Communication

Enantioselective 1,2-Difunctionalization of Dienes Enabled by Chiral Palladium Complex-Catalyzed Cascade Arylation/Allylic Alkylation Reaction

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Enantioselective 1,2-Difunctionalization of Dienes Enabled by Chiral Palladium Complex-Catalyzed Cascade Arylation/ Allylic Alkylation Reaction

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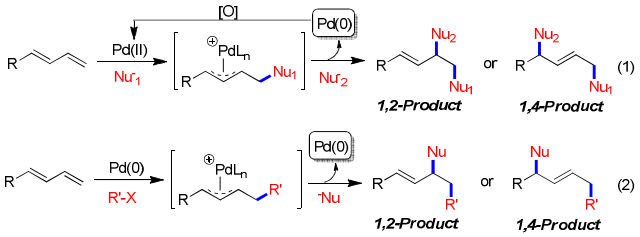
Supporting Information Placeholder

ABSTRACT: A Pd-catalyzed highly enantioselective three-component coupling of 1,3-dienes with aryl iodines and sodium dialkyl malonates has been successfully established by using a H_8-BINOL-based phosphoramidite ligand. This reaction proceeded *via* a palladium-catalyzed cascade arylation and asymmetric allylic alkylation reaction, providing an efficient strategy for the enantioselective 1,2-difunctionalization of 1,3-dienes.

The difunctionalization of alkenes is able to provide a wide range of structurally diverse functionalized chemicals, which hold great importance in organic synthesis, and has hence been considered a powerful strategy in synthetic organic chemistry.[1] 1,3-Dienes are easily accessible chemicals[2] and basically able to participate in a wide spectrum of reactions by acting on the carbon-carbon double bonds. Indeed, last several decades have witnessed that 1,3-diene derivatives are versatile reagents to render the invention of a large number of fundamentally important and synthetically significant methodologies, as exemplified by stereoselective cycloaddition reactions and polymerizations, which have shown widespread applications in the medicinal chemistry and material science.[3] It has been recognized that the 1,3-dienes can undergo nucleopalladation with palladium (II) and one nucleophile (Nu_1^-) to generate a π-allyl palladium intermediate, which can then be trapped by another nucleophile (Nu_2^-) to afford either 1,2- or 1,4-products, and releasing Pd(0) that is oxidized into catalytically active Pd(II) for the next catalytic cycle (eq. 1, Figure 1).[4-7] Palladium(0) complexes have also been identified to afford various 1,2-difunctionalization reactions upon undergoing oxidative addition with a high oxidation state compound and subsequent Heck insertion of a 1,3-diene to form a π-allyl palladium species, which ultimately reacts with a nucleophile to generate a 1,2- or 1,4-addition-like product (eq. 2, Figure 1).[8-12] However, among these transformations, highly enantioselective 1,2-difunctionlization reactions of 1,3-dienes, in particular, the protocols for the formation of two carbon-carbon bonds, have rarely been reported.[10,11] Very recently, Sigman and co-workers established a Pd(0)-catalyzed intermolecular 1,2-diarylation reaction of 1,3-dienes with aryldiazonium salts and aryl boronic acids, allowing the installation of two different aryl groups.[12] In the presence of a chiral bicyclo[2.2.2]octadiene ligand, the reaction was able to give a good enantiomeric excess, but a rather low yield (Figure 2a). As a consequence, highly efficient and enantioselective 1,2-difunctionlization reactions of 1,3-dienes remain highly challenging and are in great demand. Herein, we will describe a highly regioselective and stereoselective 1,2-difunctionalizaton of terminal 1,3-dienes with iodoarenes and stabilized carbon nucleophiles catalyzed by chiral palladium complexes (Figure 2b).

Figure 1. Pd-catalyzed Difunctionlization of 1,3-Dienes



As shown in Figure 2c, the Pd(II) intermediate **I**, generated from an oxidative addition reaction of a Pd(0) complex to an aryl iodine **2**, undergoes a Heck insertion reaction to give an allylic palladium intermediate **II**, which will be able to undergo isomerization to form a π-allyl palladium intermediate **III**[8-12] and then to participate in allylic alkylation reaction with a stabilized carbon nucleophile, principally giving rise to either a 1,2-product **4** or a 1,4-product **5**. Alternatively, the intermediate **II** would experience sequential events including *β*-hydride elimination, reinsertion reaction via palladium complex **IV** and isomerization via palladium species **II'** to yield a π-allyl palladium intermediate **III'**, as indicated by Sigman.[8p,8q,9] The π-allyl palladium species **III'** will also undergo the allylic alkylation reaction, to basically generate two regiomers **6** and **7**. Apparently, the simultaneous control of both the regio- and stereoselectivity renders the proposed three-component reaction much more challenging than similar reactions established already.[8-11] Since the chiral ligands principally coordinates to all of the palladium species formed in whole reaction process, we believe that the use of chiral ligands will be able to provide solutions to formidable issues associated with selectivities. However, the requirement for the chiral ligands to allow the proposed three-component reaction proceeding smoothly is quite critical: they not only enable the palladium to smoothly undergo the oxidative addition to aryl iodine and the subsequent insertion reaction, but also are able to efficiently control the stereoselectivity of the asymmetric allylic alkylation.

Figure 2. Pd-catalyzed Asymmetric 1,2-Difunctionlization of 1,3-Dienes

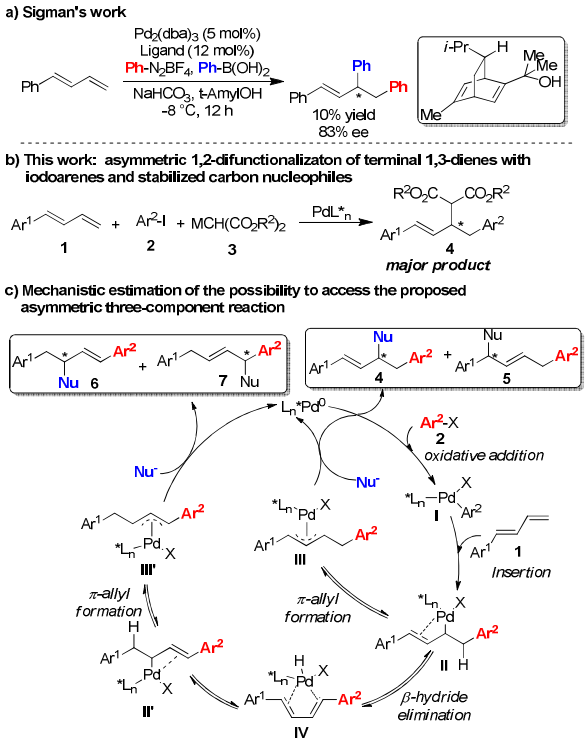
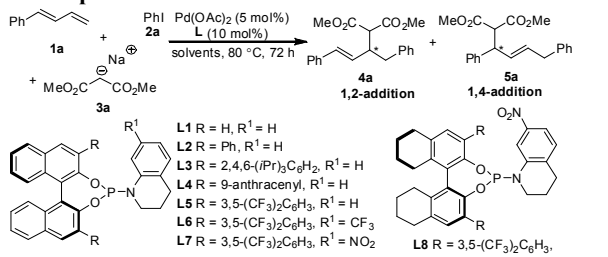


Table 1. Optimization of the Reaction Conditions[a]



entry	ligand	solvent	yield (%)[b]	ee (%)[c]	ratio (**4a**/**5a**)[d]
1	**L1**	THF	77	0	>15:1
2	**L2**	THF	84	5	>15:1
3	**L3**	THF	21	11	>15:1
4	**L4**	THF	74	9	>15:1
5	**L5**	THF	82	74	>15:1
6	**L6**	THF	90	79	>15:1
7	**L7**	THF	73	81	>15:1
8	**L8**	THF	90	83	>15:1
9	**L8**	MTBE	89	87	>15:1
10	**L8**	DMF	trace	-	-
11	**L8**	DCM	5	74	>15:1
12	**L8**	MeCN	27	87	>15:1
13[e]	**L8**	MTBE	38	88	>15:1
14[f]	**L8**	MTBE	89	87	>15:1

[a]Unless indicated otherwise, reactions of **1a** (0.10 mmol), **2a** (0.15 mmol), **3a** (0.50 mmol), $Pd(OAc)_2$ (0.005 mmol), and **L** (0.010 mmol) were carried out in a solvent (2 mL) at 80 ºC for 72 h. [b]Isolated yields. [c]Determined by HPLC analysis. [d]Determined by ^1H NMR analysis. [e]The reaction was carried out at 60 ºC. [f]The reaction was carried out at 100 ºC.

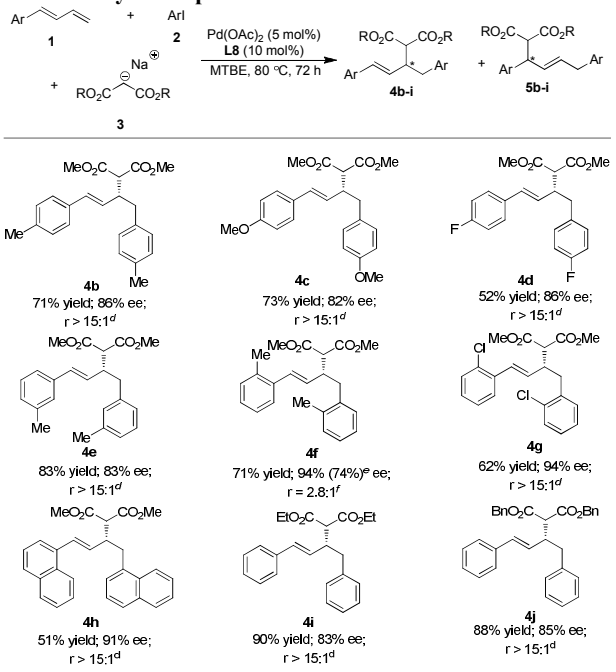
The feasibility of the hypothesis was initially explored by screening chiral ligands for the three-component reaction of (*E*)-1-phenylbutadiene (**1a**) with iodobenzene (**2a**) and sodium dimethyl malonate (**3a**) (Table 1). The chiral ligands commonly employed in the asymmetric allylic alkylation, including Trost ligands,[13] chiral phosphinooxazoline-type P,N ligands[14] and others, which were reported to deliver excellent levels of enantioselectivity in palladium catalysis,[15] were initially evaluated. However, they were unable to give good results (Table S1, in Supporting Information). Then, chiral phosphoramidite ligands that perform well in controlling the stereoselectivity of allylic substitutions[16] were examined. In the presence of 10 mol % of BINOL-based phosphoramidite **L1**,[16] $Pd(OAc)_2$ was indeed able to catalyze the three-component reaction in THF at 80 ºC and the desired 1,2-arylalkylation product **4a** was isolated in 77% yield and with excellent regioselectivity, but without enantioselectivity (entry 1). Finely tuning the structure of BINOL-derived phosphoramidites found that ligands **L2**-**L7** bearing substituents at the 3,3'-positions of the binaphthyl backbone and 7-position of 1,2,3,4-tetrahydroquinoline, enabled the reaction to deliver even more promising levels of asymmetric induction (up to 81 % ee, entries 2-7). A little higher enantiomeric excess was provided by H_8-BINOL-based phosphoramidite **L8** (83% ee, entry 8). The examination of solvents found that the reaction performed well in ether solvents (entries 9-12) and the highest enantioselectivity of 87% ee was observed in MTBE (entry 9). The variation of reaction temperature was unable to significantly alter the stereoselectivity (entries 13 and 14), but a much diminished yield was given at lower temperature (entry 13). The palladium source did not show significant effect on the reaction (Table S2, in Supporting Information).

After the optimal reaction conditions were established, the generality of the asymmetric transformation was subsequently examined. A variety of arylbutadienes (**1b**-**h**) and aryliodides (**2b**-**h**), possessing same aryl groups, were firstly examined in the presence of 5 mol % of $Pd(OAc)_2$ and 10 mol % of **L8** in MTBE at 80 °C (Figure 3). It is necessary to mention that the structures of **4** and **5** are respectively identical to those of **6** and **7** (Figure 2c) in these cases, and thus only two different regiomers are generated. The presence of either electron-releasing or deficient substituent at the *para*-position was nicely tolerated and highly regioselectively generated the target products in high yields and enantioselectivity (**4b**-**4d**). Obviously, the substitution pattern had considerable effect on both regio- and stereoselectivities (**4b**, **4e** and **4f**). For instance, an excellent enantiomeric excess, but a moderate regioselection was obtained in the reaction involving 2-methylphenylbutadiene and 2-methyliodobenzene (**4f**). In contrast, a little lower ee value, but an excellent regioselection was given to the case with either *meta*- or *ortho*-methylphenyl substrate (**4b** or **4e**). Comparing with the results of the substrate with a methyl group at the *ortho*-position (**4f**), the presence of an electron-withdrawing group such as chloride at the *ortho*-position of aryldiene and aryliodine led to a high regio- and enantioselectivities, together with a good yield (**4g**). Further, the sterically hindered naphthyl substrates also underwent a smooth three-component coupling reaction in a satisfactory yield and with high levels of regio- and enantioselectivities (**4h**). Moreover, different malonates were also examined, providing excellent yields (**4i**, 90% yield and **4j**, 88% yield) and high levels of enantioselectivities (**4i**, 83% ee and **4j**, 85% ee).

Next, the generality for a number of arylbutadienes **1** and aryliodides **2**, which contain different aryl substituents, was investigated (Figure 4). Basically, four different regiomers are generated from the reaction, and hence will bring even more challenges to the simultaneous control of both the regio- and stereoselectivities.

To our delight, the application of the optimal conditions to the three-component reaction of (*E*)-1-phenylbutadiene (**1a**) with different iodobenzenes **2** was quite successful to give the corresponding chiral products **4k-4r** in high yields ranging from 74% to 93% and with excellent levels of enantioselectivity of up to 98% ee. Notably, the regioselectivity to preferentially generate **4** over other regiomers was nicely controlled (**4k-4q**) while less regioselective control of 1,2-addition was observed for 2-methyliodobenzene reacting with (*E*)-1-phenylbutadiene to afford **4r**. However, the regiomeric ratios of 1,2-addition product to other regiomers seemingly suffer from the *ortho*- or *meta*-substitution with an electron-releasing group (**4p** and **4r** vs **4q**). Using iodobenzene (**2a**) as the cross coupling partner, a variety of arylbutadienes were finally evaluated. Obviously, both the regio- and enantioselectivities are highly sensitive to the aryl substituents (**4s-4u**). For example, low regioselectivity was obtained for the reaction with *ortho*-substituted phenylbutadiene, albeit with a high enantioselectivity (**4s**), while 2-thiophenyl and 1-naphthyl substituted-butadienes could lead to 1,2-products with high regio- and enantioselection (**4t** and **4u**). The structure and absolute configuration of product **4m** was assigned by X-ray analysis (see Supporting Information).

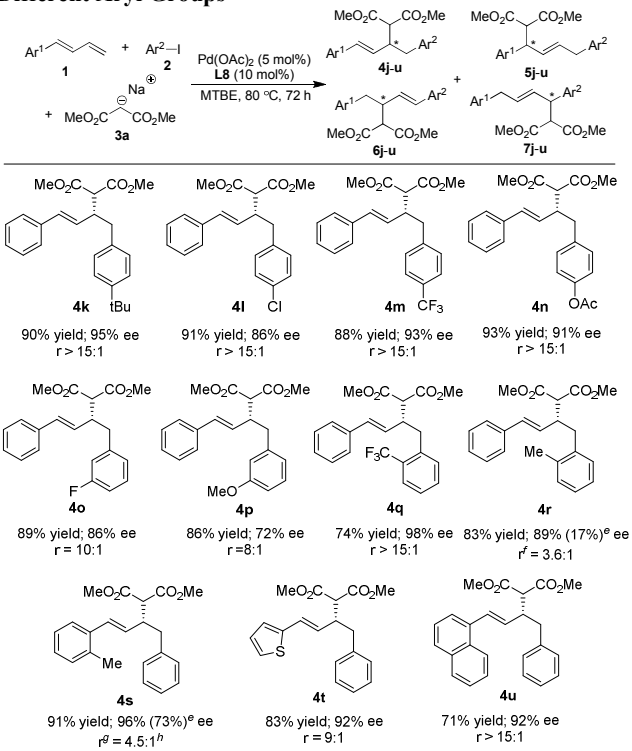
Figure 3. Scope of Arylbutadienes and Aryliodides Containing the Same Aryl Groups[a-d]



[a]Reactions of **1a** (0.10 mmol), **2a** (0.15 mmol), **3a** (0.50 mmol), $Pd(OAc)_2$ (0.005 mmol), and **L8** (0.010 mmol) were carried out in 2 mL of MTBE at 80 ºC for 72 h. [b] Yields are reported as a mixture of regioisomers of **4** and **5**. [c]The *ee* values were determined by HPLC analysis. [d]The ratio (r) represented **4**/**5** and was determined by ^{1}H NMR analysis. [e]The number in the parenthesis is the *ee* value of regiomer **5f**, and was determined by HPLC analysis. [f]For the characterization of the minor regiomer **5f**, see Supporting Information.

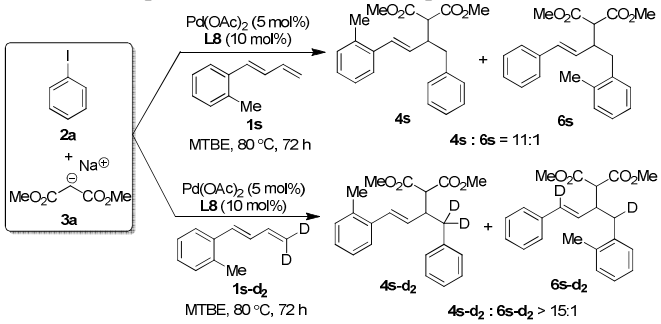
As shown in Figure 2c, all of the regiomers are generated from the nucleophilic substitution of two π-allyl-Pd intermediates **III** and **III'**. To understand how the π-allyl-Pd species are generated, experimental studies on the isotope effect were conducted by the reaction of d_2-*ortho*-methylphenylbutadiene (**1s-d_2**), iodobenzene (**2a**) and sodium dimethyl malonate (**3a**). A similar isotope labeling experiment was reported by Sigman and identified that no deuterium migration occurs.[8p] However, the deuterium migration was found in the minor regiomer **6s-d_2** (Scheme 1). More interestingly, an obvious isotope effect was observed for the regioselectivity. An enhanced regioselectivity (> 15/1 *vs* 11/1) was obtained for the d_2-*ortho*-methylphenylbutadiene (**1s-d_2**), probably due to that the *β*-deuteride elimination and reinsertion reactions proceed much more slowly than the similar transformations with **1s**,[17] and thereby rendering the allyl-Pd intermediate **III'** to be much more slowly formed than **III**. These experimental results aggregately indicated that the *β*-hydride elimination and reinsertion reaction to form allyl-Pd intermediate **II'** indeed occurred, leading to minor products **6** and **7** (Figure 2c).

Figure 4. Scope of Arylbutadienes and Aryliodides Containing Different Aryl Groups[a-e]



[a]Reactions of **1** (0.10 mmol), **2** (0.15 mmol), **3a** (0.50 mmol), $Pd(OAc)_2$ (0.005 mmol), and **L8** (0.010 mmol) were carried out in MTBE (2 mL) at 80 ºC for 72 h. [b]Yields are reported as a mixture of regioisomers of **4**, **5**, **6** and **7**. [c]The *ee* values of major products **4** were determined by HPLC analysis. [d] Unless stated otherwise, the ratio (r) represented major products (**4**)/regiomers (**5**+**6**+**7**), and was determined by ^{1}H NMR analysis. [e]The numbers in the parentheses are the *ee* values of regiomers **6**, and were determined by HPLC analysis.[f]The ratio of **4r/6r** /(**5r+7r**) is 1.0 : 0.10 : 0.18. [g]The ratio of **4s**: **6s**: (**5s+7s**) is 1.0: 0.09: 0.13. [h]For the characterization of the minor regiomer **6s**, see Supporting Information.

Scheme 1. Experimental Studies on Isotope Effect



In summary, we have established a chiral palladium complex-

catalyzed asymmetric three-component reaction for the difunctionalization of 1,3-dienes with aryl iodines and sodium dialkyl malonate, resulting in high yields and excellent levels of regio- and enantioselectivities. The H_8-BINOL-based phosphoramidite turned out to be the optimal ligand, which not only provides high catalytic activity, but also is able to efficiently control the regio- and stereoselectivity. The reaction proceeds via a palladium-catalyzed cascade arylation and asymmetric allylic alkylation, capable of tolerating a broad scope of substrates, including 1,3-dienes and iodoaryl compounds. Two different types of π-allyl palladium intermediates, respectively generated from migratory insertion of the 1,3-diene to aryl Pd(II) and sequential events, including Heck insertion, *β*-hydride elimination and reinsertion reactions, are both involved in the whole reaction process. Notably, this protocol actually provides an important alternative strategy for the enantioselective difunctionalization of 1,3-dienes, leading to synthetically useful chiral chemicals that were hardly prepared from the classical asymmetric allylic alkylation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:
X-ray data of **4m** (CIF)
Experimental procedures; compound characterization data (PDF)

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Author Contributions

§The authors contribute equally to this work.

Notes

The authors declare no competing financial interests.

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