Cross-Coupling

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Regioselective and Stereospecific Cross-Coupling of Primary Allylic Amines with Boronic Acids and Boronates through Palladium-Catalyzed C–N Bond Cleavage**

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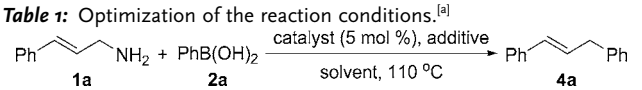
The cross-coupling of allylic electrophiles with boronic acids and boronates is extremely useful for the formation of C–C bonds and for the introduction of the allyl moieties to target compounds.[1,2] Allylic halides,[3] esters,[4] carbonates,[4f,g,5] phosphates,[6] and alcohols[7] have been identified as allylic electrophiles with significantly different reactivity and selectivity. It is noteworthy that the employment of an allylic alcohol as the allylic electrophile is very attractive with respect to atom economy because the leaving OH group has a mass of 17 amu, which is much smaller than that of a halo or an OR ($R \neq H$) group. Nevertheless, the coupling of an α-chiral allylic alcohol with a boronic acid has been reported to afford a racemic product.[7f] To our knowledge, a leaving group with a mass smaller than 17 amu has not yet been reported for the coupling of an allylic electrophile with an organoboron.

In contrast to allylic halides and alcohol derivatives, allylic amines have rarely been employed to deliver allyl moieties to final products in the cross-coupling reactions owing to the poor leaving ability of the amino group.[8] Notably, in 1995 Trost et al. described a nickel-catalyzed cross-coupling of terminal tertiary allylic amines with boronic acids.[8g] Although the reaction suffers from narrow substrate scope and poor selectivity, this study, together with our interest in C–N bond cleavage,[9] prompted us to investigate the possibility of using primary allylic amines as the allylic electrophiles. Herein, we report that the NH_2 group, having a mass of 16 amu, acts as an effective leaving group in the palladium-catalyzed regioselective and stereospecific cross-coupling of primary allylic amines with boronic acids and boronates. Notably, complete transfer of chirality was achieved when using α-chiral primary allylic amines as the allylic electrophiles.

Initially, we found that 5 mol% of $[Pd(PPh_3)_4]$ could catalyze the cross-coupling of primary allylic amine **1a** with boronic acid **2a** in dioxane at 110°C to give alkene **4a** in 70% yield (Table 1, entry 1). This reaction proceeded with exclusive α selectivity, and no *E*/*Z* isomerization was observed for the allyl C=C bond. The major byproduct generated from amine **1a** was $N(CH_2CH{=}CHPh)_3$, which could barely be transformed into alkene **4a** through prolonging reaction time. The replacement of $[Pd(PPh_3)_4]$ with $[Pd_2(dba)_3]$ led to the formation of $N(CH_2CH{=}CHPh)_3$ as the major product (Table 1, entry 2), and the reaction was very sluggish in the presence of a palladium(II) catalyst (Table 1, entry 3). Furthermore, switching solvents did not improve the yield (Table 1, entries 4–5). On the assumption that the NH_2 group of amine **1a** might serve as a better leaving group under acidic conditions, we added a selection of acids to the reaction mixture and found that the yield was enhanced to 89% when using the inexpensive $B(OH)_3$ as the additive (Table 1, entry 9). Finally, the loading of $[Pd(PPh_3)_4]$ was reduced to 2 mol% without affecting the yield significantly (88%).

Table 1: Optimization of the reaction conditions.[a]



Entry	Catalyst	Additive (equiv)	Solvent	Yield [%][b]
1	$[Pd(PPh_3)_4]$	none	dioxane	70
2[c]	$[Pd_2(dba)_3]$	none	dioxane	0
3	Pd^{II}[d]	none	dioxane	trace
4	$[Pd(PPh_3)_4]$	none	toluene	62
5[c]	$[Pd(PPh_3)_4]$	none	solvent[e]	trace
6[c]	$[Pd(PPh_3)_4]$	$PhCO_2H$ (1)	dioxane	36
7[c]	$[Pd(PPh_3)_4]$	TsOH (1)	dioxane	40
8	$[Pd(PPh_3)_4]$	$B(OH)_3$ (1)	dioxane	76
9[f]	$[Pd(PPh_3)_4]$	$B(OH)_3$ (3)	dioxane	89

[a] Reaction conditions: amine **1a** (0. 50 mmol), boronic acid **2a** (0.60 mmol), catalyst (5 mol%), additive (if any), solvent (3.0 mL), 110°C, 12 h. [b] Yield of the isolated product. [c] $N(CH_2CH{=}CHPh)_3$ was obtained as the major product. [d] $[Pd(PPh_3)_2Cl_2]$ or $Pd(OAc)_2$. [e] Dimethyl sulfoxide, *N*,*N*-dimethylformamide, or *n*-butanol. [f] 5.0 mL of dioxane was used. dba = dibenzylideneacetone, Ts = *p*-toluenesulfonyl.

Under the optimized reaction conditions, a range of primary *E*-allylic amines bearing various β and γ substitutents

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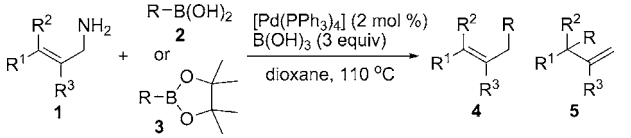
smoothly coupled with boronic acid **2a** or **2b** in an excellent α-selective fashion to give alkenes **4** in good to excellent yields and with excellent retention of alkene geometry (Table 2, entries 1–7 and 9–11). In contrast, the reaction with *Z*-allylic amine **1h** gave only the *E* alkene **4a** in 86% yield (Table 2, entry 8).[10] On the other hand, the reaction worked well with a variety of aryl-, heteroaryl-, and alkenylboronic acids (Table 2, entries 12–22). Moreover, the scope for the reaction was significantly extended by employing aryl-, alkenyl-, allyl-, and benzylboronates as the carbon nucleophiles (Table 2, entries 23–29). As demonstrated by the results summarized in Table 2, this reaction well tolerated a variety of functional groups, such as alkoxy, aromatic nitro, halo, ester, vinyl, and ketone.

Such reaction conditions were applied to α-chiral primary allylic amine **6a** (95% *ee*), and the reaction gave racemic alkene **7a** in 75% yield (Table 3, entry 1). To achieve an effective transfer of chirality, we optimized the reaction conditions again. Replacement of $[Pd(PPh_3)_4]$ with $[Pd_2(dba)_3]$ did not lead to racemization, but decreased the yield to 19% (Table 3, entry 2). The yield and stereochemical outcome were significantly affected by the ligand, and gratifyingly, the use of TMEDA as the ligand improved the yield to 46% and completely inverted the chiral center (Table 3, entry 6). Finally, the yield was enhanced to 59% by removing $B(OH)_3$, increasing the concentration of the reaction mixture, and prolonging the reaction time (Table 3, entry 7).

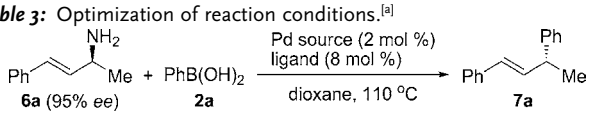
Table 2: Cross-coupling of primary allylic amines with boronic acids and boronates.[a,b]



Entry	**1**, R^1, R^2, R^3	**2** or **3**, R	Product (**4**/**5**)[c]	Yield [%][d]
1	**1a**, Ph, H, H	**2a**, Ph	**4a** (>99:1)	88
2	**1b**, 4-$MeOC_6H_4$, H, H	**2a**, Ph	**4b** (>99:1)	88
3	**1c**, 2-$MeOC_6H_4$, H, H	**2a**, Ph	**4c** (>99:1)	87
4	**1d**, 2-$NO_2C_6H_4$, H, H	**2a**, Ph	**4d** (>99:1)	84
5	**1e**, 3-pyridinyl, H, H	**2a**, Ph	**4e** (>99:1)	80
6	**1f**, 3-thienyl, H, H	**2a**, Ph	**4f** (>99:1)	72
7	**1g**, cyclohexyl, H, H	**2a**, Ph	**4g** (94:6)[e]	76
8	**1h**, H, Ph, H	**2a**, Ph	**4a** (>99:1)	86
9	**1i**, Ph, H, Me	**2a**, Ph	**4h** (>99:1)	92
10	**1j**, Ph, Ph, H	**2a**, Ph	**4i** (>99:1)	93
11[f]	**1k**, H, H, H	**2b**, 9-phenanthrenyl	**4j**	84
12	**1a**, Ph, H, H	**2c**, 4-FC_6H_4	**4k** (>99:1)	80
13	**1a**, Ph, H, H	**2d**, 4-ClC_6H_4	**4l** (>99:1)	66
14	**1a**, Ph, H, H	**2e**, 4-$(MeO_2C)C_6H_4$	**4m** (>99:1)	84
15	**1a**, Ph, H, H	**2f**, 4-PhC_6H_4	**4n** (>99:1)	89
16	**1a**, Ph, H, H	**2g**, 3-$(MeO_2C)C_6H_4$	**4o** (>99:1)	86
17	**1a**, Ph, H, H	**2h**, 3,5-$(CF_3)_2C_6H_3$	**4p** (>99:1)	85
18[g]	**1a**, Ph, H, H	**2i**, 2,6-$Me_2C_6H_3$	**4q** (>99:1)	68
19[g]	**1a**, Ph, H, H	**2j**, 2-furyl	**4r** (>99:1)	60
20	**1a**, Ph, H, H	**2k**, 2-naphthyl	**4s** (>99:1)	88
21	**1a**, Ph, H, H	**2l**, 1-naphthyl	**4t** (>99:1)	91
22	**1a**, Ph, H, H	**2m**, (*E*)-PhCH=CH	**4u** (>99:1)	88
23	**1a**, Ph, H, H	**3a**, Ph	**4a** (>99:1)	66
24	**1a**, Ph, H, H	**3b**, 4-$MeOC_6H_4$	**4v** (>99:1)	71
25	**1a**, Ph, H, H	**3c**, 4-vinylphenyl	**4w** (>99:1)	70
26	**1a**, Ph, H, H	**3d**, 4-$PhCOC_6H_4$	**4x** (>99:1)	60
27	**1a**, Ph, H, H	**3e**, (*E*)-PhCH=CH	**4u** (>99:1)	76
28	**1a**, Ph, H, H	**3f**, $CH_2=CHCH_2$	**4y** (>99:1)	71
29	**1a**, Ph, H, H	**3g**, $PhCH_2$	**4z** (>99:1)	83

[a] Reaction conditions: amine **1** (0. 50 mmol), boronic acid **2** (0.60 mmol) or boronate **3** (0.75 mmol), $[Pd(PPh_3)_4]$ (2 mol%), $B(OH)_3$ (3 equiv), dioxane (5.0 mL), 110°C, 12 h. [b] Unless otherwise stated, only the *E*-alkene product was obtained. [c] Determined by ^1H NMR spectroscopic analysis. [d] Yield of the isolated product. [e] 96:4 *E*/*Z*. [f] The reaction was run in a sealed tube. [g] The reaction was run for 24 h.

Table 3: Optimization of reaction conditions.[a]



Entry	Pd source	Ligand	Additive	Yield [%][b]	*ee* [%][c]
1	$[Pd(PPh_3)_4]$	none	$B(OH)_3$	75	0
2	$[Pd_2(dba)_3]$	none	$B(OH)_3$	19	95
3	$[Pd_2(dba)_3]$	binap	$B(OH)_3$	73	48
4	$[Pd_2(dba)_3]$	binol	$B(OH)_3$	25	95
5	$[Pd_2(dba)_3]$	$(CH_2OH)_2$	$B(OH)_3$	30	95
6	$[Pd_2(dba)_3]$	TMEDA	$B(OH)_3$	46	95
7[d]	$[Pd_2(dba)_3]$	TMEDA	none	59	95

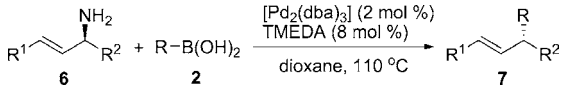
[a] Reaction conditions: amine **6a** (0. 50 mmol), boronic acid **2a** (0.60 mmol), Pd source (2 mol%), ligand (8 mol%), additive (if any, 3.0 equiv), dioxane (5.0 mL), 110°C, 12 h. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] The reaction was run in 2.0 mL of dioxane for 24 h. binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, binol = 1,1′-binaphthol, TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

In the presence of 2 mol% of $[Pd_2(dba)_3]$ and 8 mol% of TMEDA, a range of α-chiral primary allylic amines **6** smoothly coupled with boronic acids to give optically active alkenes **7** in moderate yields (Table 4).[11] As summarized in Table 4, the chiral centers of amines **6** were completely inverted and there was no loss of optical purity during the reaction.

ESI-MS analysis of the reaction mixture for the $[Pd(PPh_3)_4]$-catalyzed cross-coupling of amine **1a** with boronic acid **2a** allowed us to identify the intermediate $[Pd(CH_2CH{=}CHPh)(PPh_3)_2]^+$ according to the high resolution mass data ($C_{45}H_{39}P_2Pd^+$ calcd 747.1556, found 747.1545). This result suggests that the C–N bond of the primary allylic amine is cleaved and an allylpalladium complex is formed during the reaction.

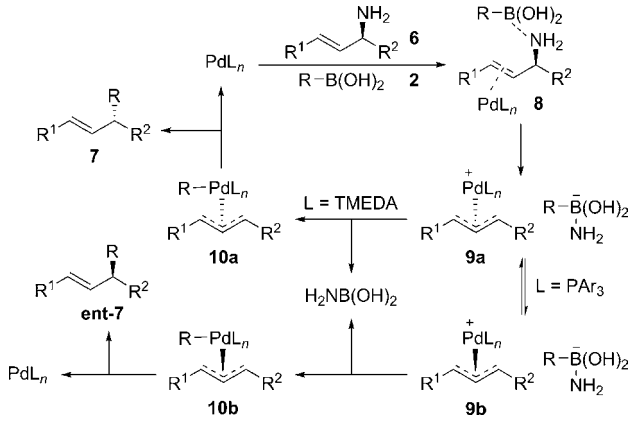
Based on our results and the general mechanism for palladium catalysis,[1,2] we propose the reaction pathways depicted in Scheme 1 for the cross-coupling of α-chiral primary allylic amines with boronic acids. The NH_2 group of amine **6** is activated by boronic acid **2** and the allylic C–N bond is cleaved by the palladium(0) catalyst with inversion of configuration to give π-allylpalladium **9a**. When TMEDA is used as the ligand, complex **9a** undergoes transmetallation followed by reductive elimination to give alkene **7** and regenerate the palladium(0) catalyst. However, racemization of complex **9a** takes place when a phosphine is used as the

Table 4: Cross-coupling of α-chiral primary allylic amines with boronic acids.[a]



Entry	**6**, R^1, R^2	*ee* [%]	**2**, R	**7**	Yield [%][b]	*ee* [%][c]
1	**6a**, Ph, Me	95	**2a**, Ph	**7a**	59	95
2	**6a**, Ph, Me	95	**2c**, 4-FC_6H_4	**7b**	60	95
3	**6a**, Ph, Me	95	**2d**, 4-ClC_6H_4	**7c**	46	95
4	**6a**, Ph, Me	95	**2e**, 4-$(MeO_2C)C_6H_4$	**7d**	56	95
5	**6a**, Ph, Me	95	**2n**, 2,6-$(MeO)_2C_6H_3$	**7e**	55	95
6	**6b**, Ph, Et	92	**2a**, Ph	**7f**	61	92
7	**6c**, 2-naphthyl, Me	90	**2a**, Ph	**7g**	56	90
8	**6d**, 4-ClC_6H_4, Me	91	**2a**, Ph	**7h**	60	91
9	**6c**, 2-naphthyl, Me	90	**2m**, (*E*)-PhCH=CH	**7i**	58	90

[a] Reaction conditions: amine **6** (0. 50 mmol), boronic acid **2** (0.60 mmol), $[Pd_2(dba)_3]$ (2 mol%), TMEDA (8 mol%), dioxane (2.0 mL), 110°C, 24 h. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase.



Scheme 1. Proposed reaction pathways.

ligand,[1] and the reaction loses optical purity by transforming a portion of amine **6** into alkene *ent*-**7**.

In summary, we have developed an unprecedented palladium-catalyzed regioselective and stereospecific cross-coupling of primary allylic amines with boronic acids and boronates, wherein the NH_2 group serves as an effective leaving group. A range of primary allylic amines bearing β and γ substitutents smoothly couple with boronic acids in an excellent α-selective fashion to give alkenes in good to excellent yields and with excellent *E* selectivity. The reaction works well with aryl- and alkenylboronic acids and aryl-, alkenyl-, allyl-, and benzylboronates, and tolerates functional groups such as alkoxy, aromatic nitro, halo, ester, vinyl, and ketone. Moreover, complete transfer of chirality has been achieved when using α-chiral primary allylic amines as the allylic electrophiles.

Experimental Section

General procedure (Table 2): A mixture of boronic acid **2** (0.60 mmol), $[Pd(PPh_3)_4]$ (11.6 mg, 2 mol%), $B(OH)_3$ (92.7 mg, 1.50 mmol), and amine **1** (0.50 mmol) in dioxane (5.0 mL) was heated at 110°C under nitrogen for 12 h. The mixture was cooled to room temperature, and purified by preparative thin layer chromatography (petroleum ether) to give alkene **4**.

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[10] The *Z*/*E* isomerization can be attributed to the generation of a π-allylpalladium intermediate during the reaction (see below).

[11] The major side reaction with amines **6** is the formation of the corresponding tertiary amines.

