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Report

Allylic compounds, Allylation, Indole, Cycloaddition, Substitution

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Design and Application of Indole-Based Allylic Donors for Pd-Catalyzed Decarboxylative Allylation Reactions

Qing-Qing Hang,[a] Si-Jia Liu,[a] Lei Yu,[a] Ting-Ting Sun,[a] Yu-Chen Zhang,*[,a] Guang-Jian Mei*[,a] and Feng Shi*[,a]

[a] *School of Chemistry and Materials Science, Jiangsu Normal University, Xuzhou, 221116, P. R. China.*

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Summary of main observation and conclusion A new class of indole-based allylic donors have been designed and developed for palladium-catalyzed decarboxylative allylations. In addition, the first application of these indole-based allylic donors in palladium-catalyzed decarboxylative [3+2] cycloaddition and allylic amination has been achieved by reacting with isocyanates and sulfonyl amines, respectively. This approach represents the first design of indole-based allylic donors, which is helpful for settling the challenge of designing and developing new class of heterocycle-based allylic donors for Pd-catalyzed decarboxylative allylation reactions. Moreover, the application of this new class of allylic donors in cycloadditions and substitutions will add new contents to the research field of decarboxylative allylation.

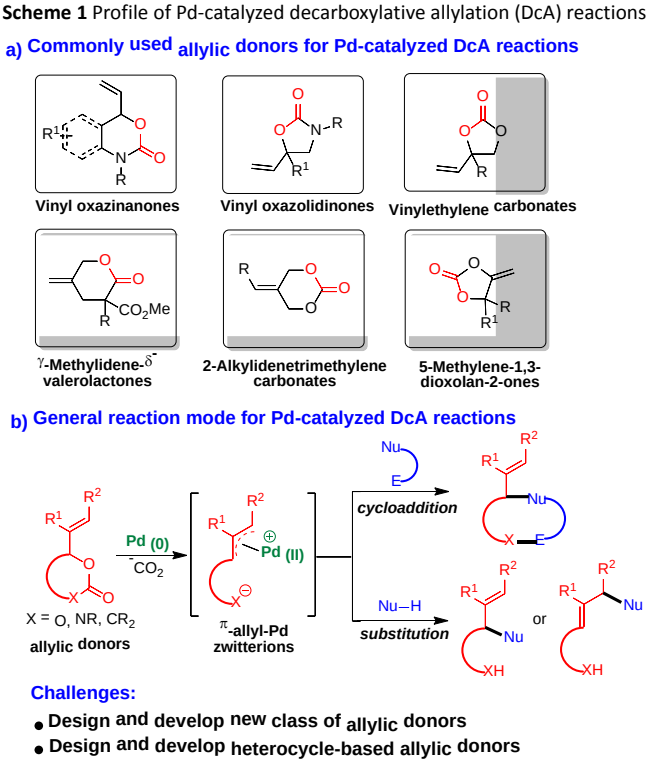
Background and Originality Content

Transition-metal-catalyzed allylation reactions belong to a class of important transformations for forming new covalent bonds.[1-2] Among them, palladium-catalyzed decarboxylative allylation (DcA) reaction has developed rapidly due to its unique characteristics such as generating organometallic intermediates via decarboxylation of allylic donors under mild conditions, which are easily intercepted by another reaction partner to construct useful frameworks.[3]

The rapid development of this class of reactions relies on the design and synthesis of decarboxylative allylic donors with high reactivity. As illustrated in Scheme 1a, commonly used allylic donors for Pd-catalyzed DcA reactions mainly include vinyl oxazinanones,[4-6] vinyl oxazolidinones,[7-8] vinylethylene carbonates,[9-10] γ-methylidene-δ-valerolactones,[11-12] 2-alkylidenetrimethylene carbonates,[13] 5-methylene-1,3-dioxolan-2-ones[14] and so on.[3] Up to date, Pd-catalyzed DcA reactions of these allylic donors have been well-established. The general reaction mode of Pd-catalyzed DcA reactions is summarized in Scheme 1b. Namely, in the presence of Pd (0) catalyst, allylic donors underwent decarboxylation to generate zwitterionic π-allylpalladium intermediate, which could further undergo cycloadditions or substitutions with another reaction partner.[3]

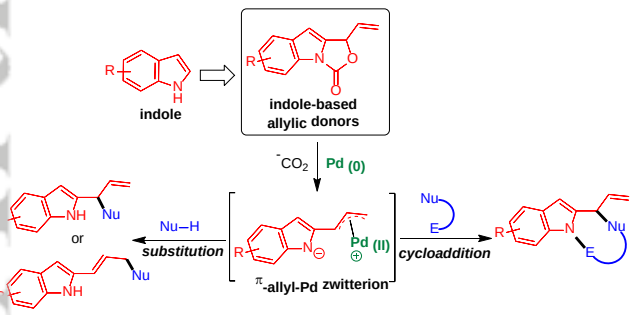
However, in spite of these progresses, there are still some challenges required to be solved in this research field. For example, the type of allylic donors for Pd-catalyzed DcA reactions is very limited, and these commonly used allylic donors were designed and first synthesized almost ten years ago. So, *it has become an urgent task to design and develop new class of allylic donors for Pd-catalyzed DcA reactions*. Furthermore, heterocycle-based allylic donors have scarcely been designed and synthesized for Pd-catalyzed DcA reactions, which nevertheless will provide an easy access to biologically relevant heterocyclic frameworks. Therefore, *it is highly desired to design and develop new class of heterocycle-based allylic donors for Pd-catalyzed DcA reactions*.

Scheme 1 Profile of Pd-catalyzed decarboxylative allylation (DcA) reactions



To fufill this task, we decided to incorporate the indole core to the structure of allylic donors based on the consideration that indole represents one of the most important heterocycles[15] and the efficient synthesis of indole derivatives has become a lasting goal in the synthetic community.[16] So, on the basis of our understanding of indole-based platform molecules,[16f,17] we designed this new class of indole-based allylic donors for DcA reactions (Scheme 2). In the presence of Pd (0) catalyst, this class of indole-based allylic donors would transform into π-allyl-Pd zwitterion intermediate, which could principally undergo cycloaddition and substitution reactions with different reaction partners, thus providing an easy access to indole derivatives. Enlightened by this design, we synthesized this new class of indole-based allylic donors and realized two different types of DcA reactions. Herein, we reported the details of our investigation.

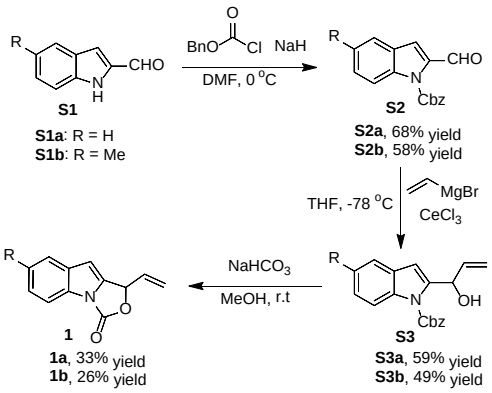
Scheme 2 Design of new class of indole-based allylic donors for DcA reactions



Results and Discussion

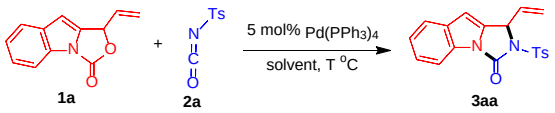
Based on our design of this new class of indole-based allylic donors, we developed a synthetic route for vinyl oxazoloindol-3-ones **1** (Scheme 3). Indole-2-carbaldehydes **S1** were utilized as starting materials, which underwent an acylation reaction with benzoyl chloride to give *N*-Cbz-protected indole-2-carbaldehydes **S2** in moderate to good yields. Then, the addition of vinylmagnesium bromide to the aldehyde group of **S2** resulted in allylic alcohols **S3** in moderate yields. Finally, an intramolecular ester-exchange led to the cyclization and the formation of vinyl oxazoloindol-3-ones **1**.

Scheme 3 Synthetic route for vinyl oxazoloindol-3-ones **1**



At first, the application of this new class of indole-based allylic donors was commenced with Pd-catalyzed decarboxylative [3+2] cycloaddition of vinyl oxazoloindol-3-one **1a** with sulfonyl isocyanate **2a** to testify our hypothesis (Table 1). Gratifyingly, in the presence of $Pd(PPh_3)_4$, this reaction in toluene at 25 °C smoothly occurred to give decarboxylative [3+2] cycloaddition product **3aa** albeit with a low yield (entry 1). Nevertheless, this preliminary result demonstrated the feasibility of our design on this new class of indole-based allylic donors for DcA reactions. To improve the yield, a series of representative solvents were evaluated for this reaction (entries 1-6), and other solvents did not display better capability than toluene in promoting the reaction (entries 2-6 vs entry 1). Then, the reaction temperature was altered (entries 7-11). It was found that lowering the temperature would decrease the yield (entries 7-8 vs entry 1), while elevating the temperature could remarkably enhance the yield (entries 9-11 vs entry 1). Among different temperatures, 70 °C was revealed to be the most suitable reaction temperature with regard to the yield (entry 10). To further enhance the yield, the reagents ratio was modulated (entries 12-15), and it was discovered that suitably increasing the amount of sulfonyl isocyanate **2a** could increase the yield to a high level of 80% (entry 13). So, these conditions as listed in entry 13 were selected as the optimal conditions for this Pd-catalyzed decarboxylative cycloaddition.

Table 1 Conditions optimization for Pd-catalyzed decarboxylative [3+2] cycloaddition[a]



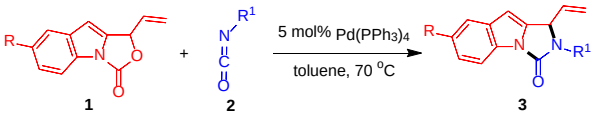
entry	solvent	T (°C)	**1a**:**2a**	yield (%)[b]
1	toluene	25	1:1.2	28
2	DCE	25	1:1.2	23
3	EtOAc	25	1:1.2	23
4	acetone	25	1:1.2	24
5	CH_3CN	25	1:1.2	trace

6	1,4-dioxane	25	1:1.2	trace
7	toluene	0	1:1.2	22
8	toluene	-10	1:1.2	11
9	toluene	50	1:1.2	49
10	toluene	70	1:1.2	70
11	toluene	90	1:1.2	65
12	toluene	70	1:2	75
13	toluene	70	1:3	80
14	toluene	70	1:4	63
15	toluene	70	2:1	51

[a]Unless indicated otherwise, the reaction was carried out at 0.1 mmol scale in a solvent (0.5 mL) for 12 h. [b]Isolated yield. DCE = 1,2-dichloroethane.

Then, we performed the application of indole-based allylic donors **1** in Pd-catalyzed decarboxylative [3+2] cycloaddition with a wide range of isocyanates **2** under the optimal reaction conditions (Table 2). Apart from sulfonyl isocyanate **2a** (entry 1), a variety of phenyl isocyanates **2b-2l** could be utilized as suitable reaction partners to undergo decarboxylative [3+2] cycloadditions with vinyl oxazoloindol-3-one **1a** in generally high yields of 59% to 98% (entries 2-12). In detail, either *para*-substituted (entries 2-5), *meta*-substituted (entries 6-8) or *ortho*-substituted (entries 9-12) phenyl groups could serve as competent R^1 groups for isocyanates **2**. Among them, *para*-chlorophenyl isocyanate **2e** reacted with vinyl oxazoloindol-3-one **1a** in the highest yield of 98% (entry 5). In addition, isocyanate **2m** bearing an aliphatic substituent could smoothly participate in the decarboxylative [3+2] cycloaddition with **1a** in a good yield of 70%. Moreover, cyclopentyl isocyanate **2n** could undergo the desired [3+2] cycloaddition with **1a** although the yield was unsatisfying (entry 14). In addition to substrate **1a**, methyl-substituted vinyl oxazoloindol-3-one **1b** could also serve as a suitable indole-based allylic donor, which successfully underwent decarboxylative [3+2] cycloadditions with a series of phenyl isocyanates **2** in overall high yields of 72%-92% (entries 15-19).

Table 2 Application of indole-based allylic donors **1** in Pd-catalyzed decarboxylative [3+2] cycloaddition[a]

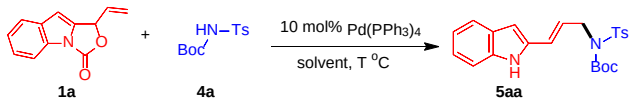


entry	R (**1**)	R^1 (**2**)	**3**	yield (%)[b]
1	H (**1a**)	*p*-$CH_3C_6H_4SO_2$ (**2a**)	**3aa**	80
2	H (**1a**)	*p*-$CH_3C_6H_4$ (**2b**)	**3ab**	90
3	H (**1a**)	*p*-$OMeC_6H_4$ (**2c**)	**3ac**	66
4	H (**1a**)	*p*-FC_6H_4 (**2d**)	**3ad**	66
5	H (**1a**)	*p*-ClC_6H_4 (**2e**)	**3ae**	98
6	H (**1a**)	*m*-$CH_3C_6H_4$ (**2f**)	**3af**	63
7	H (**1a**)	*m*-$OCH_3C_6H_4$ (**2g**)	**3ag**	67
8	H (**1a**)	*m*-FC_6H_4 (**2h**)	**3ah**	70
9	H (**1a**)	*o*-$CH_3C_6H_4$ (**2i**)	**3ai**	79
10	H (**1a**)	*o*-$OCH_3C_6H_4$ (**2j**)	**3aj**	80
11	H (**1a**)	*o*-FC_6H_4 (**2k**)	**3ak**	59
12	H (**1a**)	*o*-ClC_6H_4 (**2l**)	**3al**	81
13	H (**1a**)	$ClCH_2CH_2CH_2$ (**2m**)	**3am**	70
14	H (**1a**)	cyclopentyl (**2n**)	**3an**	39
15	Me (**1b**)	*p*-$CH_3C_6H_4SO_2$ (**2a**)	**3ba**	92
16	Me (**1b**)	*p*-$CH_3C_6H_4$ (**2b**)	**3bb**	72
17	Me (**1b**)	*p*-ClC_6H_4 (**2e**)	**3be**	80
18	Me (**1b**)	*m*-FC_6H_4 (**2h**)	**3bh**	90
19	Me (**1b**)	*o*-$OCH_3C_6H_4$ (**2j**)	**3bj**	90

[a]Unless indicated otherwise, the reaction was carried out at 0.1 mmol scale in toluene (0.5 mL) at 70 °C for 12 h, and the molar ratio of **1**:**2** was 1:3. [b]Isolated yield.

After establishing the decarboxylative [3+2] cycloaddition, we then performed the application of this new class of indole-based allylic donors in Pd-catalyzed decarboxylative substitution. As shown in Table 3, the decarboxylative allylic amination reaction of vinyl oxazoloindol-3-one **1a** with sulfonyl amine **4a** was employed as a model reaction to examine the possibility of our design. Indeed, in the presence of $Pd(PPh_3)_4$, the reaction in toluene at room temperature occurred to generate allylic amination product **5aa** with a linear selectivity in a moderate yield of 56% (entry 1), which demonstrated the feasibility of our design on this new class of indole-based allylic donors in Pd-catalyzed decarboxylative substitution. Then, the evaluation of representative solvents revealed that toluene is much better than other solvents in terms of the yield (entry 1 vs entries 2-6). To further enhance the yield, the reaction temperature was changed by either lowering or elevating the reaction temperature (entries 7-10). It was found that the yield could be greatly enhanced to 90% when the reaction temperature was lowered to 0 °C (entry 7 vs entry 1). Finally, the modulation of reagents ratio (entries 11-12) discovered that properly increasing the amount of sulfonyl amine **4a** could further improve the yield to 95% (entry 11). It should be noted that only (*E*)-isomer of **5aa** was observed in all cases. So, these conditions as listed in entry 11 were chosen as the optimal reaction conditions for this allylic amination reaction.

Table 3 Conditions optimization for Pd-catalyzed decarboxylative substitution[a]



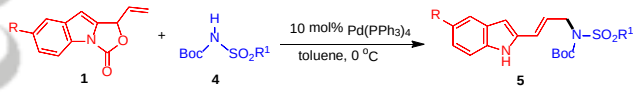
1a 4a 5aa

entry	solvent	T (°C)	**1a**:**4a**	yield (%)[b]
1	toluene	25	1:1	56
2	DCE	25	1:1	30
3	EtOAc	25	1:1	40
4	acetone	25	1:1	30
5	CH_3CN	25	1:1	40
6	1,4-dioxane	25	1:1	46
7	toluene	0	1:1	90
8	toluene	-10	1:1	54
9	toluene	-30	1:1	45
10	toluene	50	1:1	26
11	toluene	0	1:2	95

[a]Unless indicated otherwise, the reaction was carried out at 0.1 mmol scale in a solvent (0.5 mL) for 12 h. [b]Isolated yield and only (*E*)-isomer of **5aa** was observed in all cases.

With the optimal reaction conditions in hand, we carried out the investigation on the application of indole-based allylic donors **1** in Pd-catalyzed decarboxylative substitution (Table 4). As shown in entries 1-10, vinyl oxazoloindol-3-one **1a** could undergo decarboxylative allylic amination with sulfonyl amines **4a-4j** bearing various *para*-, *meta*-, and *ortho*-substituted phenyl groups, and these reactions successfully generated allylic amination products **5aa-5aj** with uniformly linear selectivity in overall high yields (61%-98%). In addition, methyl-substituted vinyl oxazoloindol-3-one **1b** could also be utilized as an allylic donor to undergo decarboxylative allylic amination with different sulfonyl amines **4** with exclusively linear selectivity in good yields (90%, entries 11-16). Notably, this reaction has an excellent (*E*/*Z*)-selectivity, and only (*E*)-isomers of **5** were observed in all cases.

Table 4 Application of indole-based allylic donors **1** in Pd-catalyzed decarboxylative substitution[a]



1 4 5

entry	R (**1**)	R^1 (**4**)	**5**	*E*/*Z*[b]	yield (%)[c]
1	H (**1a**)	*p*-$CH_3C_6H_4$ (**4a**)	**5aa**	>95:5	95
2	H (**1a**)	*p*-FC_6H_4 (**4b**)	**5ab**	>95:5	75
3	H (**1a**)	*p*-BrC_6H_4 (**4c**)	**5ac**	>95:5	70
4	H (**1a**)	*p*-$CF_3C_6H_4$ (**4d**)	**5ad**	>95:5	61
5	H (**1a**)	*m*-FC_6H_4 (**4e**)	**5ae**	>95:5	85
6	H (**1a**)	*m*-BrC_6H_4 (**4f**)	**5af**	>95:5	88
7	H (**1a**)	*o*-$CH_3C_6H_4$ (**4g**)	**5ag**	>95:5	95
8	H (**1a**)	*o*-FC_6H_4 (**4h**)	**5ah**	>95:5	98
9	H (**1a**)	*o*-ClC_6H_4 (**4i**)	**5ai**	>95:5	91
10	H (**1a**)	Ph (**4j**)	**5aj**	>95:5	76
11	Me (**1b**)	*p*-$CH_3C_6H_4$ (**4a**)	**5ba**	>95:5	67
12	Me (**1b**)	*p*-FC_6H_4 (**4b**)	**5bb**	>95:5	87
13	Me (**1b**)	*m*-BrC_6H_4 (**4f**)	**5bf**	>95:5	84
14	Me (**1b**)	*o*-$CH_3C_6H_4$ (**4g**)	**5bg**	>95:5	89
15	Me (**1b**)	*o*-FC_6H_4 (**4h**)	**5bh**	>95:5	64
16	Me (**1b**)	*o*-ClC_6H_4 (**4i**)	**5bi**	>95:5	90

[a]Unless indicated otherwise, the reaction was carried out at 0.1 mmol scale in toluene (0.5 mL) at 0 °C for 12 h, and the molar ratio of **1**:**4** was 1:2. [b]Determined by ^1H NMR. [c]Isolated yield.

The structures of products **3** and **5** were unambiguously determined by NMR, IR and HR MS. In addition, the structures of products **3aa** and **5bi** were confirmed by their single-crystal X-ray diffraction analysis (Figure 1).[18]

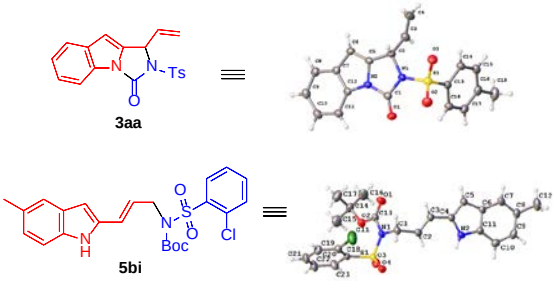
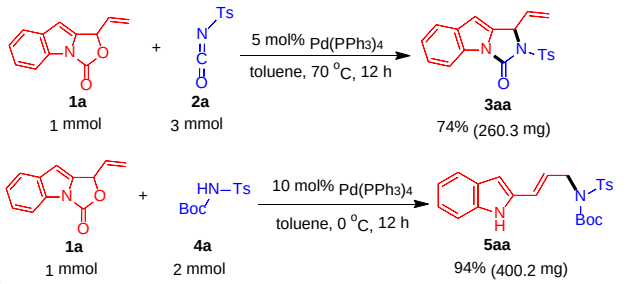


Figure 1 Single-crystal structures of products **3aa** and **5bi**

In addition, to examine the practicability of the Pd-catalyzed decarboxylative [3+2] cycloaddition and allylic amination, we performed two one-mmol-scale reactions (Scheme 4). Compared with small-scale reactions (Table 2, entry1 and Table 4, entry 1), these one-mmol-scale reactions smoothly occurred to give products **3aa** and **5aa** in nearly retained high yields, which demonstrated that these reactions could be scaled up.

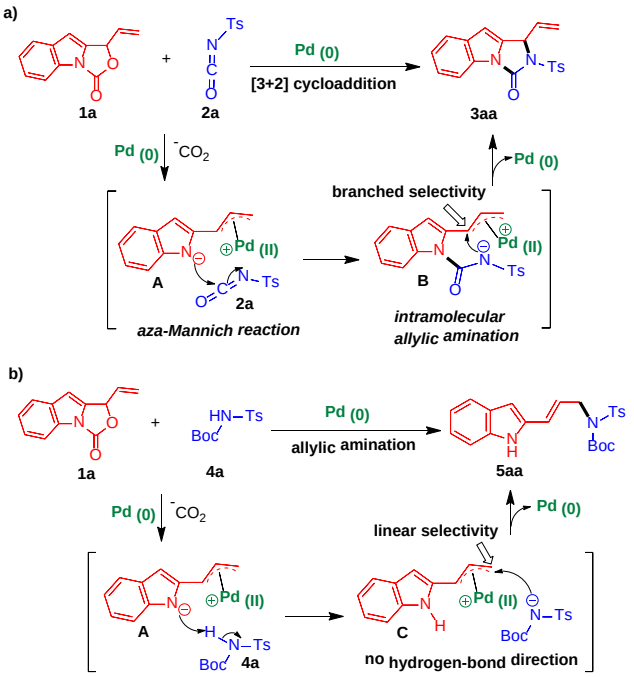
Scheme 4 One-mmol-scale reactions



Based on the experimental results, we suggested possible reaction pathways to explain the chemistry and regioselectivity of the two decarboxylative allylation reactions (Scheme 5). As exemplified by the formation of products **3aa** and **5aa**, the two reactions commenced with the generation of zwitterionic π-allylpalladium intermediate **A** via decarboxylation in the presence of Pd (0). In the [3+2] cycloaddition (Scheme 5a), this intermediate **A** first attacked sulfonyl isocyanate **2a** to undergo an aza-Mannich reaction, producing another intermediate **B**. Then, an intramolecular allylic amination of intermediate **B** occurred with a branched selectivity to form a five-membered ring. If the intramolecular allylic amination occurred with a linear selectivity, a seven-membered ring would be constructed. Perhaps because five-membered ring is easier to form than seven-membered ring, the second step of intramolecular allylic amination occurred with a branched selectivity, thus accomplishing the observed [3+2] cycloaddition. Instead, the linear selectivity of intermolecular allylic amination of **1a** with **4a** could be explained by the absence of hydrogen-bond direction (Scheme 5b), which was reported to be a crucial factor to control the regioselectivity in Pd-catalyzed allylic reactions.[3b] Namely, π-allylpalladium intermediate **A** could transform into intermediate **C** via deprotonation of sulfonyl amine **4a**. There was no hydrogen-bond direction between the NH group of intermediate **C** and the deprotonated amine anion, thus leading to the linear selectivity of the allylic amination.

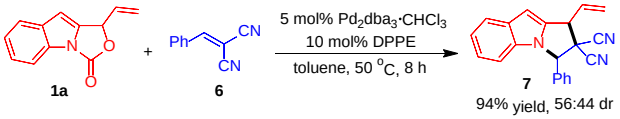
Notably, the allylic amination reaction (Scheme 5b) proceeded well at 0 °C, while the [3+2] cycloaddition reaction (Scheme 5a) occurred at a higher temperature of 70 °C. The rate difference between the two reactions might stem from the first step after the formation of π-allylpalladium intermediate **A**. Specially, in the [3+2] cycloaddition reaction (Scheme 5a), the first step was the nucleophilic addition of intermediate **A** to the C=N bond of sulfonyl isocyanate **2a**, which displayed the nucleophilicity of intermediate **A**. While in the allylic amination reaction (Scheme 5b), the first step was the deprotonation of sulfonyl amine **4a** by intermediate **A**, which exhibited the basicity of intermediate **A**. Because the basicity of intermediate **A** (nitrogen anion) was very strong, the deprotonation of sulfonyl amine **4a** by intermediate **A** could occur easily. However, the nucleophilic addition of intermediate **A** to the C=N bond was relatively difficult compared with the deprotonation of sulfonyl amine **4a** by intermediate **A**. These reasons might result in the observed rate difference between the two reactions.

Scheme 5 Suggested reaction pathways



Furthermore, to examine the utility of vinyl oxazoloindol-3-ones in [3+2] cycloadditions, we utilized benzylidene malononitrile **6**, an electron-deficient alkene, as a dipolarophile[4b,5b,19] to react with oxazoloindol-3-one **1a** under the catalysis of palladium (Scheme 6). This [3+2] cycloaddition smoothly occurred to generate product **7** in a high yield of 94% albeit with a low diastereoselectivity of 56:44 dr. Nevertheless, this result indicated that oxazoloindol-3-ones could be utilized in palladium-catalyzed 1,3-dipolar [3+2] cycloadditions.

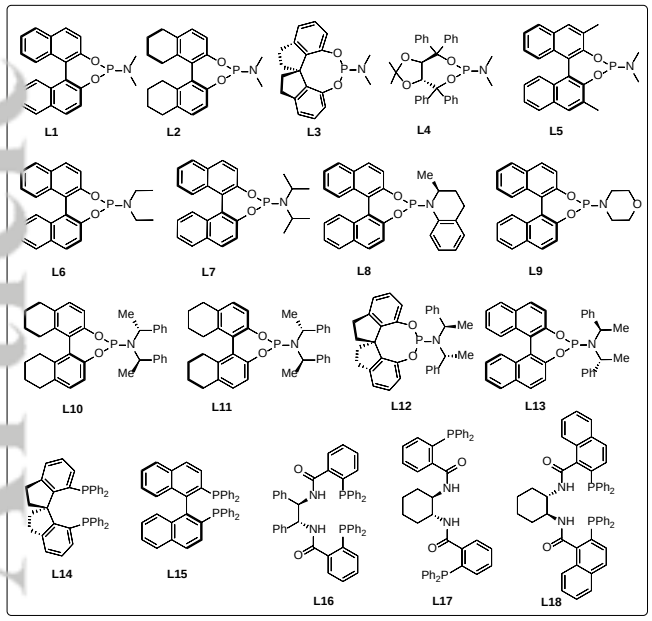
Scheme 6 Using electron-deficient alkene **6** as a dipolarophile

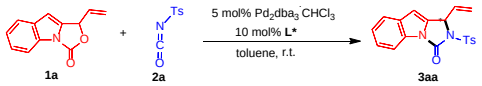


Finally, we performed an investigation on the catalytic asymmetric version of the [3+2] cycloaddition between **1a** and **2a** (Table 5). As listed in entries 1-13, a variety of BINOL, H_8-BINOL, and SPINOL-derived chiral phosphoramidites **L1-L13** were utilized as chiral ligands for this palladium-catalyzed allylation reaction. However, in most cases, very weak enantio-control of product **3aa** was observed. Among these ligands, **L5**, **L10** and **L12** could deliver the [3+2] cycloaddition with some extent of enantioselectivity (around 20% ee). In addition, several chiral bidentate phosphine ligands **L14-L18** were tested for this reaction (entries 14-18). Nevertheless, these chiral ligands could hardly control the enantioselectivity of the [3+2] cycloaddition (< 8% ee). So, it seemed that **L10** was a promising chiral ligand for this reaction considering the relatively higher yield and better

enantioselectivity of the [3+2] cycloaddition in the presence of **L10** (entry 10). However, it is still a challenging task to realize a highly enantioselective [3+2] cycloaddition between **1a** and **2a**, which might require exquisite elaboration of reaction conditions and structural modifications of chiral ligands.

Table 5 Preliminary investigation on the catalytic asymmetric version[a]





entry	L*	yield (%)[b]	ee (%)[c]
1	**L1**	15	<5
2	**L2**	20	<5
3	**L3**	15	8
4	**L4**	11	<5
5	**L5**	11	20
6	**L6**	20	<5
7	**L7**	16	11
8	**L8**	19	<5
9	**L9**	18	-8
10	**L10**	66	-20
11	**L11**	23	<5
12	**L12**	12	22
13	**L13**	40	6
14	**L14**	18	<5
15	**L15**	23	<5
16	**L16**	33	<5
17	**L17**	33	<5
18	**L18**	12	8

[a]Unless indicated otherwise, the reaction was carried out at 0.05 mmol scale in toluene (1 mL) for 12 h, and the molar ratio of **1a**:**2a** was 1:1.2. [b]Isolated yield. [c]The ee value was determined by HPLC.

Conclusions

In summary, we have designed and developed a new class of indole-based allylic donors for palladium-catalyzed decarboxylative allylations. In addition, we have realized their first application in palladium-catalyzed decarboxylative [3+2] cycloaddition and allylic amination, respectively, by reacting with isocyanates and sulfonyl amines. This approach represents the first design of indole-based allylic donors, which is helpful for settling the challenge of designing and developing new class of heterocycle-based allylic donors for Pd-catalyzed decarboxylative allylation reactions. Moreover, the application of this new class of allylic donors in cycloadditions and substitutions will add new contents to the research field of decarboxylative allylation.

Experimental

General Procedure for the synthesis of products 3:

A flame-dried 10 mL flask tube was charged with indole-based allylic donors **1** (0.1 mmol) and $Pd(PPh_3)_4$ (0.005 mmol), sealed with a septum, and evacuated and backfilled with argon for three times. Then, isocyanates **2** (0.3 mmol) and toluene (0.5 mL) was added via syringe. The reaction mixture was stirred at 70 °C for 12 h. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography on silica gel to afford pure products **3**.

General Procedure for the synthesis of products 5:

A flame-dried 10 mL flask tube was charged with indole-based allylic donors **1** (0.1 mmol), sulfonyl amines **4** (0.2 mmol) and $Pd(PPh_3)_4$ (0.01 mmol), sealed with a septum, and evacuated and backfilled with argon for three times. Then, toluene (0.5 mL) was added via syringe. The reaction mixture was stirred at 0 °C for 12 h. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography on silica gel to afford pure products **5**.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2018xxxxx.

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Entry for the Table of Contents

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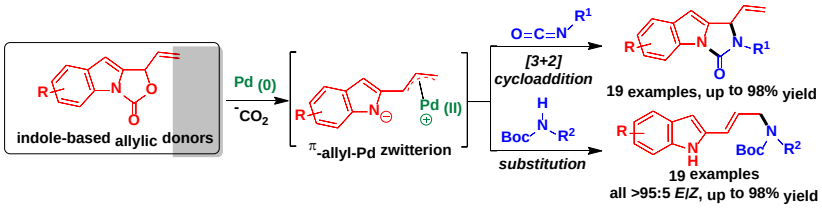
Design and Application of Indole-Based Allylic Donors for Pd-Catalyzed Decarboxylative Allylation Reactions



Qing-Qing Hang, Si-Jia Liu, Lei Yu, Ting-Ting Sun, Yu-Chen Zhang,* Guang-Jian Mei* and Feng Shi*

A new class of indole-based allylic donors have been designed and applied in palladium-catalyzed decarboxylative [3+2] cycloaddition and allylic amination.

