Organic LETTERS

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Regio- and Stereoselective Allylic C−H Arylation with Electron-Deficient Arenes by 1,1′-Bi-2-naphthol−Palladium Cooperation

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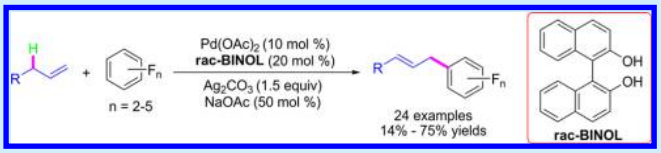
Supporting Information

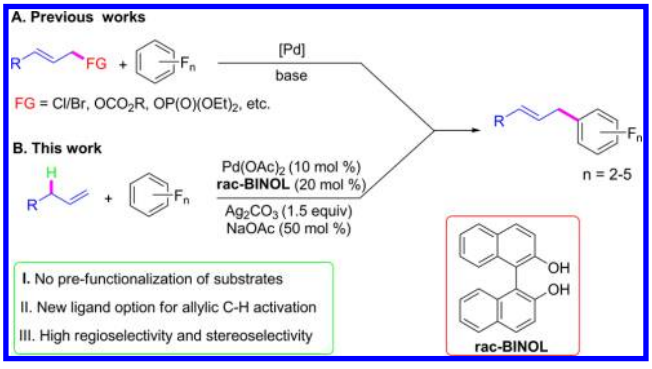
ABSTRACT: A palladium-catalyzed allylic C−H arylation reaction with electron-deficient arenes with high regio- and stereoselectivity is reported. This work represents the first successful use of 1,1′-bi-2-naphthol as the ancillary ligand in allylic C−H activation, which is the key factor for chemoselectivity. Furthermore, high selectivity allylic C−H acetoxylation and amination were also successfully achieved under the same catalytic system.



Allylic C−H bond activation has emerged as a highly valuable strategy for sp^3 C−X (X = C, N, O, etc.) coupling reactions because of its wide variety of substrates and high atom economy compared with traditional Trost−Tsuji-type reactions.[1] The activation has also demonstrated promise as an excellent example of C−H functionalization[2] with high selectivity, which represents a frontier challenge for synthetic chemistry. During the past decade, great efforts have been expended in order to develop high-selectivity allylic C−H functionalization. Numerous groundbreaking results have been achieved, including allylic C−H oxygenation,[3] alkylation,[4] and amination,[5] as well as other types of allylic C−H functionalizations.[6] In particular, palladium-catalyzed allylic C−H activation has shown great advantages in both the substrates scope and selectivity. Among these works, ancillary ligands play important roles in many cases: they favor the formation of π-allylpalladium intermediate and they also control regioselectivity and stereoselectivity. As the most successful and effective ligand, the bis-sulfoxide ligand has shown powerful applicability in catalytic allylic C−H esterification,[3c,d,h,l,n] alkylation,[4c,e,g] amination,[4b,d,f,j] Heck addition,[7] dehydrogenation,[6h] and fluorination.[6l] Although a few other different ligands such as sulfoxide derivatives[3b,j,o] (including DMSO[3a,k,5a,6s]) and 4,5-diazafluorenone were also used,[3i] further investigation into cheaper and universal ligands to promote palladium-catalyzed allylic C−H activation with excellent regioselectivity and stereoselectivity are particularly desirable.

In recent years, polyfloroarenes have been shown to exhibit unique properties for pharmaceutical, material, and electronic devices.[8] The number of reports describing the synthesis of allylic electron-deficient polyfloroarenes has seen a recent surge. These researches, however, elegant, nevertheless require prefunctionalized substrates such as allylic phosphates,[9] allylic carbonate,[10] and allylic halides,[11] which put limits on the scope of the substrate and lead to tediously long steps (A, Scheme 1). Thus, we focus our attention on directly allylic C−H arylation with polyfloroarenes with the hope of avoiding these defects. To the best of our knowledge, reports of allylic C−H arylation in high selectivity, either with electron-rich or electron-deficient arylation reagents, have been rare.[6s,7a,12] Herein, we wish to disclose a novel palladium-catalyzed high selectivity allylic C−H arylation with a series of electron-deficient arenes. For the first time, 1,1′-bi-2-naphthol was used as the ancillary ligand for allylic C−H activation and proved to be the key element for reaction selectivity (B, Scheme 1). More specifically, allylic C−H acetoxylation and amination also proceed within the catalytic system in moderate yield with excellent selectivity. In particular, the easily accessible 1,1′-bi-2-naphthol and its derivatives will enrich choices for allylic C−H activation with high selectivity.

Scheme 1. Approaches for Allylic Arylation with Electron-Deficient Arenes



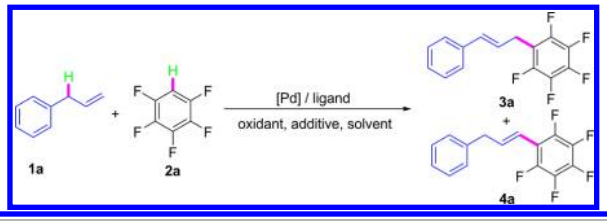
To begin our study, we chose allylbenzene **1a** and pentafluorobenzene as model substrates to identify suitable reaction conditions. In many cases, the ligands usually play an important role in allylic C−H activation; a series of commonly

Received: May 1, 2014
Published: May 12, 2014

   dx.doi.org/10.1021/ol501247b | Org. Lett. 2014, 16, 3118−3121

used *N*- and *P*-ligands for palladium-catalyzed C−H activation were first evaluated[2g,13] in the presence of 10 mol % of $Pd(OAc)_2$ as catalyst, 1.5 equiv of Ag_2CO_3 as oxidant, as well as the base for initial deprotonation of pentafluorobenzene to afford nucleophilic reagent.[14] The results showed that 2,2-bipyridine (L1), 1,2-diphenylethane-1,2-diamine (L5), and monoprotected amino acid ligand L9 were totally ineffective for this transformation (Table 1, entries 1, 5, and 9), and L2, L3, and L8 provided only trace amounts of the desired product (Table 1, entries 2, 3, and 8). When 1,4-bis(oxazol-2-yl)benzene (L4) was used as the ligand (Table 1, entry 4), the desired linear allylated product **3a** was obtained in low yield with poor regioselectivity. Triphenylphosphine (L6) and 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (L7) gave the same results of low yield and relatively poor regioselectivity (Table 1, entries 7 and 8). However, we were delighted to observe that 1,1′-bi-2-naphthol (L10) had a substantial influence on the reaction (Table 1,entry 10) and furnished the intermolecular allylic C−H arylation product **3a** in 24% yield with excellent regio- and stereoselectivity (**3a**/**4a** > 97:3 and no branched or *Z*-allylated isomers were observed). We subsequently used 1,1′-bi-2-naphthol as the ligand to further test the solvent, and DME (1,2-dimethoxyethane) was found to be the best choice (Table 1, entries 11−13). Other effective palladium catalysts such as $PdCl_2$ and $Pd(TFA)_2$ also were examined and only gave trace amounts of the desired product (Table 1, entries 16 and 17). Other screenings of silver sources proved inferior to Ag_2CO_3 for the catalytic system (Table 1, entries 14 and 15). We then examined various additives in order to improve catalytic efficiency. Indeed, the introduction of basic additives significantly increased the yield of allylic arylation product, and the desired product was obtained in 73% yield with excellent regio- and stereoselectivity in the presence of 50 mol % of NaOAc. In fact, this yield is relatively high yield compared to many other allylic C−H activation reactions. As the 1,1′-bi-2-naphthol could efficiently control regio- and stereoselectivity of the allylic arylation, we finally concentrated our optimization on various derivatives of 1,1′-bi-2-naphthol ligands[15] with the goal of increasing the yield of **3a** even higher. Although the products were obtained in excellent yield, the relatively low selectivity acted to reduce the overall efficiency of L11 (Table 1, entry 22). Compared to 1,1′-bi-2-naphthol (L10), L14 obtained the products in a slightly lower yield with excellent selectivity (Table 1, entry 25); L12, L13, and L15 provided relatively worse results both in yield and selectivity (Table 1, entries 23, 24, and 26). If the 1,1′-bi-2-naphthol was removed from the reaction system, the regio- and stereoselectivity of the allylic arylation would be decreased (Table 1, entry 27). Finally, we fixed on Table 1, entry 21, as the optimal reaction conditions.

Table 1. Reaction Conditions Screening[a]



entry	[Pd]	ligand	oxidant	additive	solvent	yield of **3a**[b]	**3a**:**4a**[c]
1	$Pd(OAc)_2$	L 1	Ag_2CO_3	----	DCE	0%	----
2	$Pd(OAc)_2$	L 2	Ag_2CO_3	----	DCE	<5%	----
3	$Pd(OAc)_2$	L 3	Ag_2CO_3	----	DCE	<5%	----
4	$Pd(OAc)_2$	L 4	Ag_2CO_3	----	DCE	11%	79:21[d]
5	$Pd(OAc)_2$	L 5	Ag_2CO_3	----	DCE	0%	----
6	$Pd(OAc)_2$	L 6	Ag_2CO_3	----	DCE	16%	89:11
7	$Pd(OAc)_2$	L 7	Ag_2CO_3	----	DCE	14%	67:33
8	$Pd(OAc)_2$	L 8	Ag_2CO_3	----	DCE	<5%	----
9	$Pd(OAc)_2$	L 9	Ag_2CO_3	----	DCE	0%	----
10	$Pd(OAc)_2$	L 10	Ag_2CO_3	----	DCE	24%	>97:3
11	$Pd(OAc)_2$	L 10	Ag_2CO_3	----	THF	29%	>97:3
12	$Pd(OAc)_2$	L 10	Ag_2CO_3	----	DMF	26%	>97:3
13	$Pd(OAc)_2$	L 10	Ag_2CO_3	----	DME	43%	>97:3
14	$Pd(OAc)_2$	L 10	AgTFA	----	DME	0%	----
15	$Pd(OAc)_2$	L 10	AgOAC	----	DME	11%	>97:3
16	$PdCl_2$	L 10	Ag_2CO_3	----	DME	<5%	----
17	$Pd(TFA)_2$	L 10	Ag_2CO_3	----	DME	<5%	----
18	$Pd(OAc)_2$	L 10	Ag_2CO_3	HOAc	DME	41%	>97:3
19	$Pd(OAc)_2$	L 10	Ag_2CO_3	$LiOAc{\cdot}2H_2O$	DME	46%	>97:3
20	$Pd(OAc)_2$	L 10	Ag_2CO_3	KOAc	DME	55%	>97:3
21	**$Pd(OAc)_2$**	**L 10**	**Ag_2CO_3**	**NaOAc**	**DME**	**73%**	**>97:3**
22	$Pd(OAc)_2$	L 11	Ag_2CO_3	NaOAc	DME	81%	88:12
23	$Pd(OAc)_2$	L 12	Ag_2CO_3	NaOAc	DME	66%	91:9
24	$Pd(OAc)_2$	L 13	Ag_2CO_3	NaOAc	DME	70%	92:8
25	$Pd(OAc)_2$	L 14	Ag_2CO_3	NaOAc	DME	65%	>97:3
26	$Pd(OAc)_2$	L 15	Ag_2CO_3	NaOAc	DME	67%	91:8
27	$Pd(OAc)_2$	----	Ag_2CO_3	NaOAc	DME	79%	85:15[d]

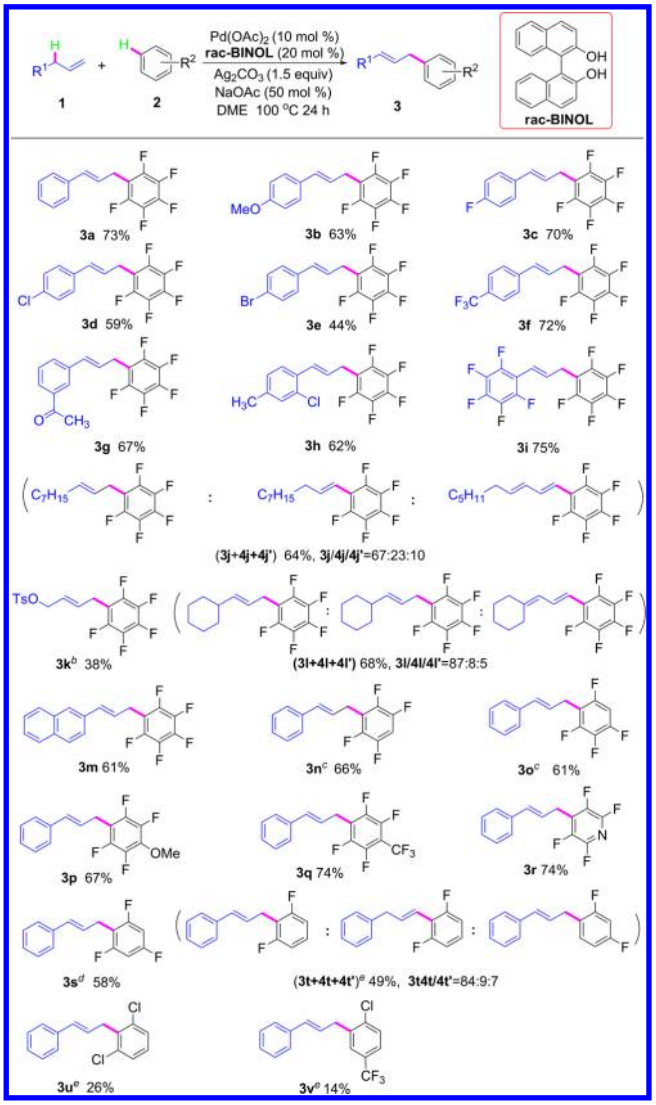
[a]The reaction was carried out with palladium (10 mol %), ligand (20 mol %), oxidant (1.5 equiv), additives (50 mol %), **1a** (0.30 mmol), and **2a** (1.20 mmol) in solvent (1.0 mL) at 100 °C for 24 h under argon. For L1−L15 see the Supporting Information. [b]Yield of isolated product. [c]Determined by ^1H NMR and ^{19}F NMR spectroscopy. [d]Trace amounts of branch product were detected.

In order to demonstrate the generality of this allylic C−H arylation reaction, the substrate scope was investigated under optimized conditions (Scheme 2). We first surveyed the compatibility of the olefin partners. Arylation products were obtained in moderate to good yields with excellent regio- and stereoselectivity, regardless of whether an electron-donating group (CH_3, OCH_3) or electron-withdrawing group (F, Cl, Br, CF_3, $C(O)CH_3$) was introduced on the aryl moiety. Aryl C−Cl and aryl C−Br bonds were well tolerated under the catalytic system, which provided opportunities for further functionalization (**3d**, **3e**). Allylpentafluorobenzene could work well with pentafluorobenzene and obtain the highest yield of desire product (**3i**). Besides substituted allylbenzene, aliphatic alkenes, for example, 1-decene and 4-substituted-1-butene, were also suitable substrates for this allylic arylation. Indeed, the products were obtained in synthetically useful yields, although the ratios of Heck-type isomers were increased, and no branched isomers were detected (**3j**, **3k**). Allylcyclohexane provided the desired product in a moderate yield with relatively good selectivity (**3l**). Subsequently, a series of electron-deficient arenes were introduced into the reaction system. Substituted tetrafluorobenzenes with different electronic substituents (OCH_3, CF_3) were found to be complete substrates and afforded the products in good yields with excellent selectivity (**3p**, **3q**). 1,2,4,5-Tetrafluorobenzene and 1,2,3,5-tetrafluorobenzene furnished the products in moderate yields without *Z*-allylated or branched isomers, and only trace amounts of diallylated products were detected by GC (**3n**, **3o**). 2,3,5,6-Tetrafluoropyridine could give a relatively high yield of the desired product exclusively (**3r**). 1,3,5-Trifluorobenzene and 1,3-difluorobenzene were also successfully allylated in reasonable yields with good selectivity (**3s**, **3t**). It is noteworthy that other types of electron-deficient arenes such as substituted chlorobenzene could also undergo the allylated reaction and gave products in low yields with excellent selectivity (**3u**, **3v**). Since these substrates had a relatively low reactivity and often failed to give the corresponding product even in the allylic substitution reaction, this result was truly an exciting breakthrough.

In order to demonstrate the broad applicability of this catalytic system, we carried out allylic C−H acetoxylation and amination under standard reaction conditions. Using 4 equiv of

dx.doi.org/10.1021/ol501247b | *Org. Lett.* 2014, 16, 3118−3121

Scheme 2. Scope of Allylic C−H Arylation[a]

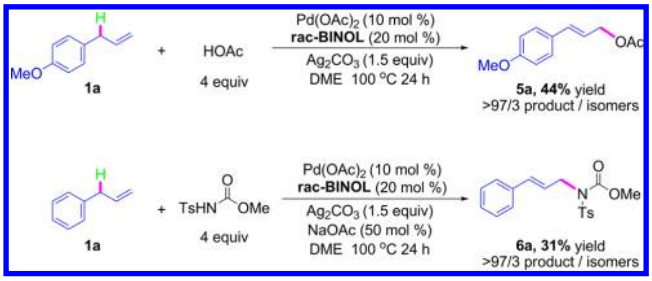


[a]The reaction was carried out with $Pd(OAc)_2$ (10 mol %), 1,1′-Bi-2-naphthol (20 mol %), Ag_2CO_3 (1.5 equiv), NaOAc (50 mol %), **1** (0.3 mmol) and **2** (1.2 mmol) in DME (1.0 mL) at 100 °C for 24 h under argon. Without a special note, the isomeric ratio (**3a**/**4a**) > 97:3. [b]Run with $Pd(OAc)_2$; 15 mol % and 18% yield of Heck-type product isomer was formed. [c]A trace amount of diallylated products were detected by GC. [d]7% yield of Heck-type product isomer was formed. [e]Reaction runs at 120 °C for 48 h.

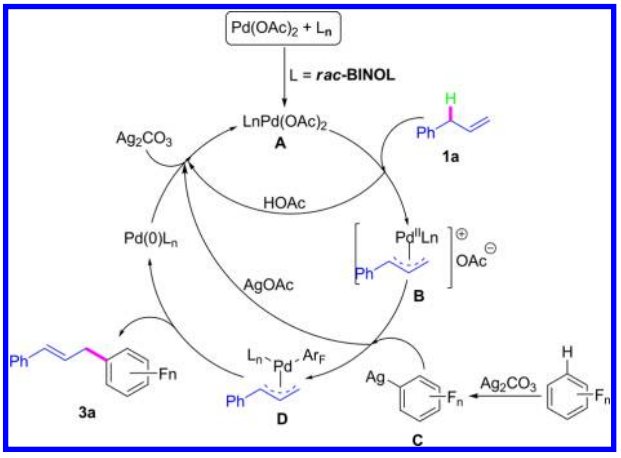
HOAc as the nucleophiles, allylic C−H acetoxylation was successfully accomplished in a synthetically useful yield with excellent selectivity. The same result was obtained in allylic C−H amination reaction (Scheme 3). We believe that after appropriate optimization of the catalytic system, yields of the product will be increased accordingly.

Primary mechanistic studies were carried out by stoichiometric reaction of a π-allylpalladium complex with pentafluorobenzene (Supporting Information). In the presence of Ag_2CO_3 and NaOAc, the product was obtained in 37% yield, and only trace amounts of desired product were formed in the absence of Ag_2CO_3. According to these results, we proposed the mechanism shown in Scheme 4. The catalytic cycle is initiated by $Pd(OAc)_2$ coordinating with *rac*-Binol to form the activated palladium complex **A**, and then through palladium-catalyzed allylic C−H activation, π-allylpalladium complex **B** is formed. At the same time, Ag_2CO_3 works as the base for initial deprotonation of pentafluorobenzene to afford nucleophilic reagent, which subsequently reacts with **B** and generates complex **D**. Finally, reductive elimination of **D** results in formation of the allylic C−H arylation products and Pd(0) species, which is oxidized by silver salts to reinitiate the catalytic cycle.

Scheme 3. Allylic C−H Acetoxylation and Amination



Scheme 4. Plausible Mechanism of Allylic C−H Arylation



In conclusion, we have developed a palladium-catalyzed allylic C−H arylation reaction with a series of electron-deficient arenes showing good to excellent regio- and stereoselectivity. This work represents the first successful use of 1,1′-bi-2-naphthol as the ancillary ligand in allylic C−H activation, and high selectivity allylic C−H acetoxylation and amination were also achieved under the catalytic system. Further investigations of asymmetric allylic alkylation reactions are in progress.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data for all new compounds are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

dx.doi.org/10.1021/ol501247b | *Org. Lett.* 2014, 16, 3118−3121

■ ACKNOWLEDGMENTS

We are grateful for the NSFC (Nos. 21272100) and Program for New Century Excellent Talents in University (NCET-11-0215 and lzujbky-2013-k07) financial support.

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