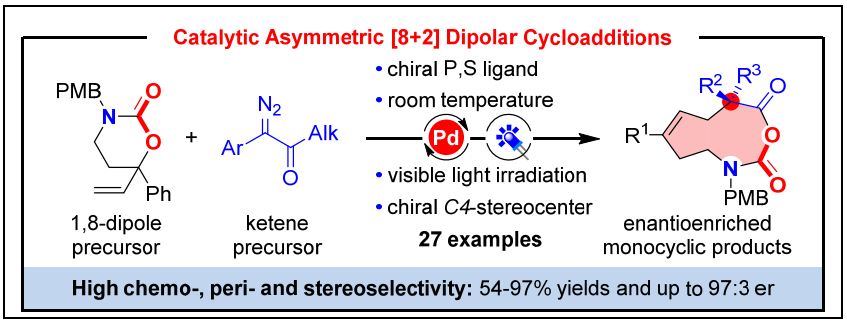

With the help of visible light irradiation and chiral palladium catalyst, an enantioselective [8+2] cycloaddition of vinyl carbomates and α-diazoketones has been accomplished with high peri-, chemo- and stereoselectivity. This protocol provides an unprecedented and straightforward route to 10-membered monocyclic products bearing chiral quaternary stereocenters under extremely mild conditions (i.e., room temperature and 6 W blue LEDs).

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