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Palladium-catalyzed asymmetric [4 + 3] cycloaddition of methylene-trimethylenemethane: access to seven-membered exocyclic axially chiral allenes†

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A palladium-catalyzed asymmetric [4 + 3] cycloaddition of the methylene-trimethylenemethane donor with an azadiene has been developed, affording benzofuro[3,2-*b*]azepine-derived exocyclic chiral allene with control of axial and point chirality. The target compounds were generated in good to excellent yields and with high diastereoselectivities and enantioselectivities (up to >20 : 1 dr, 99% ee). Furthermore, this cycloaddition reaction could be efficiently scaled-up and several synthetic transformations were accomplished for the construction of useful chiral allenol and chiral spirocyclic derivatives.

Introduction

Axially chiral allenes are important structural features in a variety of natural products, bioactive compounds, pharmaceuticals, ligands, organo-catalysts, and functional materials.[1] The reactive orthogonal π-bonds of chiral allenes render them versatile chiral building blocks in organic synthesis.[2] Developing concise approaches to synthesize axially chiral allene-containing compounds asymmetrically using readily available and inexpensive starting materials has attracted much attention.[3] Among the identified allenic natural products and pharmaceuticals, chiral exocyclic allenes constitute a major subclass, for example, allenic carbacyclin,[4] Neoxanthin,[5] Grasshopper ketone,[6] and Citroside A[7] (Fig. 1). However, compared with linear allenes, strategies to construct chiral exocyclic allenes are still rare and remain in high demand.[8]

Cycloaddition reactions involving palladium-trimethylenemethane (Pd-TMM) are extremely valuable in the construction of cyclic compounds[9] and total synthesis of natural products.[10] In the asymmetric Pd-TMM chemistry (Scheme 1a), allyl trimethylsilanes have extensively been employed as TMM donors[11] since Trost's important contribution in 1979.[12] In recent years, a number of novel self-deprotonated TMM donors have been gradually developed for the asymmetric Pd-TMM cycloadditions.[13] All these TMM donors generally behave as three-carbon synthons to react with a multitude of acceptors, giving chiral five,[11a–g,13a–i] six,[11h] seven[13j–o] and nine-membered[11i] carbo- and heterocyclic compounds. On the basis of the above, in 2013, Trost and co-workers reported a novel methylene-TMM donor, which could react with α, β-unsaturated *N*-acyl pyrroles in the palladium-catalyzed asymmetric [3 + 2] cycloaddition to provide chiral substituted vinylidenecyclopentanes.[14] And then in 2018, they developed a palladium-catalyzed asymmetric [3 + 2] cycloaddition reaction between the racemic methylene-TMM donor and electron-deficient olefins through a dynamic kinetic asymmetric transformation process, furnishing cyclopentane-derived chiral exocyclic allenes.[15] In 2019, our group also applied it in asymmetric tandem [3 + 2] cycloaddition/allylation to produce chiral hexahydropyrazolo[5,1-*a*] isoquinoline derivatives (Scheme 1b).[16] To the best of our knowledge, the catalytic asymmetric [4 + 3] cycloaddition of the methylene-TMM donor has never been achieved. On the other hand, seven-membered azepines are privileged skeletons in many natural products and pharmaceuticals.[17] Introducing an axially chiral allene moiety into the exocyclic backbone of the chiral azepine is highly challenging and may produce unexpected biological

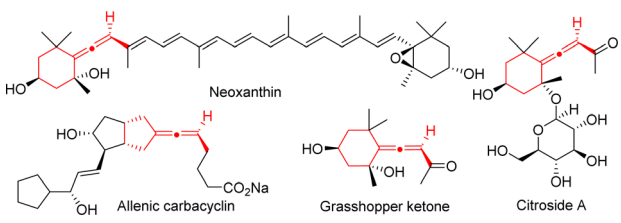

Fig. 1 Bioactive chiral exocyclic allenes.

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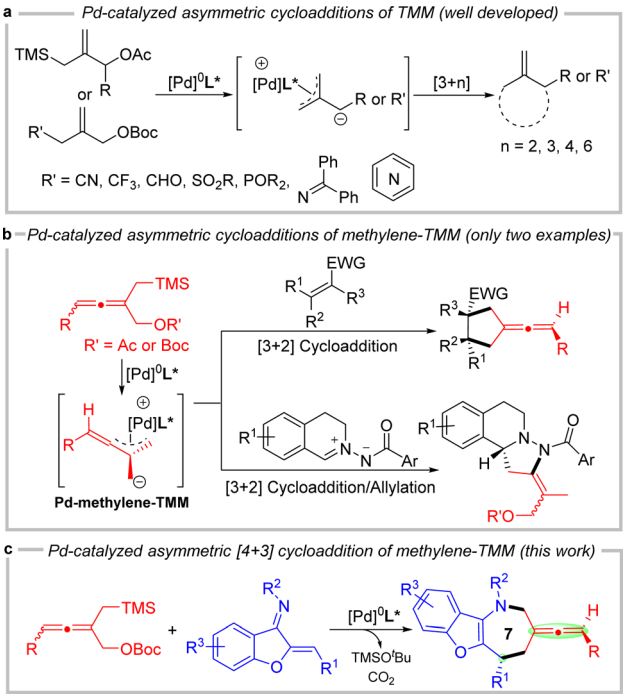


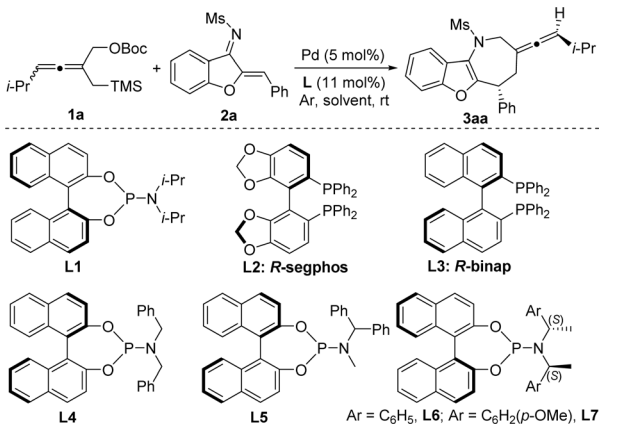
Scheme 1 Profile of Pd-catalyzed asymmetric cycloadditions involving TMM and methylene-TMM.

and pharmacological properties. In conjunction with our interest in palladium-catalyzed cycloaddition reaction and allene chemistry,[18] herein, we present the first palladium-catalyzed asymmetric [4 + 3] cycloadditions of methylene-TMM donors with benzofuran derived azadienes to furnish benzofuro[3,2-*b*]azepine-derived exocyclic chiral allenes bearing axial and central chirality (Scheme 1c).

Results and discussion

To test the feasibility of the palladium-catalyzed [4 + 3] cycloaddition, we investigated the model reaction of the racemic trisubstituted allene TMM donor **1a** and benzofuran-derived azadiene **2a** in 1,4-dioxane at room temperature (Table 1). On the basis of our previous work on palladium-catalyzed cycloadditions,[18a–c] $Pd_2(dba)_3$ was used as the precatalyst and axially chiral BINAP- or BINOL-based phosphines as the ligand. To our delight, under catalysis of a complex of $Pd_2(dba)_3$ (2.5 mol%) and **L1** (11 mol%), the [4 + 3] cycloaddition proceeded to deliver the desired cycloadduct **3aa** in 28% yield with low stereoselectivity (1 : 1.5 dr and −20% ee) (entry 1). Then several axially chiral bisphosphine ligands **L2** and **L3** were examined and did not promote the reaction (entry 2 and entry 3). Subsequently, considering that phosphoramidite ligands containing different substitutions on the nitrogen atom had a huge impact on the diastereoselectivity and enantioselectivity, several axially chiral phosphoramidite ligands **L4–L7** were then examined (entries 4–7). The reaction proceeded smoothly in the presence of **L7** to give **3aa** in 73% yield with moderate diastereoselectivity (1 : 4 dr) and a significant improvement of enantioselectivity (96% ee) (entry 7). A quick screening of several solvents such as tetrahydrofuran (THF), toluene and mesitylene

Table 1 Optimization of reaction conditions[a]



Entry	Pd source	L	Solvent	t h^{-1}	Yield[b] (%)	dr[c]	ee[d] (%)
1	$Pd_2(dba)_3$	**L1**	1,4-Diox	48	28	1 : 1.5	−20
2	$Pd_2(dba)_3$	**L2**	1,4-Diox	48	NR[f]	—	—
3	$Pd_2(dba)_3$	**L3**	1,4-Diox	48	NR	—	—
4	$Pd_2(dba)_3$	**L4**	1,4-Diox	48	Trace	—	—
5	$Pd_2(dba)_3$	**L5**	1,4-Diox	24	50	1 : 3	87
6	$Pd_2(dba)_3$	**L6**	1,4-Diox	6	72	1 : 6	−87
7	$Pd_2(dba)_3$	**L7**	1,4-Diox	10	73	1 : 4	96
8	$Pd_2(dba)_3$	**L7**	THF	2	78	1 : 3	96
9	$Pd_2(dba)_3$	**L7**	Toluene	3	76	1 : 4	97
10	$Pd_2(dba)_3$	**L7**	Mesitylene	2	80	1 : 5	98
11	$Pd(dba)_2$	**L7**	Mesitylene	2	77	1 : 4	95
12	$Pd(dmdba)_2$	**L7**	Mesitylene	6	90	1 : 5.5	98
13[e]	$Pd(dmdba)_2$	**L7**	Mesitylene	36	92	1 : 6	98

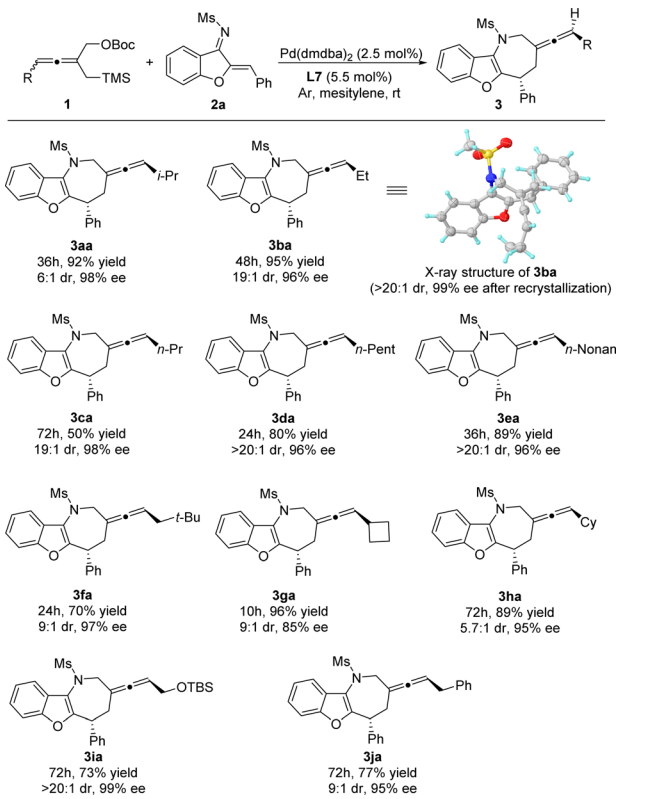
[a] Unless otherwise indicated, all reactions were performed with **1a** (0.20 mmol) and **2a** (0.10 mmol) in the presence of [Pd] (5 mol%) and a ligand (5.5 mol% for diphosphines, 11 mol% for the phosphoramidite ligand) in 1 mL of solvent under an Ar atmosphere at room temperature. Abbreviations: dba, dibenzylidene acetone; dmdba, 3,5,3′,5′-dimethoxydibenzylidene acetone. [b] Isolated yield. [c] dr values were determined by ^{1}H NMR analysis. [d] ee values of major diastereomers were determined by HPLC analysis using a chiral stationary phase. [e] 2.5 mol% Pd and 5.5 mol% ligand were used. [f] No reaction.

(entries 8–10) revealed that mesitylene is the optimal solvent, leading to the cycloadduct **3aa** in 80% yield with 1 : 5 dr and 98% ee (entry 10). Then several palladium catalysts were also evaluated, and $Pd(dmdba)_2$ displayed a better catalytic activity, resulting in the formation of the product in 90% yield with 1 : 5.5 dr and 98% ee (entry 12). Decreasing the loading of the catalyst led to a slight improvement of diastereoselectivity and yield, but the reaction time could be extended to 36 hours. Finally, the optimal reaction conditions were determined as follows: the use of $Pd(dmdba)_2$ (2.5 mol% or 5 mol%) and chiral ligand **L7** (5.5 mol% or 11 mol%) as the catalyst in mesitylene at room temperature.

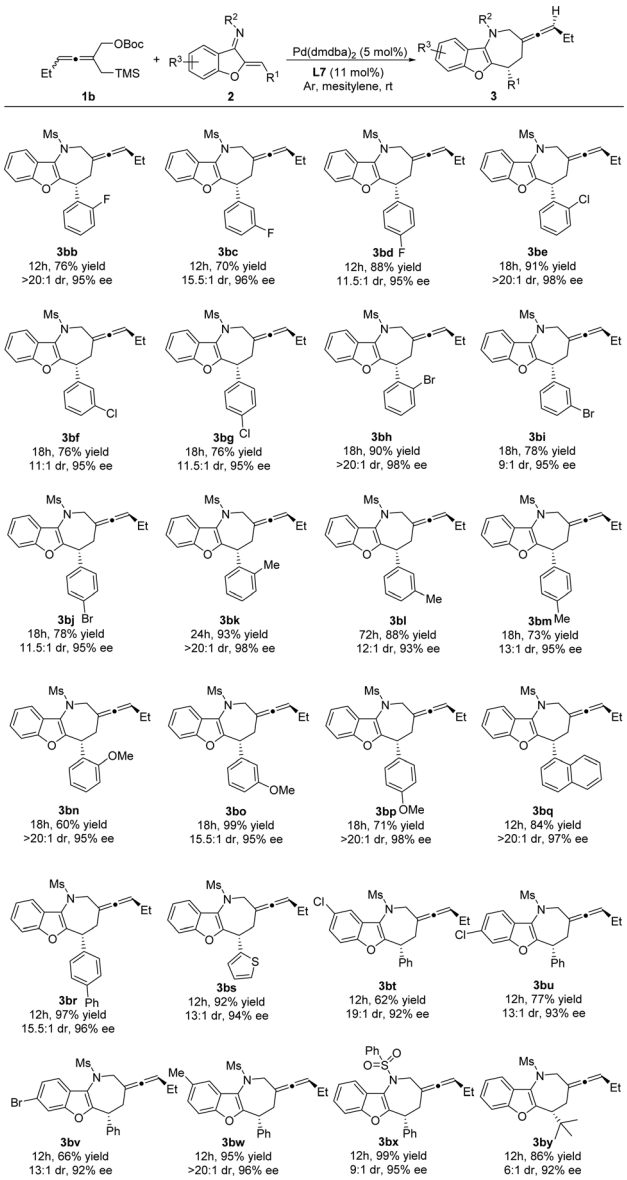
After the optimized conditions were established, we investigated the scope of allene TMM donors **1** in the Pd-catalyzed asymmetric [4 + 3] cycloaddition (Scheme 2). Generally, the reaction proceeded smoothly to give the corresponding products in good to excellent yields (50–96%) with

diastereoselectivities ranging from 5.7 : 1 to >20 : 1 and good enantioselectivities of 85–99%. The allene **1** with whether straight-chain alkyl, branch-chain alkyl or cycloalkyl substituents worked efficiently in the reaction (**3aa–3ha**). It is worth noting that higher diastereoselectivities were obtained for straight-chain alkyl substituents on the allene, probably due to the lower steric hindrance, which makes it easier to fit the spatial structure of transition states. Furthermore, the alkyl group bearing protected heteroatoms (**3ia**) and the benzyl group (**3ja**) were also well accepted, leading to the corresponding products with good to excellent levels of diastereo-and enantioselectivities. The absolute configuration of the cycloadduct was unambiguously determined through X-ray crystallographic analysis of the product **3ba**.[21]

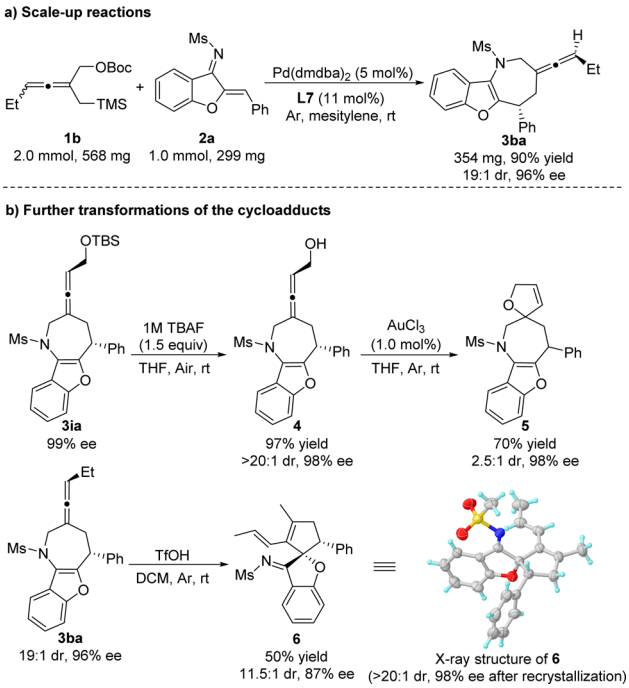
Following exploration of the variation of substituents on the allenes in Scheme 2, the generality of the asymmetric [4 + 3] cycloaddition with ethyl allene donor **1b** was investigated. As shown in Scheme 3, a series of benzofuran derived azadienes **2** were suitable substrates for this cycloaddition and afforded benzofuro[3,2-*b*]azepine-derived exocyclic axially chiral allenes **3** in moderate to excellent diastereoselectivities (9 : 1 to >20 : 1 dr) and very good enantioselectivities (92% to 99% ee). Azadienes bearing electron-donating or -withdrawing groups at the *ortho*, *meta*, and *para* positions of the aromatic R^1 group were converted into the expected products **3bb–3br** in good to excellent yields, dr, and ee. The heteroaryl substrate **3s** also performed the reaction well to produce the corresponding product **3bs** in 92% yield with 13 : 1 dr and 94% ee. Moreover, R^3 substitutions on **2** bearing halogens or a methyl group at either the C5- or C6-position of the benzofuran ring were amenable to this cycloaddition, furnishing the corresponding products **3bt–3bw**. Azadiene **2x** with a different sulfonamide substituent (phenylsulfonyl) could also deliver **3bx** in 99% yield with 9 : 1 dr and 95% ee. Gratifyingly, the alkyl-substituted benzofuran-derived azadiene **2y** was also compatible for this asymmetric [4 + 3] cycloaddition, thereby resulting in product **3by** in 86% yield with 6 : 1 dr and 92% ee.



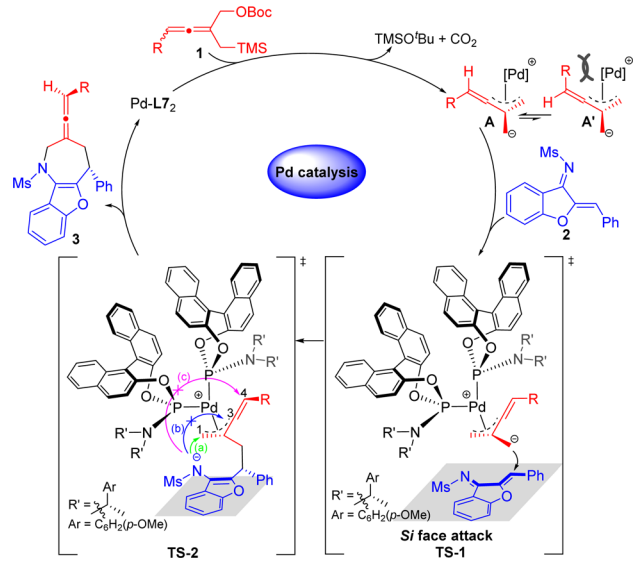
Scheme 2 Substrate scope of allene TMM donors **1**.[a] [a]Unless otherwise indicated, all reactions were carried out with **1** (0.20 mmol) and **2a** (0.10 mmol) in 1 mL of mesitylene under an Ar atmosphere at room temperature. Isolated yields were reported. The dr values were determined by ^{1}H NMR analysis, and ee values were determined by HPLC analysis using a chiral stationary phase.



Scheme 3 Substrate scope of benzofuran-derived azadienes **2**.[a] [a]Unless otherwise indicated, all reactions were carried out with **1b** (0.20 mmol) and **2** (0.10 mmol) in 1 mL of mesitylene under an Ar atmosphere at room temperature. Isolated yields were reported. The dr values were determined by ^{1}H NMR analysis, and ee values were determined by HPLC analysis using a chiral stationary phase.



Scheme 4 Scale-up experiment and further transformations of the cycloadducts.



Scheme 5 Proposed reaction mechanism for palladium-catalyzed asymmetric [4 + 3] cycloaddition.

As shown in Scheme 4a, Pd-catalyzed asymmetric [4 + 3] cycloaddition reaction of substrates **1b** and **2a** could be scaled-up with loadings of the palladium catalyst (5 mol%) and **L7** (11 mol%), producing the product **3ba** in good yield (90%) with excellent selectivities (19 : 1 dr and 96% ee). In order to further demonstrate the potential of the asymmetric [4 + 3] cycloaddition, subsequent transformations of the product **3ia** and **3ba** have been investigated (Scheme 4b). Treatment of the chiral product **3ia** with TBAF afforded the alcohol product **4** in 97% yield. Then, the gold catalyzed cyclization[19,20] of **4** gave the spirocycle product **5** in good yield with moderate diastereoselectivity and the same enantiomeric excess as that of the starting material. Finally, the seven-membered exocyclic axially chiral allene **3ba** could be efficiently converted to the five-membered spirocycle **6** by a TfOH-mediated ring contraction and the absolute configuration of the product **6** was determined by X-ray crystallographic analysis.[21]

On the basis of experimental results and previous mechanistic studies,[14–16] a plausible mechanism for the reaction is proposed in Scheme 5. In the presence of the palladium catalyst, allene TMM donors **1** were transformed into Pd-TMM complex **A** or **A′** with simultaneous release of TMSO^{t}Bu and CO_2. The dynamic kinetic asymmetric transformation process may occur between **A** and **A′**. The R-substituent of the allene and the bulky palladium complex on opposing faces leads to the more stable intermediate **A** (more details in the ESI†). According to the transition state **TS-1**, the sterically crowded chiral ligand dominates so that the carbanion of the intermediate **A** attacks at the Si face of the olefinic bond in the benzofuran-derived azadienes **2**, leading to the transition state **TS-2**. There were three possible pathways for the formation of different cyclized products in **TS-2**. For path (b), the steric effect between the *N*-Ms group and the intermediate carbon (C3) of allene blocked the cyclization reaction. For path (c), due to steric hindrance of the C4 point and its distance from the reaction site, it is difficult for the nitrogen anion to attack C4 to afford an eight-membered ring. Therefore, the transition state preferred path (a) to give rise to the seven-membered heterocyclic product **3** by intramolecular linear regioselective allylic substitution.

Conclusions

In summary, palladium-catalyzed asymmetric [4 + 3] cycloadditions of readily available racemic methylene-TMM donors with benzofuran-derived azadienes have been achieved under mild reaction conditions to give the benzofuro[3,2-*b*]azepine-derived exocyclic chiral allenes bearing axial and central chirality in good to excellent yields with good to excellent diastereoselectivities and enantioselectivities. This is the first example of asymmetric [4 + 3] cycloadditions of Pd-methylene-TMM. The cycloaddition reaction can be scaled-up, and the synthetic utility of chiral allenes has been demonstrated by their further transformations. The bactericidal activities of the novel compounds synthesized by our methodology are being evaluated.

Data availability

Experimental details and characterization of the complexes can be found in the ESI.†

Author contributions

B. M. conceived and directed the project. Y. W. performed reaction experiments and synthesis of substrates. Z. W., Y. S., Y. M. and T. L. performed synthesis of substrates and some data

collection. C. Y. helped with the crystallographic data analysis. B. M., H. G., C. Y. and Y. W. cowrote 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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21 Crystallographic data for **3ba** and **6** have been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 2335107 and 2335108, respectively.