Direct Borylation of Primary C–H Bonds in Functionalized Molecules by Palladium Catalysis**

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Abstract: Organoborane compounds are among the most commonly employed intermediates in organic synthesis and serve as crucial precursors to alcohols, amines, and various functionalized molecules. A simple palladium-based system catalyzes the conversion of primary $C(sp^3)$ -H bonds in functionalized complex organic molecules into alkyl boronate esters. Amino acids, amino alcohols, alkyl amines, and a series of bioactive molecules can be functionalized with the use of readily available and removable directing groups in the presence of commercially available additives, simple ligands, and oxygen (O_2) as the terminal oxidant. This approach represents an economic and environmentally friendly method that could find broad applications.

he direct catalytic functionalization of C–H bonds has the potential to revolutionize organic synthesis and to produce complex natural and man-designed molecules.^[1] The immediate challenge in this field is to achieve the catalytic and highly regioselective functionalization of one specific inert C–H bond in a complex molecule that contains many C–H bonds and an array of functional groups.^[2,3] Compared to the wide range of well-developed methods for the activation of aromatic C–H bonds, the precise site-selective functionalization of inert aliphatic C–H bonds in complex molecules has remained a great challenge. Potential solutions that effectively control chemo-, regio-, and site selectivity could make C–H bond functionalization more widely applicable for the synthesis of valuable molecules.

Over the past several decades, much effort has been directed towards the direct functionalization of aliphatic $C(sp^3)$ -H bonds in the presence of stoichiometric or catalytic

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amounts of transition metals.^[4–19] Compared with the selective conversion of inert $C(sp^3)$ –H bonds into carbon–carbon^[4–8] and carbon–heteroatom bonds,^[9–19] the construction of aliphatic C–B bonds directly from $C(sp^3)$ –H bonds is of great interest because organoboranes are commonly employed intermediates in organic synthesis and crucial precursors to functionalized molecules.^[20,21] Such efficient transformations could provide a new starting point for different functionalization reactions of specific $C(sp^3)$ –H bonds and have a great impact in the fields of medicinal chemistry, chemical biology, and materials science.

Significant progress has been made on the borylation of unactivated C(sp³)-H bonds, especially for primary C-H bonds of unfunctionalized hydrocarbons, using transitionmetal catalysis.^[22-28] However, the direct borylation of inert C(sp³)-H bonds in functionalized organic molecules is still challenging. The fundamental problem is to achieve direct borylation selectively and precisely at a specific position in a complex molecule. A directing-group-assisted strategy, which has been shown to be effective for the direct functionalization of both C(sp²)-H and C(sp³)-H bonds,^[29] could be employed to control site selectivity. To achieve borylation of a specific secondary C(sp³)-H bond in the presence of potentially more favored primary and other secondary C(sp³)-H bonds, the directing group must be powerful enough to achieve the desired selectivity. Furthermore, the catalyst system must be compatible with existing functional groups and the C-B unit of the product.

Although palladium catalysis is widely used for many transformations, including the direct borylation of aryl C–H bonds,^[30] the palladium-catalyzed borylation of unactivated C(sp³)–H bonds with a directing-group strategy has not been achieved because of the relatively high reactivity of C–B bonds in the presence of a palladium catalyst, other functional groups, and many oxidants as well as the steric hindrance of the target bonds.^[29] Herein, a selective oxidative borylation of unactivated primary C(sp³)–H bonds in complex structures that is based on a Pd⁰/Pd^{II} catalytic system and features an N-heterocycle as the directing group and mild reaction conditions is reported. This powerful method represents a complementary approach to the reductive borylation of C(sp³)–H bonds, which may be achieved by iridium or rhodium catalysis.^[20]

We initially chose amino acid derivatives as substrates because amino acids are among the most abundant and significant molecules and constitute the fundamental building blocks of peptides, proteins, and a number of biologically active molecules. With this choice, the potential compatibility of versatile functional groups with the developed procedure

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could be highlighted, to confirm the suitability of this method for the modification of important natural motifs. We intended to directly and selectively functionalize various unactivated $C(sp^3)$ -H bonds in amino acids through the formation of reactive C-B bonds. After installing the well-studied picolinyl directing group at the amine moiety, we performed the designed borylation reaction through the remote activation of a C(sp³)-H bond, which proceed via two fused palladacycles as intermediates (Table 1).^[31] To achieve the oxidative borylation of unactivated C(sp3)-H bonds by palladium catalysis, Pd⁰/Pd^{II} and Pd^{II}/Pd^{IV} catalytic cycles may both be considered in the presence of a proper and efficient oxidant. The oxidant, which serves to complete the catalytic cycle, must also be mild enough to avoid oxidation of the aliphatic C-B bond in the product. Furthermore, the alkyl boronic ester may easily decompose through transmetalation to a Pd^{II} species, which would lead to the conversion of the borylation product into other compounds in most cases. Moreover, to ensure the stability of the C-B bond under the reaction conditions and to complete the catalytic cycle, an alkaline environment is required. Whereas very weak bases may not be efficient enough to obtain high conversion, strong bases may accelerate the interaction of the produced alkyl boronic esters and a Pd^{II} species to afford Suzuki-Miyaura products. Finally, the previously reported intramolecular amination

Table 1: Palladium-catalyzed C-H borylation under various reaction conditions.^[a]

	IPA CO ₂ Me + : 1a	$PA = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \end{bmatrix}$	Pd(OAc) ₂ (20 mol%) Ligand, Additive Base, MeCN O ₂ , 80 °C	NHPA ,''CO ₂ Me Bpin 2a
Entry	Base	Ligand (equiv)	Additive (equiv)	Yield ^[b] [%]
1	_	_	_	< 5
2	NaOAc	_	-	16
3	NaOAc	DMF (5.0)	-	< 5
4	NaOAc	NMP (5.0)	-	< 5
5	NaOAc	phen (0.2)	-	0
6	NaOAc	<i>i</i> Pr ₂ S (5.0)	-	48
7	Li ₂ CO ₃	<i>i</i> Pr ₂ S (5.0)	-	54
8	Li ₂ CO ₃	<i>i</i> Pr ₂ S (5.0)	AcOH (2.0)	< 5
9	Li ₂ CO ₃	<i>i</i> Pr ₂ S (5.0)	H ₂ O (2.0)	44
10 ^[c]	Li ₂ CO ₃	<i>i</i> Pr ₂ S (5.0)	-	64
11 ^[c]	Li ₂ CO ₃	<i>i</i> Pr ₂ S (5.0)	LiF (3.0)	74
12 ^[c]	Li ₂ CO ₃	<i>i</i> Pr ₂ S (5.0)	NaF (3.0)	66
13 ^[c,d]	Li ₂ CO ₃	<i>i</i> Pr ₂ S (5.0)	LiF (3.0)	77
14 ^[c,d,e]	Li ₂ CO ₃	<i>i</i> Pr ₂ S (5.0)	LiF (3.0)	81
15 ^[d,e,f]	Li ₂ CO ₃	<i>i</i> Pr ₂ S (5.0)	LiF (3.0)	85 (68)

[a] Reaction conditions: **1a** (0.10 mmol), B_2pin_2 (0.20 mmol), base (3.0 equiv), MeCN (1.0 mL), O_2 (balloon), 80 °C, 12 h. [b] Determined by GC using *n*-dodecane as the internal standard. The yield of isolated product is given in parentheses. [c] B_2pin_2 (0.30 mmol), MeCN (1.5 mL). [d] NaHCO₃ (0.1 mmol) was added as an additional additive. [e] PhCN (0.1 mL) was added. [f] B_2pin_2 (0.40 mmol), MeCN (1.5 mL). DMF = *N*,*N*-dimethylformamide, NMP = *N*-methyl-2-pyrrolidinone, phen = phenanthroline.

through C–N bond formation must be avoided to obtain the desired products.^[31]

We chose valine as the standard substrate and B₂pin₂ (pin = pinacolato) as the borylation reagent in the presence of palladium acetate as the catalyst under an oxygen (O_2) atmosphere (Table 1). We were pleased to observe a trace amount of the desired borylation product by GC-MS when MeCN was used as the solvent (entry 1). When NaOAc (3.0 equiv) was added to the system, the desired product was obtained in 16% yield (determined by GC; entry 2), but the catalyst decomposed and precipitated as palladium black. Oxidants that are commonly used for palladium-catalyzed transformations, such as K₂S₂O₈, PhI(OAc)₂, benzoquinone (BQ), silver salts, copper salts, di-tert-butyl peroxide (TBP), N-fluorobenzenesulfonimide (NFSI), oxone, or $Ce(SO_4)_2$, were screened to improve the yield. Unfortunately, most of these oxidants inhibited the reaction or destroyed the desired borylation product (for details, see the Supporting Information). Therefore, we started to consider whether an atmosphere of O₂ itself might act as a mild oxidant for the regeneration of the palladium catalyst. As a result, we returned to the initial conditions and tested different ligands that could stabilize the Pd species and promote the reoxidation of the Pd⁰ species.^[32] After screening several ligands, we found that DMF, NMP, phenanthroline (phen), and bipyridine inhibited the transformation under O₂ atmosphere, albeit with no generation of palladium black (entry 3-5). A series of phosphine ligands were tested, but the yield did not improve. To our delight, when iPr_2S (5.0 equiv) was added, the yield substantially increased to 48% (determined by GC; entry 6), confirming the regeneration of the Pd^{II} species to complete the catalytic cycle. Based on preliminary kinetic studies, the ligand *i*Pr₂S only stabilizes the Pd species to prevent its precipitation and is not obviously involved in the initial reaction rate (Supporting Information, Scheme S1).

Considering that the transformation could only occur under alkaline conditions, we tested different bases. Interestingly, in contrast to sodium and lithium salts, potassium and cesium salts inhibited the reaction so that we mainly focused on sodium and lithium bases. We found that both strong bases (such as tBuONa) and very weak bases (such as NaOTf or NaOTFA; OTf = trifluoromethanesulfonate, OTFA = trifluoroacetate) are not suitable for this transformation. Finally, among several bases, such as NaOAc or Na₂CO₃ (Table S4), lithium carbonate proved to be the most suitable one, and the desired product was obtained in 54% yield (by GC; entry 7). Furthermore, to promote the re-oxidation of the Pd⁰ species by O₂, we added different acids as a proton source,^[32] but found that the reaction was very sensitive to these additional acids, such as trifluoroacetic acid (TFA), AcOH, pivalic acid (PivOH), and benzoic acid (entry 8). In the presence of H_2O , the yield was also diminished to 44% (entry 9). Fortunately, by increasing the amount of B₂pin₂ to three equivalents and diluting the solution, the yield could be increased to 64% (entry 10). While screening further additives, we observed that the addition of LiF (3.0 equiv) further improved the yield to 74% (entry 11), whereas LiCl inhibited the reaction. Finally, in the presence of four equivalents of B₂pin₂ and several other additives (entry 15), the desired borylation

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product **2a** (Table 2) was isolated in 68% yield with a good diastereoselectivity (d.r.) of 83:17. The diastereoselectivity was probably induced during the formation of two fused five-membered palladacycles as key intermediates; their relative configuration is determined by the sterically hindered carbomethoxy group.

With the optimized conditions in hand, different natural and unnatural amino acids were tested, and the desired borylated products were produced in good to excellent yields (Table 2). With isoleucine, the reaction selectively occurred at the primary $C(sp^3)$ -H bond, and the absolute configuration of the starting material did not influence the reaction efficiency (L-isoleucine vs. DL-isoleucine, 2b vs. 2c). Notably, for Lthreonine, which bears a *tert*-butoxy moiety at the β -position of the amino group, the yield improved (2d). tert-Leucine, with a quaternary carbon atom, was less reactive, possibly because of a steric effect (2e). Substituents at the α - and β positions of the amino group are necessary for this transformation, and with two methyl substituents at the β -position and one methyl group at the α -position, the corresponding product was isolated in 64% (2 f). Furthermore, for a series of easily accessible valinol substrates, valuable functional groups could be accommodated within the substrate. For example, benzyl (Bn) and benzoyl (Bz) moieties, which contain aromatic $C(sp^2)$ -H bonds, were tested as protecting groups (2g-2h). The absence of products that correspond to borylation of the $C(sp^2)$ -H bonds confirmed the key role of the picolinamide directing group.^[31] As the tetrahydropyranyl (THP) group is broadly used for protecting hydroxy groups, we tested this protecting group and found that it is well tolerated and therefore useful for masking a nearby hydroxy group (2i). An acetyl moiety could also act as a protecting group, but the corresponding product was isolated in a lower yield (2j). As silyl groups serve as valuable protecting groups in traditional organic synthesis, we tested tert-butyldimethylsilyl (TBS) and triisopropylsilyl (TIPS) moieties as alcohol protecting groups. In both cases, the corresponding products were obtained in good yield in the absence of the additive LiF (2k-2m). Notably, for a phenylalanine substrate, which bears unactivated C(sp²)–H bonds, borylation at the δ -position of the amino group was successfully achieved and thus provides a supplementary method for the functionalization of phenylalanine residues in biological structures (2n). Furthermore, targeted unactivated $C(sp^2)$ -H bonds in the lateral chain of several important antibiotics, such as Cefalexin, Cefaclor, and Ampicillin sodium, could also be functionalized in good yields (20). By employing well-established synthetic methods, a series of valuable ortho functionalization reactions could be achieved by the conversion of these C(sp²)-B bonds.^[30]

Through the preceding transformation of unactivated $C(sp^3)$ -H bonds into C-B bonds, a series of valuable functionalization reactions at the target positions were achieved (Scheme 1 a). Under simple oxidative conditions, a hydroxy group can be installed with high efficiency. In a reaction on the gram scale, the initially unactivated C-H bond was converted into methanesulfonate (OMs) and OTBS groups in moderate yields over three steps (**3a-3b**). By transforming the hydroxy group **4** into an excellent leaving group and a subsequent S_N2 reaction, a targeted C-H bond

Table 2: Substrate scope for amino acid, amino alcohol, and amine derivatives.^[a]



[a] Reaction conditions: 1 (0.10 mmol), B_2pin_2 (0.40 mmol), $Pd(OAc)_2$ (0.02 mmol), iPr_2S (0.50 mmol), Li_2CO_3 (0.30 mmol), LiF (0.30 mmol), NaHCO₃ (0.10 mmol), MeCN/PhCN (1.5:0.1), 80 °C, O_2 (balloon), 12 h. [b] Yield of isolated product. [c] d.r. determined by ¹H NMR spectroscopy. [d] Without LiF.



could be readily converted into an azide or a thioether (5, 6); these transformations are difficult to achieve from the same starting materials using traditional methods. Furthermore, the hydroxy group could be further oxidized to an aldehyde moiety to yield compound 7, which could be a new starting point for a series of further transformations, including Horner-Wadsworth-Emmons reactions to yield structures such as 8 and aldol reactions. To further demonstrate the utility of this method for organic synthesis and to confirm its efficiency in the modification of complex molecules, we explored strategies to functionalize natural product derivatives (Scheme 1b). We were pleased to discover that the inert primary C(sp³)-H bond of the angular methyl group in starting material 9, a derivative of the steroid estrone, could be successfully functionalized, and that the final product 10 was obtained as a single diastereomer.

In conclusion, the direct transformation of unactivated $C(sp^3)$ -H bonds into reactive C-B bonds was achieved by palladium catalysis. This method offers a new strategy to selectively construct C-B bonds from unactivated primary $C(sp^3)$ -H bonds and may become a powerful strategy for the synthesis of new derivatives of amino acids and other



Scheme 1. Applications of the C-H borylation reaction. [a] B₂pin₂, Pd(OAc)₂, *i*Pr₂S, Li₂CO₃, LiF, NaHCO₃, MeCN/PhCN, 80°C, O₂ balloon, 16 h. [b] NaBO₃·4 H₂O, THF/H₂O, 30°C, 1 h. [c] MsCl, NEt₃, CH₂Cl₂, 0°C, 1 h. [d] TBSCl, imidazole, DMF, RT, 0.5 h. [e] NaN₃, KI, DMF, 80°C, 1 h. [f] NaSMe, KI, DMF, 80°C, 1 h. [g] DMP, CH₂Cl₂, RT. [h] triethyl phosphonoacetate, EtONa, THF, 0°C-RT. DMP = Dess-Martin periodinane. functionalized complex molecules. Mild reaction conditions, which feature a weakly alkaline environment and oxygen as the terminal oxidant, are crucial for achieving excellent compatibility with an array of functional groups; therefore, the utility of this method for organic synthesis was confirmed. These studies are not only important for understanding the reactivity of bonds that were traditionally considered as inert, but also provide an efficient synthetic method for the construction of valuable chemicals from readily available and inexpensive natural products. Hopefully, these studies will inspire the development of new functionalization reactions for peptides, proteins, and other bioactive molecules for the postsynthetic derivatization of biomolecules.

Experimental Section

General procedure for the palladium(II)-catalyzed borylation of amino acid, amino alcohol, and amine derivatives: B₂pin₂ (101.6 mg, 0.40 mmol; white crystals after recrystallization), Li₂CO₃ (22.2 mg, 0.30 mmol; white powder), NaHCO₃ (8.4 mg, 0.10 mmol), and Pd(OAc)₂ (4.5 mg, 0.02 mmol; Acros) were added to a dried 50 mL tube under air. Then, LiF (7.8 mg; no LiF was added for 1k-1m) was added to the tube in the glove box. After degassing under vacuum and refilling with O₂ (three times), the tube was then sealed well. A mixture of 1b (25.0 mg, 0.10 mmol; colorless oil), *i*Pr₂S (75 µL, 0.50 mmol; Alfa Aesar), MeCN (1.5 mL; purified by distillation), and PhCN (0.1 mL) was quickly added to the tube under stirring at room temperature. Then, the tube was immediately moved to a Wattecs Parallel Reactor at 80 °C. The solution was stirred at 80 °C for 12 h. After the completion of the reaction, the solution was directly purified by preparative thin-layer chromatography (PTLC; petroleum ether/ethyl acetate or petroleum ether/CH2Cl2/ethyl acetate or toluene/ethyl acetate as the eluent; without concentrating the solution) to afford 2b (26.3 mg, 70 % yield) as a colorless oil.

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