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Concise Synthesis of Potassium Acyltrifluoroborates from Aldehydes by a Cu(I)-catalyzed Borylation/Oxidation Protocol

Jumpei Taguchi,[a] Takumi Takeuchi,[a] Rina Takahashi,[a] Fabio Masero,[b] Hajime Ito*[a,c]

Abstract: Potassium acyltrifluoroborates (KATs) were prepared by a copper(I)-catalyzed borylation of aldehydes and a subsequent oxidation. This synthetic route is characterized by the wide range of aldehydes accessible, a favorable step-economy, mild reaction conditions, and the tolerance of various functional groups, enabling the facile generation of KATs that bear e.g. halide, sulfide, acetal, or ester moieties. Moreover, this method was applied to the three-step synthesis of various α-amino acid analogues that bear a KAT moiety on the C-terminus, using naturally occurring amino acids as the starting material.

The chemistry of acylboron compounds represents a rapidly growing research theme in organic synthesis.[1] In 2007, Nozaki, Yamashita, and co-workers achieved the first isolation of acylboron by the reaction between boryl lithium species and benzoyl chloride.[2a] Since this seminal work, the preparation and reactivity of acylborons have been studied enthusiastically.[2–4] Among these acylboron species, potassium acyltrifluoroborates (KATs) are of particular interest due to their unique reactivity and remarkable stability toward air and moisture.[3,4d,e] In 2012, Dumas, Bode, and Molander reported the highly chemoselective and rapid amide-bond-forming reaction between KATs and hydroxylamines, i.e., KAT ligation.[3a] Although other acylboron species such as acyl *N*-methyliminodiacetyl (MIDA) boronates and monofluoro acylborates have also been used in this amide-bond-formation reaction, all these reagents can be derived from KATs; in other words: strategic importance should be attributed to KATs as precursors to a wide variety of acylboron species.[3c,d]

In 2012, Dumas and Bode reported that KATs can be synthesized by lithiation of benzotriazole-based *N*,*O*-acetals, followed by a trapping using a boron electrophile, and quenching with aqueous KHF_2 (Scheme 1Aa).[2e,f] Bode and co-workers also developed a thioformamide-derived reagent that enables a one-pot KAT synthesis from aryl lithium or alkyl cuprate compounds (Scheme 1Ab).[2g,h] Although these two approaches are practical, given that various *N*,*O*-acetals or organometallic reagents are accessible from the corresponding aldehydes or halides, the requirement for highly reactive organolithium reagents leaves still room for the improvement of the functional-group tolerance.

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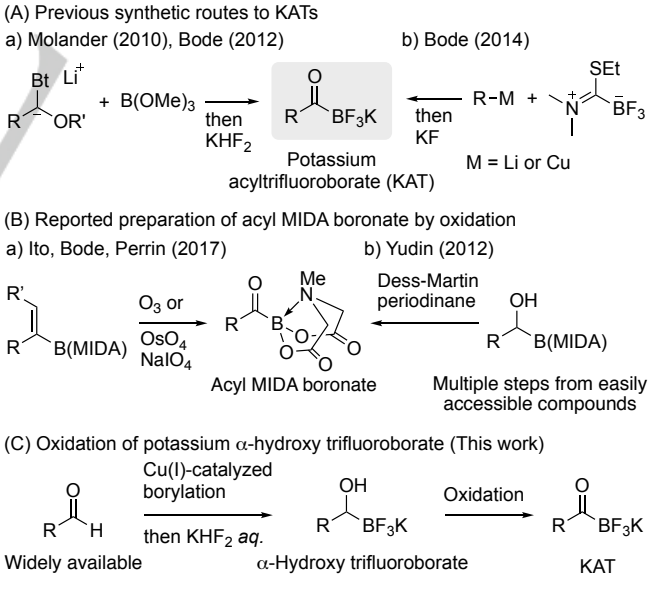
Recently, our group and that of Perrin have reported the ozonolysis and the dihydroxylation/oxidative cleavage of alkenyl MIDA boronates, respectively, which afford acyl MIDA boronates (Scheme 1Ba).[2j,k] These approaches are conducted under relatively mild conditions and are suitable for the preparation of highly functionalized acylboronates including the first examples of enantioenriched α-amino acylboron compounds. In 2012, Yudin and co-workers reported another mild synthetic route: the Dess-Martin oxidation of α-hydroxy MIDA boronates, which affords acyl MIDA boronates. Despite the mild conditions of this reaction, the tolerance toward functional groups was not explored (Scheme 1Bb).[2l,5] In any case, these three milder methods still require multiple steps from easily available materials such as alkenylboronates, and protection of the boronate moiety by MIDA against oxidative conditions, which equates to additional steps.

α-Hydroxy boronates can be directly prepared from aldehydes by Cu(I)-catalyzed borylation, followed by a treatment with KHF_2, which generates α-hydroxy trifluoroborates in a one-pot fashion.[6] Although the oxidation of α-hydroxy trifluoroborates seems to be one of the most straightforward methods to synthesize KATs, this avenue has not yet been reported. We found that KATs can be synthesized by oxidation of potassium α-hydroxy trifluoroborates using 9-azanoradamantane-*N*-oxyl (*nor*-



Scheme 1. (A) Previous synthetic routes to KATs. (B) Reported preparation of acyl MIDA boronate by oxidation. (C) Oxidation of potassium α-hydroxy trifluoroborates (Bt = benzotriazole).

AZADO) or DMSO/Ac_2O under optimized conditions (Scheme 1C). This MIDA-free approach reduces the number of synthetic steps and provides a short and scalable route to KATs that is compatible with a wide variety of functional groups. The important features of

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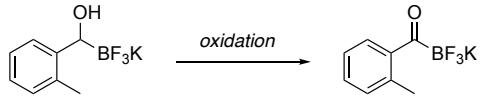
this approach are the commercial availability of a wide variety of aldehydes, its step-economy, and a wide product scope including KATs derived from biologically-related molecules including carbohydrate, steroid, and α-amino acids.

Aryl substituted α-hydroxy trifluoroborate **1a** was prepared from *o*-tolualdehyde according to the procedure reported by Molander.[6b] Our initial attempt to synthesize α-hydroxy MIDA boronates via the reaction between **1a** and $(TMS)_2MIDA/BF_3{\cdot}Et_2O$ was unsuccessful.[3c] Therefore, we investigated the direct oxidation of **1a**.[7] When **1a** was subjected to a Dess-Martin oxidation under reaction conditions similar to those for the oxidation of α-hydroxy MIDA boronates reported by Yudin, the reaction afforded a complex mixture, in which the desired KAT **2a** was not detected (Table 1, entry 1). Subsequently, we investigated standard Swern oxidation conditions using $DMSO/(COCl)_2$; alas, the low solubility of **1a** hampered the reaction (entry 2). However, we found that Albright-Goldman oxidation conditions using $DMSO/Ac_2O$ at room temperature furnished **2a** in good yield (85%, entry 3).[8] Oxidation using catalytic amounts of *nor*-AZADO or AZADOL and a stoichiometric amount of the co-oxidant $NaNO_2$ with acetic acid also afforded **2a** in 92% and 66% yield (entries 4, 5), respectively, while other co-oxidants such as NaOCl or $PhI(OAc)_2$ generated complex mixtures (entries 6, 7).[9] The oxidation with Tetrapropyl ammonium perruthenate (TPAP)/NMO afforded **2a** in lower yield (38%, entry 8).

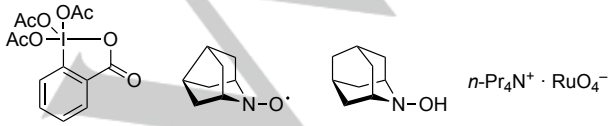
Table 1. Optimization of the oxidation conditions.



1a **2a**

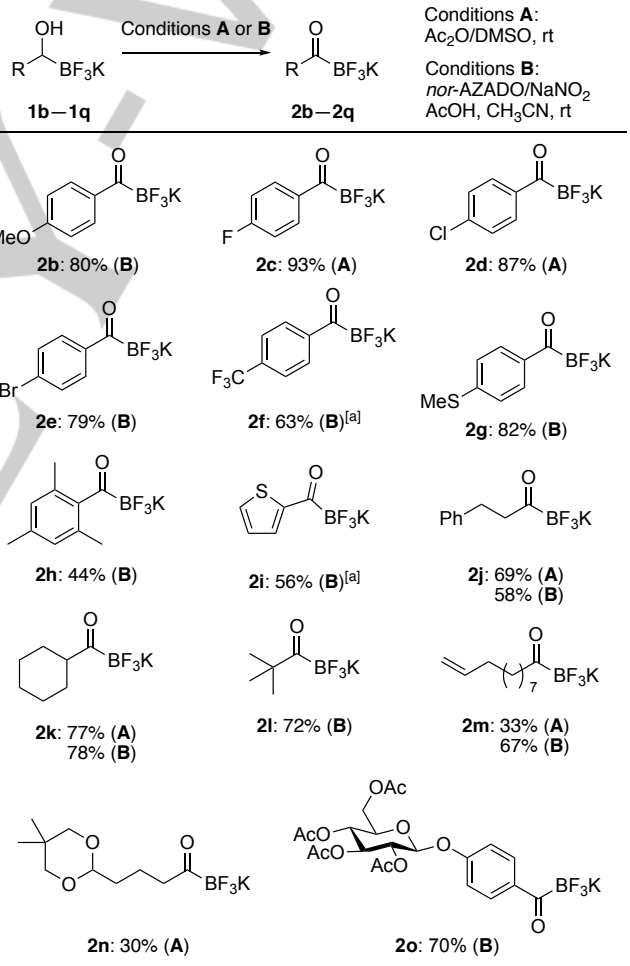
entry	oxidation conditions	yield (%)[a]
1[b]	Dess-Martin periodinane, CH_2Cl_2, rt, 1.5 h	<5
2[c]	DMSO, $(COCl)_2$, Et_3N, THF, –78 °C, 0.25 h	<5
3[d]	DMSO, Ac_2O, rt, 4 h	85
4[e]	*nor*-AZADO, $NaNO_2$, AcOH, rt, 0.5 h	92
5[f]	AZADOL, $NaNO_2$, AcOH, rt, 17 h	66
6[g]	AZADOL, NaClO, rt, 0.5 h	<5
7[h]	AZADOL, $PhI(OAc)_2$, rt, 1 h	<5
8[i]	TPAP, NMO, MS 3A, rt, 2 h	38

[a] Isolated product yield are reported. [b] **1a** (0.3 mmol), Dess-Martin periodinane (2.0 equiv), CH_2Cl_2, rt, 1.5 h. [c] **1a** (0.5 mmol), DMSO (2.2 equiv), $(COCl)_2$ (1.1 equiv), Et_3N (excess), THF, –78 °C, 15 min. [d] **1a** (0.5 mmol), Ac_2O (20 equiv), DMSO, rt, 4 h. [e] **1a** (0.5 mmol), *nor*-AZADO (10 mol%), $NaNO_2$ (1.5 equiv), AcOH (2.0 equiv), CH_3CN, rt, 18 h. [f] **1a** (0.5 mmol), AZADOL (10 mol%), $NaNO_2$ (1.5 equiv), AcOH (2.0 equiv), 17 h. [g] **1a** (0.5 mmol), AZADOL (5 mol%), NaClO (1.5 equiv), CH_3CN, rt, 0.5 h. [h] **1a** (0.5 mmol), AZADO (10 mol%), $PhI(OAc)_2$ (1.5 equiv), CH_3CN, rt, 1 h. CH_3CN, rt, 17 h. [i] **1a** (0.5 mmol), TPAP (10 mol%), NMO (6.0 equiv), MS 3A, CH_3CN, rt, 2 h.



Dess-Martin preiodinane | *nor*-AZADO | AZADOL | TPAP

Then, we investigated the scope of this reaction using two favorable procedures: oxidation with i) $DMSO/Ac_2O$ and ii) *nor*-AZADO catalyst (Scheme 2). The reaction exhibited high functional-group tolerance and afforded KATs containing methoxy (**2b**), halide (**2c**–**2e**), trifluoromethyl (**2f**), and sulfide (**2g**) moieties in good to high yield (63–93%). Sterically hindered aryl acylboron **2h** was also prepared in good yield (44%). This method can also be applied to the preparation of an acylboron bearing thiophene (**2i**: 56%). In addition to aryl or heteroaryl KATs, this method was also effective for the preparation of alkyl KATs. α-Hydroxy trifluoroborates bearing primary (**2j**), secondary (**2k**), and tertiary alkyl groups (**2l**) can also be used in this method and afford the corresponding KATs in good to high yield (69–78%).



Scheme 2. Substrate scope. Reaction conditions **A**: **1** (0.3 mmol), Ac_2O (20 equiv), DMSO, rt, 12 h–17 h. Reaction conditions **B**: **1** (0.3 mmol), *nor*-AZADO (10 mol%), $NaNO_2$ (1.5 equiv), AcOH (2.0 equiv), CH_3CN, rt, 12 h–24 h. Isolated product yields are reported. [a] NMR yields are reported.

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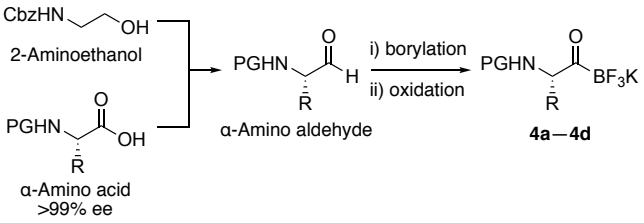
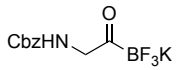
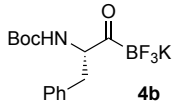
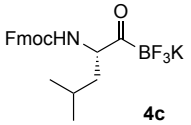
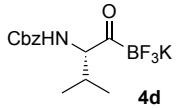
Table 2. Preparation of KAT-containing α-amino-acid analogues.[a]

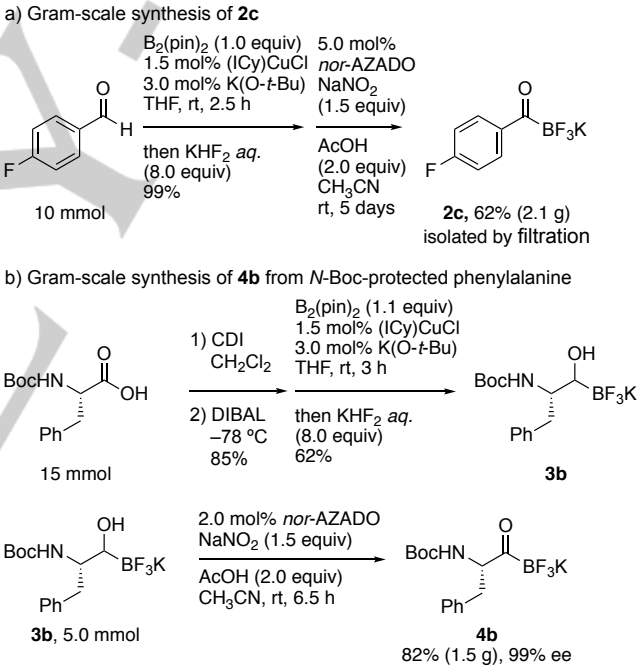


entry	product	borylation yield (%)[b]	oxidation yield (%)[b]	ee (%)
1	 **4a**	52	76[c]	–
2	 **4b**	61	80	99
3	 **4c**	62	71	99
4	 **4d**	50	77	99

[a] Borylation conditions: aldehyde, B_2pin_2 (1.1 equiv), (ICy)CuCl (3–10 mol%), K(Ot-Bu) (6–20 mol%), MeOH (2.0 equiv), THF, rt, 2–7 h. Oxidation conditions: **3**, *nor*-AZADO (10 mol%), $NaNO_2$ (1.5 equiv), AcOH (2.0 equiv), CH_3CN, rt, 4–12 h. [b] Isolated product yields are reported. [c] Reaction was performed with 2.0 mol% TBABr. (Cbz = benzyloxycarbonyl, Boc = *tert*-butoxy carbonyl; Fmoc = fuorenylmethyloxycarbonyl; [B] = potassium trifluoroborate; (ICy)CuCl = 1,3-dicyclohexylimidazol-2-ylidene-copper(I) chloride; $B_2(pin)_2$ = bis(pinacolato)diboron).

Acylboron species bearing alkene (**2m**) and acetal moieties (**2n**) were also obtained in 30–67% yield. KATs **2g**, **2m**, and **2n** are particularly important as their synthesis via the oxidative cleavage of alkenyl MIDA boronates is nontrivial.[2j,k] Based on the versatility of this method, we applied it to the preparation of KATs bearing biological molecules, which afforded glucose-bearing KAT **2o** in 70% yield. This late-stage modification of bio-active molecules to the corresponding KATs has significant potential for the preparation of glycopeptide and antibody-drug conjugates.

Subsequently, we investigated the synthesis of α-amino acid-derived KATs (Table 2). This class of compounds is very attractive due to its potential use as a building block in peptide conjugation using KAT ligation.[1b,2j,k] *N*-Cbz glycinal can be synthesized by the oxidation of *N*-Cbz-protected 2-aminoethanol. Cu(I)-catalyzed borylation afforded α-hydroxy trifluoroborate **3a** in 52% and followed by *nor*-AZADO oxidation afforded *N*-Cbz glycine type KAT **4a** in 76% (entry 1). Next, we investigated the synthesis of enantioenriched amino acid analogues. The corresponding starting materials, i.e., the α-amino aldehydes, can be prepared from commercially available α-amino acids in one step.[10b] Cu(I)-catalyzed borylation of *N*-Boc-protected phenylalanine-derived aldehyde afforded α-hydroxy trifluoroborate **3b** in 61% (entry 2). The oxidation of **3b** furnished *N*-Boc-protected phenylalanine type KAT **4b** in high yield with high enantiomeric purity (80%, 99% ee). This method can also be applied to the preparation of *N*-Fmoc-protected leucine-type KAT (**4c**), and *N*-Cbz-protected valine-type KAT (**4d**) in high yields excellent enantiopurities (entries 3, 4, borylation: 62% (**3c**), 50% (**3d**); oxidation: 71%, 99% ee (**4c**), 77%, 99% ee (**4d**)).[12] These KATs, especially for leucine-type KATs, has significant importance for peptide–peptide ligation due to their frequent appearance in natural proteins compared with serine residue, which is required in native chemical ligation (NCL).[11] Considering the accessibility of α-amino aldehydes from α-amino acids, this chiral-pool-based synthetic strategy provides a general, and scalable approach to α-amino KATs that is advantageous relative to the reported oxidative cleavage of alkenyl MIDA boronates, which requires enantioenriched propargyl amine as starting materials.[2j, 10]



Scheme 3. Gram-scale synthesis of **2c** and **4b**.

This borylation/oxidation protocol is especially amenable to a gram-scale synthesis of KATs (Scheme 3). Borylation of 10 mmols of 4-fluoro benzaldehyde with 1.5 mol% of (ICy)CuCl catalyst followed by oxidation with 5.0 mol% *nor*-AZADO afforded KAT **2c** in 62% yield (2.1 g). It is the simplicity of the synthetic protocol that renders it suitable for upscaling: the oxidation does not require an inert atmosphere and the products in each step can be easily isolated by filtration. Furthermore, phenylalanine-derived α-hydroxy trifluoroborate **3b** was obtained in 53% yield from commercially available *N*-Boc-protected phenylalanine in two steps (Scheme 3b). The oxidation of **3b** (5.0 mmol) with 2.0

mol% *nor*-AZADO affords the corresponding phenylalanine-type KAT **4b** in 82% yield (1.5 g) without any loss of enantiopurity.

In summary, we have developed an operationally simple protocol for the preparation of KATs in two steps from aldehydes. This borylation/oxidation proceeds under mild conditions and exhibits high functional-group tolerance toward e.g. halide, acetal, sulfide, and ester moieties. The oxidation can be accomplished with i) DMSO/Ac_2O or ii) *nor*-AZADO catalyst, and the conditions for either oxidation are practical as the use of expensive stoichiometric oxidants is not required. Importantly, various α-amino-acid analogues containing a KAT moiety, which is expected to be essential for peptide-peptide conjugation, can be prepared from naturally occurring α-amino aldehydes without racemization. The utility of this method was demonstrated by the synthesis of a KAT-containing carbohydrate, and a column-chromatography-free gram-scale synthesis. This general method is expected to broaden the range of applications of KAT not only in the context of bioconjugation, but also in organic synthesis and material science.

Acknowledgements

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Keywords: amino acid • boron • copper • oxidation • acylboron

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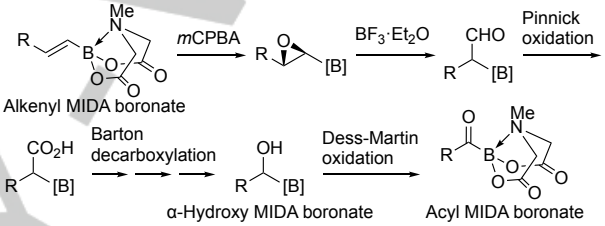
[5] Z. He; A. K. Yudin, *J. Am. Chem. Soc.* **2011**, *133*, 13770. The preparation of α-hydroxy MIDA boronates is shown below ([B] = MIDA boronate).



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[11] For amino acid distribution statistics, see: a) I. Z. Siemion, *BioSystems* **1994**, *32*, 163; b) J. L. King, T. H. Jukes, *Science* **1969**, *164*, 788; c) L. P. Kozlowski, *Nucleic Acids Research* **2017**, *45*, D1112.

[12] *N*-Cbz protected varinal was prepared via Weinreb amide-formation/reduction with $LiAlH_4$ because of the low solubility of the CDI-activated ester.

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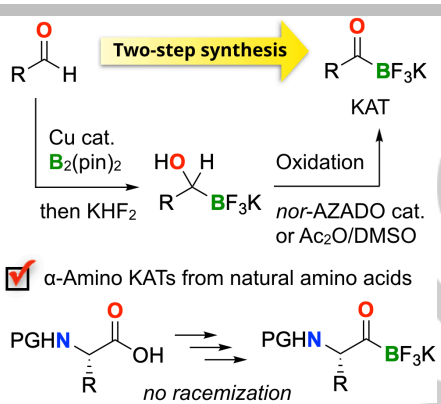
COMMUNICATION

Potassium acyltrifluoroborates (KATs) can be prepared in two steps from the corresponding aldehydes by a sequential Cu(I)-catalyzed borylation and an oxidation with either *nor*-AZADO catalyst or Ac_2O/DMSO. This method is step-economical, scalable, and exhibits high functional-group tolerance. In addition, α-amino KATs, which are expected to be essential for peptide ligations, were prepared using naturally occurring α-amino acid as starting materials.



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Concise Synthesis of Potassium Acyltrifluoroborates from Aldehydes by a Cu(I)-catalyzed Borylation/Oxidation Protocol