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Allyl—aryl coupling of allylic carbonates with arylboronic acids catalyzed by palladium nanoparticles in ionic liquid



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ABSTRACT

A practical and greener process for the allyl—aryl coupling of allylic carbonates with arylboronic acids catalyzed by in situ generated palladium nanoparticles (PdNPs) in ionic liquid (IL) has been described. The PdNPs showed high catalytic activity for the coupling reaction in the IL to afford allyl—aryl coupling products in good to high yields with complete regio- and *E*/*Z* selectivities. The PdNPs were readily immobilized in the IL phase and the catalyst can be reused several times without significant loss of catalytic activity and stereospecificity.

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1. Introduction

The Pd-catalyzed Suzuki-Miyaura coupling reaction is one of the most versatile methods for C–C bond formation in organic synthesis.¹ While the coupling reaction has most often been applied to sp²-hybridized halides and pseudohalides, significant progress toward extending the coupling process to alkyl and alkynyl electrophiles has recently been achieved.^{1,2} However, the coupling reaction of allylic electrophiles has rarely been reported,^{3–5} and in most of the reports, the allylic partners have been confined to primary allylic halides or allylic alcohol derivatives. In contrast, the coupling reaction of 1,3-disubstituted secondary allylic electrophiles with arylboronic acids has largely been unexplored⁶⁻⁸ despite the coupling products are prevalent motifs in a wide variety of important medicinally relevant agents and natural products.⁹ Until most recently, Uozumi and Yamada,¹⁰ Tian,¹¹ Watson,¹² and our group¹³ accomplished respectively Suzuki-Miyaura coupling reactions of secondary allylic electrophiles with arylboronic acids. The method also offered a possibility to conduct the stereoselective allyl-aryl coupling through the stereospecific cross-coupling of chiral secondary allylic electrophiles. Most recently, we demonstrated that the allyl-aryl coupling reaction could be catalyzed by palladium nanoparticles (PdNPs) generated in situ from homo-coupling of arylboronic acids with palladium acetate in pure water.^{13b} We found that the reaction is catalyzed by PdNPs without any ligands and additional stabilizers, furnishing the coupling products in high levels of yields with high stereospecificities. However, the PdNPs were difficult to reuse because they leached to the organic solvent during the process of product extraction. Therefore, the development of more practical and greener allyl–aryl coupling process with advantage in catalyst immobilization and recycling is highly desired.

PdNPs-catalyzed cross-coupling reactions have recently attracted great attention due to their high catalytic activity and the fact of allowing ligand-free synthesis.¹⁴ However, additional stabilizers are generally required for the protection of PdNPs to prevent aggregation into inactive palladium black. Electrostatic or steric protection methods were mainly used for stabilization of PdNPs in solution, for example, the use of polymers, dendrimers, ligands, tetraalkylammonium salts, or polyoxoanions.¹⁴ Room temperature Ionic liquids (ILs) have been extensively used as alternative reaction media in catalytic reactions.¹⁵ They have also offered to be excellent media for the formation and stabilization of PdNPs.¹⁶ The ILs, in particular imidazolium-based ILs, are probably composed of imidazolium aggregates located immediately adjacent to PdNPs surface, affording both steric and electronic protection against aggregation and/or agglomeration. In addition, PdNPs can be readily immobilized in IL phase to achieve catalyst recycling. Based on these advantageous, ligand-free cross-coupling catalyzed by PdNPs



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in IL medium has emerged as a practical and greener strategy for the amelioration of traditional cross-coupling reaction.^{16,17}

Based on our continuous effort to the development of practical and greener allyl-aryl coupling reactions, we envisioned that the allyl-aryl coupling reaction of allylic carbonates with arylboronic acids could perform in a biphasic system of 1-butyl-3methylimidazolium hexafluorophosphonate ($[bmim]PF_6$) and water. We reasoned that PdNPs, which are generated in situ from homocoupling of arylboronic acids with palladium acetate in the reaction system, could be stabilized and immobilized in IL phase. After the reaction complete, the coupling product could be extracted with organic solvents such as ether and the water-soluble byproducts of boronates could be separated in water phase, and then the catalyst recycling would be feasible (Scheme 1). Herein we report PdNPscatalyzed allyl-aryl coupling reaction of allylic carbonates with arylboronic acids in ILs. The PdNPs can be successfully immobilized in the IL layer, and reveal high catalytic activity for the allyl-aryl coupling reaction. In addition, the PdNPs can be reused three times without any loss of catalytic activity and stereospecificity.



Scheme 1. Synthetic strategy of PdNPs-catalyzed allyl-aryl coupling reaction in ionic liquids.

2. Results and discussion

Initial investigations focused on examining the allyl-aryl coupling reaction of allylic carbonate **1a** with phenylboronic acid (**2a**) as standard reaction partners in different solvents (Table 1). For comparison, we firstly conducted the reaction in different organic solvents. As our previous report,^{13b} the reaction was highly effective in water to afford the coupling product in full conversion (entry 7). However, the reaction was less effective in organic solvents (entries 1–6). With these results in hand, we next examined the coupling reaction in pure 1-butyl-3-methylimidazolium (bmim) based ILs with different counter anions. To our delight, the coupling reaction of **1a** with **2a** in the presence of 1 mol % of Pd(OAc)₂ in [bmim]PF₆ proceeded smoothly to afford allyl-aryl coupling product 3a in full conversion with complete regio- and E/Z-selectivities, and no β -H elimination product was observed (entry 8). The reaction performed well in other ILs, such as [bmim]SbF₆ (entry 9) and [bmim] NTf₂ (entry 10). However, low conversion was observed when the reaction carried out in [bmim]OTf (entry 11), and complex mixture was obtained in [bmim]BF₄ (entry 12). As our expected, The reactions were tolerated in the biphasic system of [bmim]PF₆ and water to furnish the coupling product 3a in full conversion with excellent selectivities (entry 13).¹⁸ The reaction was also highly effective in biphasic system of [bmim]PF₆ and insoluble organic solvents, such as ether, toluene and isopropanol (entries 14-16) Next, we tried catalyst recycling in biphasic system of [bmim]PF₆ and water. As expected, the palladium catalyst was efficiently immobilized in the IL, which can be reused three times without any loss of catalytic efficiency (entries 17 and 18). In the fourth run, the

Table 1

Allyl-aryl coupling of allylic carbonate 1a with phenylboronic acid (2a) in an IL^a

	OBoc	+ PbB(OH).	Pd(OAC) ₂ (1 mol%)	Ph
Ph	Me 1a	2a	solvent 25 ^o C, 4 h	Ph Me 3a
Entry		Solvent		Conversion (%) ^b
1		THF		16
2		1,4-Dioxane		12
3		Ether		31
4		Toluene		22
5		MeOH		50
6		iPrOH		47
7		H ₂ O		>99
8		[bmim]PF ₆		>99
9		[bmim]SbF ₆		>99
10		[bmim]NTf ₂		>99
11		[bmim]OTf		38
12		[bmim]BF ₄		Complex mixture
13		[bmim]PF ₆ /H ₂	0	>99
14		[bmim]PF ₆ /eth	ner	>99
15		[bmim]PF ₆ /tol	uene	>99
16		[bmim]PF ₆ / ⁱ Pr	OH	>99
17 ^c		[bmim]PF ₆ /H ₂	0	>99
18 ^d		[bmim]PF ₆ /H ₂	0	95
19 ^{e,f}		[bmim]PF ₆ /H ₂	0	>99

 a Reaction conditions: Pd(OAc)_2 (1 mol %), 1a (0.4 mmol), 2a (0.6 mmol), solvent (0.4 mL of IL or IL/other solvent=0.4 mL/0.4 mL), 25 °C, 4 h.

^b Determined by ¹H NMR of the crude reaction mixture.

^c Catalyst recycling of entry 13.

^d Catalyst recycling of entry 17.

^e Catalyst recycling of entry 18.

^f The reaction carried out for 18 h.

catalytic activity was decreased, but the reaction completed when the reaction time prolonged to 18 h (entry 19).

As our expected, we found that the reaction system turned black after few minutes no matter pure ILs or biphasic system. And for the reaction in [bmim]PF₆/water, water phase become clear after stop the stirring, which means the catalyst immobilized efficiently in the IL phase. In order to recognize the real catalytic species, the immobilized catalyst was analyzed by the transmission electron microscopy (TEM). The first sample made from after first run of coupling reaction in [bmim]PF₆/water biphasic system (entry 13). As illustrated in Fig. 1, the TME analysis indicated that PdNPs were generated and dispersed well with an average particle sized of 3.2 nm (Fig. 1a). The PdNPs was also generated in situ in neat [bmim]SbF₆ with an average particle sized of 2.8 and slightly broad size distribution (Fig. 1b). After fourth run of the catalyst recycling, the PdNPs still dispersed well in the IL phase (Fig. 1c). This result indicated that lowered catalytic activity of the fourth cycle was not resulted from the catalyst aggregation. Next, the leaching amount of the PdNPs was determined by ICP-AES analysis. 45.2 µg and 18.3 µg of Pd were leached out to the ether layer and water phase, respectively, during the phase-separation of the first run. After second cycle, 13.8 µg (ether layer) and 4.7 µg (water phase) of Pd were leached out. And after third cycle, 9.3 µg (ether layer) and 1.1 µg (water phase) of Pd were leached out. During the product extraction of the fourth cycle, 23.7 μ g (ether layer) and 5.7 μ g (water phase) of Pd were leached out. These results clearly implied that catalyst leaching is a reason for the decreased catalytic activity for the catalyst recycling.

With optimized reaction conditions in hand, the generality of the allyl–aryl coupling reaction was evaluated with a variety of allylic carbonates **1** and arylboronic acids **2** in [bmim]SbF₆ and [bmim]PF₆/ water biphasic system (Table 2). Firstly, we examined the coupling reaction of **1a** with arylboronic acids having different electronic and steric properties. The reaction performed well with arylboronic acids with electron-donating groups to afford corresponding coupling



Fig. 1. TEM image of PdNPs. a) A sample made from the coupling reaction of **1a** with **2a** in [bmim]PF₆/H₂O after full conversion. b) A sample made from the coupling reaction of **1a** with **2a** in [bmim]SbF₆ after full conversion. c) A sample made from fourth run of catalyst recycling for the reaction of **1a** with **2a** in [bmim]PF₆/H₂O.

products **3b** and **3c** in high yields with complete regio- and E/Z selectivities (entries 1–4). However, low yields were obtained when the reaction with 4-trifluoromethylphenylboronic acid (**2d**) in both of the neat IL and biphasic system (entries 5 and 6). The reaction proceeded smoothly with 1-naphthylboronic acid (**2e**) to furnish the coupling product **3e** in high yields (entries 7 and 8). Next, we

examined the reaction of a variety of allylic carbonates with phenylboronic acid (2a) in [bmim]SbF₆ and [bmim]PF₆/water biphasic system. The allylic carbonates 1b and 1c were employed successfully in the coupling reaction to afford coupling products **3f** and **3g** in high levels of isolated yields (entries 9-12). However, the reaction less effective for the substrate **1d** with sterically hindered isopropyl group (entries 13 and 14). The reaction efficiency was decreased for the reaction of 3-cvclohexvl-substituted allvlic carbonate 1e. giving the coupling product 3i in moderate yield with complete regio- and E/Z-selectivities (entries 15 and 16). Importantly, more challenging substrates such as 1-benzyl-3-phenylallylic carbonates 1f-1i, which greatly tend to undergo β-H elimination in Pd-catalyzed system to form highly conjugated 1,3-butadienes, were also tolerated in the IL system, thus affording corresponding coupling products **3j**-**3m** in good yields with complete regio- and E/Z-selectivities, and no 1,3butadienes were observed (entries 17-24). For the coupling reaction of 1f with 2a (entry 17), the catalyst recycling was performed after the product extraction with ether. Although the catalytic activity was decreased in the second and third cycles, high selectivities of the product 3j were maintained, and have no the eliminated compound was observed. The reaction of 1-carbonylmethyl allylic carbonates **1***i* and **1***k*, which also readily undergo β -H elimination to form $\alpha, \beta, \gamma, \delta$ -unsaturated carbonyl compounds, still worked well to give coupling products **3n** and **3o** in good yields (entries 25-28). The PdNPs were also effective for the coupling reaction of cinnamyl carbonate 11 with arylboronic carbonates, providing corresponding coupling products **3p**-**3t** in high levels of isolated yields (entries 29-33).

After successful realization of the allyl–aryl coupling in the IL, we subsequently turned our attention toward the examination of stereospecific allyl–aryl coupling using enantiomeric excessed allylic carbonate (*S*)-**1a**. Gratifyingly, as shown in Table 3, the coupling reaction of (*S*)-**1a** (96% ee) with phenylboronic acid (**2a**) in [bmim]PF₆ provided coupling product (*R*)-**3a** with inversion of the absolute configuration in full conversion with excellent stereospecificity (94% ee, entry 1). However, the stereospecificities were decreased when the reaction carried out in [bmim]SbF₆ and [bmim]NTf₂ (entries 2 and 3). Interestingly, the reactions proceeded well in biphasic system, such as [bmim]PF₆/water, [bmim]SbF₆/toluene and [bmim]NTf₂/water, giving coupling product (*R*)-**3a** in full conversion with high stereospecificities (entries 4–6). The PdNPs can be reused three times in [bmim]PF₆/water biphasic system without any loss of catalytic activity and stereospecificity (entries 7 and 8).

3. Conclusion

In conclusion, we have developed a practical process of the allyl–aryl coupling reaction of allylic carbonates with arylboronic acids catalyzed by in situ generated PdNPs in the IL at ambient temperature. The PdNPs showed high catalytic activity in the IL even for the coupling reaction of easily eliminated allylic carbonates, providing allyl–aryl coupling products in good to high yields with complete regio- and *E*/*Z* selectivities. The PdNPs can be readily immobilized in the IL, and the catalyst can be reused three times without significant loss of catalytic activity and stereospecificity. However, the catalytic activity still decreased for further recycling. Further studies will focus on finding better supports for the immobilization of PdNPs and the development more practical allyl–aryl coupling process.

4. Experimental section

4.1. General procedure for allyl-aryl coupling in the IL

To a 10 mL Schlenck flask equipped with a stir bar, was added $Pd(OAc)_2$ (0.004 mmol), allyl carbonates **1** (0.4 mmol), arylboronic

 Table 2

 PdNP-Catalyzed allyl-aryl coupling of 1 with 2 in the IL^a

Fatas	Allulia ambanata 1	R ₂ 2 IL, 20 0, 4 II R ₁ 3	R2	
EIIIIY		Pioduct 3	Solvent	field (%)
	OBoc	Ar I		
	Ph Me 1a	Ph		
1		3b , Ar=2-Me-C ₆ H ₄	[bmim]PF ₆ /H ₂ O	83
2		3b , Ar=2-Me-C ₆ H ₄	[bmim]SbF ₆	87
3		3c , Ar=4-MeO-C ₆ H ₄	[bmim]PF ₆ /H ₂ O	93
4		3c , $Ar=4-MeO-C_6H_4$	[bmim]SbF ₆	95
5		30 , $AF = 4 - CF_3 - C_6H_4$ 3d $AF = 4 - CF_3 - C_6H_4$	[Dm1m]PF ₆ /H ₂ O	27
7		3e, $Ar=1$ -naphthyl	[bmim]PF ₆ /H ₂ O	86
8		3e , Ar=1-naphthyl	[bmim]SbF ₆	96
9	OBoc	Ph	[bmim]PF ₆ /H ₂ O	88
10	Pn 1b	Ph 3f	[bmim]SbF ₆	93
11	OPec	Ph	[bmim]PF ₆ /H ₂ O	93
		Ph		
12	10	3g	[bmim]SbF ₆	85
13	OBoc	Ph	[bmim]PF ₆ /H ₂ O	8 ^c
	Ph	Ph		
14	1d	3h	[bmim]SbF ₆	11 ^c
15	OBoc	Ph	[bmim]PF ₆ /H ₂ O	57
16	1 e	3i	[bmim]SbF ₆	31
17 ^d	OBac	Ph	[bmim]PF ₆ /H ₂ O	85
	Ph	Ph		
18		511 3j	[bmim]SbF ₆	75
19	510.00		[bmim]PF ₆ /H ₂ O	87
		Ph []		
20	Ph 1g	Ph 3k	[hmim]SbF_	80
20	· 3 · ·		[ուլլլլ]շու։	69
21			[hmim]DE /U O	<u>ە</u> م
∠1	EtO ₂ CO	Ph	[DIIIIII]Pr ₆ /H ₂ U	δU
	Ph	Ph		
22	1h	31	[bmim]SbF ₆	85
23	FtO ₂ CO OMe	Ph	[bmim]PF ₆ /H ₂ O	60
24	n 1i	3m	[bmim]SbF ₆	76
25	EtO ₂ CO	Ph	[bmim]PF ₆ /H ₂ O	77
	COOEt	COOEt		
26	· · · 1j	511 3n	[bmim]SbF ₆	75
27			[bmim]PF ₆ /H ₂ O	73
	Ph´ 🎽 🔨 `	Ph' 🔶 🔨 🔪 30		
	~ ~			
28	Ph ```````OCO2Et	Ph	[bmim]SbF ₆	60

(continued on next page)

Table 2	(continued)
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Entry	Allylic carbonate 1	Product 3	Solvent	Yield (%) ^b
29		3p , Ar=Ph	[bmim]PF ₆ /H ₂ O	96
30		3q , Ar=2-Me-C ₆ H ₄	[bmim]PF ₆ /H ₂ O	95
31		3r , Ar=4-MeO-C ₆ H ₄	[bmim]PF ₆ /H ₂ O	97
32		3s , Ar=4-CF ₃ -C ₆ H ₄	[bmim]PF ₆ /H ₂ O	80
33		3t , Ar=1-naphthyl	[bmim]PF ₆ /H ₂ O	95

^a Reaction conditions: Pd(OAc)₂ (1 mol%), 1 (0.4 mmol), 2 (0.6 mmol), [bmim]PF₆/H₂O (0.4 mL/0.4 mL) or [bmim]SbF₆ (0.4 mL), 25 °C, 4 h.

^b The yields are of isolated material.

^c Determined by ¹H NMR of the crude reaction mixture.

^d Catalyst recycling of entry 17, second run: 55% yield; third run: 58% yield.

acids **2** (0.6 mmol), and an IL (0.4 mL) or IL/water (0.4 mL/0.4 mL). The reaction mixture was stirred at 25 °C for 4 h. The reaction mixture was extracted with ether (1 mL×3), dried over Na₂SO₄, filtered, and the solvent was evaporated. The residue was purified by flash column chromatography (ethyl acetate: petroleum ether, 1:200–1000) to furnish corresponding allyl–aryl coupling products.

4.2. General procedure for catalyst recycling

To a 10 mL Schlenck flask equipped with a stir bar, was added $Pd(OAc)_2$ (0.004 mmol), allyl carbonate **1a** (0.4 mmol), phenylboronic acid **2a** (0.6 mmol), [bmim]PF₆ (0.4 mL) and water (0.4 mL). The reaction mixture was stirred at 25 °C for 4 h. The reaction mixture was extracted with ether (1 mL×3), dried over Na₂SO₄, filtered, and the solvent was evaporated to obtain coupling product **3a**. After getting rid of the water phase by syringe, **1a** (0.4 mmol), **2a** (0.6 mmol) and water (0.4 mL) were added to run the next cycle.

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Table 3

Stereospecific allyl–aryl coupling of (S)-1a with 2a in the IL^a

		Pd(OAc) ₂ (1 mol%)	Ph
Ph (S)- 96%	Me 2a 1a ee	solvent Ph 25 °C, 4 h	Me (<i>R</i>)- 3a
Entry	Solvent	Conversion (%) ^b	ee (%) ^c
1	[bmim]PF ₆	>99 (95)	94
2	[bmim]SbF ₆	>99 (93)	83
3	[bmim]NTf ₂	>99 (94)	75
4	[bmim]PF ₆ /H ₂ O	>99 (92)	93
5	[bmim]SbF ₆ /toluene	>99 (96)	93
6	[bmim]NTf ₂ /H ₂ O	>99 (95)	93
7 ^d	[bmim]PF ₆ /H ₂ O	>99 (98)	95
8 ^e	[bmim]PF ₆ /H ₂ O	>99 (93)	96

^a Reaction conditions: Pd(OAc)₂ (1 mol %), (S)-**1a** (0.4 mmol), **2a** (0.6 mmol), IL (0.4 mL) or IL/other solvent (0.4 mL/0.4 mL) 25 $^{\circ}$ C, 4 h.

^b Determined by ¹H NMR of the crude reaction mixture. Isolated yields are shown in parentheses.

 $^{\rm c}$ Determined by HPLC using chiral stationary phase. The absolute configuration was determined by comparison the sign of optical rotation with that of the reported data. 9

^d Catalyst recycling of entry 4.

^e Catalyst recycling of entry 7.

Supplementary data

Supplementary data related to this chapter can be found at http://dx.doi.org/10.1016/j.tet.2015.01.046.

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